

Effect of PEG as a plasticizer on the electrical and optical properties of polymer blend electrolyte MC-CH-LiBF₄ based films

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ABSTRACT

Plasticized polymer blend electrolyte films based on methylcellulose (MC), chitosan (CH), lithium tetrafluoroborate (LiBF₄), and polyethylene glycol (PEG) as a plasticizer were prepared and investigated. The effect of different concentrations of PEG was studied using AC impedance spectroscopy, and UV–Visible spectroscopy. The electrical and optical properties of polymer electrolytes have been improved upon addition of PEG. The DC conductivity was evaluated from the bulk resistance achieved from Nyquist impedance plots. Results from temperature studies reveal that all samples comply with the Arrhenius formula in the investigated temperature range. The sample with 10 wt% of PEG exhibits the highest ionic conductivity of 2.12×10^{-5} S/cm with the minimum activation energy of 0.528 eV at ambient temperature. The lowest relaxation time for highest ion conductive sample indicates the faster ion dynamics. The frequency-dependence AC conductivity was found to follow the Jonscher's power law at various temperatures, and the conduction mechanism for this system followed the overlapping large polaron tunneling (OLPT) model. The increase in absorption and a decrease in optical band-gap in the UV region was confined by UV–Visible spectroscopy.

Introduction

Currently, many research groups focus their efforts on investigating the electrical and optical properties of polymer materials, due to the wide range of possible applications of polymeric materials in optical and electronic devices [1]. Investigation of the electrical properties considered to explore the nature and mechanism of charge transport in these materials; whereas the optical properties investigated to obtain the information about materials band structure [2]. It is well established in the literature that the chemical and physical properties of polar polymers can be suitably modified by combination with different inorganic salts [3]. Several approaches have been adopted in the literature to enhance the electrical conductivity of the solid polymer electrolyte (SPE) systems at ambient temperatures, such as copolymerization, blending, and addition of additives [4,5].

Polymer blending is the most important tool to develop new polymeric materials, because of its simplicity of preparation, relatively low cost, and ease to control the physical properties by compositional change [6]. The ion transport in polymer electrolyte is believed to

predominant mainly through the amorphous phase of polymer rather than the crystalline phase [7]. Thus to enhance the ionic conductivity of SPE, many studies have focused on increasing the amorphous phase of the host polymer matrix [8–10]. On the other hand, many research studies have focused on the development and improvement of the polymer electrolyte based on the natural carbohydrate and different bio-organic materials, such as chitin, chitosan, cellulose, methylcellulose, carboxymethyl-cellulose, hydroxyethyl-cellulose, etc. [11,12]. Among all biopolymer materials, cellulose and chitin are two of the most abundant bio-organic compound in nature [13]. Methylcellulose (MC) and chitosan (CH) derived, respectively, from cellulose and chitin, attracted significant consideration in recent works due to some advantages, such as biocompatible, biodegradable, non-toxic, abundance, water-soluble, excellent film-forming properties, and dopant dependent properties [14,15].

In recent years, particular attention has been devoted to developing lithium-ion batteries (LIB) for their use in modern electric vehicles. The development of new organic materials for LIB is the focus of prominent research groups throughout the world in the field of advanced materials

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science [16]. Consequently, lithium-ion-conducting SPEs have received a great deal of interest in the last two decades due to their growing demand for LIB [17]. Rechargeable LIB based on SPEs, introduces a wide variety of advantages such as lightweight, low-cost, ease of fabrication, flexible geometry, and improved safety due to the absence of electrolyte leakage [18]. However, poor ionic conductivity (lower than 10^{-5} S/cm) at ambient temperature, due to low mobility of the lithium cations in SPEs, obstructed their spread in the battery market [19]. Several approaches have been adopted to increase ionic conductivity by enhancing ion mobility while maintaining good mechanical properties [20,21]. For instance, polymer blending, utilization of cross-linked polymer, the addition of inorganic fillers, and the incorporation of plasticizer and dopants [22].

The effective approach to improve the ionic conductivity of SPEs is to form plasticized systems by introducing chemical additives with high dielectric constants and low viscosities into the host polymer [23,24]. The relatively low molecular size of plasticizers allows them to penetrate the space between polymer chains and minimize secondary intermolecular attractive forces between adjacent polymer chains, resulting in an increase in the free volume, leading to an increase in the segmental mobility and charge carrier mobility [25,26]. Thus the enhancement in ionic conductivity of SPEs can be achieved by incorporating a different type of organic plasticizers such as ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, etc. [25,27]. Taking into consideration that the degree of plasticity of polymers is largely dependent on the chemical structure of the plasticizer, its compatibility and miscibility with the host polymer, molecular weight, and concentration of plasticizer [28].

Referring to our previous works [29,30], the most amorphous blend composition (25% MC and 75% CH) was used as a host matrix to prepare lithium-ion polymer electrolyte, the maximum ionic conductivity of 3.74×10^{-6} S/cm was achieved by incorporating 40 wt% of lithium tetrafluoroborate (LiBF_4) to the host matrix. In order to enhance the ionic conductivity of this polymer electrolyte system, varying concentrations of polyethylene glycol (PEG) as a plasticizer were added to the system. In the present work, the concentration-effect of the PEG on the electrical and optical properties of MC-CH- LiBF_4 solid polymer blend electrolyte films were presented.

Experimental procedures

Preparation of plasticized polymer blend electrolytes

Materials used in this work are chitosan (CH) powder ($\geq 75\%$ deacetylated), and methylcellulose (MC), lithium tetrafluoroborate (LiBF_4) all of them supplied by Sigma-Aldrich, Polyethylene glycol (PEG) average molecular weight 8000 supplied by Himedia, and double-distilled water was used as a solvent. The polymer blend electrolyte based on MC-CH- LiBF_4 without plasticizer were prepared by the conventional solution cast technique. As an optimized concentration, 25% MC and 75% CH were dissolved in double-distilled water separately and mixed together; this solution was used as a host matrix to prepare polymer electrolyte. Incorporating 40 wt% of LiBF_4 exhibits a maximum room-temperature ionic conductivity of 3.74×10^{-6} S/cm when compared with other salt concentrations. The detail of polymer electrolyte preparation has been described elsewhere [30]. In order to improve the ionic conductivity of MC-CH- LiBF_4 polymer blend electrolyte, different amounts of PEG as a plasticizer was added to this composition.

To prepare different compositions of plasticized polymer electrolytes, the desired weight ratio of PEG (2, 4, 6, 8, 10 wt%) were dissolved in 5 mL double-distilled water separately. The fixed amount of MC, CH, and LiBF_4 were used throughout all the samples. PEG solutions were added into the MC-CH- LiBF_4 solution, and the mixture and stirred continually without heating for 2 h to ensure the electrolytes were completely homogenous. Next, the homogeneous viscous gel plasticized

polymer electrolytes were poured into clean plastic Petri dishes and allowed the solution to evaporate for 2 weeks at ambient temperature until membranes were formed. The plasticized polymer blend electrolyte samples were coded as PPE-2, PPE-4, PPE-6, PPE-8 and PPE-10 for MC-CH- LiBF_4 incorporated with 2, 4, 6, 8, and 10 wt% PEG, respectively. Prior to characterization, the membranes were stored in a vacuum desiccator containing silica gel for further drying.

Characterizations

The ionic conductivity and dielectric properties of the prepared plasticized polymer blend electrolyte samples were investigated using the Agilent precision LCR Meter (E4980A) at the frequencies ranging from 100 Hz to 2 MHz, and in the temperature ranges between 303 and 373 K at approximately 10 K intervals. The samples were sandwiched between two aluminum blocking electrodes with a diameter of 2 cm under spring pressure. The electrochemical impedance measurements were carried out in a homemade temperature-controlled chamber. An accurate T-type thermocouple was used to measure temperature within the chamber. The sample was allowed to stabilize for 25 min for each temperature before the measurement was taken. The impedance data were presented in the complex plane (Argand diagram), to achieve information on the electrical properties of the system under investigation.

The optical properties of the present samples were investigated using a double beam UV-Visible spectrophotometer device (Perkin-Elmer Lambda 25) in the wide wavelength range from 190 nm to 1100 nm. The thickness of the thick film samples was observed in the range of 86–107 μm .

Results and discussion

Impedance spectroscopy studies

The room temperature Nyquist impedance plots for all plasticized MC-CH- LiBF_4 membranes are shown in Fig. 1. The cation migration in a polymer electrolyte membrane can be represented by an equivalent circuit element, consists of a capacitor and resistor connected in parallel. The complex plane shows two well-defined regions; a wide semicircle at high frequencies, followed by a straight linear at low-frequency region. The presence of the semicircle and the linear portion in the Nyquist plot was, respectively, attributed to the ion conduction in the bulk polymer electrolyte and the effect of blocking electrode/electrolyte interface, due to an accumulation of free charges at the interface between electrode and the electrolyte specimen [31,32]. The convergence of the Nyquist plot to the origin with the reduction in the semicircle size upon increasing PEG concentration (see Fig. 1) is an indication that the conductivity in the system is mainly ionic and not electronic.

The bulk resistance (R_b) for all present samples was obtained from the intercept of the semicircular region of the Nyquist plot with the real impedance axis, as shown in Fig. 1. It is clear that the value of R_b decreases continuously with an increase in the PEG concentration, from value 7044 Ω for PPE-2 to 857 Ω for PPE-10.

The dc conductivity (σ_{dc}) could be estimated from the bulk resistance (R_b) using the relation:

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

where l and A are the electrolyte membrane thickness, and the area of the electrode, respectively [33]. It was observed from Fig. 4 that the σ_{dc} increases with increasing PEG concentration to reach a maximum value at the highest plasticizer concentration. The ionic conductivity of 2.11×10^{-5} S/cm has been obtained for the membrane containing 10 wt % PEG. Researchers have interpreted such increase in ion conductivity with plasticizer concentration to the increase in the number of free

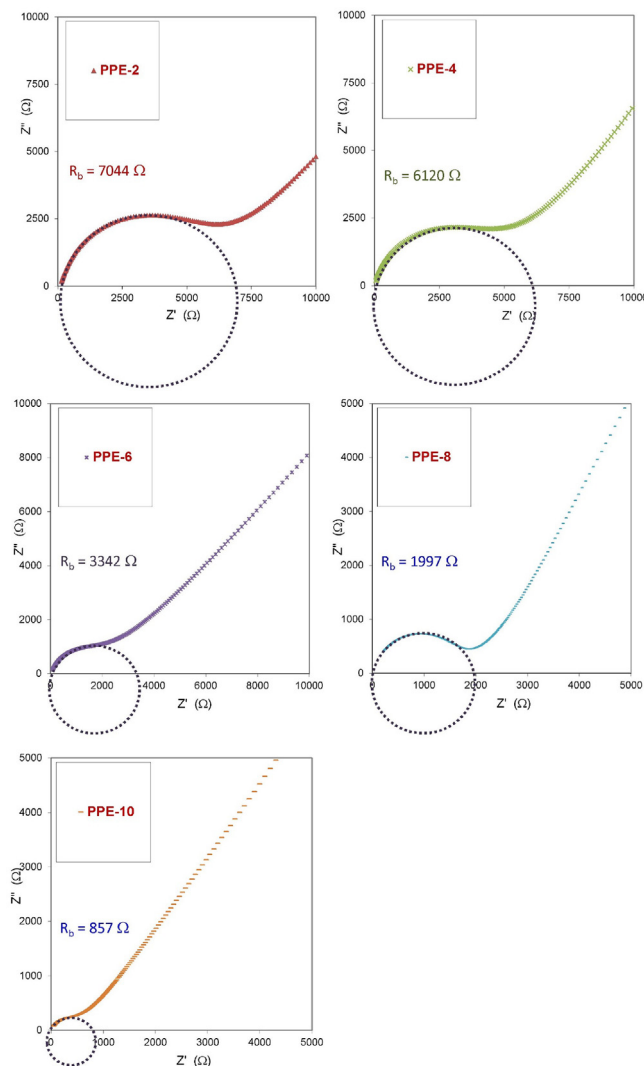


Fig. 1. Nyquist impedance plot for all plasticized MC-CH-LiBF₄ membranes at room temperature, which shows the two different regions, high-frequency semicircle, and low-frequency spike.

charge carriers and their mobility [34].

By incorporating low-viscosity PEG into the MC-CH-LiBF₄ polymer blend electrolytes, the ionic conductivity increase due to the improvement in the flexible nature of polymer chains as well as the amorphous nature of the system [35]. The formation of polymer ions complexes was also helping the transport of ions through the electrolyte [36]. In polymer electrolyte systems, the charge concentration and its mobility are two adjustable parameters which govern the ionic conductivity as described by the following equation [25]:

$$\sigma(\omega, T) = \sum_i q_i n_i \mu_i \quad (2)$$

where q_i , n_i , and μ_i are defined as the charge, concentration, and the mobility of free ion, respectively. ω here represents angular frequency ($\omega = 2\pi f$). From this equation, it can be inferred that the ionic conductivity directly proportional to both the concentration and mobility of free ions in the polymer matrix. The mobility of the ions is greatly influenced by the degree of crystallinity for a polymer. The lower the crystallinity, the higher the ion mobility as the crystalline phase have a tendency to block the conductive channels that are utilized to transport the ions across the electrolyte membrane [30,37]. On the contrary, in the amorphous phase, the polymer chains play significant role in the ionic conductivity process by facile the ion-transport mechanism [38].

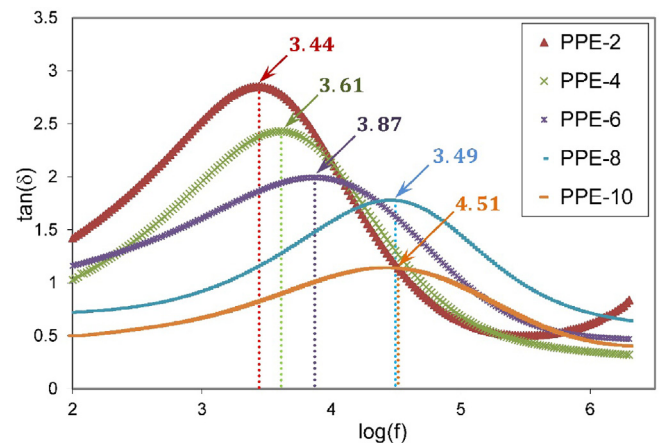


Fig. 2. Variation of $\tan\delta$ versus logarithm of frequency for all plasticized MC-CH-LiBF₄ membranes.

Dielectric relaxation studies

The Debye type relaxation peaks are exhibited in the loss tangent ($\tan\delta$) spectra of the investigated plasticized polymer blend electrolyte films, as depicted in Fig. 2. The broad nature of the observed peak in the loss tangent spectra can be interpreted as being the consequence of distributions of relaxation time [39], and the observed asymmetry in the relaxation peaks indicates the non-Debye type of relaxation [40]. The varying concentration of PEG affect the magnitude of the relaxation peaks of $\tan\delta$ as evidenced clearly in the figure. It is found that the magnitude of the relaxation peaks continually decreasing upon increasing PEG concentration in the MC-CH-LiBF₄ polymer blend electrolyte samples. Moreover, it is also observed that the relaxation peaks are gradually shifting towards higher-frequency side with the increase in PEG plasticizer content, which may relate to the increase in the amorphous domain in the SPE [41].

The peak frequency of Fig. 2, can be used to determine the values of relaxation time (τ) by the relation $\tau = 1/2\pi f_p$, where f_p is the frequency value corresponding to $\tan\delta$ peak. As the $\tan\delta$ peaks shifted toward the high-frequency side; it will decrease the relaxation time (τ). The higher plasticized sample (PPE-10) had the lowest τ value of 1.92×10^{-4} s with the highest ionic conductivity of 2.12×10^{-5} S/cm. The lower the relaxation time, the faster the segmental dynamics in this sample and hence its ionic conductivity is relatively enhancing. The reduction in τ directly indicates the increased rate of ion hopping. The inverse relationship between conductivity and relaxation time have been reported for different polymer electrolytes [42–44].

The peak frequency of $\tan\delta$ related to the activation energy for dielectric relaxation (E_a), and vary with temperature according to the Arrhenius type relationship:

$$f_p = f_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

where f_0 is the pre-exponential factor represent frequency at infinite temperature, k_B is the Boltzmann constant, and T is absolute temperature [45]. The values of E_a for all plasticized MC-CH-LiBF₄ membranes are calculated from the slope of linear fitting of $\ln f_p$ versus $1000/T$ (shown in Fig. 3). The E_a value decrease from 0.785 eV for PPE-2 to 0.528 eV for PPE-10, due to lower electrolyte viscosity at higher plasticizer (PEG) concentrations. The obtained values of E_a , and σ_{dc} for different plasticized samples were summarized in Fig. 4. From this figure, it can be observed that the value of E_a is inversely related to the ionic conductivity. The higher σ_{dc} only has lower E_a and vice versa. Based on reported studies, the lower E_a gives the faster segmental movement of the polymer backbone, thereby produce more free-volumes, which in turn promote the ionic movement through the host

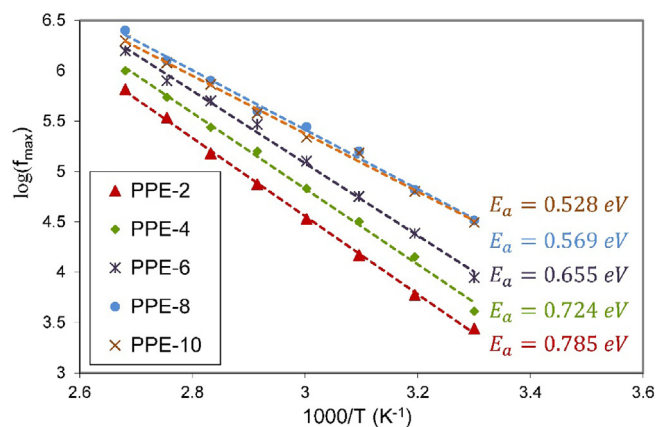


Fig. 3. The variation of $\log(f_{\max})$ versus $1000/T$ for all plasticized MC-CH-LiBF₄ membranes.

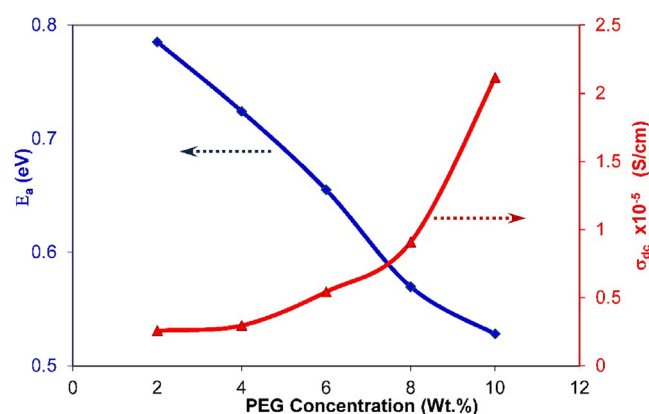


Fig. 4. The variation of activation energy and ionic conductivity for plasticized MC-CH-LiBF₄ membranes with different PEG concentrations at ambient temperature.

matrix, which leads to an increment in the conductivity [35,46]. Thus, we can conclude that incorporating PEG into the MC-CH-LiBF₄ polymer blend electrolyte helped the ion-pairs to dissociate into free ions, as well caused to increase the flexibility of segmental mobility of polymer chain, which lead to facilitates the movement of ions in the host matrix. Therefore, the ionic conductivity for plasticized composite polymers is always higher than that of the unplasticized ones [47]. Consistent with our conclusion, Zainuddin et al. [48] reported the increase in both a number of ions and their mobility upon incorporating PEG plasticizer into CMC-NH₄Br based SPE.

Ion transport mechanism studies

In order to grasp the lithium dynamics and the transport mechanism in the present plasticized MC-CH-LiBF₄ membranes, the frequency-dependence of the electrical conductivity at various PEG concentrations and temperatures has been analyzed. The AC electrical conductivities for various samples at different temperatures were obtained and summarized in Fig. 5. The AC conductivity dispersion at intermediate frequency region of the samples can be understood by the random barrier hopping mechanism model, where ions jump between different ion coordination sites of the polymer chains [49].

The results show that the AC conductivity of the present plasticized solid polymer electrolyte membranes increases as the temperature increases. The increase in ionic conductivity of this system with temperature can be linked to the increase in chain flexibility of the host polymer [50]. This is due to the fact that the segmental movement of polymer chains increases with increasing temperature, according to the

free-volume models of polymer dynamics, which assume that the rates of molecular motions are governed by the available unoccupied sites [30]. Furthermore, an increase in temperature also helps to improve the ionic conductivity by lowering the activation energy and increase the density of free mobile ions [51]. Other researchers reported the same findings for a different type of host polymers [52].

The dispersion region of electrical conductivity in the intermediate and high-frequency region of the present samples (Fig. 5) follows the Jonscher power-law behaviour. According to Jonscher power-law the total conductivity as a function of angular frequency (ω) at different temperature (T), is the combination of DC and AC conductivity [49];

$$\sigma(\omega, T) = \sigma_{dc} + A\omega^s$$

where A is the pre-exponential constant (weakly temperature-dependent), and s is the fractional exponent having values between 0 and 1. The conductivity data at dispersion region were fitted to the above equation, to find Jonscher exponent (s) value. The temperature dependence of the Jonscher exponent (s) with varying PEG concentrations is given in Fig. 6. The s values are all in the range between 0.1 and 0.6 over the temperature range studied, which suggesting that the lithium ions transported by the hopping mechanism in the present plasticized polymer electrolyte films. In this type of ion transport mechanism, the ion transport is expected to be coupled with the segmental motions of polymer chains.

The variation of the Jonscher exponent (s) against temperature is used to determine the origin of the ionic conduction mechanism. Several theoretical models have been applied to estimate the microscopic charge transport mechanism based on a variation of s with temperature [53]. Thus the temperature dependence of s plays a crucial role in the determination of the conduction mechanism in disordered materials.

In the quantum mechanical tunneling (QMT) model, the frequency exponent s is temperature independent; the s is nearly equal to 0.8. In the non-overlapping small polarons (NSPT) model, the exponent s , which is temperature-dependent, increased with the increase in temperature. In the correlated barrier hopping (CBH) model, the s value ranged between 0.7 and 1 at ambient temperature, and decrease temperature increment. In the overlapping large polaron tunneling (OLPT) model, the increase in temperature caused a decrease in the s to a minimum value and then increased again with further increases in temperature [54,55].

It is seen from Fig. 6, the exponent s decreases with increasing temperature to reach a minimum value and then increases again. Hence, the OLPT model seems to be the most valuable one to describe the conduction mechanism in present plasticized polymer electrolytes.

Optical band-gap studies

The ultraviolet-visible (UV-Vis) absorption spectra of all plasticized MC-CH-LiBF₄ membranes are given in Fig. 7. All samples are highly transparent in nature because their spectra did not display any peaks in the entire visible region, but it displays a peak in the UV region. The fundamental absorption peak is appeared at around 205 nm, and the observed peak around 270 nm for MC-CH-LiBF₄ polymer blend electrolyte is due to $\pi \rightarrow \pi^*$ transition [56,57]. In all present membranes, the absorption onset is more dominant in the UV region and tends to shifts to higher wavelength with an increase in the PEG concentration; this indicates the Li⁺ ions interaction in the host matrix via plasticizer, and it means that the electron transition between the energy levels in the band-gap is altered by creating a new sub-energy levels between the existing levels [58], which correlates with the observed enhancement in the ionic conductivity as depicted in Fig. 4.

The absorption edge position for all composites was obtained from the absorption coefficient (α) versus photon energy ($h\nu$) plot, as shown in the inset of Fig. 7. The absorption edge (E_g) value was measured by extrapolating the linear abrupt absorption portion of the graphs to the

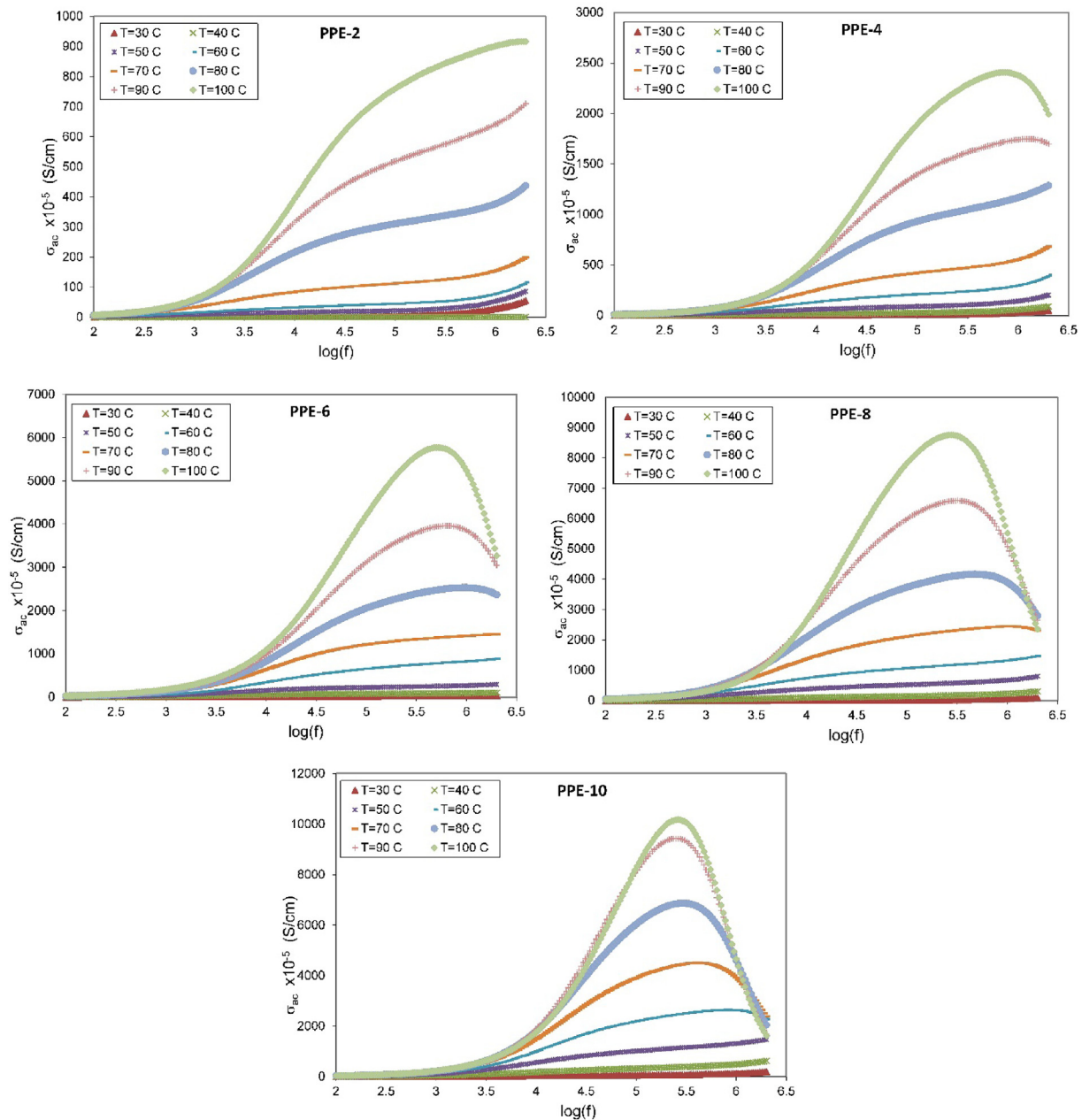


Fig. 5. The AC conductivity versus $\log f$ for all plasticized MC-CH-LiBF₄ membranes at different temperature.

energy axis of the plot. It is obvious that E_e value shifts toward lower values with the rise of PEG loadings, indicating the decrease in the optical band-gap for the composite membranes.

The observed changes in the absorption spectra can refer to the type of possible electron transitions in the samples. Fundamental absorption refers to inter-band transition. The direct band-gap energy (E_{dg}) for all present samples are calculated using the relation [59],

$$(\alpha h\nu)^2 = \beta(h\nu - E_{dg}) \quad (4)$$

where α is the absorption coefficient, β is a constant, and $h\nu$ is the incident photon energy. The optical energy gap separates the two distinct energy levels, namely, the highest occupied band (HOMO), and the lowest unoccupied band (LUMO). The values of E_{dg} were evaluated from extrapolating the linear part of $(\alpha h\nu)^2$ versus $h\nu$ to zero absorption, as provided in Fig. 8. From the graph, clearly the E_{dg} values decrease with increasing PEG wt%. The E_{dg} values decreased from 4.92 eV for polymer blend electrolyte to 3.78 eV for plasticized with 10 wt% PEG

concentration.

The reduction in E_{dg} values might be described by the density of states model, the incorporated PEG can formulate new localized state in the band-gap of the host polymer matrix, that play the role of trapping and recombination center [57].

The width of the Urbach tail is an indicator of the presence of defect levels in the forbidden band-gap [60]. The Urbach energy (E_u) is the energy width of the localized tail states in the band-gap and is calculated by using the following formula:

$$\alpha = B \exp\left(\frac{h\nu}{E_u}\right) \quad (5)$$

where, B is a constant. The E_u value for all samples was calculated by taking the reciprocal of a given slope of the straight line fitted portion of the graphs between the natural logarithm of absorption coefficient ($\ln \alpha$) against photon energy ($h\nu$), as evident in Fig. 9. It is obvious that increasing the PEG loading into the host polymer electrolyte matrix E_u

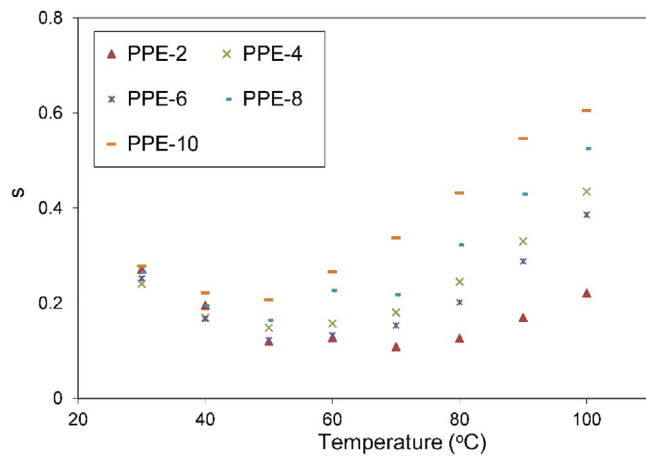


Fig. 6. The frequency exponent (s) versus temperature, for all plasticized MC-CH-LiBF₄ membranes.

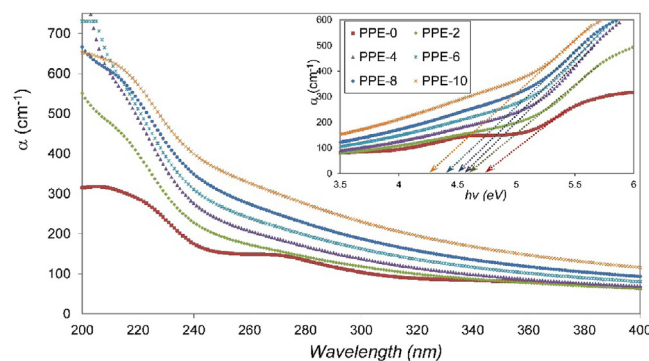


Fig. 7. Absorption coefficient (α) spectra for all plasticized MC-CH-LiBF₄ membranes. The inset is a plot of α versus $h\nu$ to find absorption edge position.

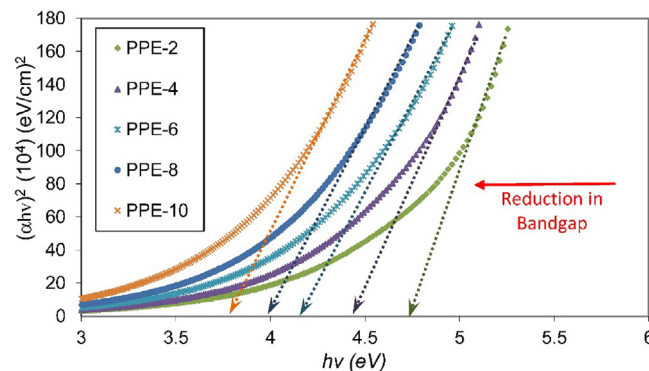


Fig. 8. Plot of $(ah\nu)^2$ versus $h\nu$ for calculating the direct band-gap of all plasticized MC-CH-LiBF₄ membranes.

increases. The increasing trend in E_u value with PEG plasticizer concentration indicates the formation of more defects in the host matrix, which form more free ions in the conduction band resulting in an increment in the conductivity. This result is in good agreement with the ionic conductivity studies shown in Fig. 4.

Fig. 10 shows the variation of absorption edge (E_e), direct band-gap energy (E_{dg}), and Urbach energy (E_u) with different PEG loadings. The observed change in E_e , E_{dg} , E_u indicate the change in energy states of valance and conduction bands, i.e., the electronic structure of the host matrix is actually changed.

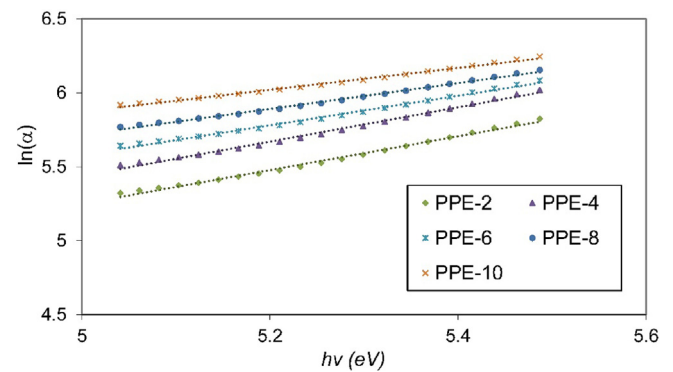


Fig. 9. Natural logarithm of the absorption coefficient ($\ln\alpha$) against photon energy ($h\nu$) for calculating the Urbach energy of all plasticized MC-CH-LiBF₄ membranes.

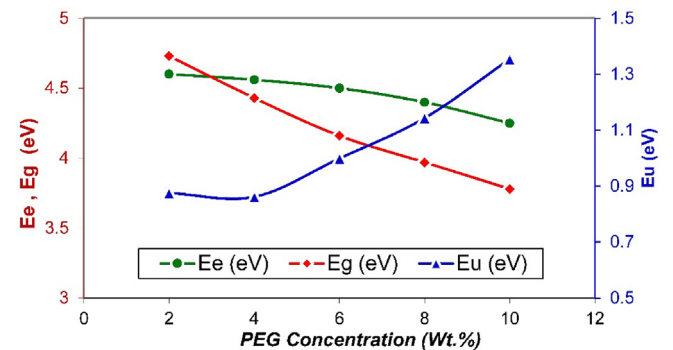


Fig. 10. Variation E_e , E_{dg} , E_u with different PEG wt% concentrations.

Conclusion

Plasticized polymer blend electrolyte films based on MC-CH-LiBF₄ and various concentrations of PEG were prepared and studied. Impedance studies showed that the conductivities of the membranes were mainly due to cation migration, which confirmed by the Nyquist plot. The maximum ambient conductivity of 2.12×10^{-5} S/cm is achieved by incorporating 10 wt% of PEG into MC-CH-LiBF₄ polymer electrolyte. PEG plasticizer tends to dissociate ion-pairs into free ions, which lead to an increase in conductivity. The increase in ionic conductivity of MC-CH-LiBF₄ polymer blend electrolyte films upon addition of PEG plasticizer is also correlated with the enhancement in the segmental motions of polymer chains. The Jonscher exponent was found to be temperature-dependent, and the conduction mechanism was best represented by the OLPT model. The optical absorption band-gap shows a decreasing tendency with an increased concentration of PEG plasticizer.

CRediT authorship contribution statement

Hawzhin T. Ahmed: Investigation, Methodology, Writing - review & editing. **Viyan J. Jalal:** Writing - original draft, Writing - review & editing. **Dana A. Tahir:** Conceptualization, Writing - original draft, Writing - review & editing. **Azhin H. Mohamad:** Investigation, Methodology, Writing - review & editing. **Omed Gh. Abdullah:** Conceptualization, Investigation, Methodology, Formal analysis, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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