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Solid Biopolymer Electrolyte Based on κ-Carrageenan for Electrochemical Devices Application

I.J. SHAMSUDIN[1,2], A. AHMAD[1,*], N.H. HASSAN[1] and H. KADDAMI[3]

[1]School of Chemical Sciences and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia
[2]Department of Chemistry, Centre for Defence Foundation Studies, National Defence University of Malaysia, 57000 Kuala Lumpur, Malaysia
[3]Department of Chemistry, Faculty of Sciences and Technology of Marrakech, Cadi Ayyad University, Av. A. Elkhattabi, B.P. 549, Marrakech 40000, Morocco

*Corresponding author: Fax: +60 3 89212115; Tel: +60 3 89287262; E-mail: azizan@ukm.edu.my

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Solid biopolymer electrolyte based on kappa, κ-carrageenan as the polymer host and ionic liquid 1-butyl-3-methylimidazolium chloride, [Bmim]Cl as the charge carrier has been successfully prepared. The ionic conductivity, (σ) of the electrolytes significantly increase with the increase of weight percentage, (wt. %) of [Bmim]Cl. The highest σ attained is 2.44×10^{-3} S cm^{-1} at ambient temperature. FTIR spectra confirmed the complexation and interactions of κ-carrageenan and [Bmim]Cl. XRD diffractograms revealed that inclusion of [Bmim]Cl has increased the amorphous nature of κ-carrageenan. SEM observations showed the smoother surface morphologies of the polymer electrolytes as the wt. % of [Bmim]Cl increases.

Keywords: κ-Carrageenan, Ionic liquid, 1-Butyl-3-methylimidazolium chloride, Biopolymer electrolytes, Ionic conductivity.

INTRODUCTION

Nowadays, the development of solid polymer electrolytes based on biopolymers has attracted lots of attention and investigations as biopolymers are abundantly available, biodegradable, non-toxic, renewable and cost effective. Carrageenan is natural polymer consist of linear-sulfated polysaccharides of D-galactose and 3,6-anhydro-D-galactose extracted from red algae[1]. There are three types of carrageenan with different position and number of ester sulfate group known as kappa, iota and lambda. Kappa, κ-carrageenan is one of the most generally known and commercially explored members of that polysaccharide family. Chemical structure of κ-carrageenan is shown in Fig. 1.

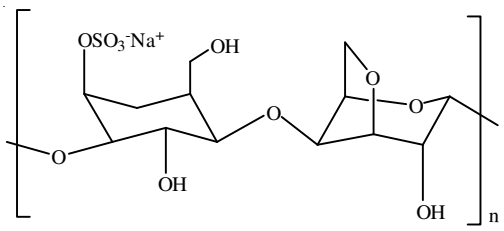

Fig. 1. Chemical structure of κ-carrageenan

Numerous researches on carrageenan have been reported in commercial applications such as agent in thickening and gelling in food and non food industries, cosmetic and pharmaceutical applications[2,3] and also hydrogel or wound healing[4,5]. More advanced technological applications of carrageenan have also been explored. Carrageenan have been used as a main material in biodegradable packaging films[6], electrical double layer capacitor[7] (EDLC), electrosynthesis process[8] dye-sensitized solar cell systems[9,10] and direct methanol fuel cell (DMFC) application[11].

Previous studies of carrageenan as the polymer host in electrolyte systems mainly use various kind of salts and platicizers in order to increase the ionic conductivity[7,9,11]. However, the usage of ionic liquid as a charge carrier in the carrageenan electrolyte system is still unexplored. Ionic liquid has lots of interesting and unique properties such as high ionic conductivity, low melting point (typically below 100 °C), high thermal stability, moderate viscosity and good stability to redox conditions[12]. In addition, the negligible volatility and flame retardant properties of ionic liquid are the important factors in enhancing the safety features of electrolytes.

Due to the fascinating features of ionic liquid, 1-butyl-3-methylimidazolium chloride, [Bmim]Cl is introduced as the

charge carrier in this system. [Bmim]Cl was reported compatible with many polysaccharides and commonly used as a dissolution media[13,14]. Hence, apart from acts as a charge carrier, [Bmim]Cl plays an important role as a co-solvent in this system and thus the problem of salt crystallization in many solid polymer electrolytes can be avoided. Chemical structure of [Bmim]Cl is shown in Fig. 2.

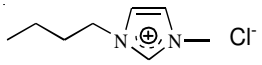

Fig. 2. Chemical structure of 1-butyl-3-methylimidazolium chloride, [Bmim]Cl

In this study, solid polymer electrolytes with κ-carrageenan as the polymer host and [Bmim]Cl served as the charge carrier is prepared and characterized. To the best of our knowledge, the study of conductive κ-carrageenan with ionic liquid, particularly 1-butyl-3-methylimidazolium chloride, [Bmim]Cl has never been reported before.

EXPERIMENTAL

κ-Carrageenan was commercially obtained from Tacara. Ionic liquid, 1-butyl-3-methylimidazolium chloride and acetic acid was purchased from Sigma-Aldrich. All materials were used without further purification.

Preparation of membrane: κ-Carrageenan was dissolved in 1 % solution of acetic acid and stirred overnight in order to obtain complete dissolution of κ-carrageenan. Various wt. % of [Bmim]Cl was then added to the dissolved κ-carrageenan solution under nitrogen gas. The mixed solution was further stirred for 2 h at 80 ºC. After complete dissolution, the solution was poured into a Teflon petri dish and left to dry for several days. The resulting membrane were then peeled and stored in desiccator to prevent any moisture contact.

Sample characterization: The measurement of the bulk resistance (R_b) of the sample was carried out by using electrical impedance spectroscopy (EIS) model HIOKI 3522 LCR Hi-Tester with the frequency range between 50 Hz to 1 Mhz. The sample was sandwiched between the blocking stainless steel under spring pressure with a contact area of 5.13 cm^2. The conductivity value, (σ) of electrolyte have been calculated from the equation $\sigma = tR_b^{-1}A^{-1}$, where t is the thickness of the sample and A is the contact area. Complex impedance plot was used to calculate the R_b. ATR-FTIR analysis was performed using Perkin-Elmer Spectrum 2000 in the range of 4000-650 cm^{-1}. The scanning resolution is 4 cm^{-1}. The analysis was carried out to observe any shifting of the peaks due to the chemical interactions of κ-carrageenan with the charge carriers. X-ray diffraction measurements were performed using model D5000 Siemens. The data were collected from range of diffraction angle 2θ from 3° to 60° at the rate 0.05° s^{-1} to determine whether the sample is crystalline, semi-crystalline or amorphous. Investigation on the morphologies of the polymer electrolytes were examined by FESEM Supra 55VP model at 1,000 magnifications.

RESULTS AND DISCUSSION

The conductivity of a material can be investigated by using electrical impedance spectroscopy (EIS) technique. Fig. 3

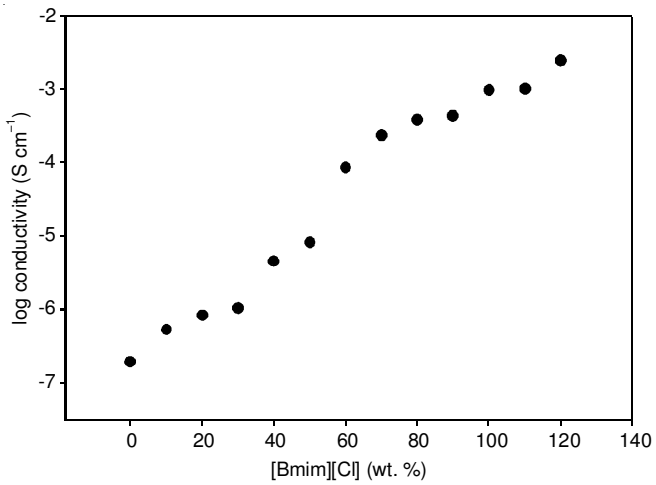

Fig. 3. log Conductivity, σ of κ-carrageenan as a function of [Bmim]Cl wt. %

depicts log conductivity, σ of κ-carrageenan *versus* [Bmim]Cl weight percentage, (wt. %) measured at ambient temperature. It is observed that the σ increases significantly as the wt. % of [Bmim]Cl increases. This might be due to the increase numbers of mobile charge carrier, [Bmim]Cl. The highest σ achieved is 2.44×10^{-3} Scm^{-1} at 120 wt. % of [Bmim]Cl. The increment of four orders of magnitude in the σ compared to the σ of pure carrageenan, where the σ was only 1.95×10^{-7} S cm^{-1}, showed that ionic liquid [Bmim][Cl] plays a significant role as a charge carriers in this system. The continuous increase in the conductivity value as the wt. % of [Bmim]Cl increases suggesting that [Bmim]Cl also plays as co-solvent in this system and this might be the reason that there is no sign of any reduction in the conductivity value.

Fig. 4 represents the ATR-FTIR spectra of pure κ-carrageenan film and κ-carrageenan with various wt. % of [Bmim]Cl in the wavenumber region (i) 1300-700 cm^{-1}, (ii) 4000-3000 cm^{-1} and (iii) 1800-1300 cm^{-1}. In Fig. 4(i), κ-carrageenan shows strong absorption bands in region 1226-1223 cm^{-1} belong to the S=O stretching of sulfate esters. Another band at 922 cm^{-1} is due to the C-O stretching of 3,6-anhydro-D-galactose and at 843 cm^{-1} attributed to the C-O-SO_3 of D-galactose-4 sulfate[15,16].

Fig. 4(ii) shows the broadening of the hydroxyl bands, O-H due to the protonation of the O-H by acetic acid, CH_3COOH during the dissolving process of κ-carrageenan. This is proven by the shift of the O-H band towards lower wavenumber[17]. New peak formation with the loading of 40 wt. % [Bmim]Cl and above has also been observed at 3151 cm^{-1} probably due to sp^2=C-H stretching in imidazolium, $[Bmim]^+$ ring[18], thus implying that complexation has occurred between the polymer matrix, κ-carrageenan and the charge carrier, [Bmim]Cl.

As can be seen in Fig. 4(iii), with the incorporation of [Bmim]Cl, several shifts of characteristic bands have been observed. The asymmetric and symmetric stretching of the carbonyl, C=O in the acetic acid are shifted to higher wavenumbers. Asymmetric C=O stretching has shifted from 1561 cm^{-1} in the pure κ-carrageenan film to 1572 cm^{-1}. An increase in the intensity is also been observed in this band with the higher amount of [Bmim]Cl which probably due to

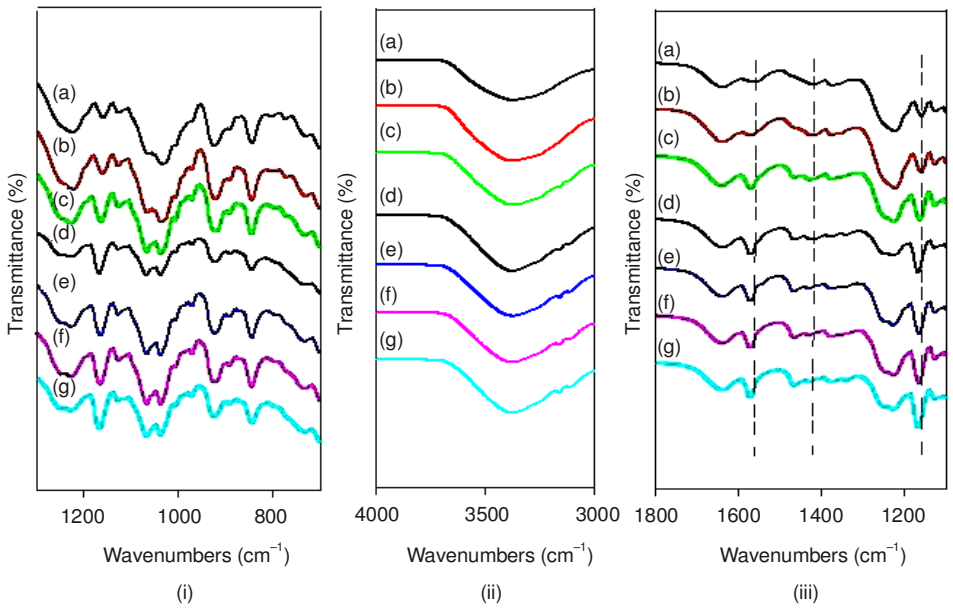

Fig. 4. ATR-FTIR spectra of (a) pure κ-carrageenan film and κ-carrageenan with (b) 20 wt. %, (c) 40 wt. % (d) 60 wt. %, (e) 80 wt. %, (f) 100 wt. % and (g) 120 wt. % [Bmim]Cl in the wavenumber region (i) 1300-700 cm^{-1}, (ii) 4000-3000 cm^{-1} and (iii) 1800-1300 cm^{-1}

the C=C stretching of the imidazolium ring[19]. The symmetric C=O band has shifted about 8 cm^{-1} of wavenumbers to 1428 cm^{-1}. Bridge C-O stretching of κ-carrageenan has also shifted to higher wavenumbers from 1157 to 1165 cm^{-1}. It is also noted that this peak tend to intensify as the wt. % of [Bmim]Cl increases. Thus, the shifts and the changes of all the characteristic bands suggest the strong interaction of the polymer matrix with ionic liquid, [Bmim]Cl. Table-1 listed the shifts and assignments of bands in κ-carrageenan/[Bmim]Cl biopolymer electrolytes.

TABLE-1
SHIFTS/CHANGES AND ASSIGNMENTS OF BANDS IN κ-CARRAGEENAN/[Bmim]Cl BIOPOLYMER ELECTROLYTES

[Bmim]Cl wt. %	Assignment of bands (cm^{-1})			
	OH stretching	Asymmetric C=O stretching	Symmetric C=O stretching	C-O stretching
0	3373	1561	1420	1157
20	3370	1573	1421	1158
40	3361	1567	1427	1162
60	3368	1567	1427	1162
80	3368	1573	1428	1163
100	3370	1572	1428	1163
120	3370	1572	1428	1165

XRD analysis has been performed in order to study the solid-state structural information of the polymer matrix, κ-carrageenan and κ-carrageenan with [Bmim]Cl films. Fig. 5 shows the XRD diffractograms of pure κ-carrageenan film and κ-carrageenan with various loading of ionic liquid, [Bmim]Cl. It is noted that the nature of the pure κ-carrageenan is amorphous, which is similar to the previous reported studies[6,20] with a broad hump at 2θ = 22.5º. As more [Bmim][Cl] is added to the polymer, the broad hump seems to be diminished and has been totally disappeared at the highest addition of [Bmim]Cl, 120 wt. %, signifying the prominent amorphousness of the

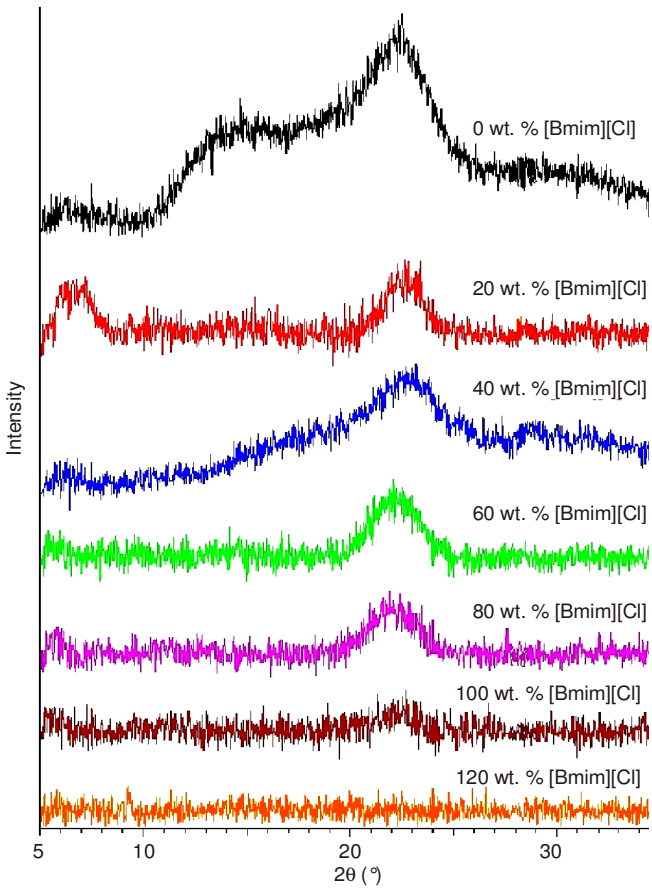

Fig. 5. XRD diffractograms of κ-carrageenan with various wt. % of [Bmim]Cl

κ-carrageenan-[Bmim]Cl films. Thus, this is a sign that the addi-tion of [Bmim]Cl has increases the amorphous phase of κ-carrageenan.

The increase in the amorphous phase in the polymer matrix of κ-carrageenan-[Bmim]Cl films with the inclusion of [Bmim]Cl is important in the ionic conduction system. As the free volume of the polymer is increased the polymer

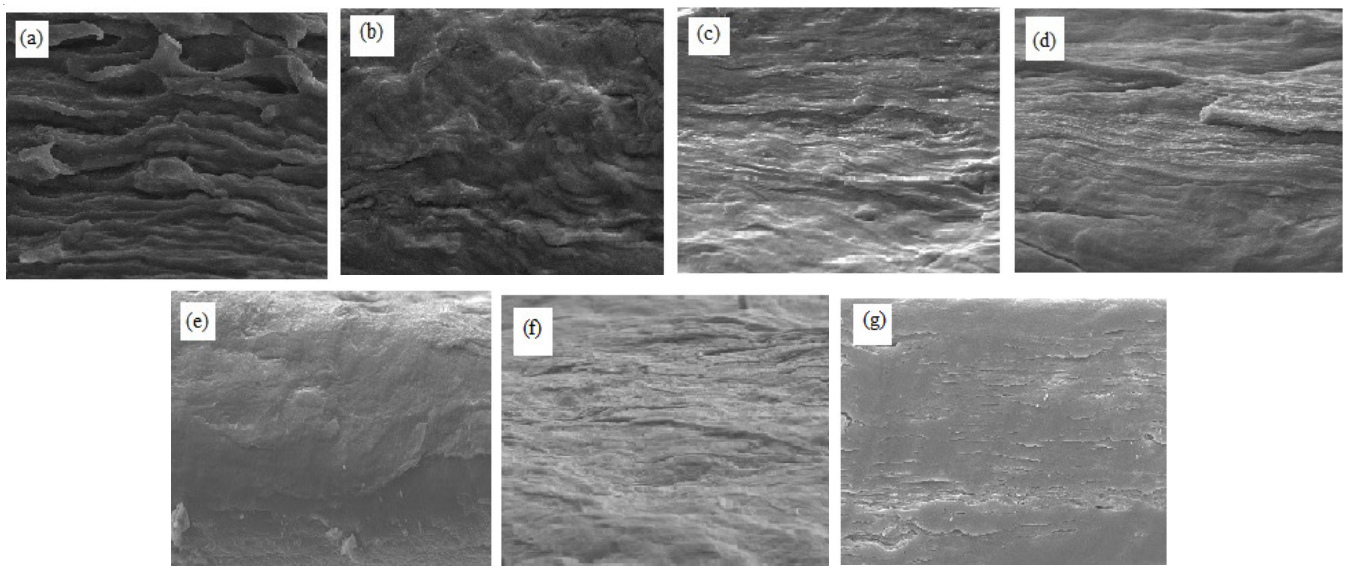

Fig. 6. SEM micrographs of (a) pure κ-carrageenan film and κ-carrageenan with [Bmim]Cl (b) 20 wt. %, (c) 40 wt. % (d) 60 wt. %, (e) 80 wt. %, (f) 100 wt. % and and (g) 120 wt. %

chain become more flexible. Thus, as the flexibility increases, the mobility of the charge carriers are more favorable and thus increase the ionic conductivity of the system. This explained the increasing trend of ionic conductivity as the wt. % of [Bmim]Cl increases.

Fig. 6a represents the SEM micrographs of pure κ-carrageenan film while Fig. 6b-g shows the micrographs of κ-carrageenan with 20 wt. %, 40 wt. %, 60 wt. %, 80 wt. % and 120 wt. % [Bmim]Cl. As can be seen, there is no presence of [Bmim]Cl agglomeration and any phase separation observed suggesting that the polymer and ionic liquid are homogeneous and compatible with each other. The morphology of the pure κ-carrageenan film shows layered and potholed structure. On the other hand, with the inclusion of ionic liquid [Bmim]Cl, the morphology tend to be smoother as the amount of [Bmim]Cl increases. This suggests strong interaction between κ-carrageenan with [Bmim]Cl. The smoother morphologies as the wt. % of [Bmim]Cl increases signifying the enhancement of amorphous phase in the polymer matrix[21] and thus supported the XRD data and explained the increasing trend of ionic conductivity as the wt. % of [Bmim]Cl increases.

Conclusion

Solid bioplymer electrolytes based on κ-carrageenan and ionic liquid [Bmim]Cl exhibits the highest ionic conductivity, 2.44×10^{-3} Scm^{-1} at ambient temperature and thus shows potential as an electrolyte in electrochemical devices.

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