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Ionic Conductivity and Conduction Mechanism Studies of CMC/ Chitosan Biopolymer Blend Electrolytes

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Abstract

The ionic conductivity of carboxymethyl cellulose/chitosan (CMC/CS) electrolyte containing various ammonium bromide (NH_4Br) compositions was prepared via solution cast method. The biopolymer blend electrolyte (BBE) films have been measured using Electrical Impedance Spectroscopy. The incorporation of 20 wt.% NH_4Br gives the optimum room temperature dc conductivity, σ_{dc} of 2.12×10^{-5} Scm^{-1}. Dielectric study shows dependence of BBE films on temperature, but independent to frequency. Based on the power law exponent result, CMC/CS-NH_4Br system can be represented by quantum mechanical tunnelling (QMT) model.

Keywords: Carboxymethyl cellulose, chitosan, ammonium bromide, dielectric behavior, quantum mechanical tunneling (QMT) model, conduction mechanism.

Introduction

Global climate change is a critical problem that everlasting and becomes a worrying environmental issue, which has resulted in actively work by public to minimize the current and upcoming environmental impact. The usage of 'bio-derived' materials in the polymer electrolyte (PE) system contributes to the white pollution[1] and will directly bring toward green nation. Since Wright and Armand discovered ionic conductivity in a PEO/Na^+ complex in 1975[2-3], there are a few numbers of natural polymer has been proposed by researchers as the application for the host polymer in the PE system, such aschitosan[4], κ-carrageenan[5], carboxymethylcellulose[6], and starch[7].

When comparing the solid polymer electrolyte to gel and liquid type, solid polymer electrolyte possess some advantages such as leakage-free and also has a simple preparation[8-9]. But it main drawback such as low in conductivity value gives an obstacle for researchers to produce high quality polymer electrolyte with good ionic conductivity[10], which then give a space for researchers to study and search on the best solution. There are many attempts has been made to enhance the conductivity of PE system, such as copolymerization[11-12], plasticization, blending, reduction of crystallinity, addition of unusual or inorganic salts, varying the salts concentration and addition of ceramic filler/additives[12].

Blending technique was proposed in this work and it is believed could enhance the conductivity and improved structural stability of the electrolyte films[13]. From the polymerist point of view, polymer blend is a mixture or combination of at least two macromolecular substances, polymers and copolymers[14-15]. This blending technique uses low cost conventional processing technique and displays several advantages such as simplicity of preparation and ease in controlling the physical properties of the polymer[16]. There are many polymeric blend have been previously discovered such as poly(vinyl chloride) (PVC)/ poly(ethyl methacrylate) (PEMA)[17-18], starch/ poly(ethylene oxide)(PEO)[14], poly(ethylene oxide) (PEO)/ poly(vinylpyrrolidone) (PVP)[19], poly(vinyl alcohol) (PVA)/ chitosan (CS)[20], poly(ethyl methacrylate) (PEMA)/ poly(vinyl alcohol) (PVC)[12], poly(vinyl chloride) (PVC)/ poly(methyl methacrylate) (PMMA)[21], poly(vinyl alcohol) (PVA)/ poly(vinylpyrrolidone) (PVP)/ chitosan[15], poly(vinyl chloride) (PVC)/ poly(vinylacetate) (PVAc)/ poly(ethylene glycol) (PEG)[22].

From the literatures, there is no report so far suggesting CMC and CS blend as natural polymer electrolyte film. In facts, organic polymer is usually known as insulator based in electronic component which gives the lowest ionic conductivity value (10^{-12}-10^{-18})[23]. With the blending technique applied to the system, it can enhance the conductivity value to the range of 10^{-8} Scm^{-1} though it is still cannot satisfy the conductivity required for electrolyte in battery system[9]. However, with the incorporation of dopant it is believed could further increase the conductivity value. Most of the previous reports show that the conductivity increase after the addition of salts into the polymer host, for example, 10^{-6} Scm^{-1} for PVC/ PEO-KBr salt[24], 10^{-7} Scm^{-1} for PEO/PVP-NaBr salt[19] and $10^{-6}Scm^{-1}$ for CS/PVA-NH_4I salt[25].

Besides that, the investigation of conduction mechanism involved in the system also becomes vital information in PE study in order to understand the conduction process of the blend polymer system. Various models have been proposed and explained by many researchers such quantum-mechanical tunnelling (QMT) model[23,25-26], correlated barrier-hopping (CBH) model[27-29], overlapping large polaron-tunnelling (OLPT) model[30] and small polaron-hopping (SPH) model[31]. This paper reports the ionic conductivity and dielectric study for CMC/CS with various compositions of ammonium bromide (NH_4Br) and investigate the conduction mechanism involved in the system.

Material and Methods

Preparation of BBE film: The BBEs were prepared via solution cast method. The 2:1 ratio of natural polymer blend, CMC (Acros Organic Co.) and CS (W.A. Hammond Drierite Company LTD) were dissolved in 1% acetic acid solution. To this solution, 5-30 wt.% of ammonium bromide (NH_4Br) were added separately and stirred continuously until it is completely dissolved. The solutions were casted into different Petri dishes and dried in the oven at 60 °C for the film formation. The yellow-ish BBE films were then kept in a desiccator for further drying to remove any traces of water before characterization process.

Impedance spectroscopy: Impedance spectroscopy measurements were performed to determine the ionic conductivity of BBE films. A round shape of BBE films were cut into 2 cm diameter and sandwiched between two stainless steel electrodes. The BBE films were then characterized using electrical impedance spectroscopy (EIS) equipped with HIOKI 3532-50 LCR Hi-Tester in the frequency range of 50 Hz to 1 MHz. Dc conductivity, $\sigma_{dc}$was expressed by using equation 1[9].

$$\sigma_{dc} = \frac{t}{R_b A} \quad (1)$$

Where A (cm^2) is the electrode-electrolyte contact area and t is the thickness of the electrolyte[9]. The bulk resistance, R_b can be obtained from the plot of negative imaginary impedance, $-Z_i$ versus real part of impedance, Z_r[9].

Dielectric constant, ε_r and dielectric loss, ε_i were calculated using equation 2 and equation 3, respectively.

$$\varepsilon_r(\omega) = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \quad (2)$$

$$\varepsilon_i(\omega) = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \quad (3)$$

Here, $C_o=\varepsilon_o A/t$ and $\omega=2\pi f$, where ε_o is the permittivity of free space[8].Based on Jonscher's Universal Power Law (UPL), the total ac conductivity, $\sigma(\omega)$ of biopolymer electrolyte is equal to the sum of dc conductivity, σ_{dc} and ac conductivity, σ_{ac}[32].

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac} \quad (4)$$

Ac conductivity can be expressed using equation 5 and equation 6 as reported by Majid and Arof[30] and Samsudin and Isa[33].

$$\sigma_{ac} = A\omega^s \quad (5)$$

$$\sigma_{ac} = \varepsilon_o \varepsilon_i \omega \quad (6)$$

Consolidating equation 5 and equation 6 gives equation 7 and equation 8.

$$\varepsilon_r \varepsilon_i \omega = A\omega^s \quad (7)$$

$$\varepsilon_i = \frac{A}{\varepsilon_o}\omega^{s-1} \quad (8)$$

By applying natural logarithm rule to equation 8, it gives

$$ln\, \varepsilon_i = ln \frac{A}{\varepsilon_o} + (s-1)\, ln\, \omega \quad (9)$$

Here, A is a parameter dependent on temperature and s is the power law exponent in the range of $0 < s < 1$[33]. In ac conductivity study, plot of s against T was investigated to determine the conduction mechanism involved in the system[25]. The value of s can be calculated from the slope, m of ln$\varepsilon_i$againstln ω, where $m= s$-1[33].

Results and Discussion

Dc conductivity study: Figure-1 shows the typical Cole-cole plot of BBE films with different NH_4Br compositions at 303 K. From the plots, two-well defined regions, namely a high frequency region semicircle arc and low frequency region inclination spike can be observed. In this present work, the semicircle represents the bulk effect of BBE which is due to the parallel combination of bulk resistance, R_b (proton migration) and bulk capacitance, C_b (immobile polymer chain)[29,34-36]. The inclination spike denotes the effect between two blocking electrodes which represent the formation of double layer capacitance of BBE film interface[37]. The value of R_b can be retrieved from the interception between low-frequency and high-frequency region on Z_r-axis.

It can be observed that the value of R_b decreased with the addition of NH_4Br composition up to 20 wt.%, and beyond that the R_b started to increase. With the decreasing in R_b value, the high semicircle arc seems to gradually faded away and completely disappeared at 20 wt.% of NH_4Br The depressed semicircles and inclines spikes (figure-1a, figure-1b and figure-1d) showed that the ions have different relaxation times and reveals non-Debye behaviour of the sample[27,34]. Incorporating with 20 wt.% of NH_4Br gives the highest dc conductivity, σ_{dc} value of 2.12 x 10^{-5} Scm^{-1}. The enhancement in σ_{dc}value is assumed due to the presence of ammonium salts (ionic dopant) in the system which was believed to be a good proton donor in a polymer matrix and expected to enhance in conductivity value [31,35]. On the other hand, the low-frequency inclined spike at 20 wt.% of NH_4Br in the plot indicates that the system is dominated by the only resistive component as illustrated in figure-1c [27,33].

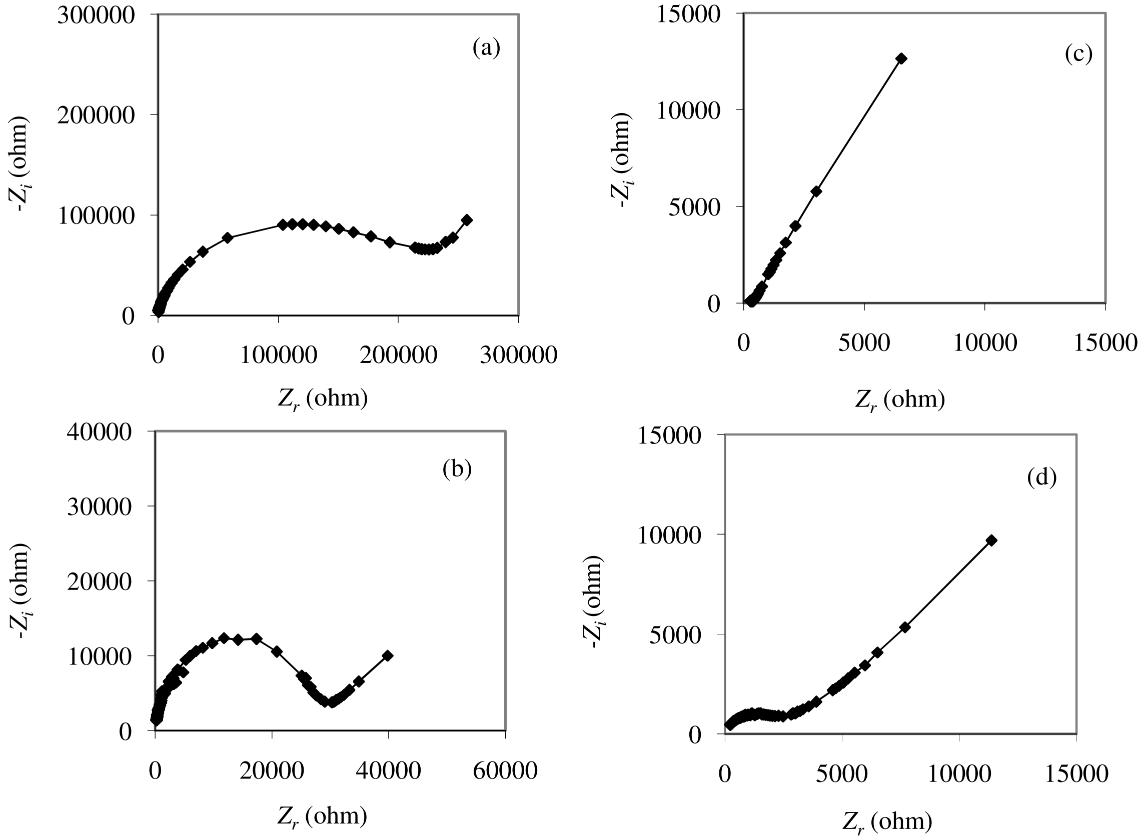

Figure-1
The Cole-cole plots of the imaginary impedance, $-Z_i$ against real impedance, Z_r biopolymer blend electrolyte system for (a) BBE film, (b) BBE-10 wt.% NH_4Br, (c) BBE -20 wt.% NH_4Br and (d) BBE-30 wt.% NH_4Br, respectively at 303 K

Figure-2 shows the NH_4Br composition dependence of dc conductivity, σ*dc* value of BBE film at selected temperatures. From the figure, the σ_{dc} of 20 wt.% NH_4Br seems to increase from 2.12 x 10^{-5} Scm^{-1} to 1.61 x 10^{-4} Scm^{-1} at higher temperature. According to Rajendran and Bama[38], the increasing in σ_{dc} with the temperature is due to the increase in free volume which then allowed ion to move freely through the polymer backbones. Besides that, the increasing in σ_{dc} can also be related to three phenomenons which are 1) ionic transport mechanism and its coordinating sites, 2) local structural relaxation and 3) segmental motion of BBE chains in free volume system[39]. As the temperature increases, the segmental motion of BBE chains have enough vibration energy to push against hydrostatic pressure exerted by its neighbouring atom and created a small amount of space surrounding for vibrational motion to occur in which causes augmentation in mobility ion, thus instantly boosted up the σ_{dc}[38-39]. In BBE films, there are two different ionic mobile species involved in the system, which are cation (+ve) and anion (-ve). In this present work, it is believed that proton ion (cation) takes fully responsible for ionicconductivity of BBE films since Samsudin and Isa[29] have reported that H^+ is the predominant conducting species in ammonium salts.

Dielectric study: The study of dielectric in polymer electrolyte brings a deep insight into the characteristic of ionic and molecular interaction[23,40]. In figure-3, it shows the NH_4Br compositions dependence of dielectric constant, ε_r at selected frequencies. From figure-3, ε_r found to increase by the addition of NH_4Br and reached maximum value at 20wt.% of NH_4Br and beyond that it is begin to decrease. The increasing of ε_r value together with the addition of NH_4 Br composition is due to the increase in number density of store charge as a result of salt dissociation in the polymer matrix[41]. However, at above 20 wt.% of NH_4Br, the distance between ions become smaller and easy for ion to form neutral pair which then leads to the clustering ion. Thus, limit the mobility of ions in the system and instantly reduce in σ_{dc} and also ε_r[6, 32].

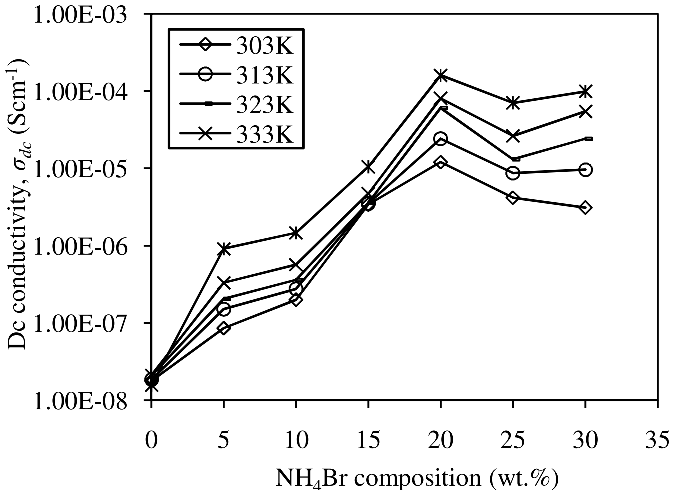

Figure-2
NH$_4$Br composition dependence of dc conductivity, σ_{dc}BBE films at selected temperatures

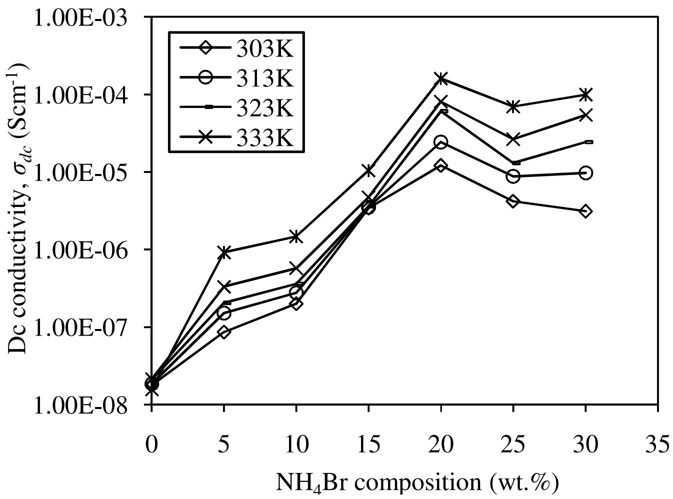

Figure-3
NH$_4$Br composition dependence of dielectric constant, ε_r at selected frequencies

Figure-4 displays the temperature dependence of dielectric constant, ε_r for the highest dc conductivity, σ_{dc} sample at selected frequency. Based on figure-4, the value of ε_r rise sharply at higher temperature, but it decreases with the increasing of frequency. As temperature increase, ions have sufficient energy to dissociate and produce higher mobile charge carrier in the system. Besides that, the degree of re-dissociation process of pairing or clustering ion can also be improved by heating up the samples, hence increase the concentration of free charge carriers which are favourable for transportation[42]. Furthermore, the value of ε_r as depicted in figure-4 also found closed to zero at 100 kHz. At this frequency, ε_r tends to be temperature independent. This can be attributed to the electrode polarization effect at the optimum degree of dissociation[40].

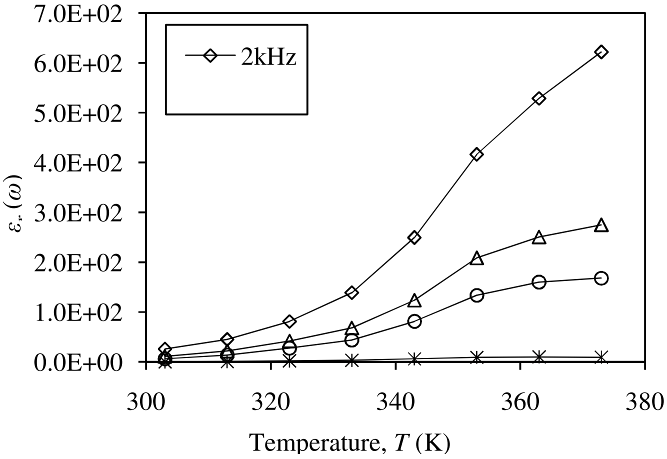

Figure-4
Temperature dependence of dielectric constant, ε_r for BBE - 20 wt.% NH$_4$Br film at selected frequencies

Acconductivity study: Ac conductivity: Ac conductivity measurement of BBE system was performed to investigate the conductionmechanism[43]. Figure-5 represents the frequency dependence of dielectric loss for the highest conductivity sample (20 wt.% of NH$_4$Br) at selected temperature in the higher frequency region. Based on the figure, the value of exponent s can be obtained from the slope of ln $\varepsilon_i$against ln ω, where there is assign no or minimal space charge polarization occur at this acceptable frequency range of 12.0<ln ω<14.0[25]. According to Buraidah et al.[25], the reduction of electrodes polarization nearest to zero in higher frequency region is due to the shorter period taken for the direction of electric field to change at faster rate.

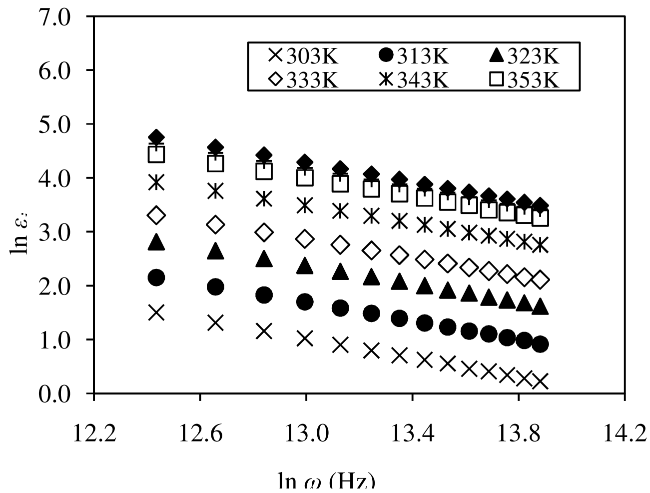

Figure-5
Ln ε_i against ln ω at selected temperature for BBE-20 wt.% NH$_4$Br film

The plot of s against T is shown in figure-6. From the plot, it directly evidenced that BBE system follows quantum mechanical tunnelling (QMT) model, in which the exponent s is temperature independent and nearly consistent as the temperature increase[23, 26]. Shukur et al.[26] stated that the ionic hopping between two sites is not only occurs by jumping over a barrier, but can also accompanied by QMT. In this work, the plot of s against T can be fitted to the equation $s = 0.0001T + 0.1106$. From this fitting equation, a small gradient values of s almost independent to temperature and tend to go constantly with temperature. Thus, it indicates that the ionic conduction of BBE system is accompanied by QMT model as similar reported for other polymer-salt systems[23,26,32]. In this quantum mechanical phenomenon, the polaron which is made up of conducting proton together with their stress fields, are attempting to travel and tunnels through the potential barrier that exist between two possible complexation sites with the addition of NH_4Br in the present BBE system[23, 30].

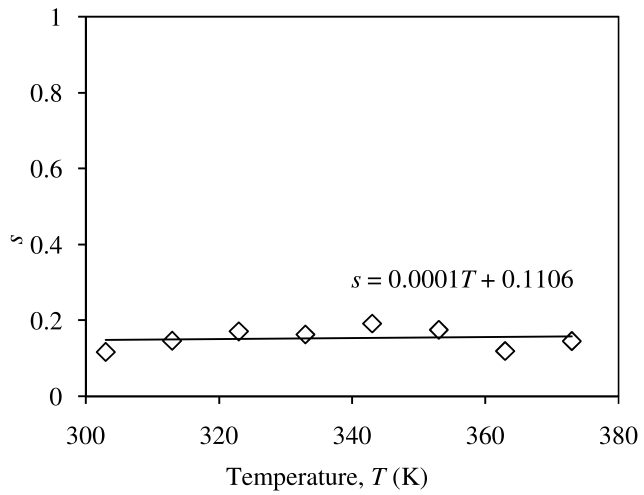

Figure-6
Plot of exponent s against T for BBE-20 wt.% NH_4Br film

Conclusion

A yellow-ish transparent CMC/CS-NH_4Br BBE films were successfully prepared using solution casting technique. Dc conductivity for the highest BBE film of 2.12 x 10^{-5} Scm^{-1} containing 20 wt.% NH_4Br was obtained at room temperature, and gradually increases with temperatures. From dielectric analysis, ε_r was observed to increase with the increasing inNH_4Br composition. This is due to the increase in charge density which provides more space for ion mobility. The ε_r also found to increase with temperature but decrease with the frequency. As temperature increase, pairing ions gain enough energy to break away from its coordination thus formed free charge ions for transportation. The conduction mechanism studies showed that the BBE film for 20 wt.% NH_4Br was accompanied by quantum mechanical tunnelling (QMT) model in which the value of s is independent to temperature.

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