

Incorporating 1-butyl-3-methylimidazolium Chloride Ionic Liquid into Iota Carrageenan Solid Biopolymer Electrolyte for Electrochemical Devices Application (Pencampuran Cecair Ionik 1-butyl-3-metilimidazolium Klorida ke dalam Elektrolit Biopolimer Pepejal Iota Karagenan bagi Aplikasi Peranti Elektrokimia)

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ABSTRACT

Solid biopolymer electrolyte based on iota carrageenan and 1-butyl-3-methylimidazolium chloride, [Bmim]Cl were successfully prepared by solution casting technique. Weight percentage (wt. %) of [Bmim]Cl was varied from 0 wt. % to 100 wt. % and the highest ionic conductivity achieved was $2.70 \times 10^{-3} \text{ S cm}^{-1}$ for 70 wt. % [Bmim]Cl at ambient temperature. The interaction between iota carrageenan and [Bmim]Cl was confirmed by the formation of new peak on the ATR-FTIR spectrum. The reduction in crystallinity of iota carrageenan as the inclusion of [Bmim]Cl was observed based on X-ray diffraction (XRD) spectroscopy. FESEM morphology showed the compatibility and homogeneity between iota carrageenan and [Bmim]Cl while the LSV analysis showed that solid biopolymer electrolyte-based iota carrageenan-[Bmim]Cl possess high electrochemical stability up to 3.0 V. The transference number (TN) analysis indicated that ions are the main contributor for the ionic conduction.

Keywords: Iota carrageenan; ionic conductivity; ionic liquid; solid polymer electrolyte

ABSTRAK

Elektrolit biopolimer pepejal berasaskan iota karagenan dan 1-butyl-3-metilimidazolium klorida, [Bmim]Cl berjaya dihasilkan melalui teknik pengacuan larutan. Peratus berat (% bt.) [Bmim]Cl divariasikan daripada 0 % bt. sehingga 100 % bt. dan kekonduksian ionik tertinggi adalah $2.70 \times 10^{-3} \text{ S cm}^{-1}$ bagi 70 % bt. [Bmim]Cl pada suhu ambien. Interaksi antara iota karagenan dan [Bmim]Cl disahkan dengan pembentukan puncak baru pada spektrum ATR-FTIR. Pengurangan dalam penghabluran karagenan apabila [Bmim]Cl dimasukkan diperhatikan berdasarkan spektroskopi belauan sinar-X (XRD). Morfologi FESEM memperlihatkan keserasian dan kehomogenan antara iota karagenan dengan [Bmim]Cl manakala analisis LSV menunjukkan bahawa elektrolit biopolimer pepejal berasaskan iota karagenan-[Bmim]Cl mempunyai kestabilan elektrokimia yang tinggi sehingga 3.0V. Analisis nombor pemindahan (TN) membuktikan bahawa ion adalah penyumbang utama bagi pengkonduksian ionik.

Kata kunci: Cecair ionik; elektrolit biopolimer pepejal; iota karagenan; konduksian ionik

INTRODUCTION

Biopolymers offer renewable, abundant, biodegradable and non-hazardous properties compared to synthetic polymers (Mobarak et al. 2015; Shamsudin et al. 2015a, 2015b). Previous studies showed that biopolymer had the potential to be used in various applications such as drug delivery, water treatment and filler. Biopolymer also has the ability to function as a polymer host for solid polymer electrolyte application (Agrawal & Pandey 2008; Ng & Mohamad 2006; Osman & Arof 2003; Tanner et al. 2002).

Carrageenan, which is extracted from red seaweed (Rhodophyceae) is a family of anionic polymers that share a common backbone of alternating (1 → 3)-linked β-D-galactopyranose and (1 → 4)-linked α-D-galactopyranose. There are three primary types of carrageenan: *kappa* (possesses one sulphate per disaccharide), *iota* (two sulphates per disaccharide) and

lambda (three sulphates per disaccharide) (Borderias et al. 2005; Campo et al. 2009; Moniha et al. 2018). Normally, carrageenan has been used widely in food, pharmaceutical, and cosmetic industry as gelling agents, stabilizer and viscosity builder (Borderias et al. 2005; Coggins et al. 2000; Mobarak et al. 2015; Paula et al. 2015). Recent studies showed that carrageenan has potential to be used as host polymer as it managed to achieve ionic conductivity in the range of 10^{-8} - $10^{-6} \text{ S cm}^{-1}$ depends on types of carrageenan.

However, the minimum requirement of ionic conductivity for the electrolyte in order to be fabricated into electrochemical devices is in the range of $\times 10^{-3} \text{ S cm}^{-1}$. In a study reported by Jumaah et al. (2014), the ionic conductivity of *iota* carrageenan was only $2.19 \times 10^{-8} \text{ S cm}^{-1}$ (Jumaah et al. 2014, 2013). On the other hand, in our previous studies on a purified *iota* carrageenan, the ionic

conductivity was found to be $1.57 \times 10^{-5} \text{ S cm}^{-1}$ (Ghani et al. 2018). Guided by these results, imidazolium ionic liquid has been chosen to be added into a purified iota carrageenan. It is expected that the ionic conductivity will increase and electrochemical stability of iota carrageenan will be enhanced as ionic liquids can act as a carrier and plasticizer in the system. Ionic liquid is also known due to its negligible vapour pressure and low flammability that enhanced the safety features. Besides that, ionic liquids also possess a wide electrochemical window in the range of 2.0 to 5.0 V which is applicable to the electrochemical device application (Anderson et al. 2006; Armand et al. 2009; Liu et al. 2011; Sun & Armstrong 2010).

1-Butyl-3-methylimidazolium chloride, [Bmim]Cl was chosen because of its compatibility and ability to dissolve biopolymer (Bester-Rogac et al. 2011; Liu et al. 2011). The high ionic conductivity value (Bester-Rogac et al. 2011; Vila et al. 2007) of [Bmim]Cl plays an important role as a charge carrier in the system. Besides that, Shamsudin et al. (2015a) also reported that the addition of [Bmim]Cl into carboxymethyl κ carrageenan-based polymer electrolyte had achieved the highest ionic conductivity value of $5.76 \times 10^{-3} \text{ S cm}^{-1}$ at 30 wt. % of [Bmim]Cl. They reported that [Bmim]Cl does not only act as charge carriers but also as a plasticizer with the development of amorphous phase (Liew et al. 2014; Shamsudin et al. 2015a). Meanwhile, the electrochemical stability for [Bmim]Cl was up to 2.5 V as reported by Giridhar et al. (2007) and Jayakumar et al. (2007). They concluded that the utilization of [Bmim]Cl into the polymer electrolyte system not only had improved the ionic conductivity and amorphous phase of the electrolyte but also the electrochemical stability of the polymer electrolyte. Therefore, this study will discuss the effects of ionic liquid [Bmim]Cl on physical, chemical and electrochemical properties of iota carrageenan (Liew et al. 2014).

MATERIALS AND METHODS

CHEMICALS AND MATERIALS

Ionic liquid 1-butyl-3 methyl imidazolium chloride and acetic acid were purchased from Merck (Kenilworth, NJ, USA) and Sigma Aldrich (St. Louis, MO, USA). Iota carrageenan was purified prior to use. Other chemicals listed were used without further purification.

PREPARATION OF FILM

The purified iota carrageenan powder was dissolved in 1% solution of acetic acid and stirred overnight in order to ensure a complete dissolution of iota carrageenan (Mobarak et al. 2012). [Bmim]Cl was added to the solution of iota carrageenan at weight percentages (wt. %) of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 under the nitrogen gas. The mixtures of purified iota carrageenan-[Bmim]Cl were stirred for 24 h at 40°C. After that, each solution was poured into a Teflon petri dish and left to dry at room temperature

for several days to allow complete evaporation of the solvent. The films formed were peeled and stored in a vacuum desiccator with silica gel desiccant for the further drying process.

SAMPLE CHARACTERIZATION

The ATR-FTIR analysis was performed using Perkin-Elmer Spectrum 2000 in the range 4000-650 cm^{-1} . The analysis was carried out in order to investigate any shifting of the peak arising from the chemical interactions between iota carrageenan and [Bmim]Cl. The alternating current (AC) impedance measurements were conducted by using a high-frequency response analyser (HFRA) model Solartron 1260 Schlumberger in the frequency range of 1 Hz to 10 MHz at room temperature. The polymer electrolytes were sandwiched between the stainless steel blocking electrodes with a contact surface area of 2.0 cm^2 . The bulk resistance, R_b was analysed from the equivalent circuit analysis by using the Zview analyser software. The conductivity value (σ) of the polymer electrolytes was calculated using equation (σ) = $t/R_b A$, where t is the thickness of the film sample ranged between 0.03 and 0.08 cm and A is the contact area. The X-ray diffraction (XRD) was performed using model D5000 Siemens. Data were collected ranging from 2θ from 3° to 60° at rate 0.05° s^{-1} to determine the level of amorphous properties of complexes. Investigation on the morphologies of the polymer electrolyte was examined using the FESEM Supra 55VP model at 10000 magnifications. The electrochemical stability window of the polymer electrolyte system was determined by applying the linear sweep voltammetry (LSV) technique in which the sample was placed between two stainless steel blocking electrodes using 1 mVs^{-1} scan rate from 0 to 5 V. The DC polarization method was used to measure the transference number (TN) of polymer electrolyte system in order to determine the main conducting element in the system. A fixed 1.0 V dc current was applied across the sample sandwiched between two stainless steels. The Wagner's polarization technique was applied to calculate the ion transference number, t_{ion} value from the current versus time plot by using equation $t_{ion} = (I_i - I_{ss})/I_i$ where I_i and I_{ss} are the initial and steady-state current, respectively.

RESULTS AND DISCUSSION

INTERACTION STUDY

The ATR-FTIR spectroscopy was utilized to investigate the interactions that occurred between the ionic liquid, [Bmim]Cl and polymer host, iota carrageenan. Figure 1 represents the infrared spectrum of the ionic liquid, iota carrageenan and iota carrageenan with different weight percentages of ionic liquid, [Bmim]Cl. We will focus on three different band regions between (a) 4000-2600 cm^{-1} , (b) 1600-1300 cm^{-1} and (c) 1300-700 cm^{-1} that represent hydroxyl, carbonyl and ether groups as the interaction that was expected to occur between imidazolium cation and oxygen

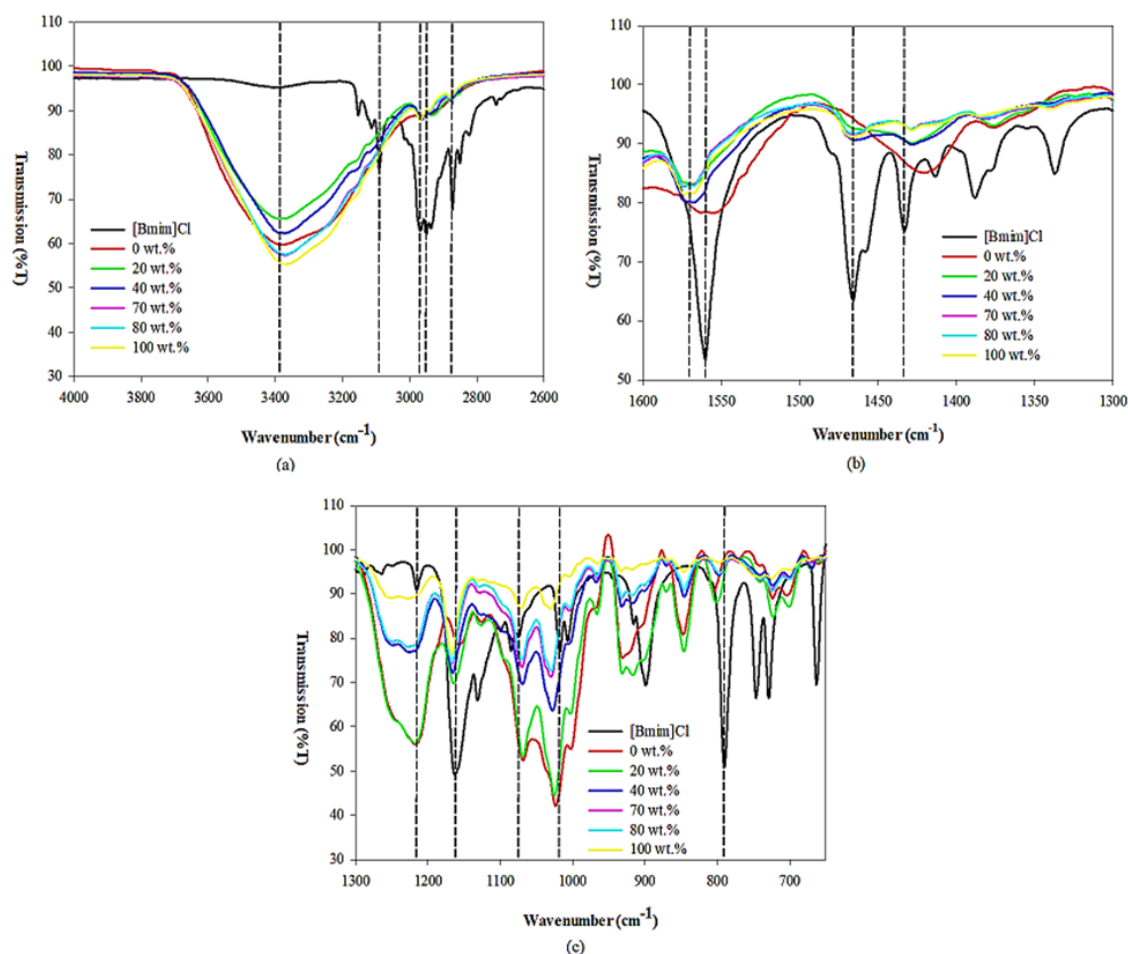


FIGURE 1. FTIR spectra of [Bmim]Cl and iota carrageenan at different weight percentage of [Bmim]Cl

atoms. Based on Figure 1(a)-1(c)), there are four new peaks that can be observed when [Bmim]Cl was added into iota carrageenan. These new peaks represent C-H stretching for cyclic [Bmim]⁺ at 3152 cm⁻¹, C-H stretching of the methyl group of alkyl chain at 2967 cm⁻¹, 2958 cm⁻¹ and 2876 cm⁻¹, symmetric and asymmetric stretching of CH₃ at 1464 cm⁻¹ and 1430 cm⁻¹ and CH₃-N stretching mode of [Bmim]⁺ at 1162 cm⁻¹. Meanwhile, some of the characteristic bands of iota carrageenan experienced few changes in terms of wavenumber and intensity.

Based on the previous studies, the O-H group in the iota carrageenan structure go through protonation as 1% acetic acid solution had been used as a solvent (Jumaah et al. 2014). The disappearance of C-Cl stretching mode of [Bmim]Cl at 791 cm⁻¹ on Figure 1(c) (Liew et al. 2014) can be observed. This phenomenon indicates the chloride dissociation from [Bmim]Cl and further interaction with OH₂⁺ as chloride ion, Cl⁻ has the ability to form an ionic bond with OH₂⁺ (Claudio et al. 2014; Shamsudin et al. 2015a). The protonated OH and basic Cl⁻ anion will exhibit electrostatic attraction that eventually pulls away the hydrogen from the centre atom (Shamsudin et al. 2015a). This resulted in the shifting of the O-H stretch towards lower wavenumber for about 9 cm⁻¹ because less energy is required to vibrate the particular bond (Shamsudin et al.

2015a). As the concentration of [Bmim]Cl was increased, the peaks that represented the O-H group became more intense. These changes proved that there were interactions between the hydrogen of the hydroxyl group with chloride ions.

Meanwhile, the imidazolium cation, [Bmim]⁺ which has the ability to donate hydrogen will form a coordination interaction with C-O-H, C-O-C and O-SO₃⁻. Basically, hydrogen at the C2 position of [Bmim]⁺ has the most acidic hydrogen (H2) (Avent et al. 1994), therefore, possesses a high tendency to donate hydrogen to form a hydrogen bond with the C-O-H, C-O-C and O-SO₃⁻ groups. This interaction had caused the sharp peak of CH₃-N stretching shifted from 1163 cm⁻¹ to 1167 cm⁻¹ with reduced peak intensity as shown in Figure 1(c) (Liew et al. 2014).

Besides that, the peaks at 1070 cm⁻¹, 1024 cm⁻¹ and 1215 cm⁻¹ which belong to C-O-H, C-O-C and a symmetric stretch of O=S=O had shifted to higher wavenumber regions, 1075 cm⁻¹, 1031 cm⁻¹ and 1228 cm⁻¹, respectively. The strong interaction of H2 in the imidazolium ring might have pushed the C-O-H, C-O-C and O=S=O bond closer and thus shortened the bond length (Shamsudin et al. 2015). As a result, more energy is required to vibrate the bonds and resulted in the shift of wavenumber towards higher region as the concentration of [Bmim]Cl increased.

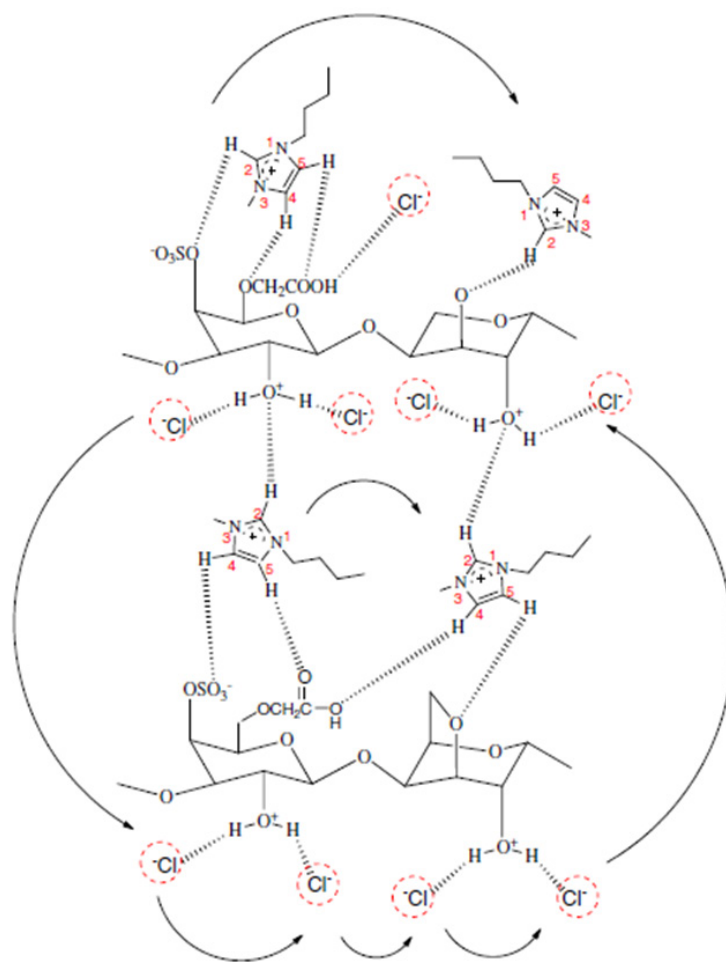


FIGURE 2. The proposed conduction mechanism of [Bmim]Cl with CM-carrageenan reported by Shamsudin et al.(2015b)

Figure 1(b) shows the peak at 1556 cm^{-1} which belongs to the asymmetric stretch of carboxylate ion, COO^- from acetate ion shifted to 1573 cm^{-1} as more [Bmim]Cl had been added. Carboxylate ion, COO^- ion has the ability to interact with H4 and H5 located at C4 and C5 position in the imidazolium ring as it has the ability to form the resonance structures (Mobarak et al. 2015; Shamsudin et al. 2015a). Avent et al. (1994) stated that all hydrogen molecules in the imidazolium ring (H2, H4 and H5) are able to participate in the hydrogen bonding interaction (Avent et al. 1994). Thus, the resonance effects resulted in the attraction and repulsion of COO^- ion with H2, H4 and H5 in imidazolium ring that will form a hydrogen bond with an anion, COO^- . Furthermore, the bulky size of imidazolium cation, $[\text{Bmim}]^+$ will ensure the cation to keep intact with an anion, COO^- in order to be mobile in this system.

The changes involved the C-O-C stretching of 3,6-anhydrogalactose at 930 cm^{-1} , C-O-C stretch at 1024 cm^{-1} , O=S=O symmetric stretching at 1215 cm^{-1} , -O-SO₃ stretching vibration of D-galactose-4-sulfate at 846 cm^{-1} and D-galactose-2-sulfate at 802 cm^{-1} . These peaks were reduced in intensity as the [Bmim]Cl increased, indicated the changes in the dipole moment of the molecule bonds

(Shamsudin et al. 2015a). Again, these observable changes signify the interaction between ionic liquid, [Bmim]Cl and iota carrageenan.

The changes in the ATR-FTIR spectra as the [Bmim]Cl was added into the iota carrageenan-based biopolymer electrolyte system suggest that ionic liquid, [Bmim]Cl acts as a charge carrier in this system. Imidazolium cation and chloride anion play an important role as mobile ion throughout the system by interacting with the active site of the polymer host, iota carrageenan. Hence, continuous coordination of the ions with the active site increased the ion mobility thus will generate the ionic conductivity. Shamsudin et al. (2015a) reported the proposed conduction mechanism of [Bmim]Cl with carboxymethyl carrageenan shown in Figure 2 that depicts a similar mechanism for the interaction between polymer host and the ionic liquid in this system.

CRYSTALLINITY INDEX

Figure 3 shows the X-ray diffraction pattern of iota carrageenan and iota carrageenan with 20, 40, 70, 80 and 100 wt. % of [Bmim]Cl. Iota carrageenan is a semicrystalline polymer that contains both crystalline and amorphous phase (Arof et al. 2010). However, the ionic conduction

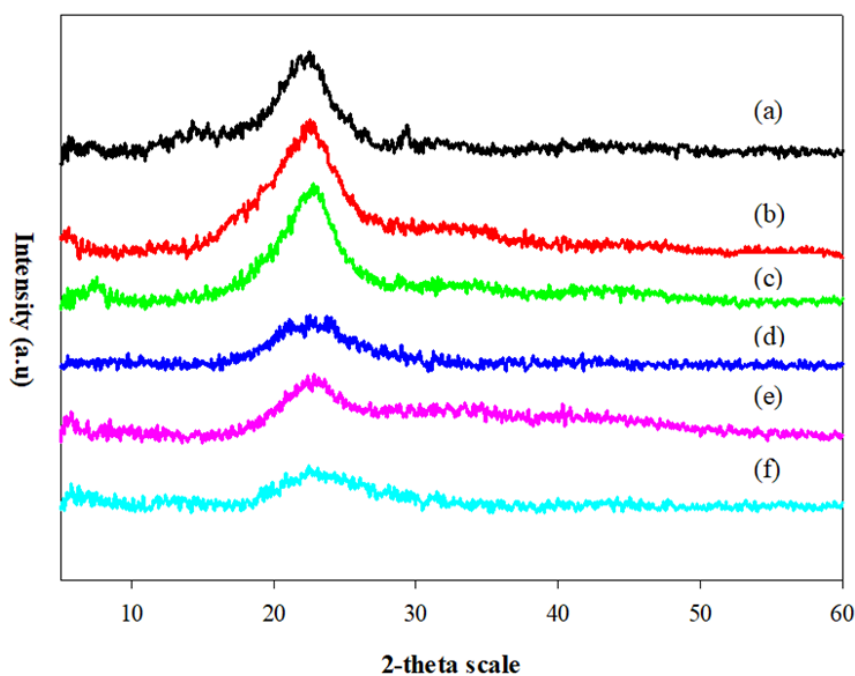


FIGURE 3. X-ray diffractogram of iota carrageenan at (a) 0 wt. %, (b) 20 wt. %, (c) 40 wt. %, (d) 70 wt. %, (e) 80 wt. % and (f) 100 wt. % of [Bmim]Cl

takes place primarily in the amorphous region. Based on Figure 3, the crystallinity of iota carrageenan decreases upon the increasing concentration of the ionic liquid, [Bmim]Cl. The degree of crystallinity (DC) of the iota carrageenan is 36.9%. Upon the addition of ionic liquid at 20 wt. % of [Bmim]Cl, the DC has decreased to 27.9% and gradually declined to 24% at 40 wt. % of [Bmim]Cl. At 70 wt. % of [Bmim]Cl, the polymer electrolyte system has

achieved the lowest DC which is 14.1%. The decrease in the DC value with the addition of [Bmim]Cl into the iota carrageenan has proven that [Bmim]Cl not only act as charge carrier but also give plasticizing effect in iota carrageenan system. However, the DC was then increased to 16.8% and 16.3% at 80 wt. % and 100 wt. % of [Bmim]Cl which is probably due to the high amount of ionic liquid loaded. This is also supported by impedance analysis result

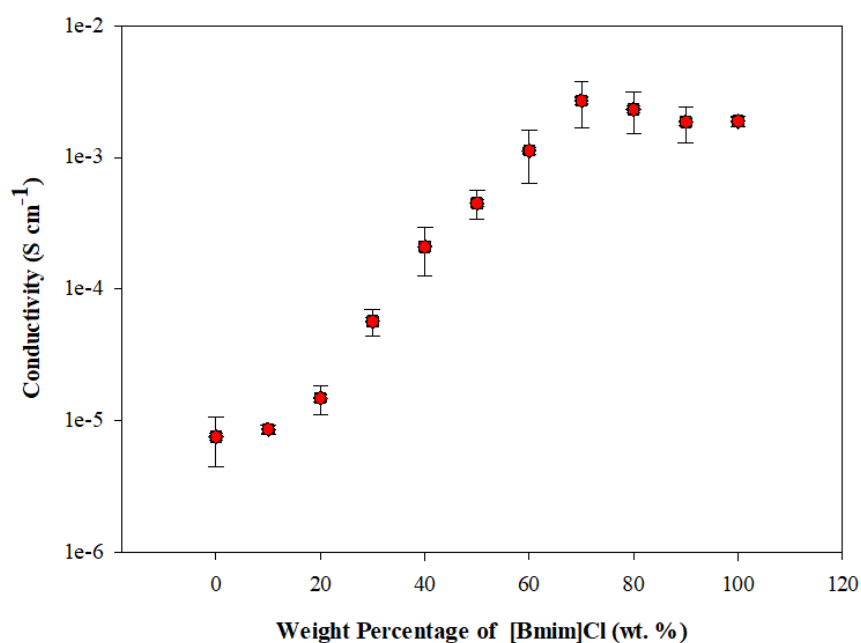


FIGURE 4. Ionic conductivity (σ) of iota carrageenan as a function of [Bmim]Cl (wt. %)

whereby the ionic conductivity started to drop at 80 wt. % and 100 wt. % of [Bmim]Cl.

IONIC CONDUCTIVITY

The ions of ionic liquid; imidazolium cation [Bmim]⁺ and chloride anion Cl⁻ interactions are weak and easily detached from each other due to the bulky size of the imidazolium cation (Shamsudin et al. 2014). Based on Figure 4, the ionic conductivity at ambient temperature of iota carrageenan was increased sequentially with the increasing concentration of [Bmim]Cl concentration. The increment starts from $7.57 \times 10^{-6} \text{ Scm}^{-1}$ at 0 wt. % of [Bmim]Cl to $1.48 \times 10^{-5} \text{ S cm}^{-1}$ with the addition of 20 wt. % of [Bmim]Cl. The optimum ionic conductivity value recorded was $2.70 \times 10^{-3} \text{ S cm}^{-1}$ achieved at 70 wt. % of [Bmim]Cl with the increment of ionic conductivity up to three orders of magnitude. The increment of ionic conductivity value is related to the increase of mobile charge carriers number in the iota carrageenan system and a decrease of crystallinity as proved by XRD spectrum.

However, the ionic conductivity gradually decreased upon addition of more than 70 wt. % of [Bmim]Cl. The decline in ionic conductivity in this system may be contributed by the re-association of ions. As the concentration of ionic liquid increases, the polymer host becomes saturated with ions which then lead to the formation of an ion pair and eventually, ion cluster. This reduces the number of mobile ions and hence, decreasing the ionic conductivity in the system (Rani et al. 2016; Woo et al. 2011).

FESEM

The morphology of iota carrageenan and iota carrageenan with 20, 40, 70, 80, and 100 wt. % of [Bmim]Cl is depicted in Figure 5. Based on Figure 5(a), the morphology of 0 wt. % of [Bmim]Cl shows the cratered surface of iota carrageenan film due to the semicrystalline nature of its polymer. Upon the addition of 20 wt. % of [Bmim]Cl, (Figure 5(b)) it can be seen that the addition of ionic liquid, [Bmim]Cl has altered the cratered surface of iota

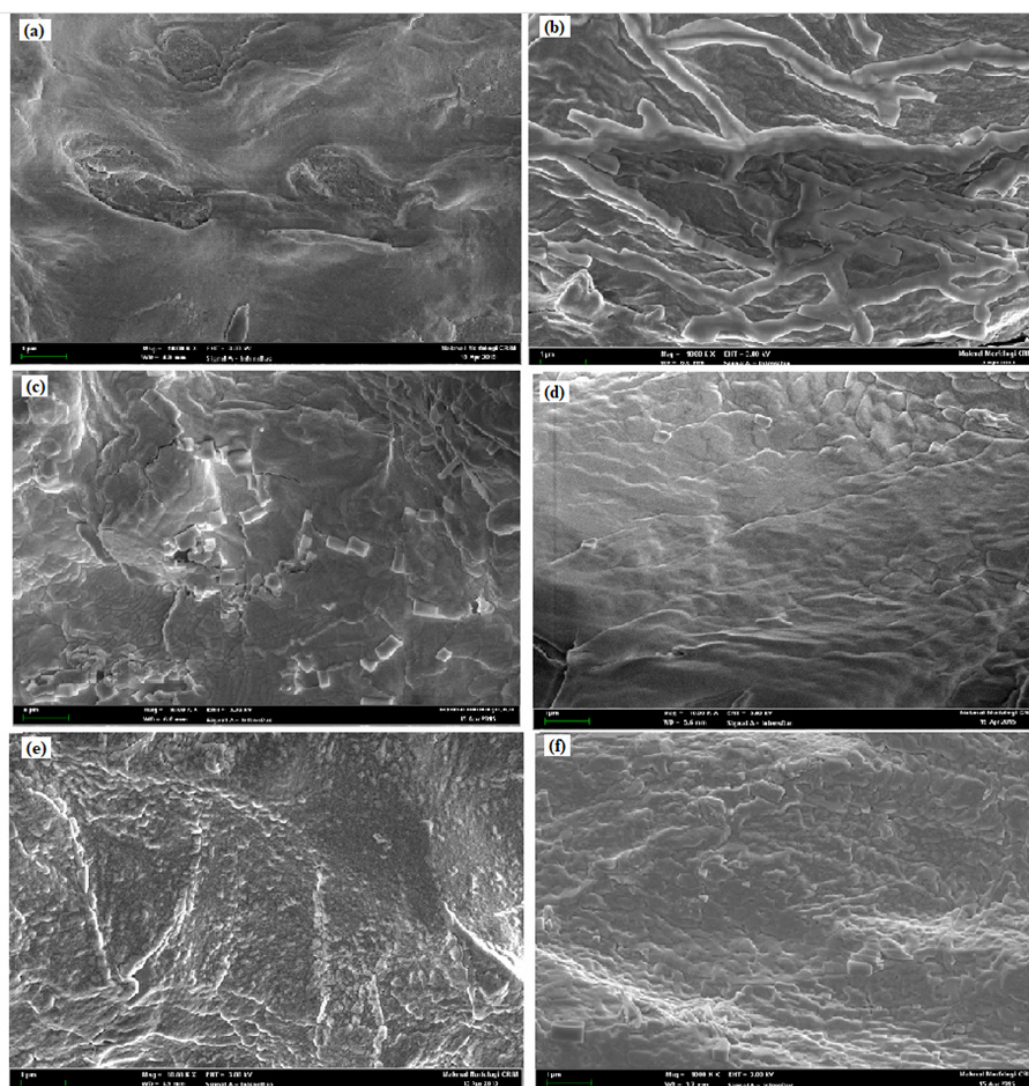


FIGURE 5. Surface morphology of (a) pure iota carrageenan film, (b) 20 wt. %, (c) 40 wt. %, (d) 70 wt. %, (e) 80 wt. % and (f) 100 wt. % of [Bmim]Cl

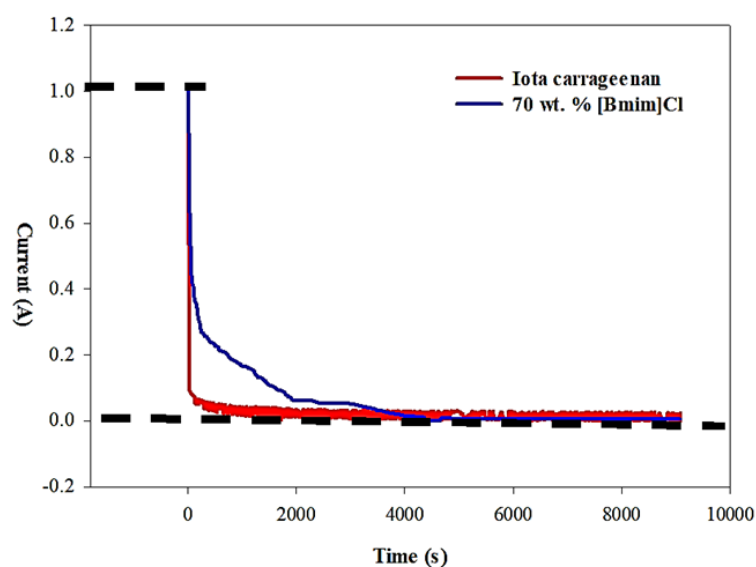


FIGURE 6. (a) Linear sweep voltammetry of pure iota carrageenan and iota carrageenan with 70 wt. % [Bmim]Cl, (b) Current versus time of iota carrageenan and highest conducting iota carrageenan film at 70 wt. % [Bmim]Cl

carrageenan film. At 40 wt. % of [Bmim]Cl, the morphology of the film encountered some disruption and the rearrangement of the polymer has taken place as shown in Figure 5(c). Nevertheless, the homogeneity of the polymer electrolyte is achieved at 70 wt. % of [Bmim]Cl as shown in Figure 5(d). This result shows the compatibility between iota carrageenan and [Bmim]Cl. Further increment of [Bmim]Cl at 80 wt. % has caused the morphology of the electrolyte to become protruded and has less homogeneity compared to 70 wt. % [Bmim]Cl (Figure 5(e)). The occurrence of this phenomenon can also be observed at 100 wt. % [Bmim]Cl (Figure 5(f)). These morphological changes of the iota carrageenan polymer electrolyte have indicated that the plasticizing effects of [Bmim]Cl help to increase the ionic conductivity of the electrolyte with the development of an amorphous phase. Hence, the morphology study of iota carrageenan with the addition of different wt. % of the ionic liquid is in accordance with the XRD results of the polymer electrolytes.

ELECTROCHEMICAL STABILITY

Figure 6(a) depicts the linear sweep voltammetry (LSV) curves for the iota carrageenan and 70 wt. % [Bmim]Cl. A small current was observed through the working electrode until the applied voltage reached a potential of 2.8 and 3.0 V for iota carrageenan and 70 wt. % [Bmim]Cl, respectively. This analysis provides information on the electrochemical stability of an electrolyte in which it notified the potential range where neither oxidation nor reduction is experienced by the electrolyte for it to be applied in the electrochemical device's applications. Figure 6(a) shows that iota-carrageenan exhibits electrochemical stability up to 2.8 V which is lower compared to iota carrageenan with 70 wt. % [Bmim]Cl in which the value is up to 3.0 V as shown in Figure 6(a). The anodic current was negligible below 2.0 V but then it increased gradually which might be attributed

to the decomposition of the chloride anion (Shamsudin et al. 2015a). Hence, the utilization of ionic liquid has improved the stability of iota carrageenan electrolyte system as it increased dissociation of ion inside the polymer host.

TRANSFERENCE NUMBER

The transference number of the solid biopolymer electrolytes- based iota carrageenan with the ionic liquid, [Bmim]Cl is depicted in Figure 6(b). The value of the transference number was calculated from the normalized polarization current versus time. Based on the graph, the initial total current was found to decline with time due to the depletion of ionic species in the electrolytes and become constant in the fully depleted condition as shown in Figure 6(b). At steady state, the current flows because of the electronic species that migrate across the electrolyte and interfaces (Mobarak et al. 2015). Based on the calculated value, the t_{ion} for iota carrageenan was found to be 0.97 whilst the t_{ion} with the addition of [Bmim]Cl was calculated to be 0.98. Both of these values imply that ions are the main contributor to the ionic conduction of the electrolytes and the effects of the electrons which are 0.03 and 0.02 can be neglected for both systems. The increased value of t_{ion} of 0.98 suggests the increased of ionic species in the system due to the incorporation of [Bmim]Cl.

CONCLUSION

The influence of ionic liquid on iota carrageenan based solid biopolymer electrolyte was investigated. The highest ionic conductivities achieved for iota carrageenan was $2.70 \times 10^{-3} \text{ S cm}^{-1}$ at 70 wt. % [Bmim]Cl. ATR-FTIR spectra demonstrated that the imidazolium cation of [Bmim]Cl has interacted with hydroxyl, carbonyl, ether and sulfate groups of the polymer host. Meanwhile, chloride ion was

preferable to interact with a protonated hydroxyl group, OH_2^+ . The slight decrease of ionic conductivity value at 80 and 100 wt. % of [Bmim]Cl has shown that the plasticizing effect of [Bmim]Cl has softened the polymer backbone thus maintained the magnitude $10^{-3} \text{ S cm}^{-1}$ of the conductivity. These results can be attributed with the XRD analysis of the film in which the lowest DC exhibited by iota carrageenan is 14.1% at 70 wt. % of [Bmim]Cl. The morphology result has shown that ionic liquid, [Bmim]Cl is compatible with iota carrageenan and possesses the most homogeneous film at 70 wt. % of [Bmim]Cl. The LSV analysis indicated that the electrochemical stability of iota carrageenan with the addition of ionic liquid was stable up to 3.0 V. The transference number measurement shows that ions are the main contributor for the polymer electrolyte conduction. These results indicated that iota-carrageenan based solid polymer electrolyte with the ionic liquid, [Bmim]Cl has a potential to be applied for electrochemical device application.

ACKNOWLEDGEMENTS

The authors would like to thank UKM for the provision of grants 07-01-02-SF1321 and GUP-2017-014.

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Received: 5 December 2018

Accepted: 27 October 2019

