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Effect of BMITFSI to the Electrical Properties of Chitosan/ MethylCellulose Based Polymer Electrolyte

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Abstract. Blended polymer electrolyte of methylcellulose (MC) / chitosan were prepared with different weight percentage of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMITFSI) via solution casting technique. The film was characterized by impedance spectroscopy to measure its ionic conductivity. Samples with 45% of BMITFSI exhibit the highest conductivity of $(1.51 \pm 0.13) \times 10^{-6} \text{ S cm}^{-1}$ at ambient. Dielectric data were analysed using complex permittivity and complex electrical modulus for the sample with highest conductivity. Dielectric data proved that the increase in conductivity is mainly due to the increase in number of charge carriers.

INTRODUCTION

Solid bio polymer electrolyte (BPE) is an electrolyte that exist in solid state and made up from natural substance [1,2]. Recently, solid BPE has become more attractive since it has better shape and easy to handle with no electrolyte leakage possibility [3]. Solid BPE needs to full fill certain requirement such as good ionic conductivity, low cost, good dimensional and good mechanical stabilities in order to be used in electrochemical devices [4]. Nowadays, many researcher has proposed the use of natural polymer to develop polymer electrolyte such as chitosan [5] and methyl cellulose [6]. To improve physical properties of polymer, blending technique has been used [7]. In order to enhance conductivity of BPE, ionic liquid are added to the electrolyte system. Ionic liquid is salt at room temperature due to its low melting point [1]. Previous study also shown that, ionic liquid can act as a plasticizer [2]. However, according to Radzir et al., ionic conductivity of BPE increases with concentration of ionic liquid due to the rise of charge carrier donor by ionic liquid. Hence, it can replace salt as the ion donor in the electrolyte system. Ionic liquid that contain fluorine atom, such as 1 butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMITFSI) are commonly used in electrochemical application. They are less sensitive to moisture due to their hydrophobic properties [8]. Thus, the objectives of the study is to produce a thin film of polymer electrolyte using polymer blending method of chitosan and methyl cellulose, doped with BMITFSI as charge carrier and plasticizer.

MATERIAL AND METHOD

Sample Preparation

A mixture of chitosan – methyl cellulose containing different weight percentage of BMITFSI was prepared by using solution casting technique. Methylcellulose and chitosan were dissolved separately in 60:40 ratio in which 0.6g chitosan was dissolved in 50ml in 1% diluted acetic acid while 0.4g methyl cellulose in 50ml distilled water. An amount of 10 w.t%, 15 w.t%, 20 w.t%, 25 w.t%, 30 w.t%, 35 w.t%, 40 w.t%, 45 w.t% and 50 w.t% of BMITFSI solution was added into the polymer solution. The solution was then further stirred to obtain homogenous solution and then casted onto plastic petri dish and left to dry at room temperature before further analysis.

Conductivity Measurement

The conductivity of the sample was measured by using Impedance Spectroscopy via HIOKI 3532 LCR Hi Tester Bridge interfaced to a computer. The impedance values were measured within the frequency of 50Hz to 1 MHz. A negative imaginary impedance, Z_i versus real impedance, Z_r with same scale of horizontal and vertical axes were then plotted where the bulk resistance, R_b could be obtained. Hence, the conductivity of the sample in room temperature can be calculated by using the following equation:

$$\sigma = t / R_b A \quad (1)$$

where R_b is bulk resistance, t is the thickness of the thin film and A is the surface area of contact. In order to measure the thickness of the thin film, a digital micro meter screw gauge was used.

RESULT AND DISCUSSION

Conductivity Studies

A cole-cole plot at ambient temperature was plotted in Fig. 1(a) and (b). It can be observed that, the value of bulk resistance, R_b decreases with the increase in BMITFSI concentration. The value of R_b can be determined by the intersection of spike and semicircle line. The semicircle on the plot indicate the characteristic of a corresponding combination of bulk resistance, R_b and bulk capacitance, while the inclined spike is the capacitance nature of the boundary and absence of electronic conductivity [9].

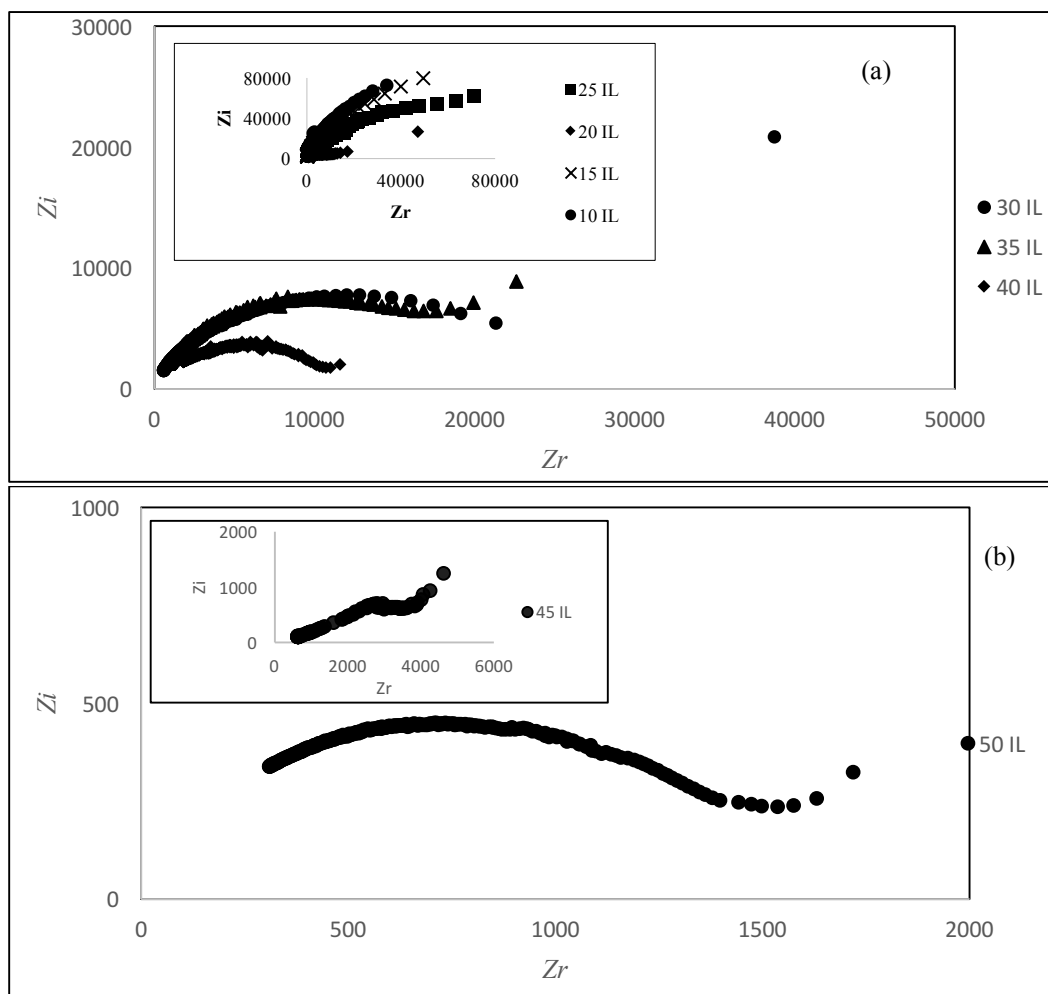


FIGURE 1. (a) Impedance plot at ambient temperature (onset figure shows impedance at low concentration of BMITFSI)
(b) Impedance plot at ambient temperature for 50 w.t % BMIMTFSI (onset figure shows impedance at 45 w.t % of BMITFSI).

The optimum conductivity recorded was at $(1.51 \pm 0.13) \times 10^{-6} \text{ S cm}^{-1}$ with addition of 45 wt% BMITFSI. Unfortunately the conductivity value decreased beyond 45 wt% of BMIMTFSI. The increase of ionic conductivity with increasing ionic liquid content could be due to the increase in concentration of mobile charge carrier [10]. The decrease of conductivity beyond the 45 wt% of ionic liquid can be inferred due to the excess concentration of ion in the polymer electrolyte host. Thus the distance between ion become closer, hence the rate of ion association is higher than rate of ion dissociation. As a result, the ion can react and produce neutral ion pair which is do not contribute to conductivity [2]. The plot of variation of ionic conductivity against BMIMTFSI concentration has been plotted in Fig. 2.

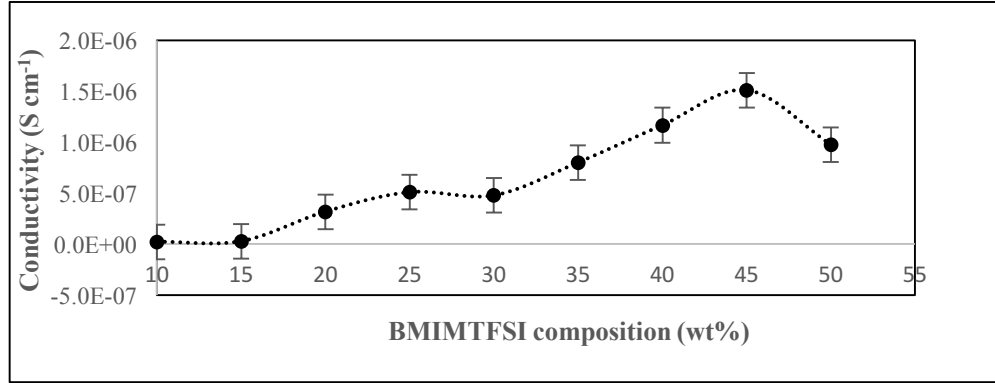


FIGURE 2. Variation of ionic conductivity as a function of BMITFSI concentration.

Dielectric behaviour study is the analysis of complex permittivity data. This analysis provides the information about the material electrode polarization, information on ion transport behaviour and ionic or molecular interaction in solid polymer electrolyte [11]. The increase in dielectric constant give arise in the number of charge carriers and is always taken to have high dissociation ability for ion-pair formation and eventually result in higher conductivity. The dielectric constant, ϵ_r , charge carrier, η and the dissociation energy, U are related according the equation:

$$\eta = \eta_0 \exp \left(-\frac{U}{\epsilon_r kT} \right) \quad (2)$$

where k is Boltzmann constant and T is absolute temperature.

In contrast, there will be also dielectric loss that will affect the conductivity of ions. Dielectric loss describes a direct measure of dissipation of energy and generally comprises the contribution from the ionic transport and also from polarization of a charge or a dipole. Both dielectric constant and dielectric loss can be represented by the following equations:

$$\epsilon_r = Z_i / \omega C_0 (Z_r^2 + Z_i^2) \quad (3)$$

$$\epsilon_i = Z_r / \omega C_0 (Z_r^2 + Z_i^2) \quad (4)$$

Here $C_0 = \epsilon_0 A/t$ where ϵ_0 is the permittivity of the free space, t the thickness of the sample, A is the area of contact and $\omega = 2\pi f$, which f representing the frequency in Hz respectively.

Figure 3 shows the variations of dielectric constant and dielectric loss as a function of frequency for Chitosan/Methyl Cellulose /BMIMTFSI complexes. As shown in the figure, there are no appreciable relaxation peaks: hence the dielectric constant in this present study act as an indicator to show that the increase in conductivity is due to an increase in the number of mobile ion.

Further analysis of the dielectric behaviour can further be confirmed by using the formulation of dielectric moduli, which highlight the bulk dielectric behaviour and suppresses the effect of electrode polarization [12]. Figure 4 shows the variations of real and imaginary part of dielectric modulus. The trend shows it is a conjugate result from the dielectric constant, hence it explains the negligible contribution of electrode polarization at low frequencies as the value are approaching zero [13]. The curve peaks at higher frequencies indicates the bulk effect which means that the polymer electrolytes are ionic conductor [14]. On another hand, the plot gives long tail at low frequencies which shows the contribution of large capacitance associated with the electrode [15].

The equation for the real modulus, M_r and the imaginary modulus M_i can be expressed as follows.

$$M_r = \varepsilon_r / (\varepsilon_r^2 + \varepsilon_i^2) \quad (5)$$

$$M_i = \varepsilon_i / (\varepsilon_r^2 + \varepsilon_i^2) \quad (6)$$

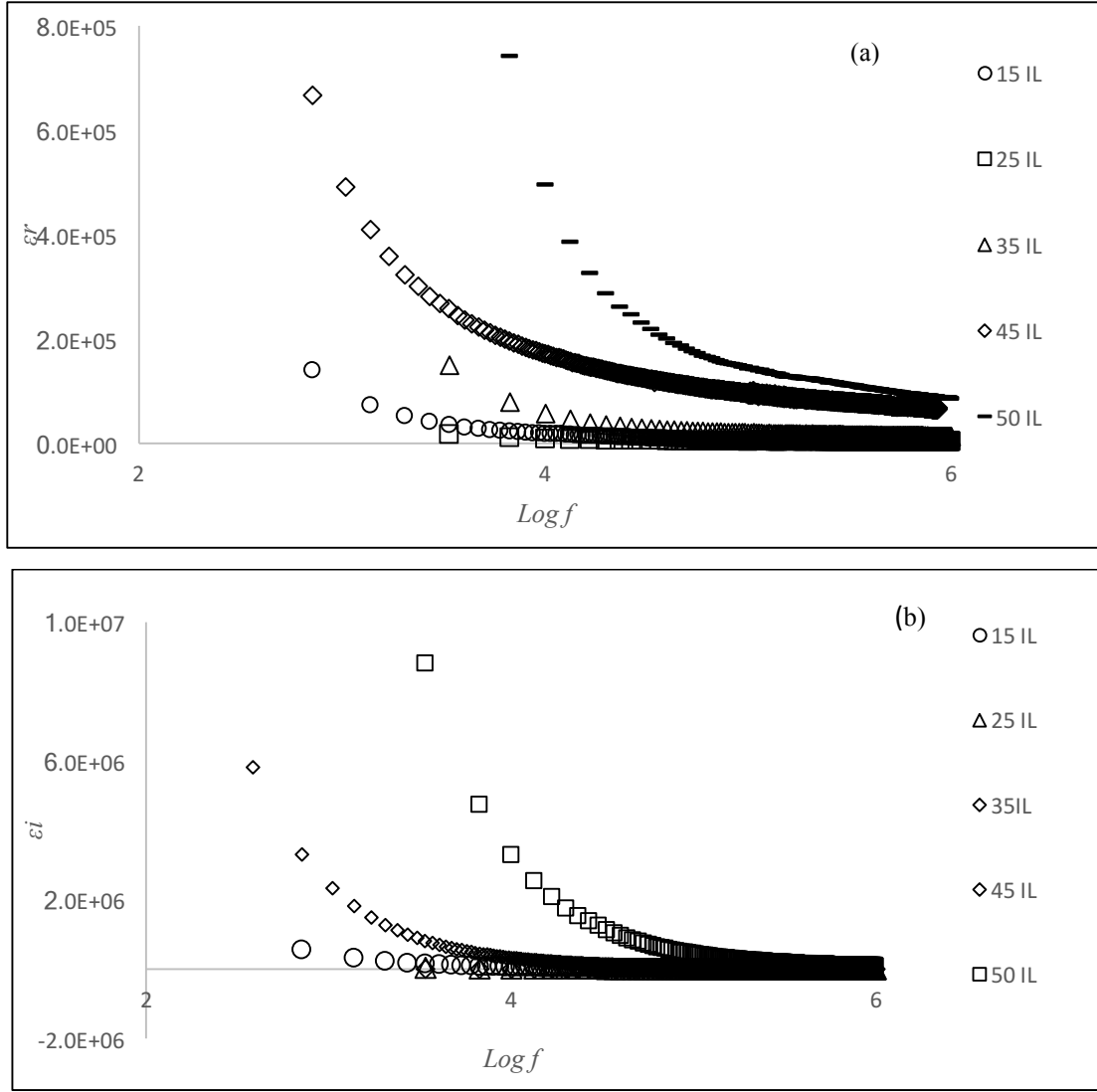


FIGURE 3. Variations of dielectric constant (a) and dielectric loss (b) as a function of frequency for CS/MC/BMIMTFSI complexes.

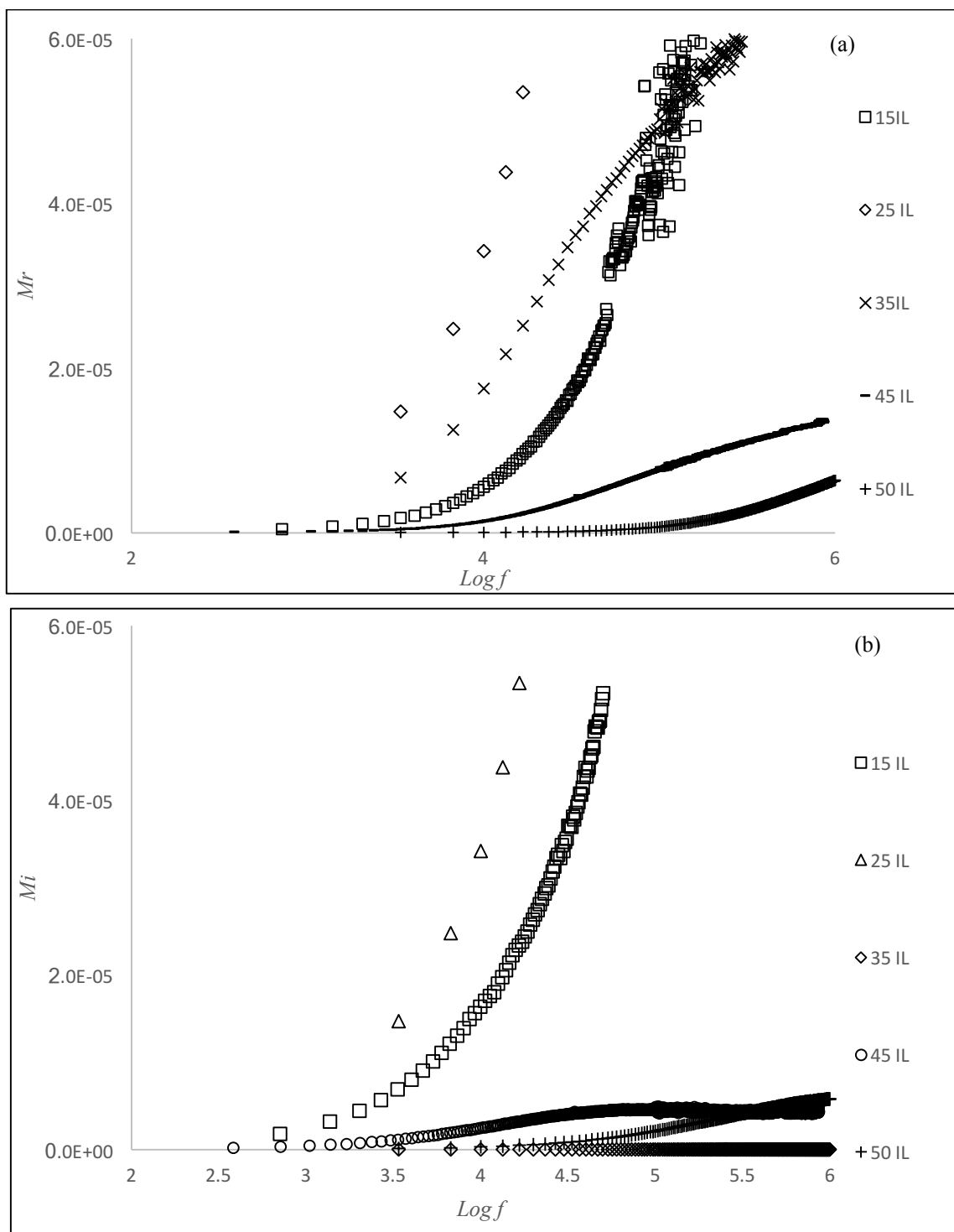


FIGURE 4. Variations of real (a) and imaginary (b) part of dielectric modulus as a function of frequency for Chitosan/Methyl Cellulose /BMIMTFSI complexes.

CONCLUSION

The polymer blend of solid polymer electrolyte from chitosan/ methylcellulose with different weight percentage of BMITFSI (10 to 50 w.t %) has been prepared via solution casting technique. The conductivity and dielectric behaviour of electrolyte system have been studied at room temperature as a function of frequency. The addition of BMITFSI gradually increases the ionic conductivity of polymer electrolyte when a maximum of $(1.51 \pm 0.13) \times 10^{-6} \text{ S cm}^{-1}$ for 45 w.t % of BMIMTFSI. The tendencies of dielectric constant, over the

concentration of BMITFSI propose that the number of charge carriers strongly influences the increase in conductivity.

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