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Influence of Polyethylene Glycol (PEG) in CMC-NH₄BR Based Polymer Electrolytes: Conductivity and Electrical Study

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Abstract

The present work was carried with new type and promising polymer electrolytes system by development of carboxyl methylcellulose (CMC) doped NH₄Br and plasticized with polyethylene glycol (PEG). The sample was successfully prepared via solution casting with no separation phase and good mechanical properties. The electrical conductivity and thermal conductivity of CMC-NH₄Br-PEG based PE system have been measured by the electrical impedance spectroscopy method in the temperature range of 303–373 K. The highest ionic conductivity gained is $2.48 \times 10^{-3} \text{ Scm}^{-1}$ at ambient temperature for sample contain with 8 wt. % PEG. It can be concluded that the plasticized is accountable for the conductance and assist to enhancing the ionic conductivity of the CMC-NH₄Br-PEG electrolyte system. The addition of PEG to the CMC-based electrolyte can enhance towards the cation mobility which is turn increases ionic conductivity. The conductivity-temperature of plasticized BdPEs system was found obeys the Arrhenius relation where the ionic conductivity increases with temperature and activation energy for the ions hopping of the highest conducting PE system only required small value to migrate. The electrical studies show a non-Debye behaviour of BdPEs based on the analyzed data using complex permittivity, ϵ^* and complex electrical modulus, M^* of the sample at different temperature.

Abstrak

Pengaruh Polietilena Glikol (peg) di dalam Elektrolit Polimer berbasis CMC-NH₄BR: Studi Konduktivitas dan Kelistrikan. Pekerjaan yang sekarang ini dilaksanakan dengan sistem elektrolit polimer tipe baru dan yang menjanjikan dengan pengembangan NH₄Br yang didoping karboksil metil selulosa (CMC) dan diplastisasi dengan polietilena glikol (PEG). Sampel dibuat secara sukses melalui penuangan larutan tanpa fase pemisahan dan dengan sifat-sifat mekanik yang baik. Konduktivitas listrik dan konduktivitas panas sistem PE berbasis CMC-NH₄Br-PEG telah diukur melalui metode spektroskopi impedansi listrik di dalam kisaran temperatur 303–373 K. Konduktivitas ionik tertinggi yang diperoleh adalah $2,48 \times 10^{-3} \text{ Scm}^{-1}$ pada temperatur lingkungan untuk kandungan sampel dengan 8% berat PEG. Dapat disimpulkan bahwa pemlastisan tersebut bertanggung jawab atas konduktansi dan membantu meningkatkan konduktivitas ionik sistem elektrolit CMC-NH₄Br-PEG. Penambahan PEG ke elektrolit berbasis CMC dapat meningkat ke arah mobilitas kation yang pada akhirnya meningkatkan konduktivitas ionik. Konduktivitas-temperatur sistem BdPEs yang diplastisasi terbukti mengikuti hubungan Arrhenius di mana konduktivitas ionik naik karena temperatur dan energi aktivasi untuk lompatan ion pada sistem PE konduksi tertinggi hanya memerlukan sedikit energi aktivasi untuk bermigrasi. Studi kelistrikan menunjukkan perilaku non-Debye pada BdPEs berbasis pada data yang dianalisis dengan menggunakan permitivitas kompleks, ϵ^* dan modulus listrik kompleks, M^* dari sampel tersebut dengan temperatur yang berbeda.

Keywords: carboxyl methylcellulose, ionic conductivity, plasticized, activation energy, electrical studies

1. Introduction

Recently, plasticized polymer electrolytes have been extensively used in the electrochemical devices, like secondary batteries, fuel cells, sensors, and smart windows. In order to improve their electrical and

electrochemical properties for technical and industrial application, structural modification through plasticized polymer electrolytes is extensively used. In order to overcome these drawbacks, adding plasticizers in SPEs was considered one of the most effective ways to bring a desirable enhancement in their conductivity by

improving the mobility of ionic or/and the interfacial interaction among ionic and polar groups in polymer chains by several researchers [1,2–5]. In the previous researcher's reported on CMC doped with NH_4Br system and have found that the sample containing 25 wt.% NH_4Br achieved the highest conductivity value of $1.12 \times 10^{-4} \text{ Scm}^{-1}$ [6]. In the present work, CMC doped with NH_4Br is plasticized with 8 wt. % PEG shows the highest ionic conductivity value of $2.48 \times 10^{-3} \text{ Scm}^{-1}$. It can be noted here that the plasticizer is the best method to enhance the ionic conductivity of the BdPEs electrolytes. The addition of plasticizers in polymer electrolyte is one of the most effective approaches to improve the mobility of ionic or/and the interfacial interaction among ionic and polar groups in polymer chains. The choice of plasticizer and its concentration can affect film permeability and mechanical properties by several researchers [7, 8].

for biopolymer electrolyte is carboxyl methylcellulose (CMC). CMC is one of cellulose derivatives, which displays biodegradable and non-hazardous properties [9]. In this research, ammonium bromide (NH_4Br) has been taken as the depend seat in the development of CMC–salt complexes based polymer electrolytes (BdPEs) system. Ammonium salts have already known with its properties as a good proton donor to the polymer host. In the present study, we outline the effect of plasticizers that is PEG on electrical properties of electrolyte that is ionic conduction and ionic behaviour (electrical and dielectric response).

2. Methods

Preparation of biopolymer electrolyte films. Formulation of carboxyl methyl cellulose (CMC) doped NH_4Br based biopolymer electrolytes have been prepared via solution cast technique with distilled water was used as a solvent. For the preparation, 2 g of CMC was dissolved into distilled water and then, 25 wt. % of NH_4Br (due to the highest ionic conductivity from the previous report) [10] with a varied amount of plasticized, PEG in weight percentage (2-20 wt. %) was added into CMC solution. The mixture was stirred with magnetic stirrer until homogenous solution was obtained with no phase separation. The mixture was then poured into several petri dishes and left dry in the oven at temperature of 55°C for the plasticized biopolymer film to be formed. The film will be kept in desiccators before being characterized to ensure no water content in the polymer electrolyte system.

Characterization of CMC BdPEs system electrical impedance spectroscopy (EIS). The CMC- NH_4Br -PEG BdPEs films were analyzing via Electrical Impedance Spectroscopy model HIOKI 3532-50 LCR Hi-Tester at varies frequency of 50 Hz to 1 MHz. The films was cut into a suitable size of diameter 2 cm and placed between

two stainless-steel blocking electrodes of the sample holder which connected to the EIS. The software controlling the measurement recorded the real and imaginary impedance at various frequencies. The bulk resistance (R_b) value was obtained from the plot of imaginary impedance (Z_i) versus real impedance (Z_r) and the conductivity of the samples was calculated using the eq.(1) below:

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

where t is thickness of the film and A the cross-sectional area. The dielectric constant, ϵ_r , the dielectric loss, ϵ_i the real electrical modulus M_r and the imaginary electrical modulus M_i can be determined from complex impedance calculated using the eq.(2), eq(2), eq(3), eq(4) and eq(5) below :

$$\epsilon_r = \frac{z_i}{wC_o(z_r^2 + 1)} \quad (2)$$

$$\epsilon_i = \frac{z_r}{wC_o(z_r^2 + z_i^2)} \quad (3)$$

$$M_r = \frac{\epsilon_r}{wC_o(\epsilon_i^2 + \epsilon_r^2)} \quad (4)$$

$$M_i = \frac{\epsilon_i}{wC_o(\epsilon_i^2 + \epsilon_r^2)} \quad (5)$$

The plot from Figure 4 can be considered Arrhenian by the relation according to the in eq (6) :

$$\sigma = \sigma_0 \exp\left(\frac{Ea}{KT}\right) \quad (6)$$

where σ_0 is the pre-exponential factor, Ea is the activation energy and k is the Boltzman constant.

3. Results and Discussion

Conductivity study. The resultant Cole-Cole plot for various samples were obtained and tabulated as shown in Figure 1. The high frequency semicircle can be related to the ionic conduction process in the bulk of the polymer electrolytes and the low frequency spike has been attributed to the effect of blocking electrodes since in this research used stainless steel as an electrode, Nitya et al., [11]. From the individual Cole-Cole plots, the bulk resistances, R_b , were obtained and equation (1) was used to calculate the conductivity, σ , for each sample. The graph of conductivity versus plasticizer contents (wt. %) at room temperature is shown in Figure 2.

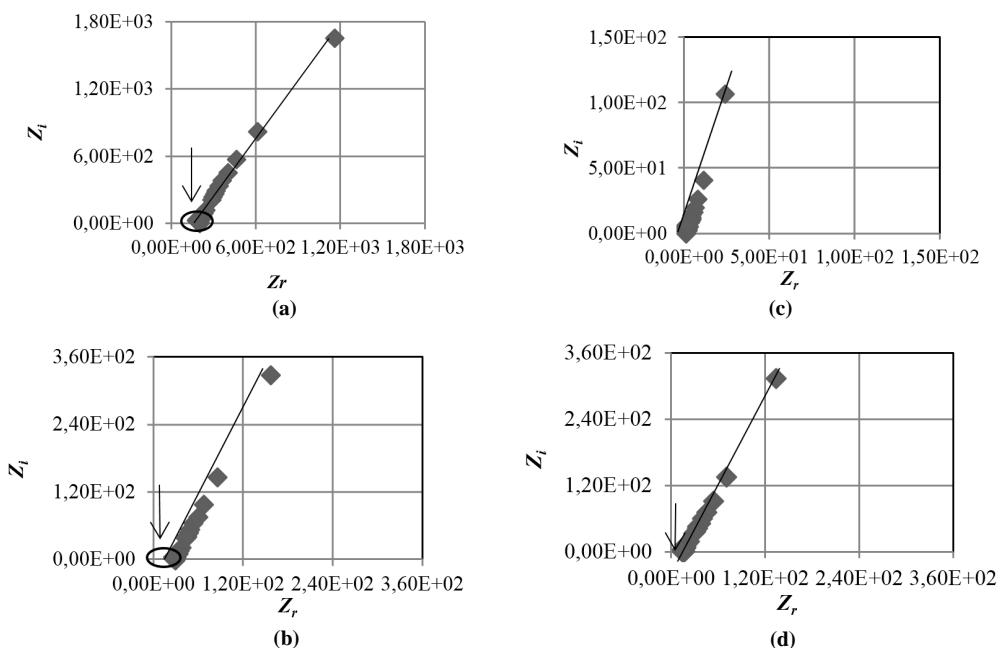


Figure 1. The Cole-Cole plot from EIS results

The R_b value for all samples starts to decrease when plasticizer was added and affect the ionic conductivity of the system. According to the previous report which using plasticizer in polymer electrolytes system, similar observation was found where addition of 8 wt. % of PEG the ionic conductivity increases compare to unplasticized sample from 1.12×10^{-4} to $2.48 \times 10^{-3} \text{ Scm}^{-1}$ [6]. It can be inferred that the PEG as plasticized is the best method to increase the dissociation of salt which promote the higher ionic conductivity [12]. It can be proven also based to the result of Samsudin et al., [13], the ionic conductivity increased to $3.31 \times 10^{-3} \text{ Scm}^{-1}$ when 8 wt. % ethylene carbonate (EC) was added. The conductivity increased by three orders of magnitude when PEG was added into solid biopolymer electrolyte system. According to Samsudin et al., [14], this phenomena can be explained in terms of the two factors, where are plasticizer had a function to act as an agent in enhancing the conductivity of the biopolymer electrolyte system. The weakly bound of H^+ of NH_4^+ can easily be dissociated due to increase in amorphous and these H^+ ions can hop from one site to another leaving a vacancy which will be filled by another H^+ ion from a neighboring [15, 16]. PEG does not supply ions to the electrolyte system. It is a plasticizer that is able to dissociate more salt into ions and has a low viscosity that can increase ionic mobility. The factors are; a higher percentage of plasticizer would give a greater ionic transport and to provide a large conducting phase. More salt could be dissociated with the present of plasticizer. Beyond the content of plasticizer (8 wt. %) which give the maximum value of ionic conductivity, will cause accumulation of ions which then will limit the movement of mobile ions, thus reducing the ionic

conductivity of BdPEs system.

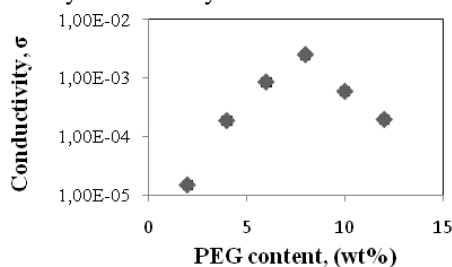


Figure 2. Conductivity against PEG Contents wt. at Room Temperature

Temperature dependence. Figure 3 shows the temperature dependence of ionic conductivity for BdPEs system at various temperatures. It can be observed that the conductivity increase linearly with temperature, which showing that the conductivity is thermally assisted. According to Samsudin et al., [14], the increasing of conductivity value with temperature because the internal modes are activated where, semi-crystalline nature of the electrolytes turn into amorphous nature. The relationship between log conductivity and $1000/T$ is almost linear. The regression value, R^2 was found close to unity. From this observation, it revealed that the temperature relationship of BdPEs system obey Arrhenius rule.

The activation energy, E_a can be obtained from the slope and each value for all samples were plotted as depicted in Figure 4.

Activation energy is the energy required for anion to begin movement. In the context of polymer electrolytes, the ion is usually “loosely bound” to a site with donor

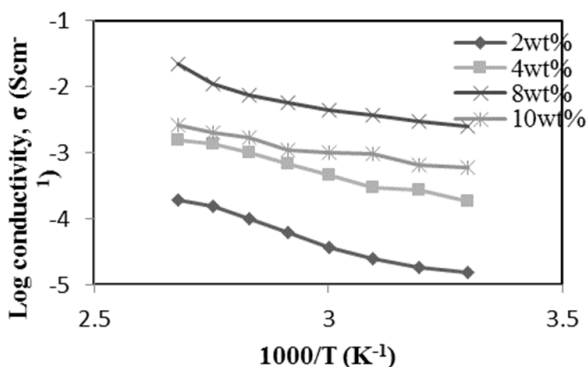


Figure 3. Temperature Dependence of Ionic Conductivity for BdPE System

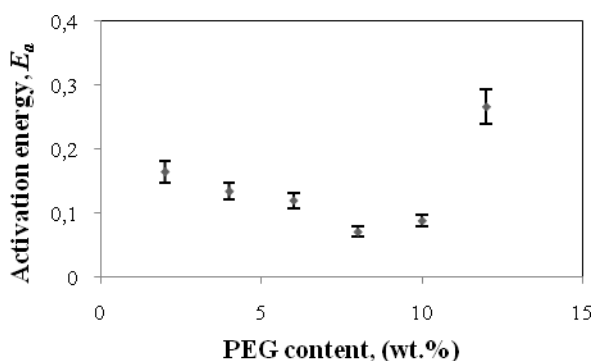


Figure 4. Activation Energy Against Plasticizer Content

electrons. When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site. The movement from one site to other which results in the conduction of charge and the energy for this conduction is the activation energy. According to the Anderson–Stuart model [17], the activation energy is the sum of the binding energy of the ion to its site and the kinetic energy for migration. If the energy of the ion is only sufficient to overcome the binding energy, then it will be dislocated from its site but will still be at the same location. Only if it has more energy than this binding energy will it be a free ion. It can be observed that E_a decreases as conductivity of sample increases implying that the ions in highly conducting samples require lower energy for migration. As shown in Figure 4, it can be observed that, the activation energy is reduced when PEG was added. The highest content of plasticizer in the CMC based BdPEs system shows the lowest activation energy. It can be noted here; the low activation energy to the ion transport, which completely amorphous in nature and speed up the H^+ ion motion when plasticizer was introduced in the polymer system Samsudin et al., [18]. The variation in E_a could be attributed to a variation in the polymer segmental movement. An increase in E_a with further addition of PEG as a plasticizer suggests a decrease in segmental motion of polymer chains. Since the ion transfer is

greatly affected by the polymer segmental motion an electrolyte with lower value of E_a implies rapid ionic conduction and hence higher conductivity. Moreover, Srivastava et al., [19] have also ruled out the possibility of vehicular NH_4^+ motion. It is known that plasticizer can make the sample more amorphous thus can enhance the ionic conductivity [20, 21]. Also, the enhancement in conductivity is normally accompanied by the decrease in activation energy [22].

Dielectric constant and loss study. The dielectric constant and dielectric loss curve for BdPEs system at different temperature were presented in Figure 5 and Figure 6 respectively.

Figure shows the frequency dependence of dielectric constant, ϵ_r and dielectric loss, ϵ_i respectively for sample at 8wt.% of plasticizer. This sample confirms non-Debye dependence based on sharp rise of the dielectric value towards low frequencies and can be attributed to dielectric polarization [23]. This implies that the mobile ions tend to accumulated at this point. The increasing in conductivity with the addition of 8wt. % of plasticizer also can relate to the high dielectric value obtained from result. The effect of the plasticizer in increasing the ability of a polymer to dissociate the salt has also been observed by other workers Forsyth et al., [24].

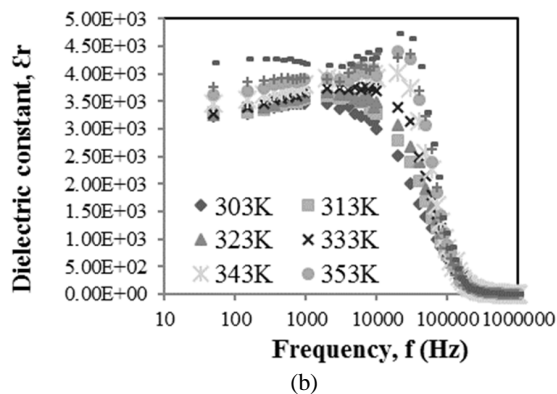
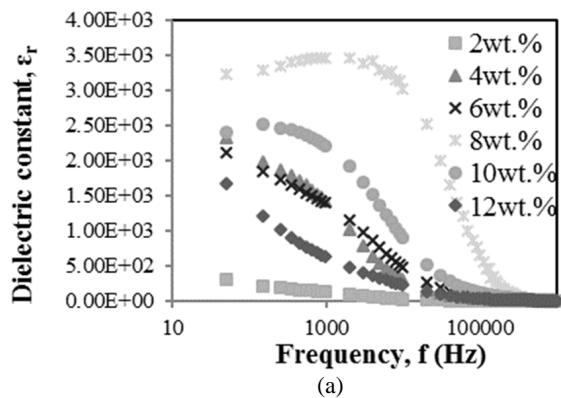
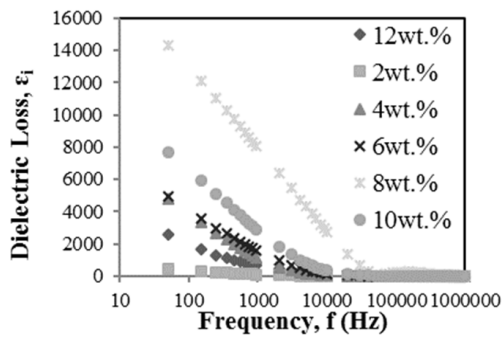
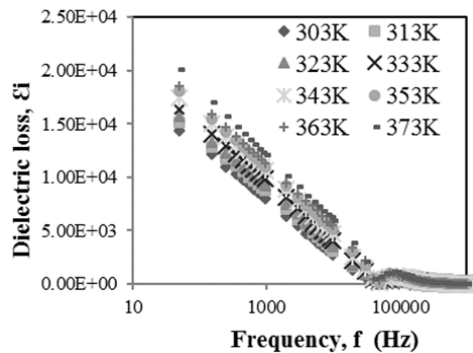


Figure 5. Dielectric Constant of Sample Plasticized CMC BdPEs System at Different Temperature

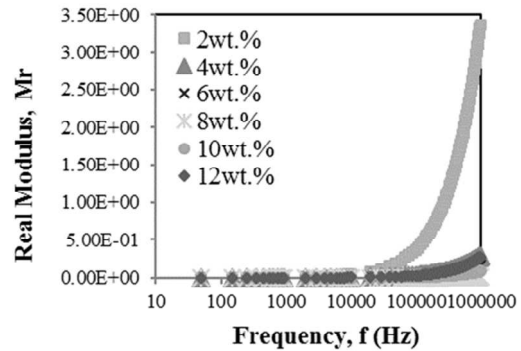


(a)

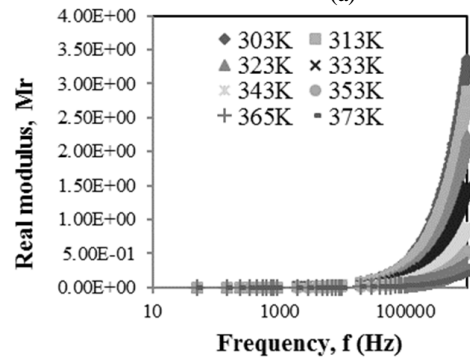


(b)

Figure 6. Dielectric Loss of Plasticized CMC BdPE System at Different Temperature



(a)



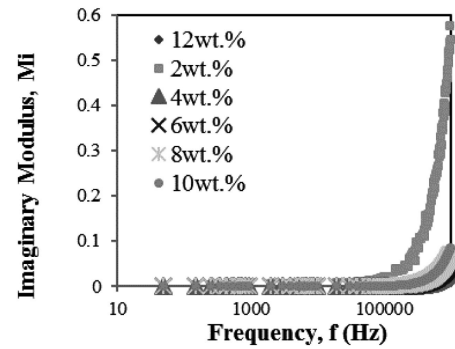
(b)

Figure 7. Real Modulus Study of Plasticized CMC BdPEs System at Different Temperature

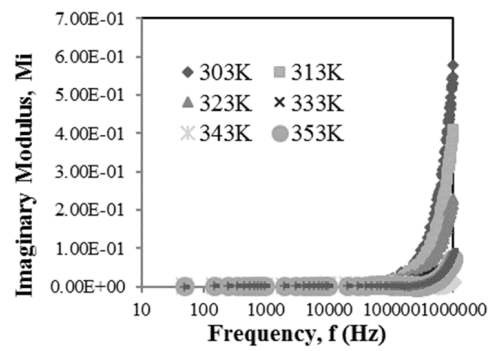
Alternatively, plasticization can also increase ionic mobility by reducing the potential barrier to ionic motion as a result of the decreasing cation–anion coordination of the salt [24]. In this present research, the conductivity of BdPEs system exhibits relaxation which non-exponential in time and this turn to a direct proportional relationship between the rates of reversal of the electric field, so there was no time to charge to build up at the interface. Thus, the polarization due to charge accumulation decreased that led to the lessening in the value of dielectric constant and loss when PEG was added.

Modulus study. Figure 7 and Figure 8 show the frequency dependence of the real and imaginary parts of modulus formalism respectively.

Figure 7 (a) and (b) depicts that both Modulus real, M_r and Modulus imaginary, M_i formalism show an increase at the high frequency end. According to Ramesh et al., [25], the presence of peaks in the modulus formalism at higher frequencies for all samples with increasing temperature is an indicator that the polymer electrolyte films are ionic conductors. It shown an increase in the higher frequency without any relaxation peaks was observed M_r and M_i approaches to zero at low frequency and this long tail is attributed to the large capacitance associated with the electrode polarization.



(a)



(b)

Figure 8. Imaginary Modulus Study of Plasticized CMC BdPEs System at Different Temperature

The visual aspect of a long tail at low frequencies indicates that in that respect might be a large capacitance associated with the electrodes used in the EIS. This further confirms the non-Debye behaviour in the BdPEs system [23].

4. Conclusion

Conductivity and electrical studies of polymer electrolytes (BdPEs) film based on carboxyl methyl cellulose (CMC) doped NH_4Br and plasticized with polyethylene glycol (PEG) have been prepared by the solution-casting technique. For the plasticized system, with 8 wt.% PEG the electrolyte exhibits the highest ionic conductivity of $2.48 \times 10^{-3} \text{ Scm}^{-1}$. The temperature dependence of ionic conductivity found obeys the Arrhenius relation where the ionic conductivity increases with temperature. The activation energy was revealed to be inversely proportional to ionic conductivity. The electrical studies confirmed of the highest conductivity sample shows non-Debye behaviour of ionic conduction of CMC doped NH_4Br and plasticized with PEG system. From the performance of this BdPEs system was found that plasticizer play an important role to improve the ionic conductivity of BdPEs.

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