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Full Length Research Paper

Electrical study of plasticized carboxy methylcellulose based solid polymer electrolyte

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The electrical conductivity and thermal conductivity of carboxyl methylcellulose doped with oleic acid and plasticized with glycerol have been measured by the electrical impedance spectroscopy method in the temperature range of 303 – 393 K. The composition of glycerol was varied between 0 and 50 wt. % and the samples were prepared via solution casting technique. The highest ionic conductivity at room temperature, σ_{rt} (303K) is 1.64 x 10^{-4} S cm^{-1} for sample containing 40 wt. % of glycerol. The system was found to obey Arrhenius rule where $R^2 \approx 1$. The dielectric study (ε^*,M^*) shows a non-Debye behavior.

Key words: Solid polymer electrolyte, carboxyl methylcellulose, oleic acid, glycerol.

INTRODUCTION

Solid Polymer Electrolytes (SPEs) are the great interests for researchers nowadays, due to their wider range of tremendous applications in electrochemical devices. SPEs also offer numerous of advantages, for example, they can eliminate corrosive solvent and harmful gas formation, have wider electrochemical and thermal stability range as well as low volatility with easy handling. Recently, biodegradable materials attract enormous attention worldwide as a result of white pollution, one of the environmental crises.

According to Guo et al. (2011), plasticizers would make the polymer softer and more flexible, and enhance the chemical and mechanical stability of membranes since they could penetrate and increase the distance of molecules and decrease the polar groups of polymer. In addition, it could overcome the main shortcoming of synthetic polymer, which is mostly insoluble in the solvents. In SPEs, the polymer acts as solvent for a salt which will be partially dissociated in the matrix, leading to ionic conductivity. The electrochemical properties of such polymers are limited by the solvent and the conductivity occurs via interconnected structures of solvent and ions.

To fulfill the stipulations on biodegradable and environmental friendly materials which are significant toward the development of a green nation, carboxy methylcellulose (CMC) has been chosen in this research due to its superior properties as the polymer host. To enhance the conductivity of SPEs, the contribution of mixing polymer and ionic dopant based on the modified double lattice (MDL) is necessary (Pai et al., 2005) thus oleic acid (OA) was chosen to be used as the ionic dopant. In addition, glycerol as plasticizer is introduced

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into the polymer-dopant system in order to enhance the conductivity and the mechanical properties of the SPEs.

EXPERIMENTAL METHODS

Sample preparation

The CMC based SPEs were prepared by using the solution casting technique. 1 g of CMC (weighted by a digital mass balance) was mixed with 33 ml distilled water and stirred continuously until the CMC dissolved. 20 wt. % (0.25 g) of OA was dissolved in the CMC solution. The CMC-OA composition is following the research of Chai and Isa (2013) of the highest ionic conductivity SPE. In addition to the previous work, the CMC-OA solution was added with different composition of glycerol (0 – 50 wt. %) as plasticizer for each sample respectively. The mixture of CMC-OA-glycerol was poured into Petri dishes and dried in an oven at 60°C. The samples were then kept in desiccators for further drying process.

Electrical impedance spectroscopy (EIS)

The EIS (HIOKI 3532-50 LCR Hi-Tester) are interfaced to a computer with frequency of 50 Hz to 1 MHz. The films was cut into a fitting size and placed between the stainless steel blocking electrodes of the sample holder which connected with the LCR (Inductance, Capacitance, and Resistance) tester. The software controlling the measurement also calculates the real and imaginary impedance. The bulk impedance, R_b value was obtained from the plot of negative imaginary impedance; $-Z_i$ versus real part, Z_r of impedance and the conductivity of the sample was calculated as follow:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

Where A= area of film–electrode contact and t=thickness of the film. Complex dielectric constant, and complex electrical modulus, are evaluated from the recorded complex impedance data, for each temperature. The complex permittivity and complex electrical modulus is given by:

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

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

$$M_r(\omega) = \frac{\varepsilon_r}{({\varepsilon_r}^2 + {\varepsilon_i}^2)} \tag{4}$$

$$M_i(\omega) = \frac{\varepsilon_i}{({\varepsilon_r}^2 + {\varepsilon_i}^2)} \tag{5}$$

Here, $C_o = \varepsilon_o A/t$ (ε_o is permittivity of free space, A is electrode–electrolyte contact area, and t is thickness of the electrolyte) and $\omega = 2\pi f$

RESULTS AND DISCUSSION

Conductivity study

The ionic conductivity is depending of various factors, such as cation and anion types, salt concentration and temperature. The ionic conductivity, *σ,* of CMC-OA-glycerol was depicted in Figure 1. From Figure 1, it is noted that by the addition of plasticizer affected the conductivity of the CMC-OA-glycerol SPEs. It can be observed that the ionic conductivity in this system increases until 40 wt. % of glycerol and decreases with the addition of higher than 40 wt. % of glycerol. The dependence of ionic conductivity on the plasticizers concentration provides more information on the specific interaction among ionic dopant, polymer matrix and plasticizer. The initial increase of ionic conductivity can be explained by association of ions at higher plasticizer concentration, which leads to the formation of ion clusters and the number of charge carriers and their mobility. When the amount of plasticizer is increased, the ions would transport mainly in the plasticizer-rich phase (Ibrahim et al., 2012). According to Bandara et al. (1998) by postulating the existence of separate ionic pathways for the migration of free ions through the plasticizer, it is possible to explain the enhancement of ionic conductivity when plasticizer is introduced. On the other hand, the decrement of conductivity is mainly due to the higher amount of glycerol which contributed to the overcrowd of ions thus reduces the number of charge carriers further gives limitation on the mobility of ions (Selvasekarapandian et al., 2005; Khiar et al., 2006). For further understanding on the ionic conductivity mechanism, the ionic conductivity of SPEs were tested at elevated temperature ranges from 313 to 393 K. From Figure 2, the relationship between conductivity and temperature of the SPEs are naturally Arrhenius behaviour. The regression values, R^2, obtained for the temperature dependence is R^2~1. Hence, proven the samples obey the Arrhenius law and it is thermally activated similar to the work done by Khiar et al. (2006); Nik Aziz et al. (2010) and Chai and Isa, 2012). The relation of Arrhenius law can be explained by:

$$\sigma = \sigma_o \exp(-E_a / kT) \tag{6}$$

Where σ_o is the pre-exponential factor, E_a is activation energy, k is Boltzmann constant and T is absolute temperature. The activation energy, E_a was calculated from the equation and shown in Figure 3.

Dielectric study

The dielectric constant is a measure of stored charge in a material (Khiar et al., 2006) where in polymer electrolytes, the charge carriers are ions. Meanwhile, dielectric loss explained the loss of energy which eventually produces a rise in temperature of a dielectric placed in an alternating electrical field. In the dielectric constant and dielectric loss plotted shown in Figure 4, no appreciable relaxation peaks observed in the frequency

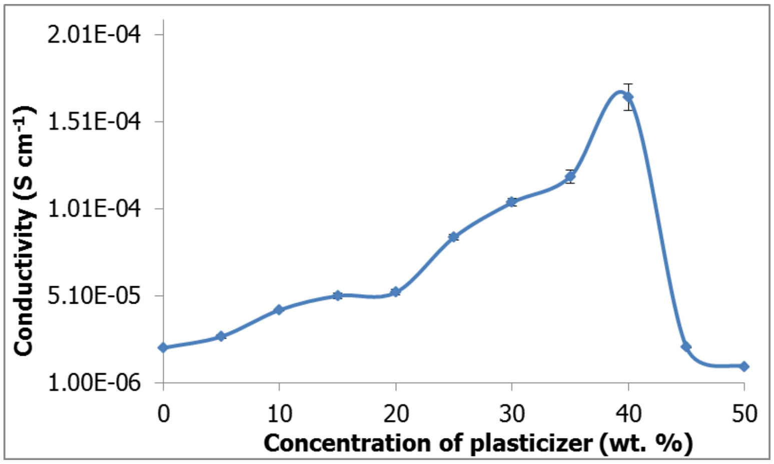


Figure 1. The conductivity of CMC-OA-glycerolSPEs at room temperature.

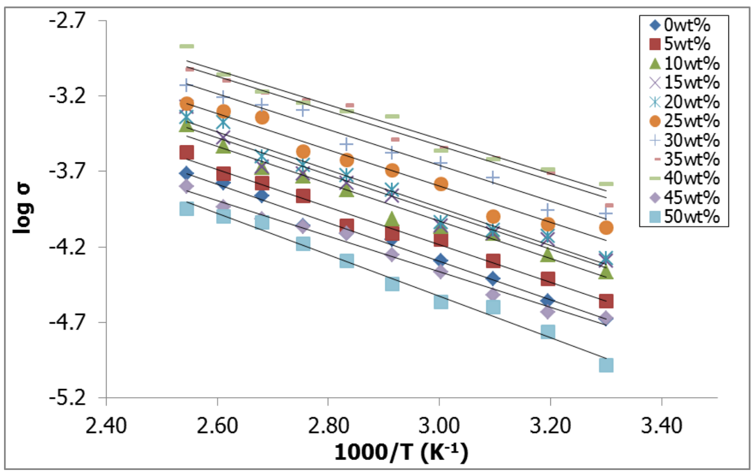


Figure 2. The Arrhenius plot of plasticized SPEs with different wt% of plasticizer.

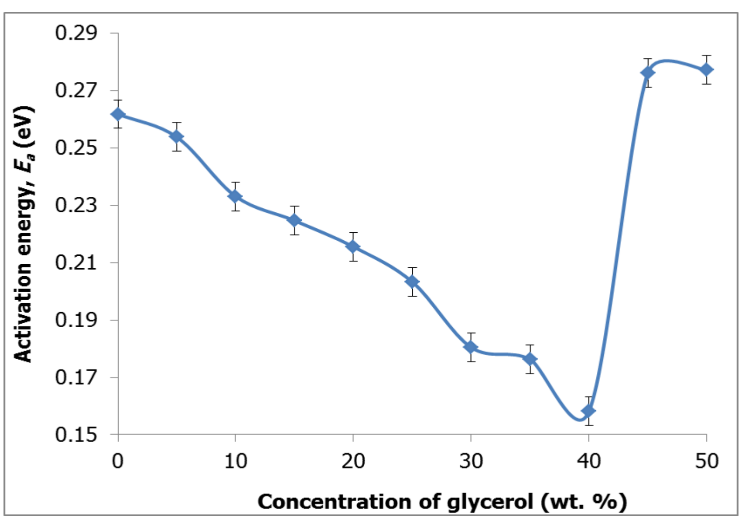
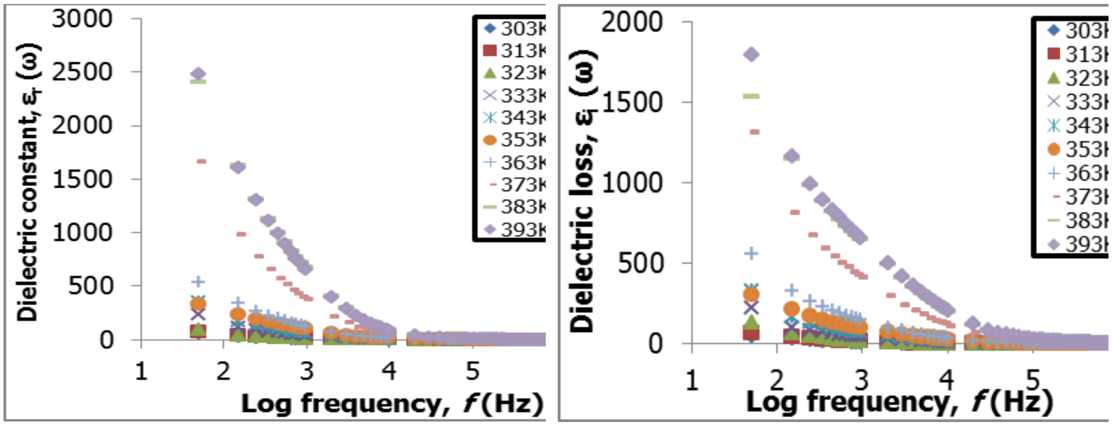
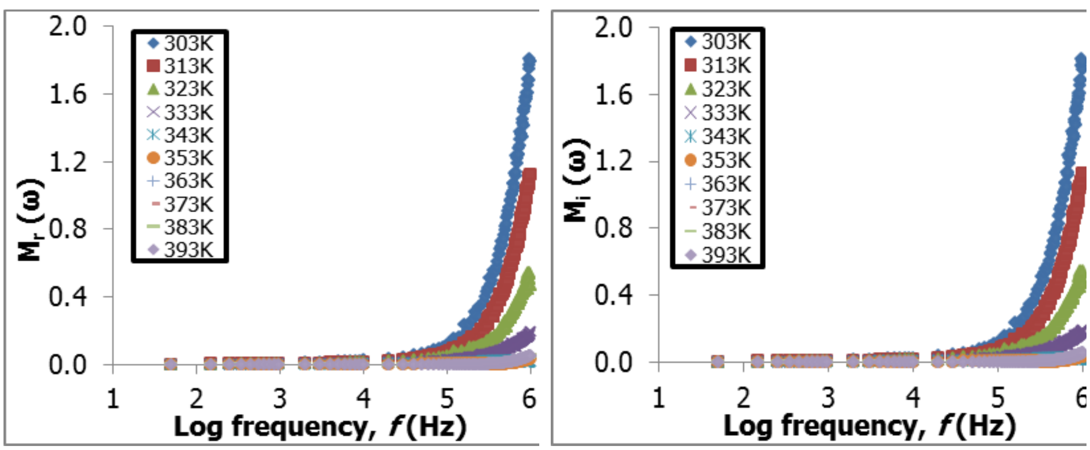


Figure 3. The activation energy of CMC-OA-glycerol SPEs.



(a) (b)

Figure 4. Frequency dependence of (a) dielectric constant, ε_r and (b) dielectric loss, ε_i at various temperatures for sample with 40 wt. % of glycerol.



(a) (b)

Figure 5. Frequency dependence of (a) real part, M_r and (b) imaginary part, M_i of modulus study at various temperatures for sample with 40 wt. % of glycerol.

range employed in this study. Both dielectric constant and loss rise sharply at low frequencies indicating that electrode polarization and space charge effects have occurred confirming non-Debye dependence. According to Khiar et al. (2006), this implied that the conductivity exhibits relaxation that is non-exponential in time. The dielectric constant in this present study indicates the increase in conductivity is mainly due to the increase in the number density of mobile ions which was also found in Majid and Arof (2007) and Khiar and Arof (2010). Based on their work and the similar result obtained in this current study, it can be deduced that as the frequency increases, the rate of reversal of the electric field also increases, as such; there is no charge build up at the interface which brings about a decrease in the values of the dielectric loss due to the decrease of the polarization effect by the charge accumulated. Further analysis of the dielectric behaviour would be more successfully achieved using dielectric modulus, which suppresses the effect of electrode polarization.

Modulus study

The variations of real, M_r and imaginary, M_i parts of electrical modulus are shown in Figure 5 (a) and (b) respectively. It can be observed from Figure 5, both M_i and M_r value are approaching zero at low frequency and increases at the higher frequency but no relaxation peaks can be observed. According to Khiar et al. (2006) the presence of peaks in the modulus formalism at higher frequencies for all polymer systems and temperatures is an indicator that the polymer electrolyte films are ionic conductors. The value of both M_r and M_i at low frequencies indicates that electrode polarization is negligible. The appearance of a long tail at low frequencies indicates that there might be a large capacitance associated with the electrodes which further confirms non-Debye behavior in the samples (Nik Aziz et al., 2010).

Conclusion

Solid polymer electrolytes based on CMC-OA plasticized with glycerol were prepared. Sample with 40 wt. % of glycerol was found to have the highest ionic conductivity at room temperature (303 K) of 1.64 x 10^{-4} S cm^{-1}. The ionic conductivity results as a function of temperature exhibited Arrhenius rule and the value of activation energy is capsized of conductivity. Dielectric study and modulus study suggests that samples in this study show non-Debye behaviour.

Conflict of Interest

The authors have not declared any conflict of interest.

ACKNOWLEDGMENT

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