Ethylene Carbonate and Polyethylene Glycol as Efficient Plasticizers in CMC-PVA-NH₄NO₃-Based Polymer Electrolyte

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Abstract

This study investigated the influence of plasticizers (polyethylene glycol [PEG] and ethylene carbonate [EC]) on the ionic conduction of CMC-PVA-NH$_4$NO$_3$. Blended biopolymer electrolytes (BBEs) based on carboxymethyl cellulose–polyvinyl alcohol (CMC-PVA) doped with ammonium nitrate (NH$_4$NO$_3$) were obtained via casting solution technique incorporated with PEG and EC, which acted as plasticizers. Electrical impedance spectroscopy (EIS) was conducted to evaluate the effect of plasticization on the ionic conduction properties. The ionic conductivity improved from 1.70×10^{-3} S/cm for un-plasticized BBEs to 3.92×10^{-3} S/cm for plasticized BBEs with EC and 3.00×10^{-3} S/cm for plasticized BBEs with PEG. The improvement indicated that the plasticizers weakened the Coulombic force and promoted further dissociation in the ionic dopant. The highest ionic conductivity was achieved for BBEs plasticized with EC, thereby suggesting the suitability of EC as plasticizer in this present system. The BBE system showed the Arrhenius characteristic at elevated temperatures and demonstrated increasing ionic conductivity. Dielectric properties of all BBE systems were found to improve upon the addition of EC and PEG, demonstrating their correlation with ionic conductivity.

Abstrak

Etilen Karbonat dan *Polyethylene Glycol* (PEG) sebagai Pemlastis yang Efisien dalam *Polymer Electrolyte* Berbasis CMC-PVA-NH₄NO₃. Kajian ini berkenaan dengan penyiasatan pengaruh campuran plastik (polietilena glikol [PEG] dan etilena karbonat [EC]) pada kekonduksian ion di dalam CMC-PVA-NH$_4$NO$_3$. Elektrolit biopolimer campuran yang diadaptasi berdasarkan kandungan karboksimetil selulosa-polivinil alkohol (CMC-PVA) yang didopkan dengan ammonium nitrat (NH$_4$NO$_3$) dihasilkan melalui teknik tebaran larutan yang mengandungi PEG dan EC. Spektroskopi impedan elektrik (EIS) digunakan untuk menilai kesan campuran plastik kepada sifat pengaliran ionik. Kekonduksian ionik telah meningkat kepada 1.70×10^{-3} S/cm untuk campuran plastik EC dan 3.00×10^{-3} S/cm untuk campuran plastik PEG. Penambahbaikan itu sepadan dengan keupayaan campuran plastik untuk melemahkan daya Kulumbik dan meningkatkan penceraian selanjutnya dalam ionik dopan. Kekonduksian ionik tertinggi dicapai untuk BBEs yang mengandungi EC dan menunjukkan kesesuaian EC sebagai campuran plastik dalam sistem ini. Sistem BBEs menunjukkan ciri-ciri Arrhenius pada suhu tinggi dan menunjukkan peningkatan kekonduksian ion. Sifat-sifat dielektrik untuk semua sistem BBEs didapati bertambah baik apabila penambahan EC dan PEG dan menunjukkan perkaitan antara hubungan mereka dengan corak kekonduksian.

Keywords: carboxylmethyl cellulose/polyvinyl alcohol, plasticized polymer electrolyte, impedance studies

1. Introduction

Tremendous initiatives have been recently made in blended biopolymer electrolyte (BBE), which has emerged as a powerful platform in the use of energy devices [1], [2]. As reported in previous research, blending [3] and doping [4] are the simplest approaches that can improve the physical, mechanical, barrier, thermal, and electrical conductance properties. The main problem involving BBEs is that they exhibit relatively low ionic conductivity. Consequently, most researchers focused on enhancing the ionic conductivity (10^{-6} S/cm to 10^{-3} S/cm) of BBEs by incorporating various plasticizers such as polyethylene carbonate [1], glycerol

[5], ethylene carbonate (EC) [6], and polyethylene glycol (PEG) [7].

Plasticization is a promising platform to enhance the conductivity of polymer electrolytes. Plasticizers have been reported to have a high dielectric constant, which can solvate more salt and increase the ion mobility that can enhance the ionic conductivity. Shuhaimi *et al.* [8] found that the plasticization of methyl cellulose–ammonium nitrate (MC-NH$_4$NO$_3$) with PEG obtained an ionic conductivity value of 1.14×10^{-4} S/cm. Meanwhile, another study on plasticized polymer electrolyte based on CMC-NH$_4$Br that used EC as plasticizer reported a high conductivity of 3.31×10^{-3} S/cm [9]. These materials can modify the 3D molecular organization of the polymers, reduce the energy required for molecular motion, and promote the formation of hydrogen bonding between the chains [10]. Such changes are highly dependent on the chemical characteristics of the plasticizer, including composition, molecular weight, and functional groups used during plasticization [11].

BBEs have been developed using ammonium nitrate (NH$_4$NO$_3$) salt because they offer advanced dynamics for the ionic association in the ionic dopant [12]. Upon doping NH4NO3 into CMC-PVA, the ionic conductivity was optimized at 1.70×10^{-3} S/cm, and a nonplasticized (PZ0) sample was considered [13]. Herein, we investigated the effect of plasticization on CMC-PVA-NH$_4$NO$_3$ using different ratios of EC and PEG as plasticizer. In this study, the influence of these plasticizers were correlated and compared in terms of electrical characteristics.

2. Methods

Materials. The host polymer was prepared using carboxymethyl cellulose (CMC; MW: 90,000) obtained from ACROS Organic Co. and polyvinyl alcohol (PVA; MW: 70,000) supplied by Merck Schuchardt. Ammonium nitrate NH$_4$NO$_3$ (MW: 80.04) used as ionic dopant was purchased from Merck. Two plasticizers, namely, EC (MW: 88.06) and polyethylene glycol (PEG; MW: 1100) supplied from Sigma Aldrich, were used in the present study.

Sample preparation. CMC/PVA hybrid (80/20 wt. %) [14] complexed with 30 weight percentage ratios of NH$_4$NO$_3$ [13] were prepared via solution casting. Various amounts of EC and PEG (2–10 wt. %) as plasticizers were added to the highest conducting CMC-PVA-NH$_4$NO$_3$ sample solutions with 56:14:30 composition. The mixture was stirred continuously until homogenous, and the resulting solution was cast into clean Petri dishes. The solution was left in an oven at 60 °C for drying purposes [15]. Semi-dried BBEs were further dried in a desiccator filled with silica gel.

Impedance spectroscopy. Impedance measurements were performed via 3532–50 LCR HiTester (Hioki, Japan) at elevated temperature conductivity (303–353 K). Frequency ranges from 50 Hz to 1 MHz were applied to samples that were sandwiched between two stainless steel electrodes. The ionic conductivity was calculated using Equation 1, where *y* is the thickness of the BBEs, *A* is the cross-sectional area, and R_b is the bulk resistance determined from the Cole–Cole plot.

$$\sigma = y/R_b A \qquad (1)$$

Complex permittivity. Complex permittivity (ε^*) is significant in the evaluation of the ionic mechanism and interaction within biopolymer electrolyte complexes. The following equation corresponds to ε^*:

$$\varepsilon* = \varepsilon_r + j\varepsilon_i \qquad (2)$$

where $j = \sqrt{-1}$, and ε_r is the real part of the complex permittivity, which is called the dielectric constant. This parameter is useful to measure the ability to store charges in BBEs. Meanwhile, ε_i is the imaginary complex permittivity or dielectric loss that determines the energy dissipation during an ion's migration when the electric field is applied. Both parameters were calculated by using the following equations:

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

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \qquad (4)$$

where Z_r is the real part and Z_i is the imaginary part of the impedance $\omega = 2\pi f$; f is frequency; $C_o = \varepsilon_o A/t$; and ε_o is the permittivity of free space.

3. Results and Discussion

Impedance analysis. The ionic conductivity of various amounts of EC and PEG incorporated into CMC-PVA-NH$_4$NO$_3$ is presented in Figure 1. Notably, the ionic conductivity increased with increasing amount of plasticizer. The ionic conductivity values for these plasticizers were 3.92×10^{-3} and 3.00×10^{-3} S/cm for samples containing 6 wt. % EC and 8 wt. % PEG, respectively. EC could provide an alternative pathway that creates additional free ions for superior ionic transport as it possessed relatively high ionic conductivity [16]. Given that EC is a well-known material with high electric constant, it is capable of weakening the interaction between NH$_4^+$ and NO$_3^-$ and promoting further H$^+$ dissociation. After each optimization of plasticizer, the conductivity was found to decrease. A possible explanation for this trend might be due to the saturation from the addition of plasticizer. This
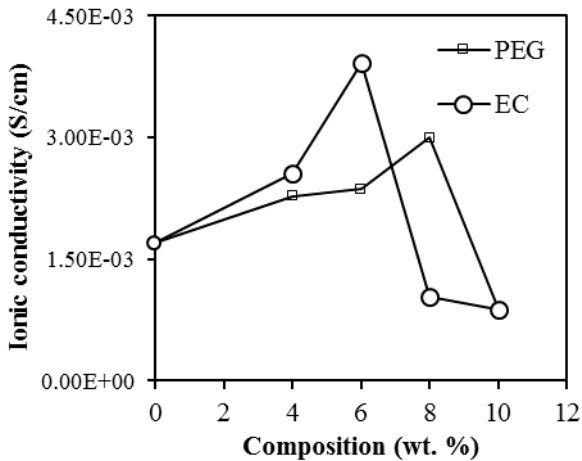
Figure 1.   Variation in Ionic Conductivity of the BBEs

Figure 2.   Temperature Dependence of the BBEs

Tabel 1. Activation Energy for the BBEs

Sample	Activation energy, E_a (eV)
PZ0	0.086
EC6	0.010
PEG8	0.026

phenomenon could drive the hindrance effect, which causes a delay in ionic transportation toward the polymer backbone and decreases conductivity [17].

Elevated temperature analysis. Figure 2 depicts the linear relationship between the logarithm of ionic conductivity against the reciprocal temperature for nonplasticized (PZ0) and the highest conducting plasticized samples (EC6 and PEG8). PZ0 showed lower conductivity than the samples containing EC and PEG. The ionic conductivity increased linearly at various temperatures. This result indicated that the ionic conduction mechanism of these BBE systems obeyed the Arrhenius characteristics, where H^+ as the conducting species rapidly hopped from one site to another due to the high kinetic energy (PAW). A similar mechanism was proposed by Dragunsaki *et al.* [18], who reported that lithium ion (Li^+) is the conducting species in the other plasticized polymer electrolyte. The Arrhenius characteristics are expressed in the following equation:

$$\sigma = \sigma_0\, exp\left(-\frac{E_a}{kT}\right) \tag{5}$$

where σ is the conductivity, σ_0 is pre-exponential factor, E_a is the activation energy, and k is the Boltzmann constant. On the basis of the temperature dependence plot, the activation energy was calculated and presented in Table 1.

The calculated value of E_a proved that EC with optimum composition showed the least amount of activation energy for the migration of the conducting species H^+ throughout the system, because EC possess a higher dielectric constant than PEG [19]. These results may be due to the characteristic of EC itself that can assist in the dissociation of NH_4^+ and produce additional conducting species H^+ as temperature increases.
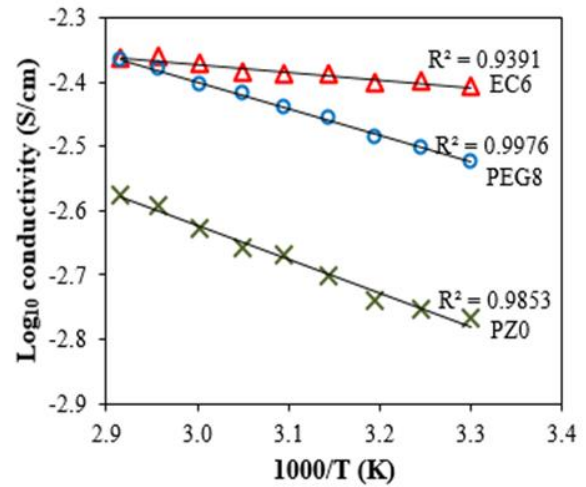
By contrast, ion hopping in PEG8 was decoupled from segmental motion in the polymer, which was due to the weak attraction between PEG and NH_4NO_3, leading to high E_a values [20]. Consequently, BBEs containing PEG8 demonstrated low ionic conductivity compared with BBEs containing EC. These results suggested that the present BBEs are suitable to be applied in electrochemical devices due to their low E_a values because the activation energy threshold is below 1 eV [21].

Dielectric analysis. The dielectric study is frequently based on frequency-dependent complex permittivity, as shown in Equation (2), to assess the capability of a material to store or lose energy. Figure 3 shows the frequency dependence of dielectric constant ($\mathcal{E}_r$) for PZ0, EC6, and PEG8 at room temperature (303 K). This graph shows that the incorporation of plasticizer increased the $\mathcal{E}_r$ values of plasticized sample at low frequency. This result could be inferred by the function of plasticizer, which promotes the dissociation of ionic salt by weakening the Coulombic force experienced by NH_4^+ and NO_3^- and releasing more free delocalized ions (H^+). The dielectric properties exhibit similar behavior to ionic conductivity where EC6 possessed the highest value; thus, EC6 has greater capability to store more charges in the sample than other materials. Interestingly, these trends matched those observed in a previous study, which revealed that the main contribution was the increasing number of free delocalized ions that were responsible for dipole alignment [22].

This finding was consistent with the earliest explanation, which mentioned that the incorporation of 6 wt. % EC increases the delocalization of conducting ions and is responsible in increasing the amount of stored charges and increasing the ionic conductivity [23]. In addition, dielectric relaxation occurs at high frequency due to space charge polarization at the electrode–electrolyte interface and causes $\mathcal{E}_r$ to plateau. Moreover, no excess ion diffusion takes place throughout the path of the field. This dielectric constant shows that all BBEs obey the non-Debye characteristic with no single relaxation.

Figure 4 presents the dielectric loss ($\mathcal{E}_i$) against a wide frequency range to explain energy dissipation, polarization properties, and relaxation energy. Ramly *et al*. [24] disclosed that the phenomenon of polarization will experience inertia involving energy dissipation due to the deviation of the proton conduction mechanism under the applied electric field. In general, frequency ranging from 50 Hz to 1 MHz significantly affected the $\mathcal{E}_i$ value for PEG8 sample, which was predicted to demonstrate a relaxation peak due to the dynamic of the segmental motion of the ion dipolar complexes of the BBEs [25]. Furthermore, the BBEs are regarded as semiconducting, which reveals their dielectric properties at low frequency. Consistent with the literature, this study found that PEG8 showed a definitive peak at low frequency, conforming to the relaxation process involving polymer segmental chain that governs the ion hopping mechanism [26],[27]. Nevertheless, this finding reflects the results of Tsuboi *et al*. [28], who also found that the molecular weight of PEG only slightly affects the polymer structure and gives rise to the bulk effect, which then causes the mobility of the polymer's segmental chain to decrease.

Given that EC can improve the dissociation of NH_4NO_3, the number of mobile ions increased, resulting in an increasing amount of charge carriers that affect the ionic
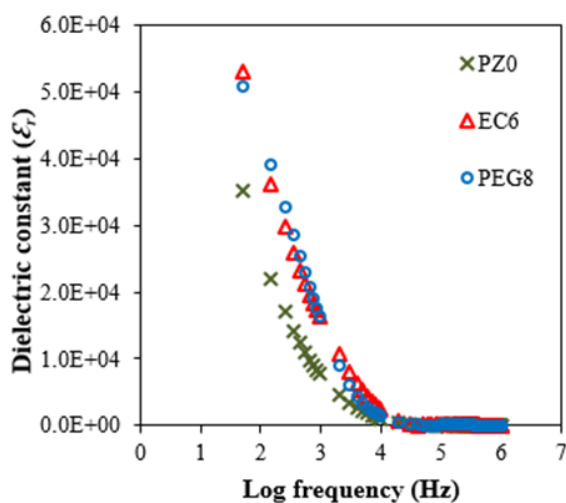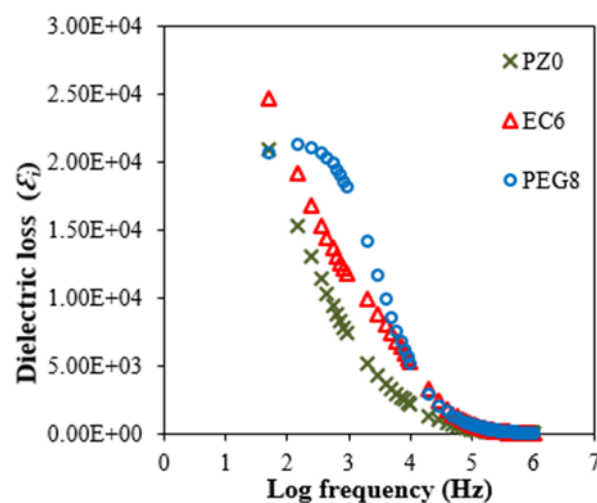

Figure 4.   Dielectric Loss of the BBEs

conductivity. This phenomenon corroborates with earlier observation shown in both Figures 3 and 4. EC6 presented the highest dielectric loss values, which corresponded to a decrement in local viscosity at the region of charge-transporting ions [29]. This decrement resulted in the accumulation of the charges at the electrode–electrolyte interface, which increased the ionic conductivity.

4. Conclusion

Polymer electrolyte based on plasticized CMC-PVA-NH_4NO_3 involving the addition of different plasticizers was successfully prepared. The composition of plasticizer was found to affect the proton conduction where EC with 6 wt.% showed the highest ionic conductivity at room temperature than 8 wt. % of PEG with values of 3.92×10^{-3} S/cm and 3.00×10^{-3} S/cm, respectively. All BBE samples exhibited Arrhenius characteristics with the activation of 0.086 eV for PZ0, 0.026 eV for the BBEs plasticized with 8 wt. % of PEG, and 0.010 eV for the BBEs plasticized with 6 wt. % of EC. The incorporation of plasticizers was verified to enhance the electrical properties, which contributed to the high degree of NH_4NO_4 dissociated into free delocalized H^+, increased dielectric constant and loss, and elevated ionic conductivity. The present work offers insight into the tendency of BBEs to be applied as an electrolyte system because of their strong potential for electrochemical devices.

Acknowledgement

Figure 3.   Dielectric Constant of the BBEs

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