

NEW HYBRID BIOPOLYMER BASED ON
CMC/KAPPA-CARRAGEENAN FOR APPLICATION AS
ELECTROLYTE SYSTEM

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NEW HYBRID BIOPOLYMER BASED ON
CMC/KAPPA-CARRAGEENAN FOR APPLICATION AS
ELECTROLYTE SYSTEM

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Applied Science (Honours) Material Technology

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JANUARY 2017

SUPERVISORS' DECLARATION

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DEDICATION

I would like to dedicate this project report to my beloved parents, MD JAMIL BIN JUSOH and ROHAIZAH BINTI ISMAIL.

In addition, dedication also to my supervisor, DR AHMAD SALIHIN BIN SAMSUDIN who have given guidance and support me for completing this project report.

Without support and guidance from them, this project cannot be done successfully.

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ABSTRACT

Today, the uses of electrochemical devices such as cellphone are having safety issue due to the exploitation of the battery which is harmful to the user. The uses of biodegradable material in electrolyte system can enhance the performance of devices and also bring to the green technology. This research reports on the biopolymer electrolyte was produced using Carboxymethyl cellulose (CMC) and kappa-carrageenan (KC) by hybrid method. This research was divided into 3 phases which are sample preparation, samples characterization and data analysis. The hybrid CMC/KC solid biopolymer electrolytes (SBEs) with different percentage were prepared by solution casting technique. The transparent and colorless with no phase separation biopolymer electrolytes were obtained. Then, the characterization of samples were done by using Fourier Transform Infrared Spectroscopy (FTIR), X-rays Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS). The characterization was divided into two sections which were structural characterization by using FTIR and XRD, and electrical measurement by using EIS. FTIR characterization shows some shifted wavenumber and increase intensity of peak due to hybrid biopolymer electrolytes complexes between CMC and KC. In addition, there are disappear of peak when introducing which clearly shown the interaction between CMC and KC which are affect the ionic conductivity measurement of hybrid SBEs system. XRD result shown that there are increasing broadness of peak as increasing the percentage of KC in the hybrid biopolymer electrolyte. In EIS measurement, the hybrid biopolymer electrolyte of 40/60 percentage of CMC/KC shows the highest conductivity at room temperature was $9.07 \times 10^{-6} \text{ Scm}^{-1}$. The regression value R^2 was found close to unity. From this observation, it revealed that the temperature relationship of SBEs system obey Arrhenius rule. The conductivity behaviour of biopolymer electrolytes was analysed by dielectric studies by measure the dielectric constant and dielectric loss.

ABSTRAK

Hari ini, penggunaan peranti elektrokimia seperti telefon bimbit menghadapi isu keselamatan kerana eksploitasi bateri yang berbahaya kepada pengguna. Kegunaan bahan yang boleh diuraikan dalam sistem elektrolit boleh meningkatkan prestasi alatan dan juga membawa kepada teknologi hijau. Dalam penyelidikan ini, biopolimer elektrolit telah dihasilkan menggunakan carboxymethyl selulosa dan kappa-carrageenan dengan kaedah hibrid. Kajian ini dibahagikan kepada 3 fasa iaitu penyediaan sampel, pencirian sampel dan data analisis. Hibrid CMC / KC elektrolit biopolimer pepejal dengan peratusan yang berbeza telah disediakan oleh teknik tebaran larutan. Elektrolit biopolymer yang telus dan tidak berwarna telah diperolehi. Kemudian, pencirian sampel telah dijalankan dengan menggunakan Spektroskopi Infrared (FTIR), Spektroskopi sinar-X (XRD) dan Spektroskopi Impedans Elektrik (EIS). Pencirian ini telah dibahagikan kepada dua bahagian yang iaitu pencirian struktur dengan menggunakan FTIR dan XRD dan pengukuran elektrik dengan menggunakan EIS. FTIR pencirian menunjukkan beberapa beralih nombor amplitud dan meningkatkan keamatan puncak kerana berlakunya kompleks antara CMC dan KC hibrid elektrolit biopolimer. Di samping itu, terdapat hilang puncak apabila memperkenalkan yang jelas menunjukkan interaksi antara CMC dan KC yang menjejaskan pengukuran kekonduksian ionik sistem SBEs hibrid. Hasil XRD menunjukkan bahawa terdapat peningkatan luasnya bonggol berpusat sebagai meningkatkan peratusan KC dalam elektrolit hibrid biopolimer. Dalam pengukuran EIS, elektrolit hibrid biopolimer yang 40/60 peratusan CMC / KC menunjukkan kekonduksian tinggi pada suhu bilik adalah $9.07 \times 10^{-6} \text{ Scm}^{-1}$. Nilai regresi R^2 ditemui berhampiran dengan nilai satu. Dari pemerhatian ini, ia mendedahkan bahawa hubungan suhu sistem SBEs mematuhi peraturan Arrhenius. Kelakian kekonduksian elektrolit biopolimer dianalisis oleh kajian dielektrik dengan ukuran pemalar dielektrik dan kehilangan dielektrik.

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LIST OF SYMBOLS

2θ	-	Bragg angle
$^{\circ}\text{C}$	-	degree celcius
Ea	-	activation energy
wt%	-	weight percentage
t	-	thickness
Rb	-	bulk resistance
σ	-	conductivity
R^2	-	regression
ϵ_r	-	dielectric constant
ϵ_i	-	dielectric loss
f	-	frequency
Zi	-	imaginary part of the complex permittivity
Zr	-	real part of complex permittivity
ϵ_0	-	permittivity of free space
T	-	temperature
k	-	Boltzman constant

LIST OF ABBREVIATIONS

EIS - Electrical Impedance Spectroscopy

XRD - X-ray diffractometer

FTIR - Fourier Transform Infrared Spectroscopy

CMC - Carboxymethyl cellulose

KC - Kappa-carrageenan

SPEs - Solid polymer electrolytes

SBEs - Solid biopolymer electrolytes

SEM - Scanning Electron Microscopy

AFM - Atomic Force Microscopy

PEO - Polyethylene oxide

PE - Polyethylene

PVA - Polyvinyl Alcohol

PVC - Polyvinyl Chloride

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

An electrolyte is a substance that produces an electrically conducting solution when dissolved in water. The electrolytes is widely use in electrical devices which include batteries, solar cell and supercapacitors for generating. Basically, electrolyte divided by three types, liquid electrolyte, gel electrolyte and solid electrolyte. Among these electrolytes, liquid based electrolyte has higher ionic conductivity and good in application but face with lots of limitation such as corrosion, leakage, reaction with electrode and some of it will explode thus very harmful to human and environment. On the other hand, gel electrolytes have unique properties which are easily to shaped, good mechanical properties, stable performance in applications and high conductivity compared to liquid electrolyte. However, gel electrolytes are very expensive in production and also due to their two phases of solid and liquid form, it hard to produce.

Solid electrolyte have an advantages to overcome the problem in liquid electrolyte and gel electrolyte. Solid electrolytes helps to eliminate corrosive solvent, harmful gas, thermal stability and also easy to fabricate with low cost production (Isa, et al., 2014). As world is stepping development technology, the user are need the long lasting, user friendly and low cost product.

Nowadays, the development of solid polymer electrolytes systems (SPEs) is active and its ionic conductivity have been improved by year. There are some properties in SPEs such as ease of fabrications including good contact between electrode and electrolyte, good mechanical and adhesive properties, no leakage electrolytes, higher in energy density and improved in safety hazards (Samsudin et al, 2014). However, there is an increment of polymers that based on petroleum sources especially synthetic polymer. All of these products, is hard to dispose, contribute to environmental pollutions that will cause harmful to human (Rudhziah et al, 2015).

In order to reduce the dependence of petroleum based polymer, the Solid Biopolymer electrolytes (SBEs) are introduced which have its interesting due to its economic, environmental friendly, nontoxic and abundant in nature. The example natural based polymer electrolytes include starch, chitosan, cellulose, soy based and sago (Hafiza and Isa., 2015).

1.2 PROBLEM STATEMENT

Polymer based electrolyte material have great interest due to their properties such as ease of preparation into films with large surface area. But, there are increasing the use synthetic polymer such as polyethylene oxide (PEO), polyethylene (PE) and polyvinyl alcohol/polyvinyl chloride (PVA/PVC) in polymer electrolytes. All of the synthetic polymer use is hard to dispose and harmful to human and also environment. In addition, the chemical used in is expensive because source from petroleum (Rudhziah et al., 2015).

In order to overcome the issues, the research on environmental friendly and low cost fabrication is essential to explore. Natural polymers are particularly interesting due to their properties in nature and biodegradable properties (Chai & Isa, 2015). Example of biopolymer are carboxymethyl cellulose, chitosan and starch (Samsudin et al, 2014). But, the single biopolymer is still lack of performance although the single polymer is adding by its dopant (Kadir et al., 2014). The conductivity is still lower for any electrochemical devices. Therefore, it will be affect the performance of electrochemical devices.

For that reason, in this research, the using of biopolymer from cellulose derivative namely carboxymethyl cellulose (CMC) and carrageenan derivative namely kappa-carrageenan (KC) were used and the using of blending technique is one of technique to overcome the performance of single polymer electrolytes system.

1.3 OBJECTIVES

In the present research, the objective based on:

1. To formulate solid biopolymer electrolytes thin film based CMC/kappa-carrageenan with different percentage.
2. To determine the structural properties of hybrid CMC/kappa-carrageenan solid biopolymer electrolytes (SBEs) system.
3. To determine the ionic conductivity of hybrid CMC/kappa-carrageenan solid biopolymer electrolytes (SBEs) system.

1.4 THESIS OUTLINE

In this research, the literature review were presented in Chapter 2 which focusing more on the structural studies and the conductivity studies about biopolymer electrolytes based on previous works. The materials and methodology of the research were discusses in Chapter 3. The hybrid biopolymer CMC/KC films were successfully prepared using casting method and were characterized by using Electrical Impedance spectroscopy (EIS), Fourier Transform Spectroscopy (FTIR) and X-ray Diffractometer (XRD).

The result obtained from the characterization were discussed in Chapter 4. In this chapter, it contain with two studies namely structure analysis and electrical analysis. For conclusion and recommendation, it was presented in Chapter 5 based on discussion in Chapter 4.

CHAPTER 2

LITERATURE REVIEW

Nowadays, the solid polymer electrolyte is among the main concerns of modern industry and society due to their unique characteristics of polymers which make them suitable for use in wide range of devices, including supercapacitors and batteries (Rani, et al., 2014). But, most of the product based on polymer is harmful, non-bio gradable and hazardous. These will give negative impact to human health and also environment. As to overcome the depletion of polymer sources, there are more researcher focus on natural polymer or biopolymer which bio gradable to green environment.

2.1 POLYMER ELECTROLYTES (PEs)

This polymers electrolytes had received attention since the earliest breakthrough of polymer-salt complexes (Fenton et al., 1973); (Wright, et al., 1975) continued by Armand and their workers on 1978. This great interest due to excellent characteristics of a low electron conductivity, a low self-discharge, a high admissibility between electrode and electrolyte, and a coating ability of a large surface area (Wilson, et al., 1994).

There are three types of electrolyte, which are liquid electrolyte, solid electrolyte, and gel electrolyte. The advantages of liquid polymer electrolytes have higher conductivity and easy to modify its structure. However, the liquid polymer electrolyte is hard to maintain corrosion, leakage and also harmful to the human and environment. The material and

production of liquid polymer electrolyte is high. Over the past year, the electrochemical power was obtained by using liquid electrolyte due to its conductivity. However, this liquid electrolyte gives a lot of disadvantages such as leakage, reaction with electrode, and poor electrochemical stability. This disadvantages makes it unsuitable for use in electro-chemical devices (Chai & Isa, 2015). The example of liquid electrolyte is 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) and poly (ethylene glycol) methyl ether methacrylate (PEGMEMA) which use as application in solar cell (Martina, et al, 2012).

Besides, gel polymer electrolytes also have good ionic conductivity. But, its disadvantages are very expensive and not easy to form due to maintain the phase of liquid and solid. Thus, there are solid polymer electrolyte as one step to overcome the limitation of other types of polymer electrolyte. Solid polymer electrolytes are more flexible in shape, no leakage and more safe. It is easy and low cost of production.

In recent years, most of host polymer investigated are petroleum based polymer which are harmful and non-biodegradable to health and environment. Example of petroleum based polymers are polyethylene (PEO), nylon and polyester. As the ways to overcome issue of the harmful and hard to dispose, the natural polymers such as cellulose, chitosan, chitin and starch had been used as host polymer of solid polymer electrolyte system (Samsudin et al., 2012).

2.2 SOLID BIOPOLYMER ELECTROLYTES (SBEs)

The first discovered of solid polymer electrolytes was by Wright and co-workers in 1973. Then, Armand et al who found their potential as novel electrolyte in 1978. They use polyethylene oxide (PEO) that use as host for sodium and potassium salts, as result the solid electrical conductor polymer/salt complex was produced (Mohamad, et al, 2000). After comparing the advantage and limitation between liquid and gel electrolyte, SPE have more advantages such as good mechanical strength, easy to produce and high ionic conductivity. Nowadays, solid biopolymer electrolytes (SBEs) are type of electrolytes that widely used in electrochemical devices such as in batteries, this is due to low cost, easy in fabrication,

natural based products and not hazardous compared with solid polymer electrolytes. Examples of solid biopolymer electrolytes with its ionic conductivity from previous work shown in Table 2.1.

Table 2.1

SBEs with their conductivity done by previous research.

SBEs	Conductivity, σ (Scm⁻¹)	References
Carboxymethyl cellulose	1.12 x 10 ⁻⁴	Samsudin and Isa (2012)
Chitosan	1.77 x 10 ⁻⁶	Buraidah and Arof (2011)
Corn Starch	1.28 x 10 ⁻⁴	Teoh et al., 2014

2.3 THE ENHANCEMENT OF SBEs

There are a few methods are adopted to enhance the conductivity and improve properties of polymer electrolytes. First by adding dopant salt. The dopant salt is a proton donor which can improve the conductivity of polymer electrolytes. If there have direct interaction between lone pair electron of the heteroatom such as oxygen or nitrogen in the polymer and cation of the ionic dopant, it shows that the polymer can solvate the dopant (Chai and Isa., 2016). The example of dopant salt use in polymer electrolytes are PMMA-NaClO₄ (Sharma et al, 2012), CMC-NH₄Br (Samsudin and Isa, 2012) and Sogo-NH₄Br (Samsudin et al, 2012).

Secondly, by adding plasticizer also can enhance the chemical and mechanical stability of membrane since they could penetrate and increase the distance of molecules and decrease the polar group of polymer (Chai and Isa., 2016). The plasticizers assist in the dissolution and dissociation of salts and therefore increasing the number of mobile charges. Example of plasticizer use in polymer electrolytes are Lithiumtriflate (LiCF₃SO₃)+ lithium tetrafluoroborate(LiBF₄) + Polyvinyl Chloride (PVC) (Ramesh and Arof, 2001) and Carboxymethyl cellulose (CMC)+ ethylene carbonate CF(EC) (Samsudin and Isa, 2013).

Thirdly, blending technique is one of the effective technique use for modification of polymer which can enhance the polymers properties (Rani et al, 2015). It one of the easiest method and can improve the mechanical strength, thermal stability and its ionic conductivity. Example of hybrid biopolymer electrolyte of Starch/Chitosan (Kadir et al, 2011) and CMC/Chitosan (Hafiza & Isa, 2014).

2.4 HYBRID SOLID BIOPOLYMER ELECTROLYTES

The blending method is one of effective step for polymer modification which help to improve the ionic conductivity besides enhance its properties. It is the easiest method to associate different type polymer together and create new structural materials. The reason which led to increase the ionic conductivity is the miscible of polymer blend showed no phase separation between two polymers (Isa et al., 2015). Examples of blending biopolymer electrolytes with it ionic conductivity from previous work shown in Table 2.2.

Table 2.2

Hybrid SSBEs with their conductivity that was done by previous research.

Blending SBES	Conductivity σ (Scm⁻¹)	References
Carboxymethyl cellulose(CMC)/Chitosan	2.12×10^{-5}	Hafiza and Isa., (2014)
Carboxymethyl cellulose/ Carboxymethyl kappa cellulose	3.25×10^{-4}	Rudhziah et al., (2014)
Carboxymethyl cellulose(CMC)/Carboxylmethyl kappa-carrageenan	2.31×10^{-4}	Ahmad et al., (2015)
Starch/Chitosan	5.15×10^{-4}	Kadir et al., (2011)
Plasticized chitosan/PVA	2.07×10^{-5}	Majid et al., (2009)

2.5 STRUCTURAL STUDY OF HYBRID SBEs

In structural studies, Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffractometer (XRD) were used. From the previous work of Kadir et al, (2015), Figure 2.1 shows XRD pattern of chitosan/starch blending polymer electrolyte. In this figure shows that the broadness and decrease in intensity when addition of chitosan makes the sample become less amorphous. In addition there are disappearing peaks due to starch and chitosan which proved that the blend is well formed and miscible, as can be seen in Figure 2.1. In their work they claimed that the addition of 50 wt% starch and above to the blends made the electrolyte brittle due to high intermolecular bonding in starch. Hence, in the previous of Kadir and workers, they conclude that the polymers were blended at a ratio of 80 wt% starch and 20 wt% chitosan (4:1) as the blend is expected to host a reasonably fast ionic conduction due to its more amorphous nature compared with other blend compositions which had been observed in Figure 2.1 (i) (Kadir et al., 2014).

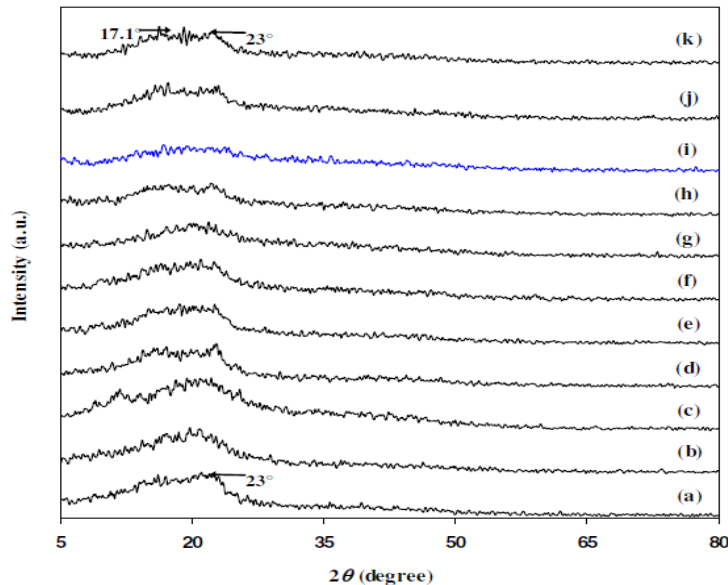


Figure 2.1. X-ray diffraction patterns of (a) pure chitosan film, (b) 10 wt% starch+90 wt% chitosan, (c) 20 wt% starch+80 wt% chitosan, (d) 30 wt% starch+70 wt% chitosan, (e) 40 wt% starch+60 wt% chitosan, (f) 50 wt% starch+50 wt% chitosan, (g) 60 wt% starch+40 wt% chitosan, (h) 70wt% starch+30 wt% chitosan, (i) 80 wt% starch+20 wt% chitosan, (j) 90 wt% starch+10 wt% chitosan and (k) pure starch film. (Kadir et al., 2014)

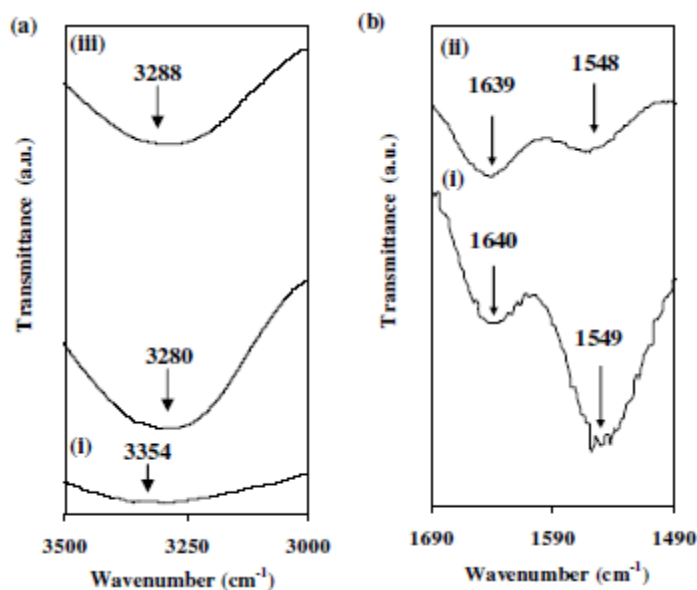


Figure 2.2. (a) FTIR spectra for (i) pure chitosan film, (ii) pure starch film and (iii) 80 wt% starch+20 wt% chitosan blend film in the region of 3000–3500 cm^{-1} . (b) FTIR spectra for (i) pure chitosan film and (ii) 80 wt% starch+20 wt% chitosan blend film in the region of 1490–1690 cm^{-1} (Kadir et al, 2014).

From the research of Kadir et al (2014), the infrared spectra of starch, chitosan and starch–chitosan films are presented in Figure 2.2. From figure 2.2 (a), the hydroxyl bands in the spectrum of pure chitosan and pure starch film appear at 3354 and 3280 cm^{-1} , respectively. The hydroxyl band of the 80 wt% starch +20 wt% chitosan blend film appears at 3288 cm^{-1} . In addition, the carboxamide band in the spectrum of the pure chitosan film is located at 1640 cm^{-1} while the amine NH_2 band appears at 1549 cm^{-1} , as shown in figure 3(b)(i). The position of the carboxamide and amine bands have shifted to 1639 and 1548 cm^{-1} , respectively, in the spectrum of pure starch–chitosan blend film, as shown in figure 3(b)(ii). Kadir et al, 2014 were suggested that interactions had taken place between the hydroxyl groups of starch and the amino groups of chitosan, even though the intensity increased with little spectra shift.

2.6 CONDUCTIVITY STUDY OF HYBRID SBEs

Electrical properties of PVA/chitosan dual-blend green polymer doped with ammonium iodide have been studied by Kadir et al., (2010). From their work, solution casting technique had been used to prepare the film and ionic conductivity was increased when NH_4NO_3 is added which is from 0 to 45 wt. %. In their work, the 36wt % PVA and 24wt% chitosan blend doped with 40wt % of NH_4NO_3 exhibited the highest conductivity at room temperature which was $2.07 \times 10^{-7} \text{ Scm}^{-1}$. On their research, they were changed the blend composition of PVA/chitosan blend but still use the same weight percent of dopant which was 40 wt.% of NH_4NO_3 in order to enhance its conductivity. For new composition of blending which is 60 wt. % PVA/40 wt. % chitosan doped which 40 wt. % NH_4NO_3 , was successfully give more value ionic conductivity $1.60 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature. This conductivity also increase due to added of plasticizer into the blend polymer electrolyte. They have study that the blend polymer electrolyte was give more site for the dopant due to more ion mobile when salt dopant was added. The plasticizer was improve the conductivity by provide more donor number. (Kadir et al., 2010)

CHAPTER 3

METHODOLOGY

The general overview for methodology in this research is presented in flow chart as shown in Figure 3.1. The research was conducted at Faculty of Sciences & Technology Industry (FIST) Laboratory, Universiti Malaysia Pahang for structural characterization and Ionic State Laboratory, Universiti Malaysia Terengganu for impedance characterization.

3.1 APPARATUS AND MATERIALS

Table 3.1

List of apparatus and materials was used in the research.

No.	Materials and Apparatus
1	Carboxymethyl cellulose (CMC)
2	Kappa-carrageenan
3	Beaker 1000ml
4	Beaker 200ml
6	Measuring cylinder 250ml
7	Magnetic Bar
8	Glass Petri Dishes
9	Sticker

3.2 RESEARCH METHODOLOGY

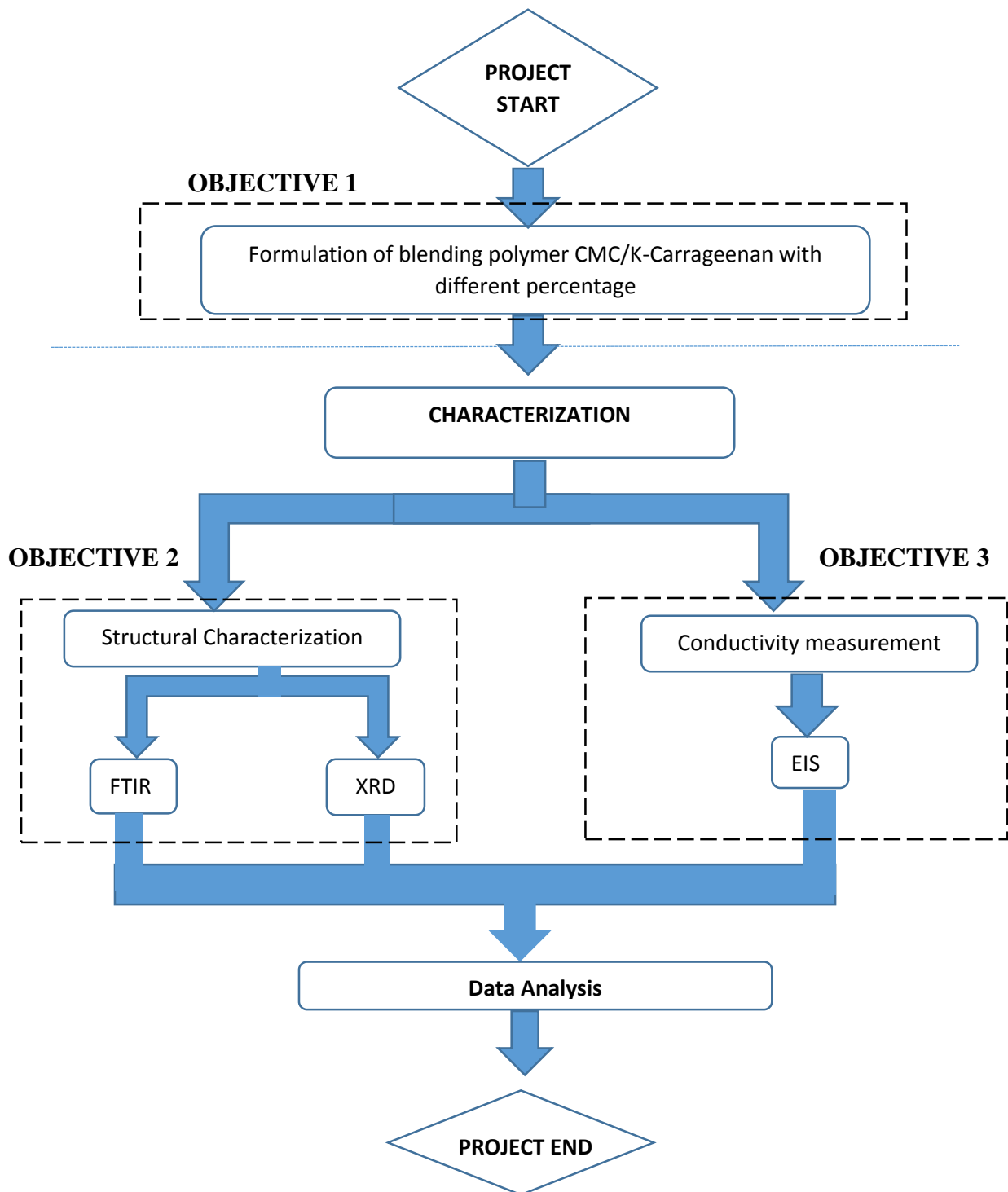


Figure 3.1. Flow chart of research procedures

3.3 SAMPLE PREPARATIONS

In this research, different amount in percentages of Carboxymethyl cellulose (CMC) from Acros Organic and kappa-carrageenan from Shanxi Orient Co. was dissolved into 98 ml of distilled water by double boiler technique. The different amount in percentage of CMC/k-carrageenan hybrid as shown in Table 3.2.

Then, the mixture was stirred by using magnetic bar until homogenous solution was obtained. The mixture then was poured and casted into several Petri dishes and left to dry at ambient temperature until film form. When hybrid biopolymer electrolytes is formed, peel sample by using knife and forceps then cut it into suitable sizes for characterization.

Table 3.2

List of sample with their composition respectively.

Designation	CMC/K-carrageenan blend	CMC (g)	K-carrageenan (g)
B1	100/0	2.0	0
B2	90/10	1.8	0.2
B3	70/30	1.4	0.6
B4	50/50	1.0	1.0
B5	40/60	0.8	1.2
B6	20/80	0.4	1.6
B7	0/100	0	2.0

3.4 SAMPLE CHARACTERIZATION

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy measurement was carried out by using Perkin Elmer Spectrum 100 which the measurement was carried out in range analysis from 400 to 4000 cm^{-1} . Then, the FTIR convert the collected spectra data from an interface pattern to a spectrum. The sample testing were cut into suitable size and placed in the specimen holder. FTIR was performed to confirm the occurrence of complexation between hybrid solid biopolymer electrolytes.



Figure 3.2. Fourier Transform Infrared Spectroscopy (FTIR)

3.4.2 X-ray Diffractometer (XRD)

In this research, the XRD measurements was performed using MiniFlex II from Rigaku. XRD was used to determine the crystallinity /amorphousness nature of CMC/kappa-carrageenan of hybrid biopolymer. The samples were cut into a desirable size (1 cm × 1 cm). Then, samples were put onto glass slide and then placed in the holder of diffractometer. The biopolymer electrolytes film was scanned at 2θ angles between 5° and 60° .



Figure 3.3.X-ray Diffractometer (XRD).

3.4.3 Electrical Impedance Spectroscopy (EIS)

The biopolymers hybrid CMC/Kappa-carrageenan film was cut into small size and sandwiched between two stainless steel electrodes of $1\pi \text{ cm}^2$ surface area. The ionic conductivity of samples was characterized by using HIOKI 3532-50 LCR Hi-Tester with frequency range between 50 Hz to 1 MHz.

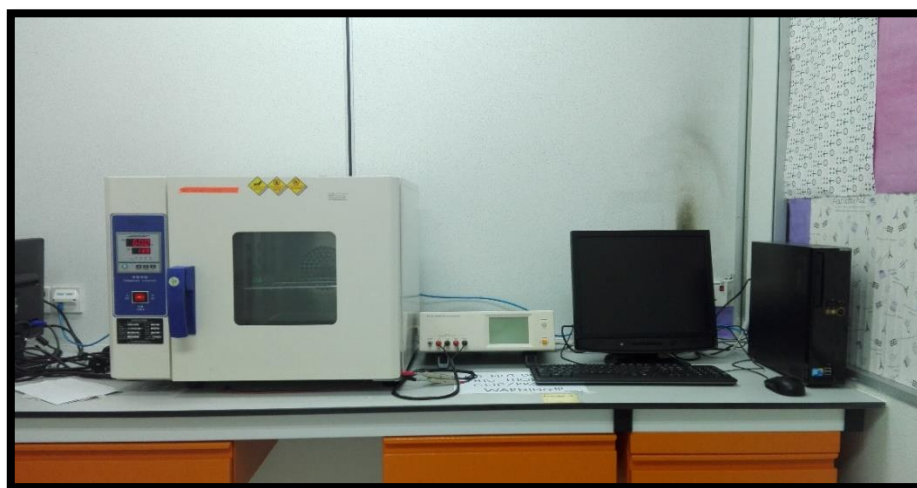


Figure 3.4. Electrical Impedance Spectroscopy (EIS).

From EIS, it's obtained negative imaginary impedance ($-Z_i$) against real impedance (Z_r). Then the bulk impedance R_b value was obtained. Thus, the conductivity, σ of the samples was calculated from the equation below (Isa et al, 2014):

$$\sigma = \frac{t}{R_b A} \quad (3.1)$$

Where t = thickness of the sample

A = area of sample

R_b = bulk resistance

For R_b it was determined from Cole-Cole plot. The data obtained from EIS was used to calculate conductivity study, activation energy and dielectric study (constant and loss) which have discuss in the Chapter 4.

Table 3.3

Summarized characterization method for hybrid biopolymer electrolytes.

Characterization	Equipment	Application
Structural characterization	X-ray diffraction (XRD)	To determine the structural properties of hybrid biopolymer electrolytes.
	Fourier Transform Infrared (FTIR)	To study the complexation of between the hybrid polymer.
Conductivity and electrical characterization	Electrical Impedance Spectroscopy (EIS)	To examine conductivity and electrical properties of CMC/Kappa-Carrageenan hybrid biopolymer samples.

3.5 DATA ANALYSIS

The data obtained from sample characterization was analyzed. The obtained data analysis was used to compare to determine the potential of the hybrid technique as advanced materials for solid biopolymer electrolytes.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter explains the results and discussion of the carboxyl methylcellulose (CMC) blend with kappa-carrageenan solid state biopolymer electrolytes (SSBEs) which was produced from the solution casting technique. The structural characterization and conductivity measurement of hybrid biopolymer electrolytes were characterized by using different technique such as Fourier Transform Infrared Spectroscopy (FTIR), X-rays Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS).

4.1 CARBOXYMETHYL CELLULOSE/K-CARRAGEENAN BLENDING BIOPOLYMER ELECTROLYTES

The transparent and colorless hybrid electrolytes with no phase separation was obtained as shown in Figure 4.1.



Figure 4.1: Transparent CMC/KC hybrid electrolyte.

4.2 STRUCTURAL CHARACTERIZATION OF CMC/K-CARRAGEENAN BIOPOLYMER ELECTROLYTE

4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4.2 shows the IR spectra of Carboxymethyl cellulose/kappa-carrageenan at different percentage in the region from 700 to 4000 cm^{-1} . According to Ahmad et al., (2015) if any significant changes in terms of the shift in wavenumber, change in the intensity or change in the band shape was observed, it shows an interaction has occurred in polymer electrolyte complexes. In this present research, the possible interaction between CMC and KC at the region from 1500 cm^{-1} to 1750 cm^{-1} is presented in Figure 4.3.

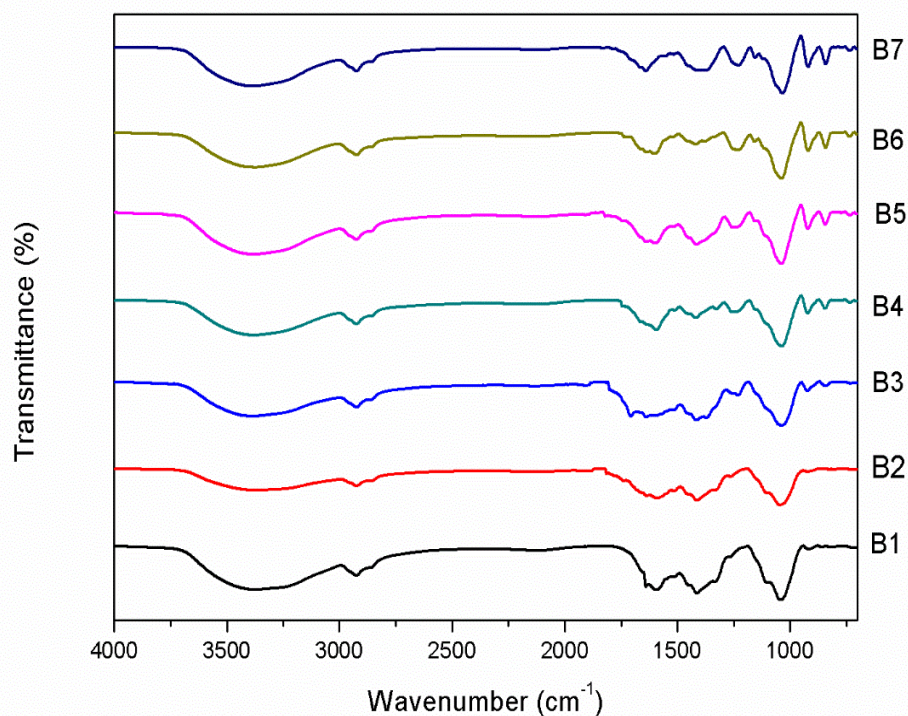


Figure 4.2. FTIR spectra of sample CMC/kappa-carrageenan SBEs system.

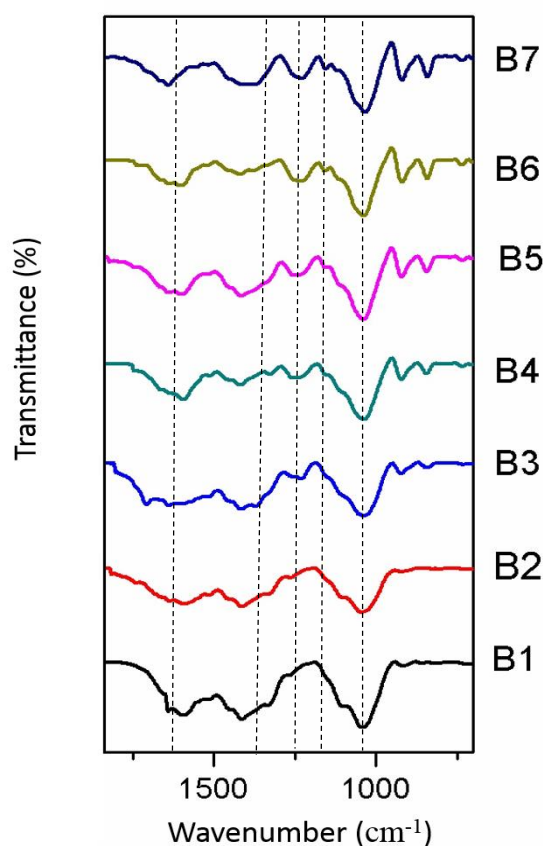


Figure 4.3. FTIR spectra of samples in the region from 750 to 1750 cm^{-1}

An absorption peak was appeared at 1510 cm^{-1} corresponding to the asymmetrical (C=O) stretching of CMC shifted to higher wavenumber when KC was increase. This may due to the interaction of hybrid biopolymer has taken place between CMC and KC. In addition, peak at 1420 cm^{-1} which correspond to O-H group moiety of CMC was found to disappear when introducing of KC until sample B5 as hybrid matrix and it shown that the hydroxyl group of CMC was dissolved with KC when it was added.

The peak at 1240 cm^{-1} indicate that the appearance of O=S=O stretching band of KC is appear in hybrid complexes where this band is identified would interact if any dopant system was added thus would lead to the protonation in polymer-salt complexes.

In addition, it clearly can be seen the shifted of C-O⁻ group in carboxylate anion of CMC towards lower value wavenumber with addition of KC. This band is found as good acceptor for CMC/KC as observed by other researcher (Rudhzhiah et al., 2015).

The changes characteristic spectra in Figure 4.3 were clearly observed due to the reflect the interaction between the hybrid CMC/KC biopolymer. It can be conclude that when the two polymers are mixed, there will be more sites for ion hopping and exchange, which will lead to an increase in conductivity (Kadir et al., 2014).

4.1.2 X-rays Diffractometer (XRD)

Figure 4.4 shows the pattern of hybrid CMC/KC SBEs system at 2θ between 5° to 60° with different percentage of CMC/KC. The sample B1 which contain 100% CMC shows that the polymer is amorphous in nature as observed by Samsudin et al., 2012. From figure 4.4 (c), the kappa-carrageenan has shown amorphous hump of $2\theta=21^\circ$. With addition of KC into hybrid SBEs system, there was crystalline peak observed until the 40/60 of CMC: KC the crystalline peak disappear due to the blend is expect are well form. According to Zakaria et al (2012), the absence of peaks revealed that structural modification has occurred in the blends. This crystalline properties also absence which important as proven the increasing in ionic conductivity. However in B6 with addition of 80% KC, causes the appearance of small peak which show that the blend has become more crystalline in nature and cause the decreasing in ionic conductivity. Majid and Arof (2005), confirmed that the conductivity of the samples will be affected if there is changes in amorphousness of polymer electrolytes system. Hence, in the 40% CMC hybrid with 60% kappa-carrageenan is the most suitable host to be doped due to its more amorphous properties resulted from XRD analysis.

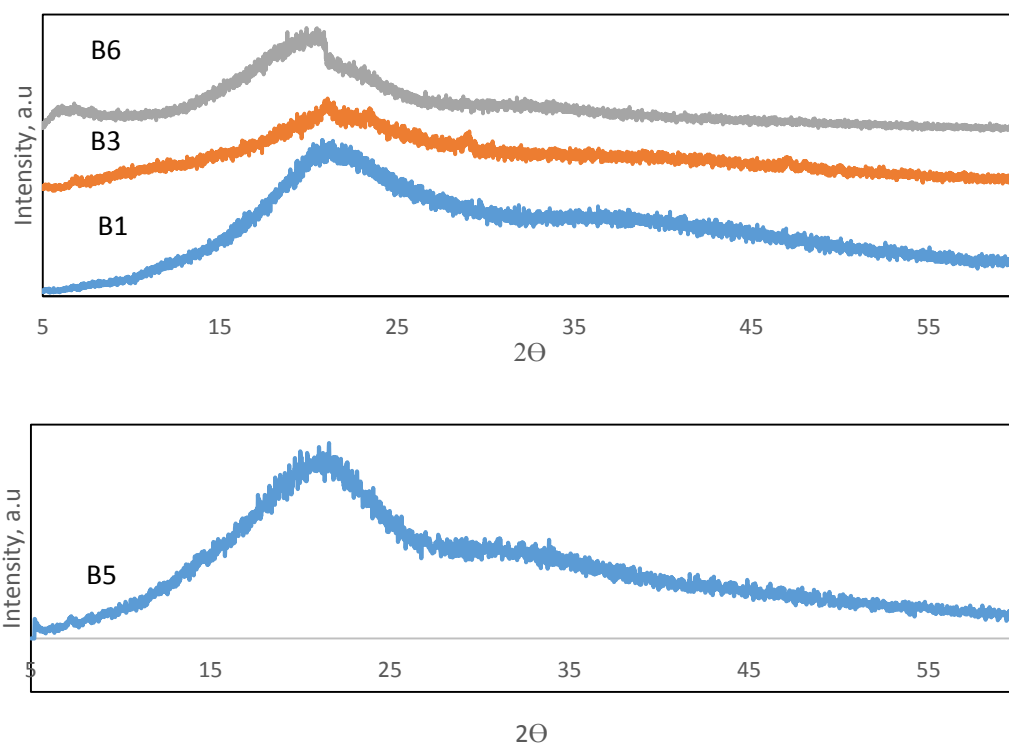


Figure 4.4. XRD pattern of B1 CMC/KC (100:0), B3 (70:30), B6 (20:80), B5 (40:60)

4.3 CONDUCTIVITY MEASUREMENT OF HYBRID CARBOXYMETHYL CELLULOSE/KAPPA-CARRAGEENAN

4.3.1 Ionic Conductivity Study of Hybrid CMC/KC Solid Biopolymer Electrolytes.

In figure, the resultant Cole-Cole plot for each sample was obtained which contain negative imaginary impedance ($-Z_i$) against real impedance (Z_r). The value of bulk resistance R_b can be obtained from the interception of low frequency and high frequency region on Z_r -axis. From the figure 4.5, the high frequency semicircle can be related to the ionic conduction process in the bulk of the polymer electrolytes and the low frequency spike has been attributed to the effect between two blocking electrodes which represent the formation of double layer of capacitance of blending biopolymer electrolyte film interface (Hafiza and Isa, 2014). From the Cole-Cole plots, the bulk resistance, R_b , were obtained as shown in the Table 4.1 and equation (3.1) was used to calculate the conductivity, σ , for each sample. The graph of conductivity against different blending composition of samples was plotted using the conductivity values in Figure 4.6.

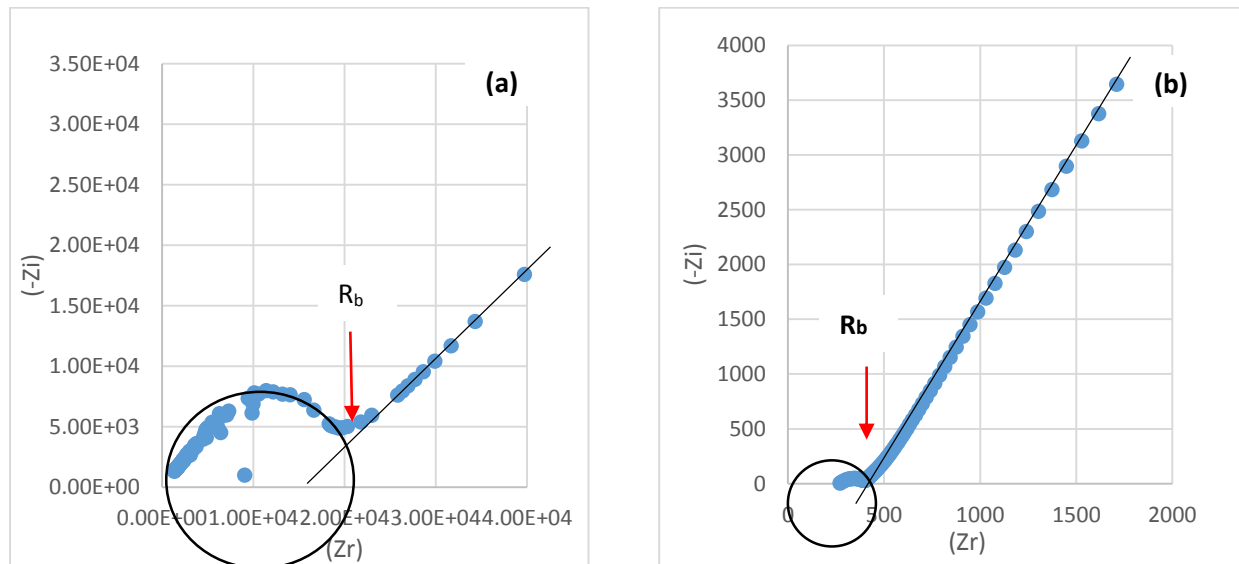


Figure 4.5. The Cole-Cole plot for (a) sample B1 (b) sample B5

Table 4.1

Bulk resistance and thickness values of prepare samples.

Samples	Thickness (cm)	Bulk Resistance (R_b)
B1	0.013	2.55×10^4
B2	0.013	8.76×10^3
B3	0.015	3.98×10^3
B4	0.011	1.64×10^3
B5	0.012	4.21×10^2
B6	0.012	2.89×10^3
B7	0.012	1.06×10^4

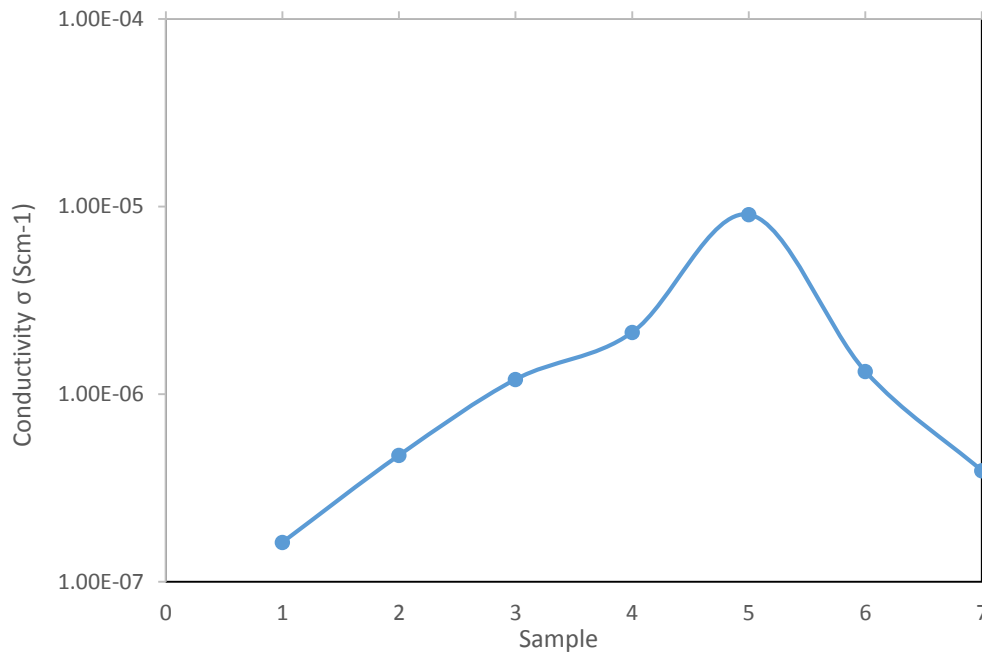


Figure 4.6: Conductivity against samples of hybrid SBE with different percentage.

From the Table 4.1, as the lower the R_b values of the sample, the higher in conductivity. It also can be referred from the equation (3.1) which show that the conductivity of sample inversely proportional to R_b . In addition, the thickness of the sample also related to the conductivity values obtained which the increasing of conductivity values is directly proportional to the thickness of the sample. From the Figure 4.6, the B5 sample which have 40:60 CMC/KC blending have higher conductivity value with $9.07 \times 10^{-6} \text{ Scm}^{-1}$.

At room temperature, the conductivity of CMC/KC hybrid solid biopolymer electrolyte were observed to gradually increase with addition of k-carrageenan up to maximum at $9.07 \times 10^{-6} \text{ Scm}^{-1}$ (sample B5). The increase in conductivity can be relate with the changes of amorphous region show by XRD studies.

4.3.2 Temperature Dependence of Ionic Conductivity Study.

Figure 4.7 shows the temperature dependence of ionic conductivity for hybrid SBEs system at various temperature. It can be observed that the conductivity increase linearly with temperature, which showing that the conductivity related to thermally assisted. According to Samsudin and Isa (2012), the increasing of conductivity value with temperature because the internal modes are activated where, semi-crystalline nature of the electrolytes turn into amorphous nature as observed from XRD analysis. The relationship between log conductivity and $1000/T$ is almost linear. The regression value, R^2 was found close to unity. From this observation, it revealed that the temperature relationship of SBEs system obey Arrhenius rule. The Arrhenius behavior can be expressed by the equation 4.1.

$$\sigma = \sigma_o \exp (-E_a/kT) \quad (4.1)$$

Where σ_o = pre-exponential factor

E_a = activation energy

k = Boltzman constant

T = absolute temperature

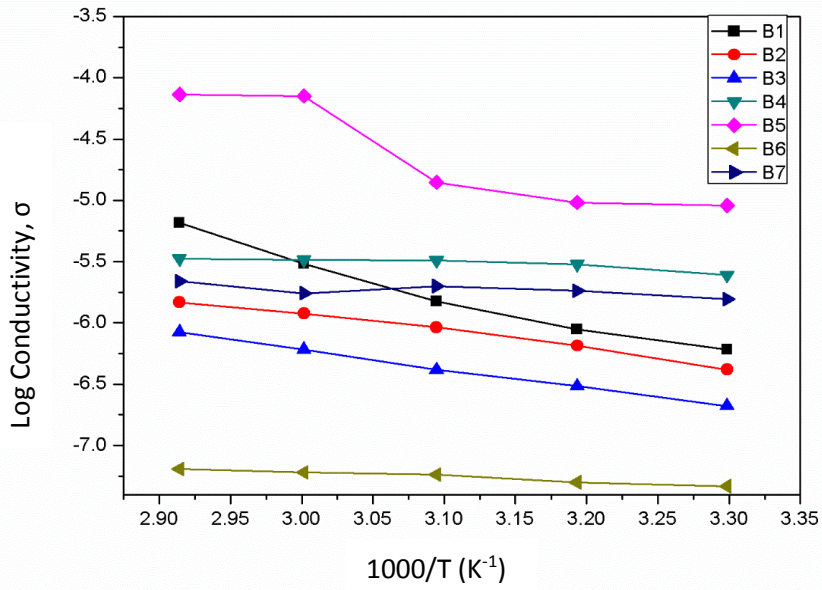


Figure 4.7. Temperature dependence of ionic conductivity for CMC/K-carrageenan biopolymer electrolyte system.

As shown in Figure 4.8 it can be observed that, the activation energy is decreased when more percentage of k-carrageenan was added. The highest percentage in the k-carrageenan, the low activation energy for highest conducting samples may due the ions in high conducting sample require lower energy for migration. The short distance between transit sites also result for lower activation energy (Kadir et al., 2014).

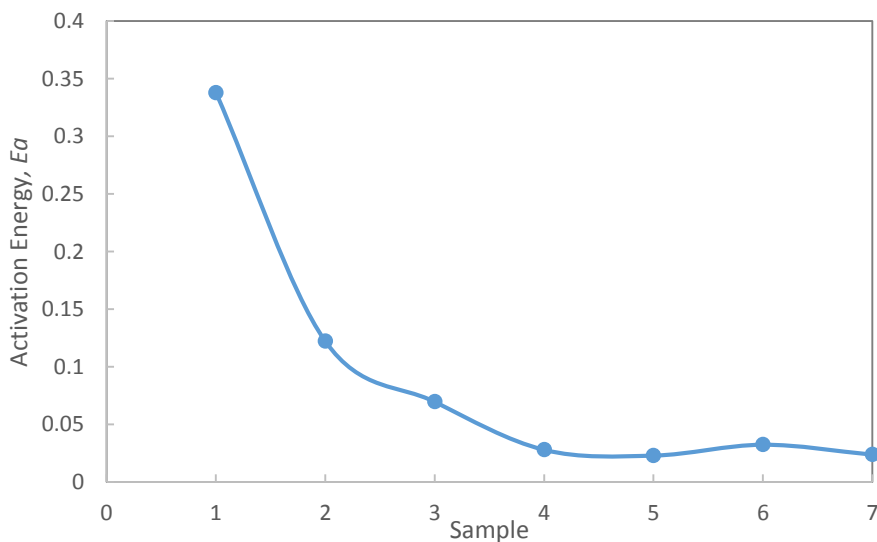


Figure 4.8: Activation energy against sample of hybrid biopolymer electrolyte with different percentage.

The conductive behavior of polymer electrolytes system can be understood from dielectric study by using dielectric constant ϵ_r which measured store charge while dielectric loss, ϵ_i measured energy loss of the applied electric field (Hafiza et al., 2014).

4.3.3 Dielectric Constant Study

The dielectric constant and dielectric lost can be calculated by using below equations (4.2):

$$\epsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_1^2)} \quad (4.2)$$

Where $C_o = \epsilon_0 \frac{A}{t}$, ϵ_0 is the permittivity of the free space

t = thickness of samples

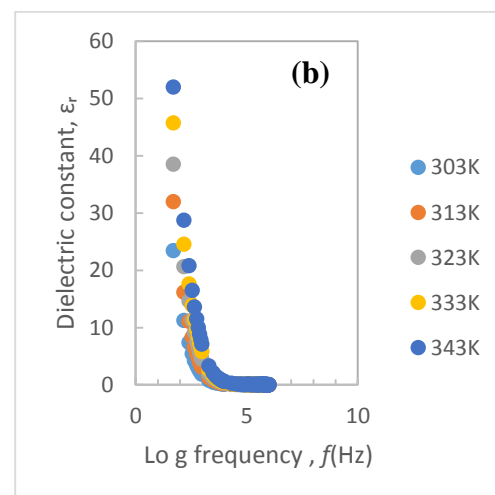
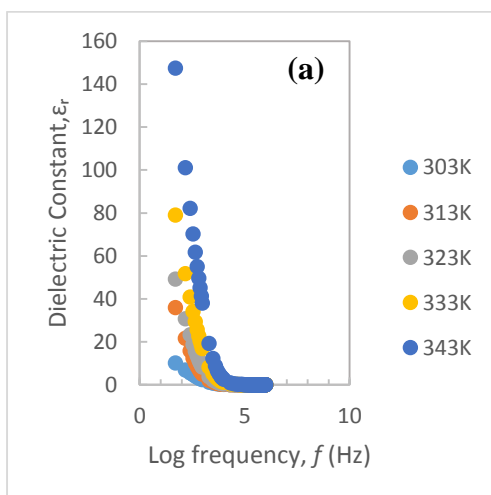
A = area electrode- electrolytes contact surface

$\omega = 2\pi f$

Z_i = negative imaginary impedance

Z_r = real impedance

The frequency dependence of real part, ϵ_r of the dielectric constant curve are shown in Figure 4.8 (a) to (g)



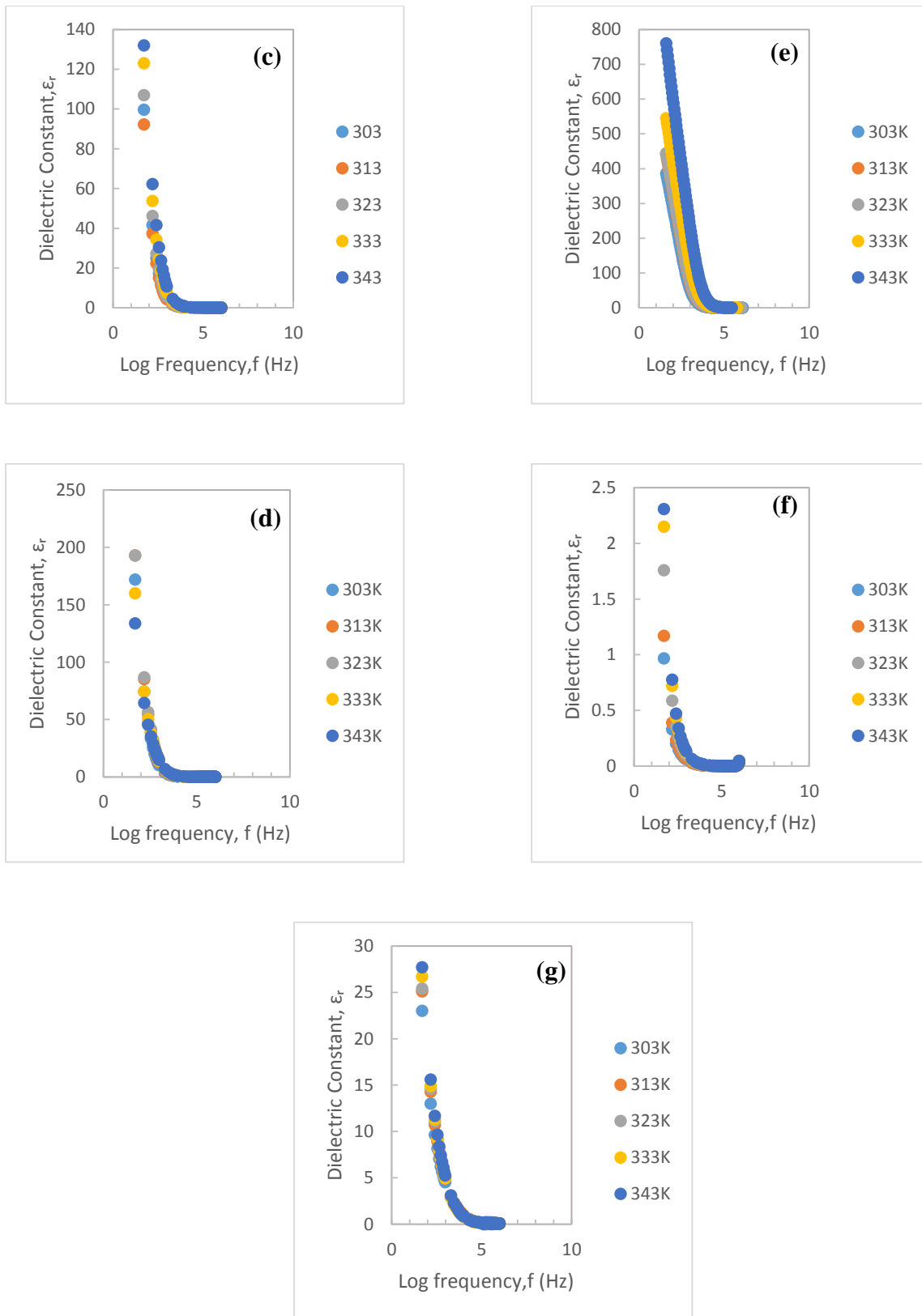


Figure 4.9. : Frequency dependence of the dielectric constant at different temperatures.

4.3.4 Dielectric Loss Study

The dielectric lost can be calculated by using below equations (4.3):

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_1^2)} \quad (4.3)$$

Where $C_o = \varepsilon_0 \frac{A}{t}$, ε_0 is the permittivity of the free space

t = thickness of samples

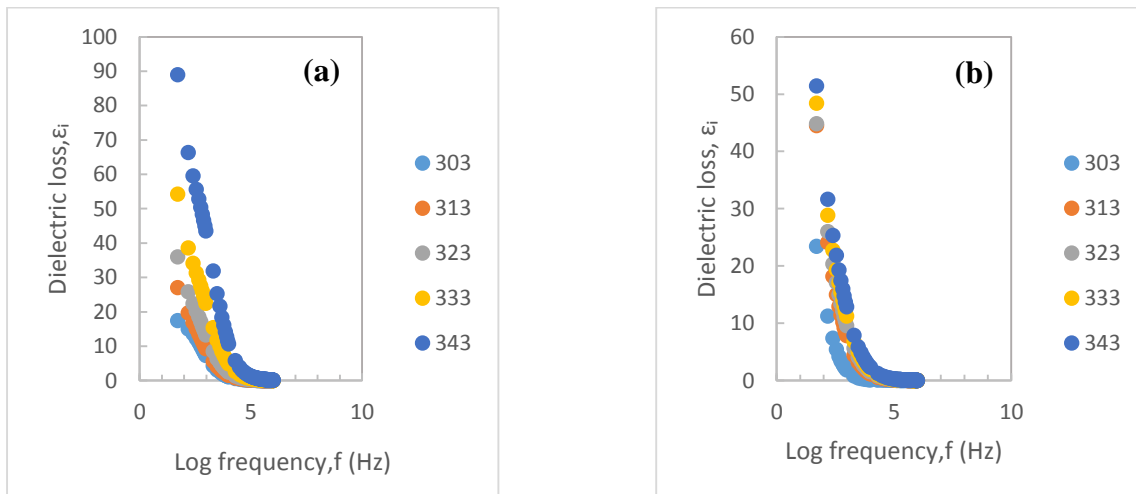
A = area electrode- electrolytes contact surface

$\omega = 2\pi f$

Z_i = negative imaginary impedance

Z_r = real impedance

The frequency dependence of real part, ε_r of the dielectric loss curve are shown in Figure 4.9 (a) to (g)



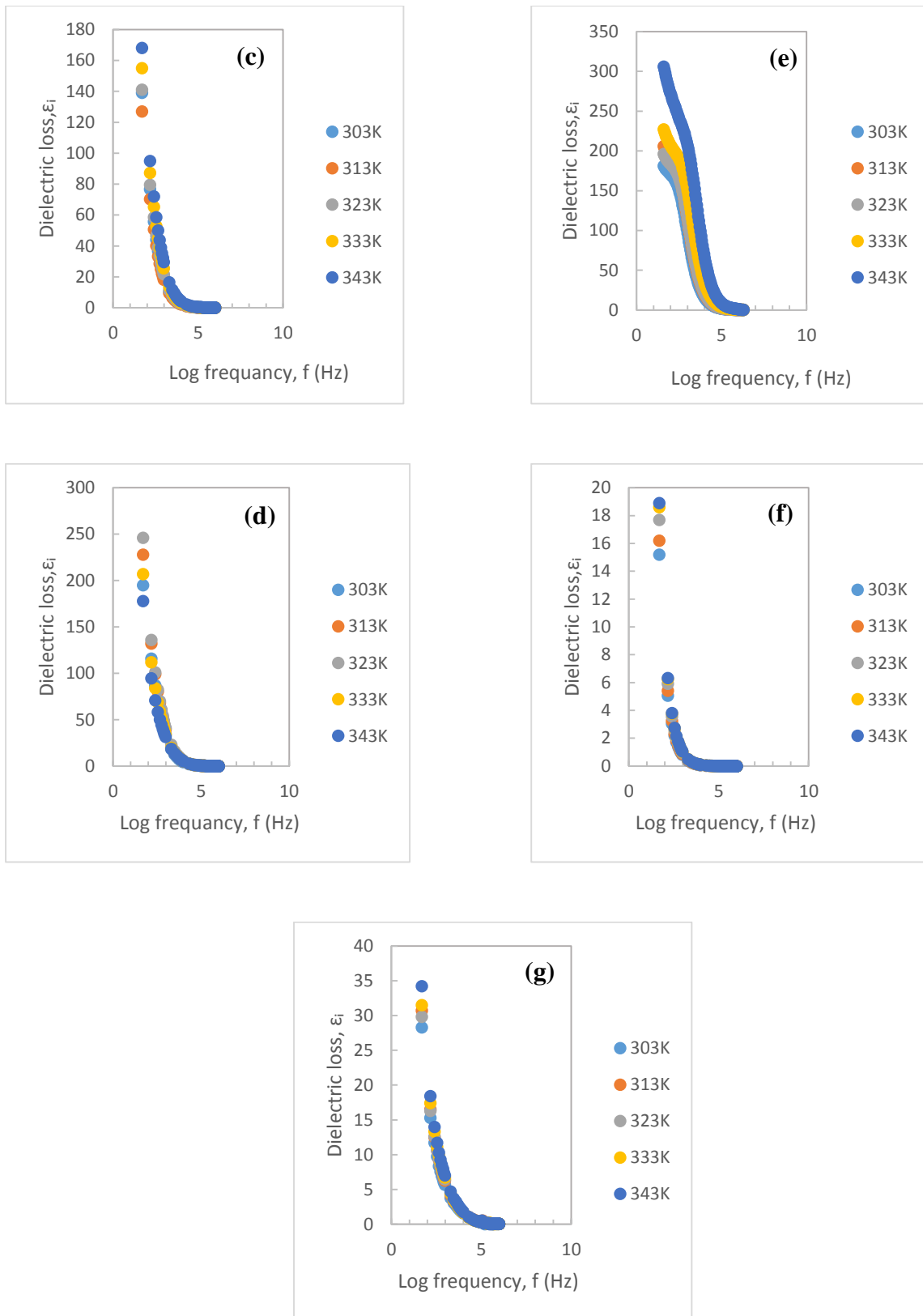


Figure 4.10. Frequency dependence of the dielectric loss at different temperature.

Figure 4.9 and Figure 4.10, shows the frequency dependence of dielectric constant (ϵ_r) and dielectric loss respectively (ϵ_i). From the figure above, it can be concluded that there were no noticeable relaxation peaks was detected in both dielectric parts. Both ϵ_r and ϵ_i sharply rise at low frequency due to electrode polarization and space-charge effects had occurred. This have confirmed that a non-Debye type. However, the rate of transposition of the electric field also increases as the frequency increase, as such there is no charge build up at the interface which brings about a decrement in the values of the dielectric loss due to the reduction of the polarization effect by the charge accumulation occur (Ramesh & Arof., 2001). In this research, the conductivity of hybrid SBEs system exhibits relaxation which non-exponential in time and this turn to a direct proportional relationship between the rates of reversal of the electric field which shows there was no time to charge to build up at the interface. Thus, the polarization due to charge accumulation decreased that led to the observed decreasing value of (ϵ_r) and (ϵ_i).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Based on the results and discussion in the previous chapter, it can be concluded that the hybrid SBEs system Carboxymethyl cellulose (CMC) with kappa-carrageenan (KC) was successfully produce by using solution casting technique. The hybrid solid biopolymer electrolytes with different percentage that produced were found to be a transparent and colorless with no phase separation.

The complexation between CMC and KC was shown from FTIR spectrum. At peak at 1420 cm^{-1} which correspond to O-H group moiety of CMC was found to disappear when introducing of KC until sample B5 as hybrid matrix and it shown that the hydroxyl group of CMC was dissolved with KC when it was added. In addition, peak at 1240 cm^{-1} indicate that the appearance of O=S=O stretching band of KC is appear in hybrid complexes where this band is identified would interact if any dopant system was added thus would lead to the protonation in polymer-salt complexes.

XRD pattern of the between $2\theta = 21^\circ$ shows that the amorphousness of biopolymer electrolytes increased with the increasing of KC percentage. The conductivity of the samples will be affected if there is change in the amorphousness of the polymer electrolyte system. Then, if more KC was added after 40/60, the crystallinity peak was appeared which shows there are low conductivity due to changes of amorphous nature of hybrid biopolymer electrolytes.

The hybrid CMC/KC solid biopolymer electrolyte have higher conductivity value with $9.07 \times 10^{-6} \text{ Scm}^{-1}$ at room temperature for sample 40/60 percentage of CMC/KC. In this case, it shown that the ionic conductivity of CMC/KC biopolymer electrolytes increased, as increasing percentage of KC. However, at sample B6 the conductivity decrease. The decreasing of ionic conductivity due to increasing of crystallinity as observed by XRD result. In addition, the temperature dependence of ionic conductivity for hybrid CMC/KC biopolymer electrolytes system revealed that the temperature relationship of SBEs system obey Arrhenius rule.

5.2 RECOMMENDATION FOR FUTURE WORK

Through this research, there are some improvement that can be done for future study on sample preparation method phase. There are some problem during sample preparation which due to the environment factor. The surrounding environment should be give attention to avoid sample contamination because carboxymethyl cellulose and k-carrageenan are very sensitive toward changes of environment temperature.

Besides, the structural characterization can be more detail by using Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), and Energy Dispersive Spectroscopy (EDS) to observe the changes morphology structure when different percentage hybrid biopolymer electrolyte are used in future work.

In addition, the ionic conductivity can be improve by adding plasticizer and dopant salt. By adding plasticizer also can enhance the chemical and mechanical stability of membrane since they could penetrate and increase the distance of molecules and decrease the polar group of polymer (Chai and Isa., 2016).

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