

Conductivity Studies on K-Carrageenan-Methyl Cellulose Blend as Bio-Polymer Electrolyte

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ABSTRACT

Solid polymer-based electrolyte materials are a great interest due to their many interesting characteristics such as flexibility, and it is easily prepared into films with a large surface area. Two sets of k-carrageenan-methyl cellulose samples were prepared using the solution casting method. Set 1, the wt% of k-Carrageenan was fixed at 0.1 wt%, while methyl cellulose and NH₄I was varied. Set 2, the wt% of methyl-cellulose was fixed to 0.1 wt%, and the carrageenan and NH₄I were varied. The functional group of samples were studied using FTIR spectroscopy, and the ionic conductivity was studied using impedance spectroscopy, EIS at room temperature. FTIR spectra from set 1 show a small hump at between the 1500 cm⁻¹ to 1000 cm⁻¹ spectra's which O=S=O symmetrical vibration from methyl cellulose component. This hump was shifted to higher wavenumber due to the increasing of NH₄I wt% in the samples. The second region of set 2's spectra shows the wavenumber between 2000 cm⁻¹ to 1500 cm⁻¹ is the deformation of H-O-H band interactions and its wavenumber decreasing as the addition



of salts increasing. The third region of spectra between 1500 cm⁻¹ to 1000 cm⁻¹ represents the band of O=S=O symmetrical vibration. This bands shifted to the lower wavenumber due to addition of salts, and it became less intense towards salt addition. On the other hand, the best conductivity is 6.00 x 10⁻⁸ S cm⁻¹ which belongs to B2 of set 2 with the composition of 0.3 wt% k-carrageenan with 0.1 wt% methylcellulose and 0.6 wt% NH₄I salt and the lowest conductivity is 3.19 x 10⁻⁹ S cm⁻¹ which its composition is 0.1 wt% k-carrageenan with 0.4 wt% methylcellulose and 0.5 wt% NH₄I salt in sample D1 of set 1. In conclusion, the optimum component by weight percentage of k-carrageenan: methyl cellulose: NH₄I is 0.3:0.1:0.6.

Keywords: *K-Carrageenan, methyl cellulose, conductivity and biopolymer blend*

INTRODUCTION

Solid polymer-based electrolyte materials are a great interest due to their many interesting characteristics such as flexibility, and it is easily prepared into films with a large surface area. Even though many researchers had studied polymer electrolytes and most of their studies reported in the literature used petrochemical-based polymers, which are associated with environmental issues and high cost. The bio-based polymers could be applied as hosts to reduce the dependence of petrochemical-based polymer as electrolytes [1,2]. Solid Polymer Electrolyte (SPE) is also an emerging field as researchers are mainly studying the green and safe electrochemical power sources. Usually, it has a more amorphous region or low degree of crystallinity which supports higher ionic transport [3,4]. The bio-based polymers are also promising candidates that meet different requirements. However, a single biopolymer may not give a satisfactory result based on its mechanical and physical or chemical properties to meet a wide range of device applications. Incorporation with other natural bio-based polymer has shown interesting result such as good conductive properties. Carrageenan is a group of linear sulfate polysaccharides that are extracted from red edible seaweeds. Among all the known biopolymers, kappa-carrageenan (k-carrageenan) and cellulose are favorable since they are abundant in nature, renewable, biocompatible, and cost-effective. It is also a family of linear sulphated polysaccharides. K-carrageenan and cellulose can form

a cross-linking network with other components in polymer electrolytes ascribed to their hydroxyl group rich molecular structure. [1, 3].

Kappa-carrageenan is well-known for its characteristics, which are low-cost material, easy to purchase, nature-like material that can be renewable [9]. The original conductivity of kappa-carrageenan is low conductivity, but it can be chemically modified, and the ionic conductivity of kappa-carrageenan could be increased. Joy Wei Yi Liew *et al.* (2018) [10] found that K-Carrageenan without any modification at $2.79 \times 10^{-6} \text{ S cm}^{-1}$ increased when it acts as a filler in the chitosan polymer chain at $1.43 \times 10^{-5} \text{ S cm}^{-1}$. So as Mobarak *et al.* (2012) [11] found the carboxymethyl κ -carrageenan is more conductive compared to green k-carrageenan when the ionic conductivity increased from $5.3 \times 10^{-7} \text{ S cm}^{-1}$ to $2.0 \times 10^{-4} \text{ S cm}^{-1}$. The incorporation of K-Carrageenan with other salts also could increase their conductivity instead of increased their elastic modulus of biopolymer thin film. It was proven by Rudhziah *et al.* (2018) [12] which the conductivity of pure seaweed k-carrageenan increased from $6.28 \times 10^{-6} \text{ S cm}^{-1}$ to $1.41 \times 10^{-4} \text{ S cm}^{-1}$ when it was incorporated with NH_4NO_3 . On the other hand, solid polymer electrolyte (SPEs) composed of cellulose acetate (CA) doped with a different stoichiometric ratio of ammonium iodide (NH_4I) could increase their conductivity up to 10^{-4} S cm [13].

In this study, the potential K-Carrageenan and Carboxyl methyl cellulose serve as the mixed bio-polymer host. At the same time, ammonium iodate was added as solid polymer as doping salt was prepared by the solution cast technique. The experiment was done by two sets of samples when the first set, the K-Carrageenan was fixed their wt% while others were varied wt% and the second set, the methyl cellulose was fixed wt% while the other's was varied in their wt% to see the effect of their conductivity.

EXPERIMENTAL

Two sets of carrageenan-methyl cellulose samples were prepared using the solution casting method. Set 1, the wt% of K-Carrageenan was fixed at 0.1 wt%, while the wt% of methyl cellulose and NH_4I was varied. While set 2, the wt% of methyl-cellulose was fixed to 0.1 wt%, and the wt% of k-carrageenan and NH_4I was varied, as shown in Table 1 and Table 2.

Table 1: The Composition of the Sample by Fixed wt% of K-carrageenan

Sample	K-carrageenan (wt.%)	Methyl-cellulose (wt. %)	NH4I (wt.%)
A1	0.1	0.1	0.8
B1	0.1	0.2	0.7
C1	0.1	0.3	0.6
D1	0.1	0.4	0.5

Table 2: The Composition of the Sample by Fixed wt% of Methyl-cellulose

Sample	K-carrageenan (wt.%)	Methyl-cellulose (wt. %)	NH4I (wt.%)
A2	0.4	0.1	0.5
B3	0.3	0.1	0.6
C4	0.2	0.1	0.7
D5	0.1	0.1	0.8

The dried thin film of the sample underwent the Fourier transforms infrared spectroscopy, FTIR and electrochemical impedance spectroscopy, EIS. The characterisation was carried out in room temperature

RESULT AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1 shows the spectra of set 1 and set 2. The spectra from set 1 shows the spectra of 0.1 wt% carrageenan with different wt% of methylcellulose and NH₄I. The spectra between 4000 cm⁻¹ to 3000 cm⁻¹ shows the OH stretching mode. This spectra of OH shifted to the higher wavenumber of the samples from sample D1 to A1 when wt% of NH₄I increased. A small hump appeared between the 2000 cm⁻¹ to 1500 cm⁻¹ spectra's shows the band of COO⁻ asymmetrical from carboxylate anion. The other hump also appeared at between the 1500 cm⁻¹ to 1000 cm⁻¹ spectra's shows the O=S=O symmetrical vibration which comes from methyl cellulose component. This hump was shifted to higher wavenumber

due to the increasing of NH_4I wt% in the samples. However, the spectra's intensity towards salts increases, which could become from the interactions between NH_4^+ ions to H^+ ions or with oxygen atoms of k-carrageenan and methylcellulose.

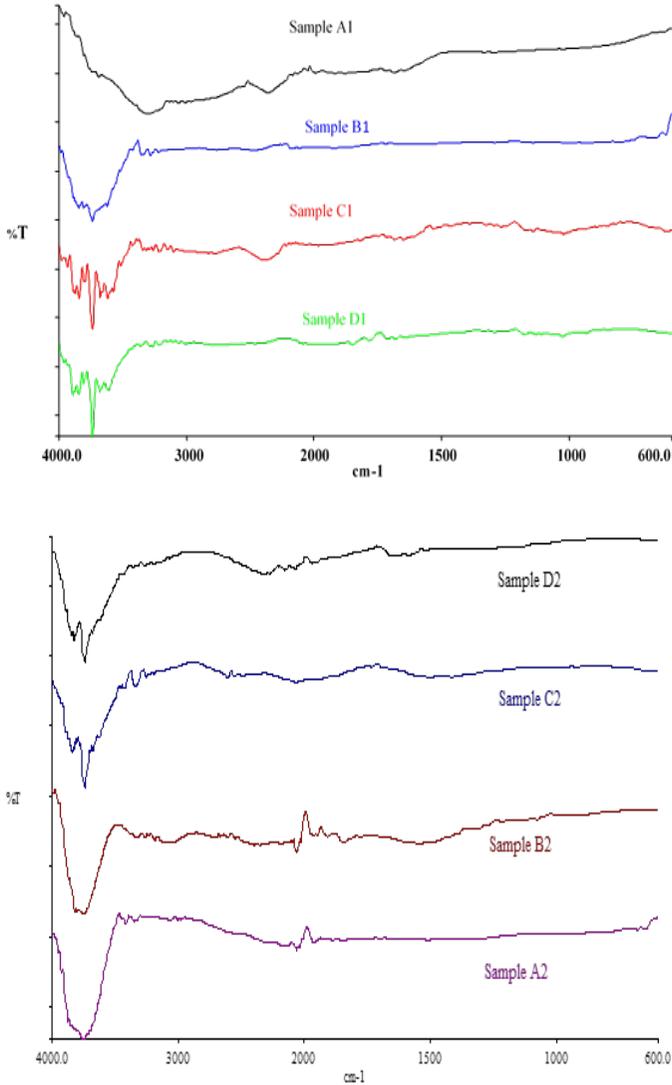


Figure1: FTIR Spectra of k-Carrageenan – Methyl Cellulose Blend in Sample Set 1 and Set 2

The spectra from set 2 show wavenumber between 3000 cm^{-1} to 2000 cm^{-1} represent the OH stretching. It is shifted to the higher wavenumber of spectra from the top to the bottom when NH_4I salt is added increasingly. The second region of spectra between wavenumber of 2000 cm^{-1} to 1500 cm^{-1} shows the deformation of H-O-H band interactions and its wavenumber decreasing as the addition of salts increasing. The third region of spectra between wavenumber of 1500 cm^{-1} to 1000 cm^{-1} represents the band of O=S=O symmetrical vibration. These bands shifted to the lower wavenumber due to the addition of salts, and it became less intense towards salt addition. This band show the H^+ ions from NH_4I salts interacts with k-carrageenan. The composition of salts higher will give more H^+ ions to withdraw towards O=S=O that will form hydrogen bonding [5,6].

Based on those two sets of spectra, it shows how the biopolymer with different composition react with salts when it is added accordingly. Set 1 in figure 1, the methylcellulose molecules interact greater towards salt than k-carrageenan due to its composition is only 0.1 wt%. This is support from previous research where the methyl cellulose is used in the study containing different concentrations of salts that are observed at the spectra regions 600 cm^{-1} to 4000 cm^{-1} . The NH was stretching and bending of NH_4I that occurs at the presence of 3077 , 1602 , and 1376 cm^{-1} , respectively [1,5,6]. The methyl cellulose1 blend bands, which are 1582 , 1408 , 1321 , and 1225 cm^{-1} show the higher shifted wavenumber and became low intense towards salts addition, respectively [1,2]. However, set 2 of samples, the k-carrageenan is varied in wt% and increased towards NH_4I salt. At the same time, the wt% of methylcellulose in the blend is fixed to 0.1 wt%, which makes it less reactive to salts. Based on previous research done by Zainuddin and Samsudin (2018) [3], it is clear that there is an excellent contribution of positions interaction of H^+ to the O=S=O between k-carrageenan and NH_4Br [3,6,7].

Electrochemical Impedance Spectroscopy. (EIS)

The EIS characterisation was measured in room temperature of the k-carrageenan-methylcellulose- NH_4I thin film. The graphs are plotted to form a semicircle where the line of the semicircle will intercept the x-axis [7,8]. The x-axis represents the bulk resistant, R_b . The conductivity, for each sample, was calculated using equation 1;

$$\sigma = t / R_b A \dots\dots\dots \text{Equation 1}$$

Where σ is the conductivity, t is the thickness of the film, and A is the area of the film.

Table 3: The Conductivity for Set 1 and Set 2 Carrageenan-Methyl Cellulose

Sample Set 1	Conductivity (σ), Scm ⁻¹	Sample Set 2	Conductivity (σ), Scm ⁻¹
A1	1.91 x 10 ⁻⁸	A2	1.13 x 10 ⁻⁸
B1	4.63 x 10 ⁻⁸	B2	6.00 x 10 ⁻⁸
C1	1.23 x 10 ⁻⁸	C2	7.21 x 10 ⁻⁹
D1	3.19 x 10 ⁻⁹	D2	1.91 x 10 ⁻⁸

The sample D1 and C2 show the lowest conductivity value at 3.19 x 10⁻⁹ S cm⁻¹ and 7.21 x 10⁻⁹ S cm⁻¹, respectively. At the same time, the highest conductivity is sample B1 and B2, where their conductivities are 4.63 x 10⁻⁸ S cm⁻¹ and 6.00 x 10⁻⁸ S cm⁻¹. Both set are experience in varied wt% of NH₄I as a proton donor. However, in set1, wt% of K-Carrageen was fixed; this means that the ionic mobility occurs between methylcellulose and NH₄I. On the other hand, for set2, wt% of methyl cellulose was fixed, and ionic mobility happened between K-Carrageen and NH₄I. The increase of salts could increase the conductivity due to the mobility of ions charged carriers [7]. It happens that sample B2 shows higher conductivity compared to B1. This means that the methylcellulose acts as a suitable host polymer for proton conduction compared to K-Carrageenan.

However, for both set, if the concentrations of salts are significantly increased, the conductivity decrease due to aggregation of ions. The composition of salts must be balanced to the composition of polymer to prepare the host polymer act as a proton conduction medium. This result is paralleled to Rudhzhiah *et al.* (2015) [12], when the biopolymer films containing more than 30 wt% of salts will becoming unstable, and impedance measurement could not be measured.

CONCLUSION

The FTIR analysis successfully identified the functional group, which contributed to the carrageenan-methyl cellulose blend, is the O=S=O, and the H⁺ ions are making a hydrogen bond. It can be seen when the peak of the spectra was shifted and become broaden in both samples, set 1 and set 2. As for the EIS results, the ionic conductivity shows that the increase of salts could increase the conductivity but the further addition of salt, which is more than 30 wt%, it will be coming to mechanically unstable. The optimum composition for the highest conductivity belongs to B2, which is $6.00 \times 10^{-8} \text{ S cm}^{-1}$ with a composition of 0.3 wt% k-carrageenan with 0.1 wt% methylcellulose and 0.6 wt% NH₄I salt. These will conclude that the optimization by weight percentage of Carrageenan: methyl cellulose: NH₄I is 0.3:0.1:0.6.

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