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Research paper

Conductivity Performance of Biopolymer Membrane based on Kappa-Carrageenan

Rosnah Zakaria[1,2]*, Asiah Mohd Nor[2], Nor Kartini Jaafar[2], Ab Malik Marwan Ali[1,2]

[1]*Institute of Science, Univerisiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*
[2]*Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*
**Corresponding author E-mail: rosna593@salam.uitm.edu.my*

Abstract

Smart energy systems are well-known among researchers who wish to introduce new technology. Biopolymer is an environmentally friendly material. Kappa-Carrageenan is one type of biopolymer with high proton conductivity and durability which has been studied for almost 10 years. The membrane based on kappa-carrageenan was prepared using solution cast technique incoorperated with ammonium thiocyanate (NH_4SCN). The solution was poured into glass petri dishes and left to dry at room temperature before further dying in an oven at 60°C to obtain thin films. The highest conductivity was obtained for 40 wt. % NH_4SCN added kappa-carrageenan. The conductivity dropped when the amount of kappa-carrageenan is equal to the amount of NH_4SCN. The maximum conductivity of kappa-carrageenan incorporated with NH_4SCN obtained is 1.64E-03 S cm^{-1}. FTIR studies show peak at 1638 cm^{-1} in pure kappa-carrageenan which slowly disappeared at 60 wt. % kappa-carrageenan. It is however characterized by a peak attributed to NH_4SCN at 1600 cm^{-1} which appeared for 50 wt. % of kappa-carrageenan and below.

Keywords: *Proton Conductivity, EIS, FTIR, kappa-carrageenan.*

1. Introduction

Biopolymers like polysaccharides are synthesized from natural sources. Most biopolymer membranes are proton conducting and offer less hazard to the environment. Carrageenan are a group of linear sulfate polysaccharides that are extracted from red edible seaweeds. There are many types of carrageenan and the three main commercial classes of carrageenan are kappa, iota, and lambda. Kappa-carrageenan is well-known with its characteristic which are low cost, easy to purchase and since it is a natural material it therefor renewable [1]. Carrageenan is also non-toxic and sustainable element of biopolymer. It has high proton conductivities at over 100˚C and under 0˚C, good water uptake above 100˚C and durable for over 10 years [1]. In this study, kappa-carrageenan is incorporated with ammonium thiocyanate as ionic dopant which acts as a source of proton for the polymer matrix.

2. Experimental

Kappa-carrageenan and ammonium thiocyanate (NH_4SCN) was purchased from Sigma Aldrich and diluted in 50 ml distilled water in various weight percent (wt. %). The sample was then stirred for 24 hours to get homogenous solution before being poured into petri dishes for drying process. It was left at room temperature for one day before heat treatment in an oven at 60°C. The sample was peeled in thin film form and stored in a dessicator before characterization with Fourier Transform Infrared Spectroscopy(FTIR) and Electrical Impedance Spectroscopy(EIS).

2.1. Electrical Impedance Spectroscopy, EIS

EIS was conducted using HIOKI 3532-50 LCR Hi-Tester interfaced to a computer for frequencies in the range of 100Hz – 1 MHz. The dried film samples were then placed between sample holders which also act as blocking electrodes, connected to a computer. Cole-Cole plots of imaginary impedance, Z_i versus real impedance, Z_r were obtained from the computer and these were used to determine bulk resistances, R_b. The ionic conductivity values were then calculated. using the equation:

$$\sigma = \frac{t}{R_b A} \text{ S cm}^{-1} \quad (1)$$

Where t - thickness of the sample (cm), R_b - bulk resistance and A - the contact area of the electrolyte film.

2.2. Fourier Transform Infrared, FTIR

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional group of kappa-carrageenan and ammonium thiocyanate. The method was utilized to identify the intensity of the FTIR spectra based on kappa-carrageenan and ammonium thiocyanate (NH_4SCN) interaction.

3. Results and Discussion

The dried thin films were characterised and analysed accordingly.

3.1. Electrical Impedance Spectroscopy, EIS

Table 1: Cole – Cole plot of kappa-carrageenan – ammonium thiocyanate at various wt. %

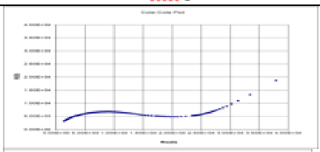
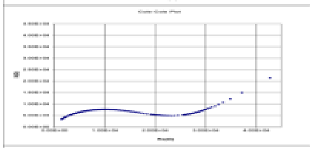
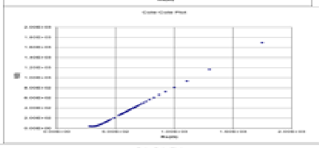
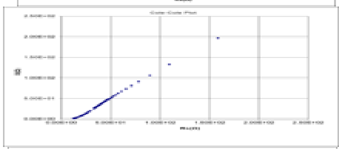
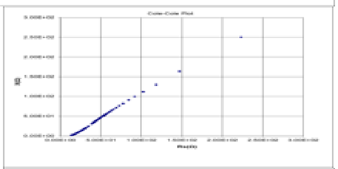
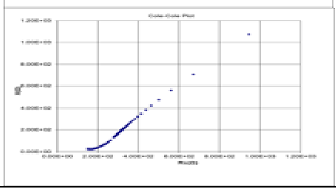
(wt %)	Cole – cole plot	(R_b)/ Scm^{-1}
0		1.82E+04
10		1.73E+03
20		3.08E+02
30		1.02E+01
40		9.50E+00
50		1.83E+02

Table 1 shows the graph of Zi vs. Zr of different kappa-carrageenan – ammonium thiocyanate weight percentage composition (wt. %). The value of R_b was obtained from the graph. The conductivity of the sample was calculated using equation (1) and tabulated in Table 2.

Table 2: Conductivity of kappa-carrageenan – ammonium thiocyanate

wt.% NH_4SCN	Conductivity
0	1.36E-06 Scm^{-1}
10	1.71E-06 Scm^{-1}
20	2.46E-05 Scm^{-1}
30	2.61E-04 Scm^{-1}
40	1.64E-03
50	2.28E-05

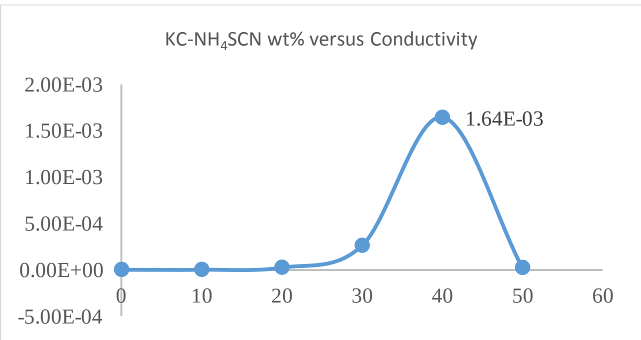


Fig. 1: Conductivity of varied wt. % NH_4SCN

The conductivity of pure sample of kappa-carrageenan is 1.36E-06 S cm^{-1} and increased as the composition of salt increased. As for the samples added with NH_4SCN at 10 wt. %, 20 wt. %, 30 wt. % and 40 wt. % the conductivities are 1.71E-06 S cm^{-1}, 2.46E-05 S cm^{-1}, 2.61E-04 S cm^{-1} and 1.64E-03 S cm^{-1} respectively. The highest conductivity was obtained for the sample with 40 wt. % NH_4SCN, after which the conductivity decreased as shown in Fig. 1.

3.2. Fourier Transform Infrared Spectroscopy

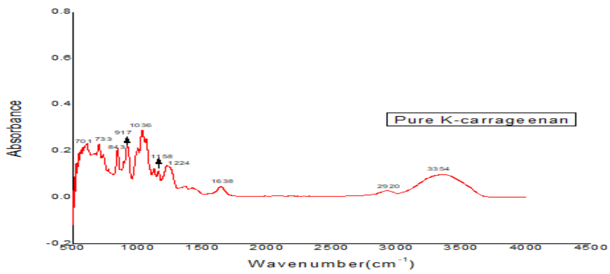


Fig. 2: FTIR spectra of pure K-Carrageenan

Fig. 2 shows the FTIR spectrum of pure kappa-carrageenan. The spectrum indicates that the C-H stretching band of pure kappa-carrageenan is observed at 2920 cm^{-1} while C-O stretching is at 1158cm^{-1}. CN stretching mode peaks at 1622 cm^{-1}. In addition, vibrational modes at 917 cm^{-1} and 843 cm^{-1} are attributed to C-S symmetric bending and SCN^{-1} polar groups respectively.

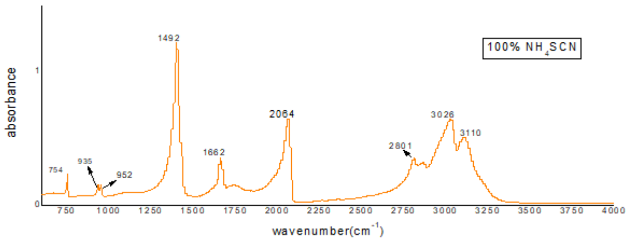


Fig. 3: FTIR spectra of pure NH_4SCN

The FTIR spectra for 100% pure NH_4SCN is shown in Fig. 3. At 3110 cm^{-1} and 2362 cm^{-1} are peaks attributed to N-H and C-N stretching respectively while the peaks at 1622 cm^{-1} and 1400 cm^{-1} belong to C asymmetric vibration and combined effect of C-S symmetric stretching respectively [2]. The vibrational band at 943 cm^{-1} and 820 cm^{-1} are attributed to C-S symmetric bending vibration and SCN^{-1} polar group. C—S symmetric bending band of pure NH_4SCN is observed at 952 cm^{-1}, C-S symmetric stretching at 1492 cm^{-1}, C asymmetric vibration at 1662 cm^{-1} and N-H stretching at 3110 cm^{-1}.

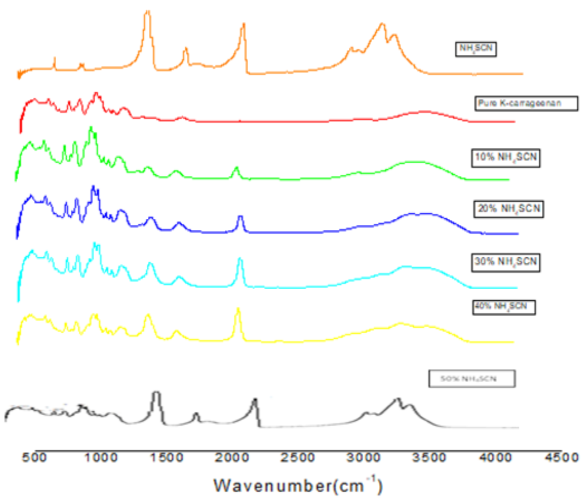


Fig. 4: FTIR spectra for varied wt. % NH_4SCN

Fig 4 depicts the FTIR spectra for the samples with various wt. % of NH_4SCN. At 1360 cm^{-1} wavenumber, the intensity increased as the wt. % of NH_4SCN increased. Meanwhile the peak at 1638 cm^{-1} in pure kappa-carrageenan slowly disappeared at 40 wt. % NH_4SCN after which the spectra is characterized by the peak attributed to NH_4SCN at 1600 cm^{-1} for 50 wt. % NH_4SCN.

4. Conclusion

The highest conductivity obtained at room temperature is 1.64E-03 S cm^{-1} for the sample with 40 wt. % NH_4SCN. FTIR studies showed complexation between kappa-carrageenan and NH_4SCN polymer electrolyte evidenced by the increase in intensity of the peak at 1360cm^{-1}.

Acknowledgement

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