



Research Article

Green Synthesis of [EMIm]Ac Ionic Liquid for Plasticizing MC-based Biopolymer Electrolyte Membranes

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Abstract

Lithium-ion batteries (LIBs) are favorable power source devices at the last two decades, owing to high energy density, rechargeable, long life cycle, portable, safe, rechargeable, good performance and friendly environment. To support their development, in this research has been successfully prepared polymer electrolyte membrane, a main component of LIBs, based on 1-ethyl-3-methylimidazolium acetate ([EMIm]Ac) ionic liquid-plasticized methyl cellulose/lithium perchlorate (MC/LiClO₄). [EMIm]Ac ionic liquid was easy synthesized by metathesis reaction between 1-ethyl-3-methylimidazolium bromide ([EMIm]Br) ionic liquid and potassium acetate (CH₃COOK) at ambient temperature, for 1 hour. [EMIm]Ac ionic liquid was functional groups analyzed with Fourier Transform Infra-red (FT-IR) and structural analyzed with ¹H-Nuclear Magnetic Resonance (NMR) and ¹³C-NMR. [EMIm]Ac ionic liquid-plasticized MC/LiClO₄ biopolymer electrolyte membrane was prepared by casting solution, with [EMIm]Ac ionic liquid content, 0, 5, 10, 15, 20, 25, and 30% (w/w). Effect of 15% (w/w) [EMIm]Ac ionic liquid incorporation to MC/LiClO₄ showed the best condition and selected as the optimum condition with conductivity, tensile strength, elongation break, and thermal stability of 9.160×10⁻³ S.cm⁻¹, 24.19 MPa, 36.43%, ~256 and ~370 °C, respectively. These results confirm that [EMIm]Ac ionic liquid can plasticize biopolymer electrolyte membranes of MC/LiClO₄ to be appealing performances to fulfill the LIB's separator requirement. Copyright © 2019 BCREC Group. All rights reserved

Keywords: Ionic Liquids; Cellulose; Methyl cellulose; Lithium Ion Batteries

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1. Introduction

Li-ion battery (LIB), nowadays, is a very important energy storage technology in human be-

ing activities [1-2]. Lithium ion batteries (LIBs) are used extensively in many applications, such as: laptop computers, mobile phones, and others, due to their high energy density, long life time, and rechargeable [3-4]. However, some issues in the development of LiBs are the cost production, environment, safety, and performances. The issues are mainly related both electrolytes and separator [5].

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Liquid electrolytes are corrosive and volatile cause leakage and explosion at high temperatures [6]. A thermally unstable separator material else tends to shrinkage at high temperatures causes memory effect. Solid polymer electrolytes (SPEs) are those macromolecules conducting ions and separating both cathode and anode electrodes [7]. However, SPEs have problem with their ionic conductivity which are lower than liquid electrolytes [8]. Some efforts to improve the ionic conductivity, they are introducing plasticizer (filler or ionic liquids), salts system mixtures, polymer blend and solvent system mixtures [9-10]. Porous SPEs are desirable due to exhibit advantages of liquid electrolyte (excellent ionic conductivity) and solid polymer electrolyte (outstanding mechanical property) [11]. It can be stated that the solid polymer electrolytes function as liquid electrolytes and common separator [12].

Applying the environmentally friendly and renewable materials overcome related-problems of LIBs. Cellulose is the most abundant biopolymer in nature and is widely used in many industrial uses, such as: paper making, food packaging, pharmaceutical applications and innovative eco-friendly application. Cellulose derivatives have been successfully applied as polymer electrolytes for LIBs separator application, they are, methyl cellulose [6,13], ethyl cellulose [14], hydroxyethyl cellulose [2], carboxymethyl cellulose [15-16].

Methyl cellulose (MC), an important ether cellulose, is widely used owing to have many advantages, they are, biocompatible, inexpensive, ease to make thin films and edible films. It also has outstanding mechanical properties compared to other biodegradable polymers such as chitosan, but it is recommended to increase ion conductivity [17].

Ionic liquids are a distinctive and interesting material due to have appealing properties. The properties are high boiling point, non-volatile, good conductivity, good thermal stability, plastic effect, wide electrochemical potential, reusable, and reproduceable [18]. These attractive properties are widely used in various purposes, such as cellulose dissolution [19-20], synthesis, electrolytes [21], as plasticizers [3,13,22], and corrosion inhibitors [23].

Ionic liquids consist of organic cations (bulky) and organic/inorganic anions (bulky / polyatom / halide). Weak ionic interactions, causing ionic liquids to easily be produced to new ionic liquid derivatives with different properties. Metathesis reaction is commonly method to derive new ionic liquids.

A microwave is one of electromagnetic energy that absorbs rotation energy of molecules with 300-300,000 MHz of frequency. This principle is used in microwave assisted organic synthesis (MAOS). Microwave-assisted heating accelerates producing product with dipole rotation and ionic conduction [24]. MAOS method is promising to ionic liquids synthesis. Both microwave heating and ionic liquids are the "hot topics" in chemistry [25]. Ionic liquids synthesis, generally, can be described in two steps, they are the desired cation formation and anion exchange (metathesis reaction) [26].

Some advantages of microwave heating utilization, practically, are mainly shorter time duration of reaction, compare to conventional heating methods. Reaction time reducing of microwave irradiation is owing to extensive heating direct to reaction system without through the vessel (conventional heating methods) [27].

The effect of ionic liquid plasticization in solid polymer electrolyte membranes has been successfully studied. Some reports approved that there are significantly improved performances of LIBs due to ionic liquids incorporation in polymer electrolyte membranes. Several researches also have succeeded to study the effects of ionic liquids plasticization of LIBs performances [3,13,22]. The properties needed as electrolyte are negligible vapor point, large liquid-phase temperature interval, nonflammable, good thermal stability and elevated electrochemical stability [28-29].

The 1-ethyl-3-methylimidazolium acetate [EMIm]Ac is popular ionic liquid which able to dissolve and deconstruct cellulose, besides 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) [30] and 1-allyl-3-methylimidazolium chloride [AMIm]Cl [31]. However, they have never been reported to be electrolytes and/or plasticizers. Only few reports used [BMIm]Cl ionic liquid in polymer electrolytes study. The potential of [EMIm]Ac ionic liquid to be electrolyte and/or plasticizer is attributed to electron withdrawing group (CH_3COO^-) which can interact to polymer chain, so it contributes ion migration.

This work investigated novel biopolymer electrolyte (BPE) membrane. The effect of ionic liquid plasticization, an environmentally friendly material, is compatible to methyl cellulose (MC)-based biopolymers. Ionic liquid was synthesized using a MAOS method, while BPE membrane was simply prepared with casting solution technique. Functional groups, structural studies, ionic conductivities, mechanical properties, crystallinities, and thermal stability were carried out with Fourier

transform infrared (FTIR), nuclear magnetic resonance (NMR), electrochemical impedance spectroscopy (EIS), tensile strength test, X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetry analysis (TGA), respectively.

2. Materials and Methods

2.1 Materials

All materials and solvents were used without further purification, they were bromoethane (Sigma-Aldrich, 98%), 1-methylimidazole (Sigma-Aldrich, 99%), potassium acetate (CH₃COOK) (Sigma-Aldrich, 99%), methyl cellulose (MC) (Sigma-Aldrich, MW = 88,000; DS = 1.5-1.9), lithium perchlorate (LiClO₄) (Sigma-Aldrich, 99%), chloroform (CHCl₃) (Merck, 99%), methanol (CH₃OH) (Merck, 99%), and distilled water (Merck, 99%).

2.2 Methods

2.2.1 The 1-ethyl-3-methylimidazolium bromide [EMIm]Br ionic liquid synthesis

[EMIm]Br ionic liquid as a precursor was synthesis using Microwave Assisted Organic Synthesis (MAOS) method. The 1-methylimidazole and bromoethane were dissolved into chloroform, then stirred for 24 hours. The solution mixture was then subjected onto microwave reactor CEM. Microwave heating was carried out at power of 100 watt, 50 °C, 15 minutes, and medium stirring. Highly purity of [EMIm]Br was obtained using extraction (water : ethyl acetate = 1 : 1). Water fraction, then, vacuum distilled to produce pure interested-[EMIm]Br ionic liquid. The purified [EMIm]Br ionic liquid was then FTIR and NMR characterized. The [EMIm]Br synthesis reaction scheme is shown in Figure 1.

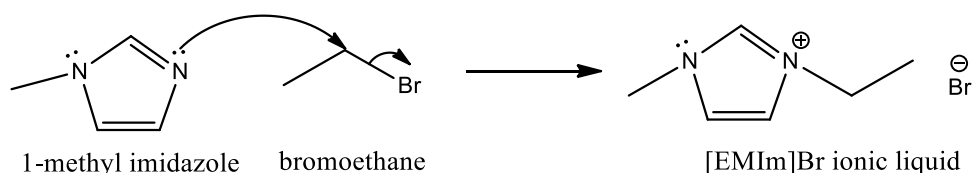


Figure 1. Reaction scheme of [EMIm]Br synthesis

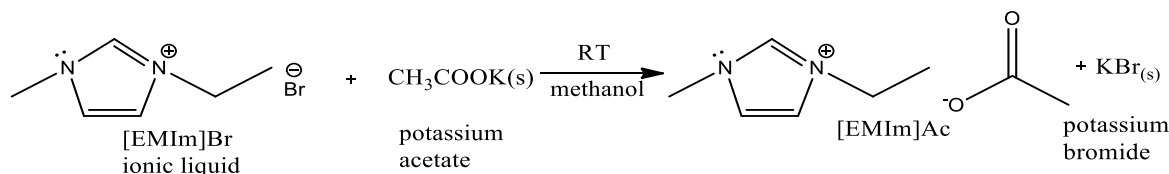


Figure 2. Reaction scheme of [EMIm]Ac ionic liquid synthesis

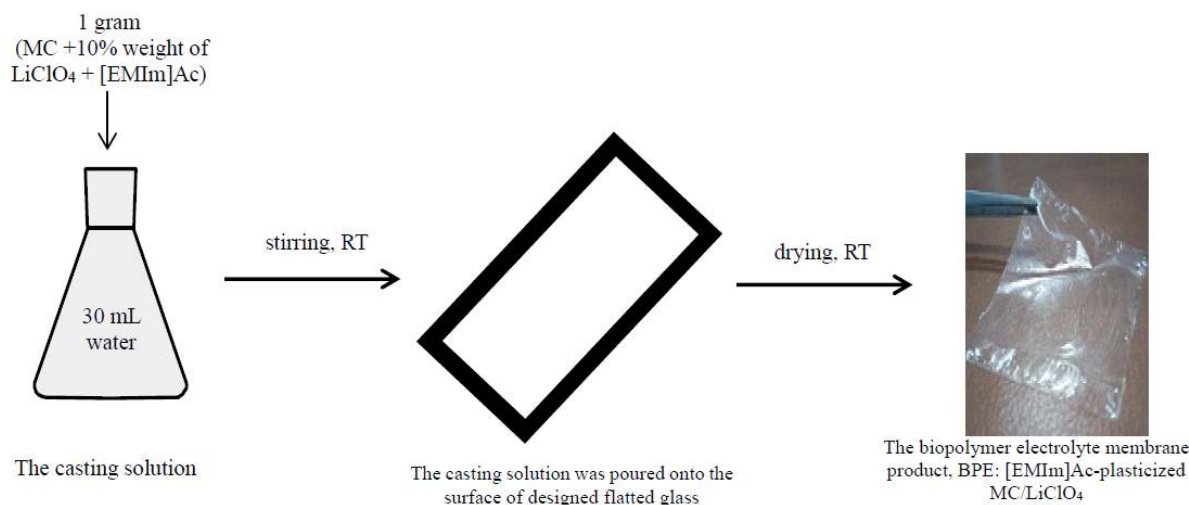


Figure 3. The preparation of biopolymer electrolyte membrane (BPE: {EMIm]Ac-plasticized MC/LiClO₄)

2.2.2 The 1-ethyl-3-methylimidazolium acetate ([EMIm]Ac) ionic liquid synthesis

[EMIm]Ac ionic liquid synthesis was employed with metathesis reaction between 0.2 mole previous produced [EMIm]Br ionic liquid and 0.2 mole CH_3COOK salt in methanol. The released potassium bromide (KBr) solid as by-product was decanted from solution phase, was then evaporated by using vacuum evaporator at 50-60 °C to remove methanol solvent. The salt solid was [EMIm]Ac ionic liquid, that was then FTIR and NMR characterized. The metathesis scheme of the [EMIm]Br ionic liquid and CH_3COOK metathesis to produce the [EMIm]Ac ionic liquid is shown in Figure 2.

2.2.3 Biopolymer electrolyte membranes preparation

Biopolymer electrolyte membranes, BPEMs: MC/LiClO₄/[EMIm]Ac were prepared using the casting solution technique (Figure 3). Total weight of prepared material was 1 gram dissolved in 30 mL of distilled water. Casting solution was then cast on the surface of the flatted glass, then evaporated at ambient temperature, continued drying in the vacuum oven. Complex of MC/LiClO₄ successfully prepared were MC/10% wt LiClO₄/x [EMIm]Ac ionic liquid (x = 5, 10, 15, 20, 25, and 30% weight).

2.3 Characterizations

Complexation study of complexed-systems of biopolymer electrolytes membranes were carried out with FT-IR (Prestige 21 Shimadzu), ionic conductivities by electrochemical impedance spectroscopy (EIS, Agilent, type E490A, precision LCR), mechanical properties by tensile tester (FAVIGRAPH), crystallinity by diffractometer XRD (Rigaku Smart Lab) and surface morphology by Scanning electromotive morphology (SEM) (Type JEOL-JSM-6510LV), and thermal properties of biopolymer electrolytes membranes were measured by thermal



Figure 4. [EMIm]Br ionic liquid product

gravimetry analysis (TGA, Linseis, type STA PT 1600).

3. Results and Discussion

3.1 Synthesis of [EMIm]Br Ionic Liquid

The 1-ethyl-3-methylimidazolium bromide ([EMIm]Br) ionic liquid was synthesized using Microwave Assisted Organic Synthesis (MAOS) method (in this research using CEM microwave reactor). The reagents used to [EMIm]Br ionic liquid synthesis were 1-methylimidazole and bromoethane (1 : 1). Setting the microwave reactor to synthesize [EMIm]Br ionic liquid were 100 watts, 15 minutes and 50 °C. The reaction involved the substitution scheme of S_N2. The free electron pair of 1-methylimidazole acts as a nucleophile that attacks the bromoethane which acts as an electrophile while releasing the bromide ion as a good leaving group.

The synthesis product [EMIm]Br ionic liquid is yellowish liquid. The product of [EMIm]Br synthesis was then washed by extraction: water/ ethyl acetate 3 times. The lower phase ([EMIm]Br) was separated, and then distilled by vacuum distillation. The purified [EMIm]Br ionic liquid has density of 1.8 g/mL (Figure 4).

[EMIm]Br ionic liquid synthesis using MAOS method fulfills what green chemistry principle is. They are especially to prevention, less hazardous chemical synthesis, designing safer chemicals and design for energy efficiency [30].

3.2 FTIR and NMR Analysis of [EMIm]Br Ionic Liquid

The result of synthesis of 1-ethyl-3-methylimidazolium bromide ([EMIm]Br) ionic liquid precursor identified functional group us-

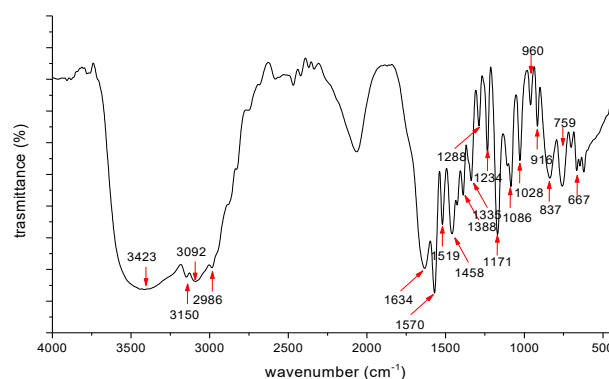


Figure 5. FTIR spectrum of [EMIm]Br ionic liquid

ing Fourier Transform Infra-red (FT-IR) and its peak absorption analysis can be seen in Figure 5. According to the Figure 5, several vibration modes for the [EMIm]Br ionic liquid are: O–H stretching at 3423 cm^{-1} , =C–H stretching of imidazole ring at 3150 cm^{-1} and 3092 cm^{-1} , C–H aliphatic stretching at 2986 cm^{-1} , C=C stretching of imidazole ring at 1635 cm^{-1} , C=N stretching of

imidazole ring at 1570 cm^{-1} , C–H (CH_3) bending at 1388 and 1335 cm^{-1} , C–N stretching imidazole at 1171 cm^{-1} , C–N interaction of CH_3 and N of imidazole at 1086 cm^{-1} , =C–H out of plane of imidazole ring at 837 cm^{-1} and 759 cm^{-1} .

To ensure the [EMIm]Br ionic liquid structure, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis

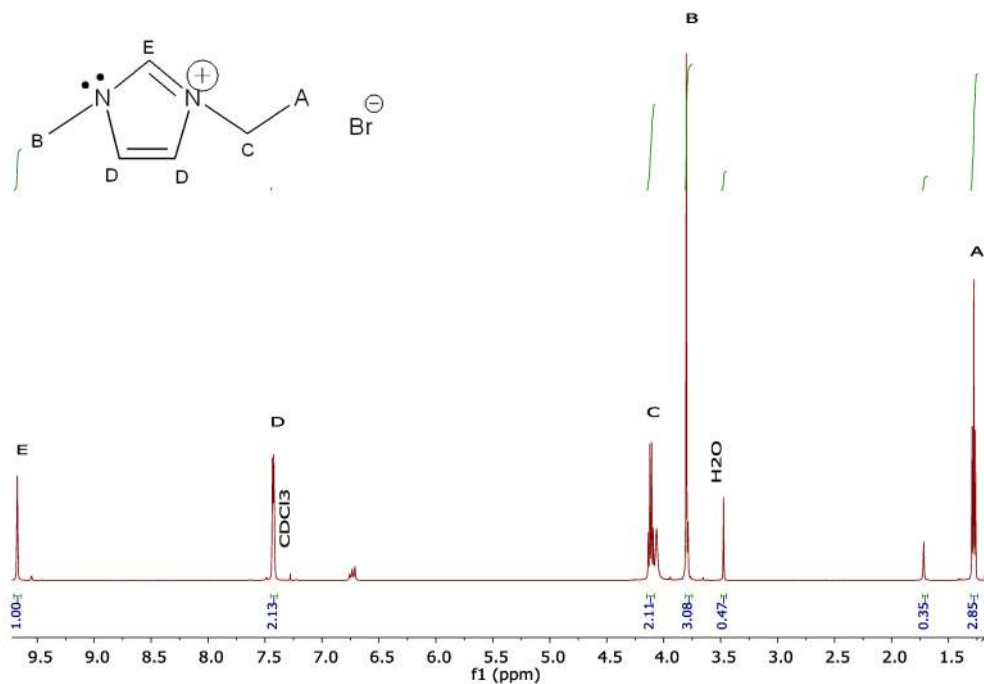


Figure 6. $^1\text{H-NMR}$ spectrum of [EMIm]Br ionic liquid

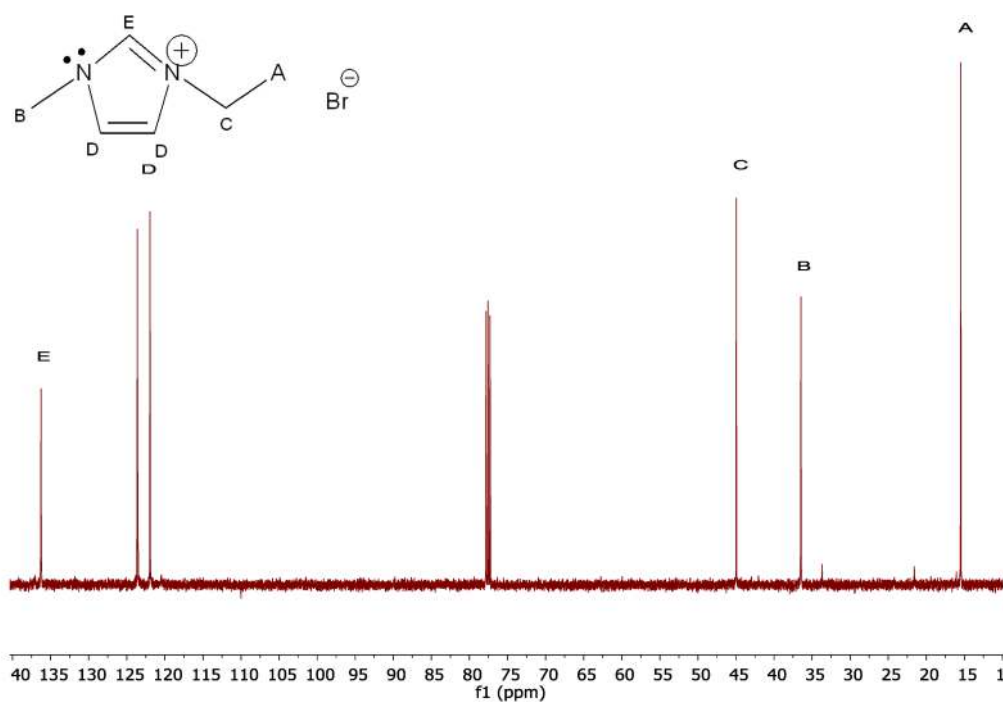


Figure 7. $^{13}\text{C-NMR}$ spectrum of [EMIm]Br ionic liquid

was performed. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra are shown in Figure 6 and Figure 7. The results of the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis of [EMIm]Br ionic liquid are as follows:

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) 1.28 (A, 3H, *t*); 3.80 (B, 3H, *s*); 4.11 (C, 2H, *q*); 7.44 (D, 2H, *dd*); 9.68 (E, 1H, *s*).
 $^{13}\text{C-NMR}$ (500 MHz, CDCl_3): δ (ppm) 15,48 (A); 36,47 (B); 44,95 (C); 123,01 (D); 136,26 (E).

Based on $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum analysis, it confirms that [EMIm]Br ionic liquid were already formed from 1-methylimidazole and bromoethane precursors.

3.3 Synthesis of [EMIm]Ac Ionic Liquid

Synthesis of [EMIm]Ac ionic liquid was employed by simply metathesis reaction by mixing 0.2 mole of [EMIm]Br ionic liquid and 0.2 mole of potassium acetate (CH_3COOK) in methanol. The potassium bromide (KBr) by-product was separated from solution. The solution was evaporated by vacuum evaporator to remove methanol solvent, released yellowish [EMIm]Ac salt solid (Figure 8). Similar to [EMIm]Br ionic liquid synthesis, so [EMIm]Ac ionic liquid synthesis also fulfill the green chemistry principle. It's especially to process performing at ambient temperature and pressure [30].

3.4 FT-IR dan NMR Analysis of [EMIm]Ac Ionic Liquid

The [EMIm]Ac ionic liquid was analyzed by FT-IR as shown in Figure 9. According to the spectrum, several vibration modes for the [EMIm]Ac ionic liquid are shown: O–H stretching at 3468 cm^{-1} , =C–H stretching of imidazole ring at 2983 cm^{-1} , C–H aliphatic stretching at 2822 cm^{-1} , C=C stretching of imidazole ring is not visible, while the C=N stretching of imidazole ring is broad at 1597 cm^{-1} , O–H bending is strong at 1408 and 920 cm^{-1} , is seen at 1338 cm^{-1} , which also still indicates a bending vibration



Figure 8. Product of [EMIm]Ac ionic liquid

of C–H(CH_3) in the region of the wave number, C–N stretching of imidazole ring at 1172 cm^{-1} , C–N interaction of CH_3 and N of imidazole ring at 1032 cm^{-1} , =C–H out of plane of imidazole ring at 756 cm^{-1} .

The substituted-bromide ion with acetate ion (CH_3COO^-) was confirmed according to the presence of a group with a strong intensity and broad at 3468 , 1596 , 1419 and 1032 cm^{-1} , as shown in Figure 9, assumed to interaction between the [EMIm $^+$] cation and polar sites of polymer chain. The NMR analysis was performed to confirm [EMIm]Ac ionic liquid structure.

The results of the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis of [EMIm]Ac ionic liquid are as follows:

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) 1.53-1.56 (A, 3H, *t*); 3.95-3.96 (B, 3H, *s*); 4.27-4.31 (C, 2H, *m*); 7.60-7.68 (D, 2H, *dd*); 9.02 (E, 1H, *s*); 1.90 (F, 3H, *s*).
 $^{13}\text{C-NMR}$ (500 MHz, CDCl_3): δ (ppm) 14.27 (A); 35.14 (B); 44.63 (C); 122.73 (D); 127.60 (E); 23.00 (F); 178.81 (G).

Based on the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum analysis, it confirms that [EMIm]Ac ionic liquid were already formed from 1-methylimidazole and bromoethane precursors.

3.5 FTIR Analysis and Complexation Study of Biopolymer Electrolyte (BPE) Membranes MC/LiClO₄/[EMIm]Ac

The biopolymer electrolyte membranes, BPE membranes: MC/LiClO₄/[EMIm]Ac produced in the form of transparent thin film, with average thickness of $\sim 22\text{ }\mu\text{m}$, meets the minimum requirements of LIB's separator application ($\sim 100\text{ }\mu\text{m}$). The FTIR spectrum of the biopolymer electrolyte membranes, BPE membranes: MC/LiClO₄/[EMIm]Ac is shown in Figure 12.

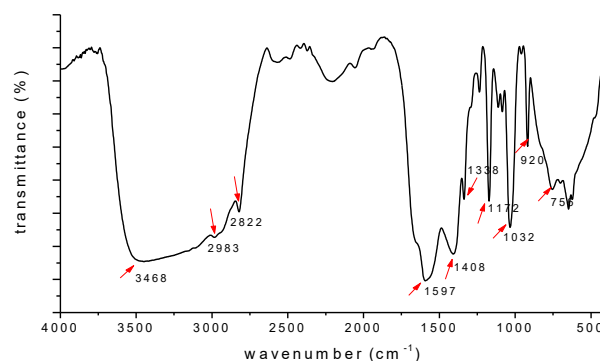


Figure 9. FTIR spectrum of [EMIm]Ac ionic liquid

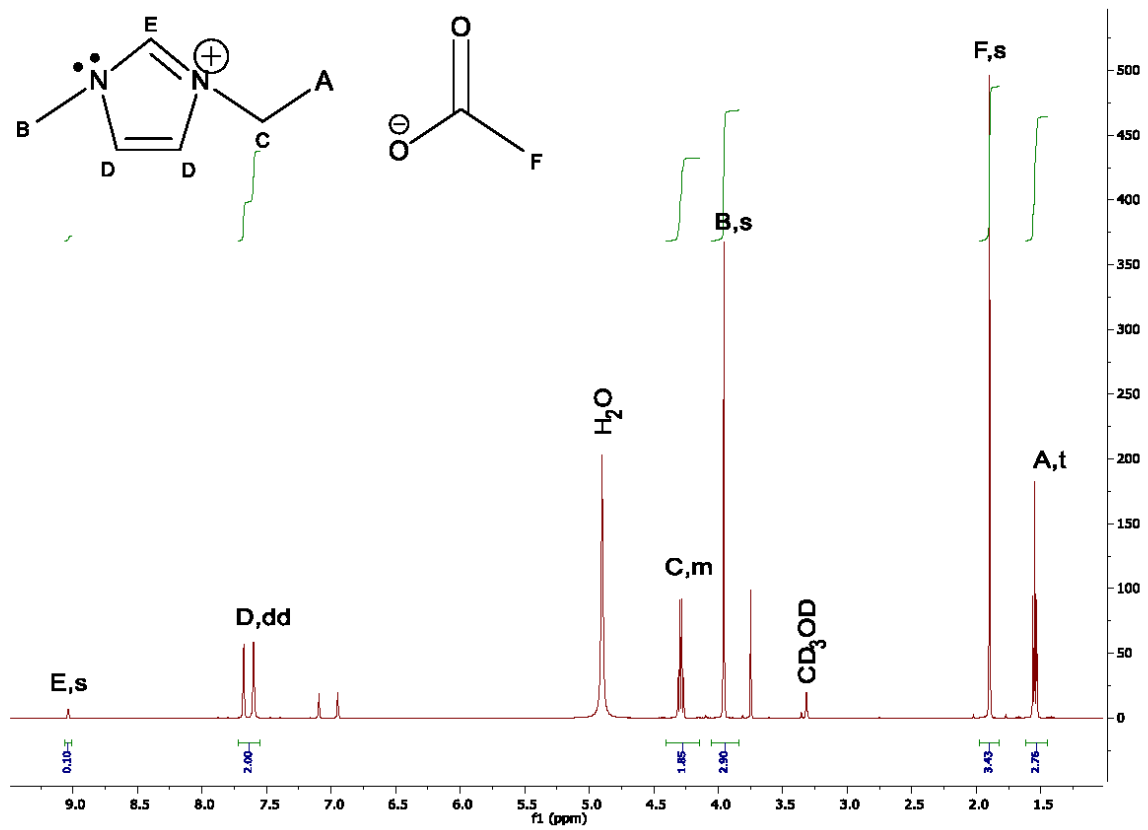


Figure 10. ^1H -NMR spectrum of [EMIm]Ac ionic liquid

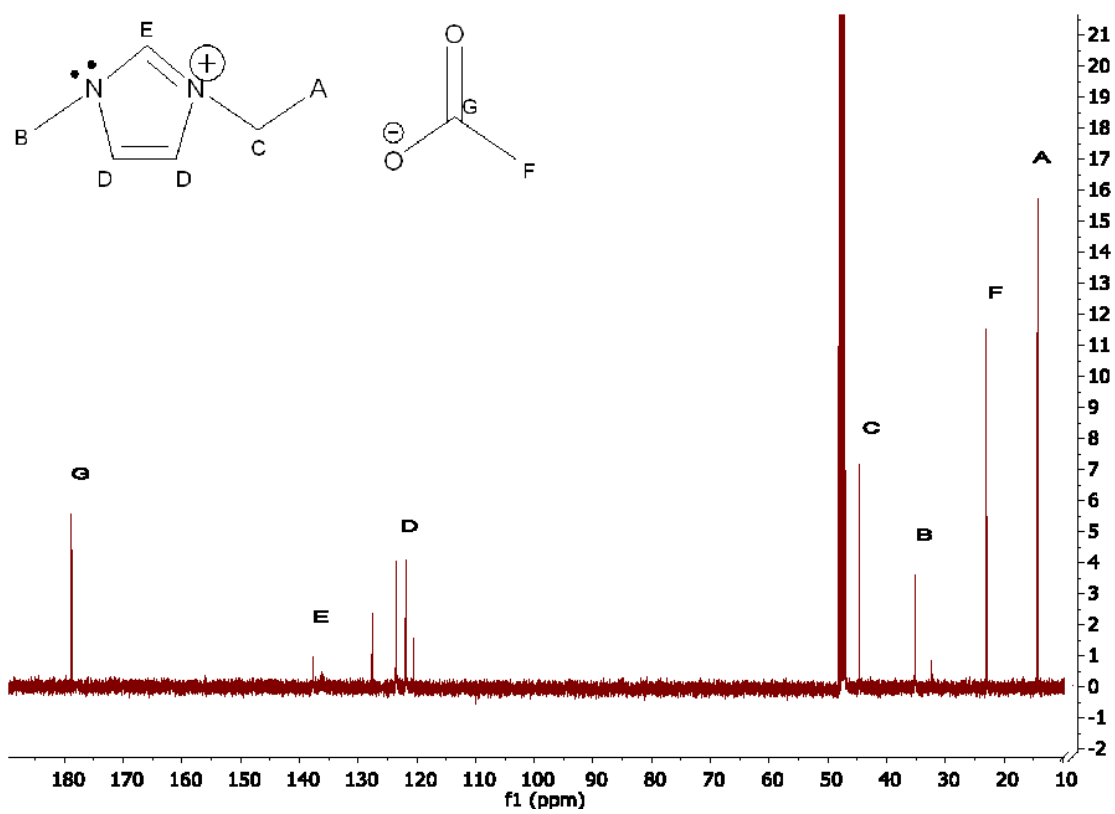


Figure 11. ^{13}C -NMR spectrum of [EMIm]Ac ionic liquid

The broad H-O-H bending vibration of methyl cellulose around 1645 cm⁻¹, is gradually reduced as an increase of [EMIm]Ac ionic liquid concentration. The incorporation of 15% to 30% (w/w) of the [EMIm]Ac ionic liquid to LiClO₄-complexed MC reduces the typical peak of MC/LiClO₄, while increasing the new absorption peak at 1570 cm⁻¹, identified as an aromatic C-C group of [EMIm]Ac ionic liquid.

In the previous FT-IR spectrum of [EMIm]Ac ionic liquid shown two typical C-C peaks absorption of imidazolium cations, could be seen at 1593.20 and 1408.04 cm⁻¹. Based on previous reports [32], the absorption bands at 1593.20 and 1408.04 cm⁻¹ are asymmetry and symmetry COO⁻ group. Thus, based on this FTIR study, C-C absorption of aromatic ring and COO-group overlap each other on the same wave number. The intensity is getting stronger at 1570 cm⁻¹, along with % weight of 5-30 % (w/w) [EMIm]Ac ionic liquid to LiClO₄-complexed MC.

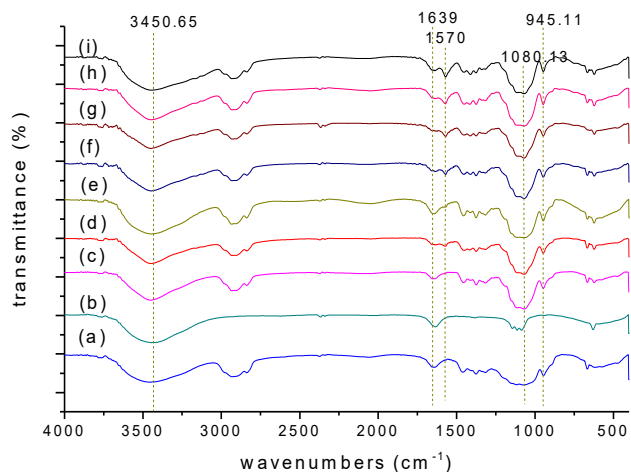


Figure 12. FTIR spectra (a) Pure MC, (b) LiClO₄, (c) MC/10% (w/w) LiClO₄, and MC/10% (w/w) LiClO₄/x% [EMIm]Ac, x (%w/w) : (d) 5, (e) 10, (f) 15, (g) 20, (h) 25, (i) 30

Table 1. Ionic conductivities of MC/LiClO₄/[EMIm]Ac

| MC content (%) | LiClO ₄ content (%) | [MIm]Ac ionic liquid content (%) | Ionic Conductivities, σ (S.cm ⁻¹) |
|----------------|--------------------------------|----------------------------------|--|
| 80 | 10 | 0 | 3.950×10 ⁻⁵ |
| 75 | 10 | 5 | 5.560×10 ⁻³ |
| 70 | 10 | 10 | 6.050×10 ⁻³ |
| 65 | 10 | 15 | 9.160×10 ⁻³ |
| 60 | 10 | 20 | 1.782×10 ⁻² |
| 55 | 10 | 25 | 3.090×10 ⁻³ |
| 50 | 10 | 30 | 1.646×10 ⁻³ |

The [EMIm]Ac ionic liquid incorporation to MC/LiClO₄ matrix biopolymer electrolytes causes some important peaks of MC/LiClO₄ are shift and even disappeared. These are due to complexation or interaction between the ether oxygen of MC and cations ([EMIm⁺] and Li⁺). The shifting and intensity reducing of several peaks absorption are mainly at hydrogen bond stretching and bending, as interacting between [EMIm]Ac ionic liquid and LiClO₄-complexed methyl cellulose. The geometry complexation of MC hydroxyl with [EMIm⁺] and Li⁺ is shown in Figure 13.

3.6 Ionic Conductivities Biopolymer-Electrolyte Membranes, BPE Membranes: MC/LiClO₄/[EMIm]Ac

The ionic conductivities of the biopolymer electrolyte membranes, BPE membranes: MC/LiClO₄/[EMIm]Ac at room temperature is shown in Table 1. The ionic conductivity of BPE membranes increases with increasing [EMIm]Ac ionic liquid concentration. [EMIm]Ac ionic liquid is fully contributing to ionic conductivity increasing, thanks to its functions as a spacer.

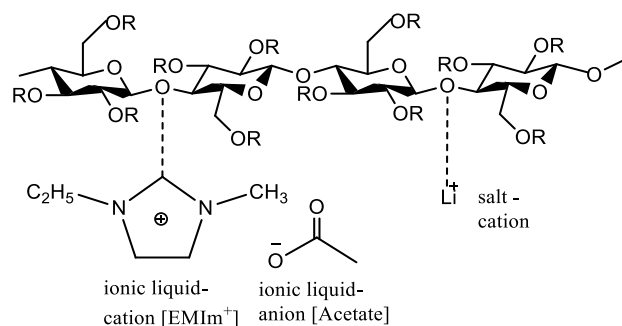


Figure 13. Proposed mechanism of complexation of MC hydroxyl with [EMIm⁺] and Li⁺ (adapted from previous report [29])

The highest conductivity is at 20% (w/w) [EMIm]Ac ionic liquid incorporation of $1.782 \times 10^{-2} \text{ S.cm}^{-1}$. After the composition, the ionic conductivities are gradually decreasing, and this is predicted due to an increasing of ionic liquid concentration providing a steric hindrance to Li^+ ion mobilization. Li^+ -ion mobilization decreases, as the interaction of the acetate ion dipole to Li^+ -ion and MC increases after the incorporation of ionic liquid under optimum conditions.

Decreased ionic conductivity is due to an increase in dipole interaction between ionic liquids and MC/ LiClO_4 compounds. This reduction in conductivity is also thought to be caused by the aggregation of ions that reduce the amount of charge carriers and limit the movement of ions [32]. This reason was also previously reported [33], which said that the empirical formulas-associations by ions cause less charge-carrying motion and form larger ion clusters that limit ionic motion, thus causing ionic conductivity to decrease. In Table 1. below, it is shown the value of biopolymer electrolyte membrane conductivities, MBE: MC/ LiClO_4 /[EMIm]Ac.

3.7 Mechanical Properties of Biopolymer-Electrolyte Membranes, BPE Membranes: MC/ LiClO_4 /[EMIm]Ac

There are two analysis to study the mechanical properties of the BPE membranes: MC/ LiClO_4 /[EMIm]Ac system, they are the tensile strength and elongation at break. In Figure 14 depicted that LiClO_4 -complexed methyl cellulose has high of tensile strength (stress), and continued by trend of effect of [EMIm]Ac ionic

liquid incorporation to tensile strength deformation. [EMIm]Ac ionic liquid incorporation decreases tensile strength of BPE membranes initially, however, following incorporation improves this property gradually until optimum condition.

[EMIm]Ac ionic liquid was incorporated to BPE membranes with various contents, i.e 5, 10, 15, 20, 25, and 30% (w/w). The [EMIm]Ac ionic liquid effect to BPE membranes tensile strength can be observed as shown in Figure 14. From the data, [EMIm]Ac ionic liquid causes tensile strength decreased drastically at its initial incorporation, but it's improved with the further incorporations up to the optimum condition at 15% (w/w) [EMIm]Ac ionic liquid. After that condition, a decreasing of tensile strength is happened. The optimum tensile strength is at 15% (w/w) of [EMIm]Ac ionic liquid incorporation to LiClO_4 -complexed MC, that is 24.19 MPa. From this data, it can be explained that presence of [EMIm]Ac ionic liquid has been succeeded to deconstruct interaction happened inter-chain methyl cellulose biopolymer in early its incorporation and after optimum condition.

Elongation break (E_{break}) analysis was conducted to both before and after [EMIm]Ac ionic liquid incorporation to LiClO_4 -complexed methyl cellulose. For the various of [EMIm]Ac ionic liquid incorporation: 5, 10, 15, 20, 25, and 30 % (w/w) as plasticizers of BPE membranes: MC/ LiClO_4 /[EMIm]Ac is illustrated in Figure 15. From the figure could be depicted the effect of [EMIm]Ac plasticization significantly increases the fabricated membrane strain up to incorporation of 30% weight of [EMIm]Ac ionic

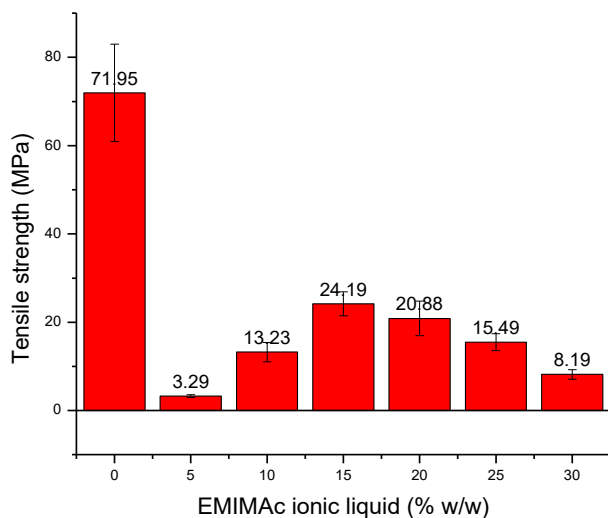


Figure 14. Tensile strength (stress) of BPE Membranes

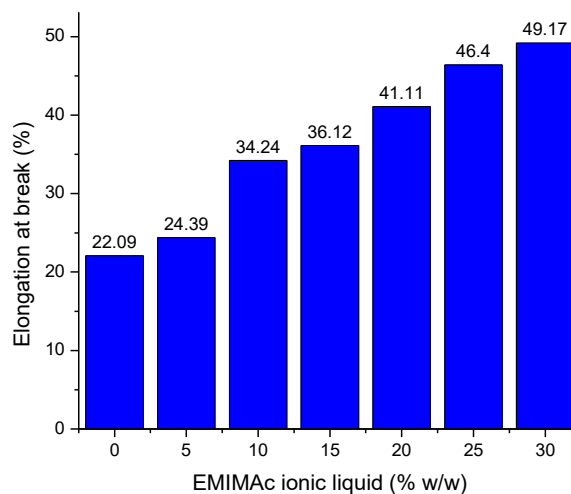


Figure 15. Elongation at break (Strain) of BPE Membranes

liquids, and release 49.7% at high value. Increasing of elongation break (E_{break}) is indicating biopolymer electrolyte membranes flexible properties. Mechanical properties with sufficient tensile strength and good elongation break indicate chain flexibility of biopolymer electrolyte that is able to support chain motions which contribute to Li-ion transport.

There is a mechanical properties difference between before and after optimum condition of tensile strength. Before the optimum condition, toughness increases, it means elongation at break increase as tensile strength increase. This property is predicted as a plastic behavior. After the optimum condition, the mechanical properties deformation is happened, where elongation at break decreases as tensile strength increases, this property called as an elastic-like behavior. It could be concluded that [EMIm]Ac ionic liquid incorporation to the MC

membranes gave plasticization and hard-elastic effect significantly at various compositions.

3.8 Crystallinity Analysis of Biopolymer-Electrolyte Membrane, BEM: MC/LiClO₄/[EMIm]Ac

Some diffraction peaks of methyl cellulose are commonly at $\sim 7.8^\circ$; 13.4° ; 20° , and 21° [34] correlate to Miller indices of (001), (100), (012), (102). Quiroz *et al.* [35] said that methyl cellulose-based films release an amorphous-crystalline structure, especially a high intensity of $2\theta = 8^\circ$, a trimethylglucose type crystalline order and broad peak at $2\theta = 21.5^\circ$.

From Figure 16, diffraction peaks patterns of LiClO₄-complexed methyl cellulose are compared to [EMIm]Ac-plasticized of LiClO₄-complexed methyl cellulose. Both are showing Miller indices but having different intensity and a little bit of 2θ -shifts. Presence of [EMIm]Ac ionic liquid weakens inter- and intramolecular hydrogen bonds, could be detected by decreasing intensity. Decreasing of peak intensity correlate to decreasing of crystallinity; vice versa, increasing of amorphous. Decreasing of crystallinity gives contribution to Li-ion migration and segmental motion of polymer chain (methyl cellulose in this case), so it can improve ionic conductivities.

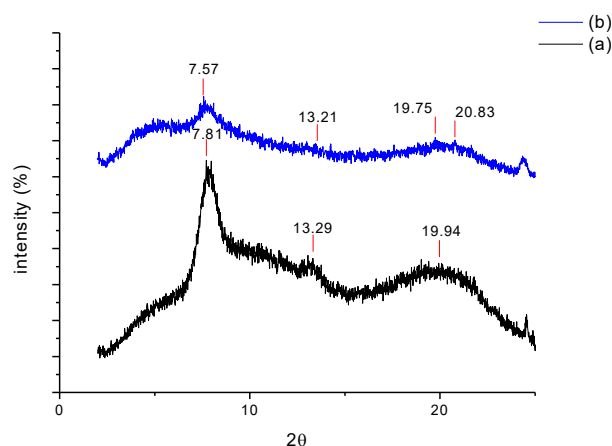


Figure 16. XRD pattern of Biopolymer electrolyte membranes, (a) MC/10% (w/w) LiClO₄; (b) MC/10% LiClO₄ /15% (w/w) [EMIm]Ac

3.9 The Morphology Study using Scanning Electron Microscopy (SEM)

Morphology studies was performed to both MC/10% LiClO₄ and MC / 10% LiClO₄ / 15% [EMIm]Ac by Scanning Electron Microscopy (SEM) (depicted at Figure 17). There is a significant difference between both samples.

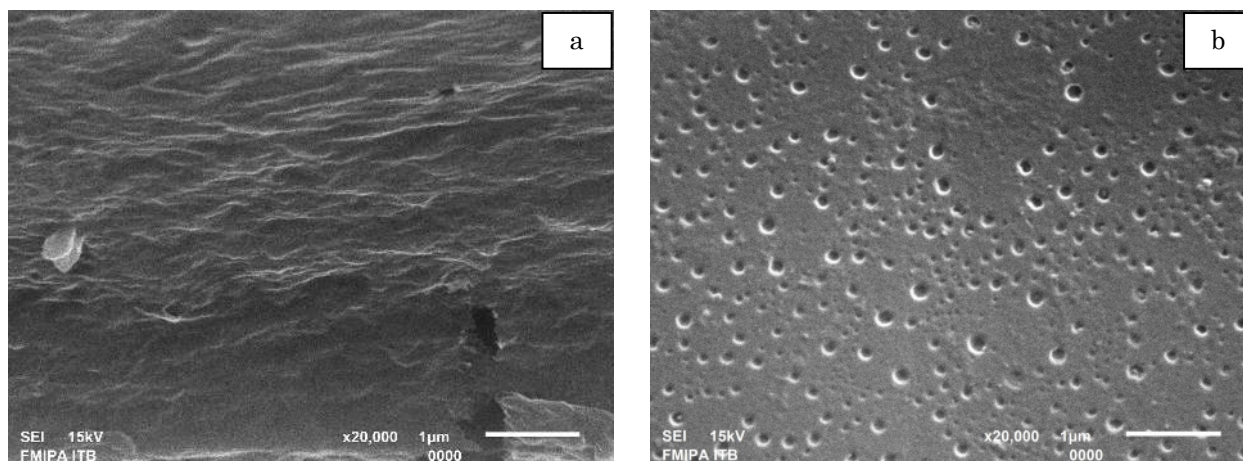


Figure 17. SEM analysis of (a) MC/10% LiClO₄; (b) MC/10% LiClO₄ /15% [EMIm]Ac

LiClO₄-complexed methyl cellulose shows morphology with no pores, while [EMIm]Ac ionic liquid-plasticized of LiClO₄-complexed methyl cellulose have some pores on its morphology.

There is a significant difference between both samples. LiClO₄-complexed methyl cellulose shows morphology with no pores, while [EMIm]Ac ionic liquid-plasticized of LiClO₄-complexed methyl cellulose have some pores on its morphology. The presence of pores indicate decreasing of crystallinity index as effect of [EMIm]Ac ionic liquid plasticization. [EMIm]Ac ionic liquid incorporation is able to weaken hydrogen interaction intra-/inter chain of methyl cellulose as polymer host. Therefore, the [EMIm]Ac ionic liquid has been succeeded to role as spacer which contribute the Li-ion diffusion and subsequently exhibited the high ionic conductivity.

3.10 Thermal Analysis of Biopolymer Electrolyte Membranes, BPE Membrane: MC/LiClO₄/[EMIm]Ac

Thermal stability of BPE: MC/LiClO₄/[EMIm]Ac was studied by Thermogravimetry Analysis (TGA), Differential Thermal Analysis (DTA) and Difference Thermo Gravimetry (DTG). The thermogram below shows TG, DTG, and DTA data of MC/LiClO₄ (Figure 18a) and MC/LiClO₄/[EMIm]Ac (Figure 18b).

If we compare to previous report [6], the onset degradation temperature of methyl cellulose-based membrane at ~300 °C, a decreasing occurred of onset degradation temperature after LiClO₄ salt incorporation to methyl cellulose. Figure 18a depicted the water removal

and the moisture desorption stages at 55.5 °C, while the onset decomposition temperature was occurred at 208.4 °C with 8.45% weight loss, and with 0.453 mg/minutes of rate at 299.1 °C, and melts at 308.7 °C. The offset decomposition temperature was occurred at 338.2 °C and remaining 24.2% of weight loss. A decreasing of LiClO₄-complexed methyl cellulose membrane onset decomposition temperature is attributed to crystallinity reducing as impacts disturb of inter-chain interaction of methyl cellulose. After the offset decomposition temperature of LiClO₄-complexed methyl cellulose, the charred at 600 °C occurred and the final residue has 24% of weight.

[EMIm]Ac ionic liquid incorporation gives new reason of thermal properties. Basically, its introduction into LiClO₄-complexed methyl cellulose matrix decreased the methyl cellulose inter-chain interactions, which contribute to Li-ion transport. Figure 18b depicted an increasing of onset decomposition temperature at 255.9 °C with 4.1% of weight loss, and with 0.355 mg of rate at 319.4 °C, due to the [EMIm]Ac ionic liquid incorporation. The offset decomposition temperature was occurred at 338.2 °C and remaining 24.2% of weight loss. The offset decomposition temperature is occurred at 369.6 °C and remaining 20.9% of weight loss. After the offset decomposition temperature of [EMIm]Ac-plasticized LiClO₄-complexed methyl cellulose, charred at 600 °C happened and remains 20.9% weight of residue. Although the crystallinity properties decrease, but the [EMIm]Ac ionic liquid acts to increase inter-molecular interaction (polymer chain and [EMIm]Ac ionic liquid), exhibits new thermal properties which is different to the

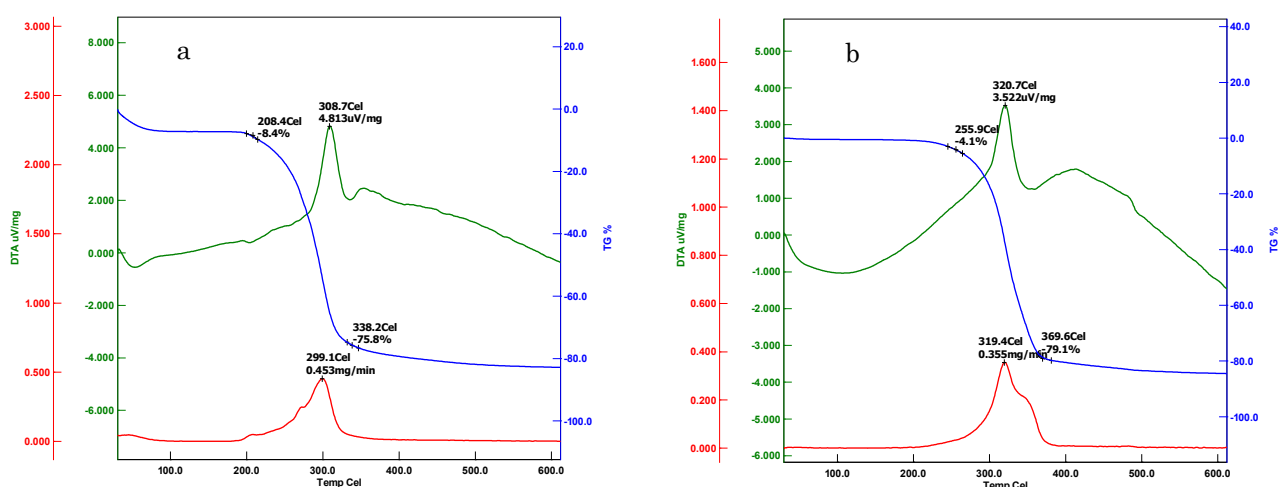


Figure 18. Thermogram of biopolymer electrolyte membranes, (a) MC/10% (w/w) LiClO₄; (b) MC/10% LiClO₄/15% (w/w) [EMIm]Ac

usual deconstruction of lithium salts to membrane matrix. This fact showed that the [EMIm]Ac ionic liquid is able to improve the biopolymer electrolytes thermal properties.

4. Conclusions

The 1-ethyl-3-methylimidazolium bromide, [EMIm]Br ionic liquid, as precursor of [EMIm]Ac, has been successfully synthesized from 1-methyl imidazole and bromoethane using Microwave Assisted Organic Synthesis (MAOS) Method, at power of 100 watts, 50 °C, 15 minutes and medium stirring. The 1-ethyl-3-methylimidazolium acetate, [EMIm]Ac ionic liquid, has been successfully synthesized from metathesis reaction between [EMIm]Br ionic liquid and potassium acetate (CH₃COOK) at room temperature for 1 hour. The [EMIm]Ac ionic liquid has the effect to increase the biopolymer electrolyte membranes of LiClO₄-complexed methyl cellulose, and at 15% [EMIm]Ac ionic liquid exhibited the optimum results in ionic conductivity, tensile strength, elongation break and thermal stability properties, which are 9.16 x 10⁻³ S.cm⁻¹, 24.19 MPa, 36.43%, ~256 and ~370 °C, respectively. These performances are sufficient to be used as a Li-ion batteries separator candidate.

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