



Effect of Plasticizer on the Structural and Transport Properties of Mg²⁺- Ion Conducting Solid Polymer Electrolytes: [PEO: Mg(CH₃COO)₂]

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Authors' contributions

This work was carried out in collaboration between all authors. Authors TOA and AI designed the study. Author TOA wrote the protocol and wrote the first draft while, authors TOA and EON carried out the experimental work and analyses. Authors TOA and EON managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this study, the use of low molecular weight Ethylene glycol [CH₂(OH).CH₂OH] as a new type of plasticizer in polyethylene oxide (PEO)/Mg(CH₃COO)₂ solid polymer electrolytes preparation was examined. The complexation of Mg(CH₃COO)₂ salt with the polymer in the presence and absence of plasticizer was confirmed using Fourier transform infrared spectroscopy (FTIR). The Optical Microscopy (OM) results showed that the microstructural evolution of the pristine polymer is as a result of doping and plasticization. The ionic conductivity was measured for the [PEO: Mg(CH₃COO)₂] systems in the temperature range 296K – 338K using standard four-probe technique. The addition of Ethylene glycol [CH₂(OH).CH₂OH] as plasticizer in the solid polymer electrolytes significantly improved the ionic conductivity. No conduction was observed in the solid polymer electrolyte systems without plasticizer except for the 15-wt-% Mg(CH₃COO)₂-doped system. The temperature dependence of the ionic conductivity reveals the conduction mechanism to be an Arrhenius-type thermally activated process.

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1. INTRODUCTION

Nowadays, device size and implementation of affordable, compact, lightweight, high-capacity, solid-state rechargeable batteries are the key contenders amongst communication and electronic industries. High ionic conductivity, strong solvating ability with a number of alkali, alkaline and transition metal salts and improved thermal, mechanical and electrochemical properties are desirable characteristics of the extensively studied polyethylene oxide (PEO) based polymer electrolytes [1]. Polyethylene oxide and poly (ethylene glycol) (PEG)-based polymer electrolytes have been regarded as the most suitable electrolytes for rechargeable batteries, amongst the family of polymers (polypropylene oxide (PPO), polyoxymethylene and polyether) with similar structure because of their semicrystalline nature at room temperature, exceptional property to dissolve high concentration of a wide variety of dopants and fast ionic conduction in its molten state when compounded into solid polymer electrolytes [2-5]. In recent years, enormous efforts and several different synthetic techniques have been employed to enhance the ionic conductivity and the cation transport number but creating one universal technique for developing polymer electrolytes is impossible due to the physicochemical differences between each system [6-11]. Most studies have been on the variation of concentration of alkali metal salts (lithium being the most used) and inorganic fillers and on conductivity enhancement of high molecular-weight polymers (e.g., PEO) using mixed phases with great interest on nanosized fillers (like TiO_2 , Al_2O_3 , SiO_2 , ZnO and MgO) [1, 12-18]. As gathered from these literatures reviewed above, the general view is that the underlying principles of the mixed-phase electrolytes is not yet well understood, but the general acceptable view is tied to the fact that fillers improve the mechanical properties and considerably stabilize the electrode-electrolyte interfaces. This implies that more systematic work is needed before these systems can be optimally designed for practical applications [1].

However, much attention has not been paid to the low-molecular-weight (MW= 4000) PEOs and complexing or plasticizing with PEGs. In our laboratory, this strategy has been exploited based on the reasoning that PEG [$CH_2(OH).CH_2OH$] has the same monomeric unit as

PEO, but with an end hydroxyl group. The Ethylene Glycol used in our studies for plasticization is a liquid at room temperature, having a melting point close to $60^{\circ}C$. Subsequently, the use of Mg^{2+} ion salt in this work is to proffer solution to the existing problem of chemical instability of Li^+ salt with the electrodes in the Li-ion batteries as claimed by many researchers [5], and to reduce cost and over dependence on Li salts for solid state rechargeable batteries. Thus, solid state rechargeable batteries based on Mg/Mg^{2+} -ion salt solid polymer electrolytes are expected to give battery performance capabilities close to those of Li/Li^+ - ion solid polymer electrolyte batteries due to the fact that Mg^{2+} - ions have ionic size and weight comparable to those of Li^+ -ions. In this work, $Mg(CH_3COO)_2$ salt was oven dried for 4hrs and subsequently blended with dissolved Poly-Ethylene Oxide (PEO) in the absence and presence of ethylene glycol employing solution mixing technique. The hybrid solid polymer electrolytes were then characterized by Fourier Transform Infrared (FTIR) spectroscopy, Optical Microscopy (OP) and conductivity measurement for possible utilization in electrochemical devices.

2. MATERIALS AND METHODS

Poly-Ethylene Oxide - magnesium acetate tetra hydrate [$PEO-Mg(CH_3COO)_2$] Solid Polymer Electrolytes (SPEs) were produced in two batches involving development with or without Ethylene glycol [$CH_2(OH).CH_2OH$]. In the development of first batch of SPEs, known weight percentages (ranging from 5-25%) of magnesium acetate tetra hydrate were mixed with PEO dissolved in de-ionized water via one-pot reaction. On the other hand, the development of second batch of SPEs was actualized through mixing of same percentages of magnesium acetate tetra hydrate with PEO dissolved in a mixture of de-ionized water (50%) and Ethylene glycol (50%) via one-pot reaction.

Following this, five (5) samples for each batch of $PEO-Mg(CH_3COO)_2$ Solid Polymer Electrolytes (SPEs) containing 5-25% of $Mg(CH_3COO)_2 \cdot 4H_2O$ were produced by solution casting into Petri dishes. The samples were oven dried at temperature lower than the melting point of PEO for 12 hrs and subsequently, flat and uniform thin samples were obtained. The samples were analyzed by a FTIR spectrophotometer in

transmission mode without KBr. The spectra were recorded in the frequency range 400 to 4000 cm^{-1} , after 25 scans, with resolution of 2 cm^{-1} . The positions and intensities of the IR bands were processed with Spectral Analysis software. Surface morphologies of SPEs were observed using Micro-Capture (Veho-VMS 004) USB microscope employing optical radiation and the images were analyzed using Imaging software (Image-J). Finally, the samples were characterized for their ionic conductivities and transference numbers from room temperature to 65°C using Four-point probe resistivity measurement system. The variation of current with time for the batches of SPEs containing 5-25% of $\text{Mg}(\text{CH}_3\text{COO})_2$ are given in Fig. 4(a-e) respectively. From these plots, the initial current (i_i) and final current (i_f) are evaluated, and total ionic transference number (t_{ion}) was calculated using the relation:

$$t_{\text{ion}} = \frac{i_i - i_f}{i_i}$$

3. RESULTS AND DISCUSSION

The micrograph presented in Fig. 1 represents the pristine polyethylene oxide film wherein the spherulitic growths are discernable with uniform contrast. The average size of the crystalline domain appearing in pristine PEO is $157.20 \pm 0.04 \mu\text{m}$ [1]. After blending the pristine polymer with $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ the surface topographies of the SPEs [Figs. 2 (a-j)], were modified and no apparent pattern of PEO crystallites is observed under microscope. This can be attributed to the strong nucleating effect of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts dispersion, leading to non-observation of the too small spherulitic growths under our experimental condition.

It can be seen from Figs. 2(a-j) that the contrast variation is mainly due to the differences in the light yield of the pristine polymer and filler atoms. The pristine polymer matrix appear in dark contrast while the filler matrix in lighter contrast. The nucleating effect of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts dispersion was observed under microscope and analyzed to bring out representative images of the SPEs with their corresponding 3D surface topography and crystalline domain size distribution. The morphological descriptions for the compositional hierarchies of the SPEs without plasticizer are presented in Fig. 2(f-j). The images presented in Fig. 2(a-e) together with the corresponding 3D surface topography and crystalline domain size distribution are the representatives of the microstructural evolution of pristine PEO polymer as a result of incorporation and plasticization with $\text{Mg}(\text{CH}_3\text{COO})_2$ and Ethylene glycol respectively.

Microscopic imaging analysis reveals the degree of the $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts dispersion in the PEO- $\text{Mg}(\text{CH}_3\text{COO})_2$ Solid Polymer Electrolytes (SPEs). The variation in contrast and appearance of the images may be attributed the lowering of the crystallinity of PEO as a result of the presence of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts. The average sizes of the crystalline domain in the SPEs containing 5%-25% $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts with and without plasticizer range from $146.70 \pm 10.99 \mu\text{m}$ to $169.39 \pm 6.32 \mu\text{m}$ while the SPEs containing 15% $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts with and without plasticizer possess discernable grain boundaries with average sizes of the crystalline domain being $153.08 \pm 6.79 \mu\text{m}$ and $155.77 \pm 17.75 \mu\text{m}$ respectively.

The FTIR spectra for the two batches of PEO- $\text{Mg}(\text{CH}_3\text{COO})_2$ Solid Polymer Electrolytes (SPEs); involving development with or without

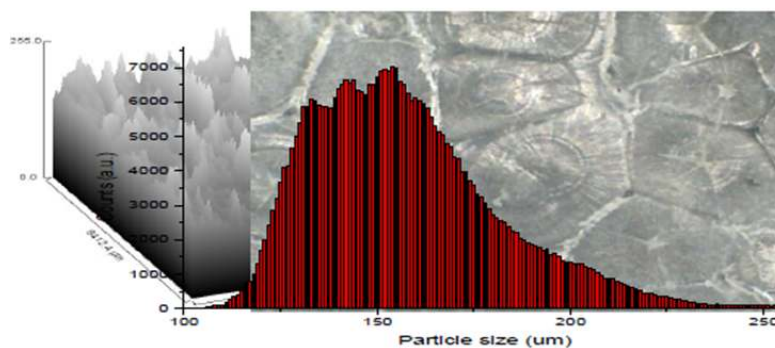


Fig. 1. Optical micrograph, surface topography and histogram of particle distribution for pure PEO film (Taken from [1])

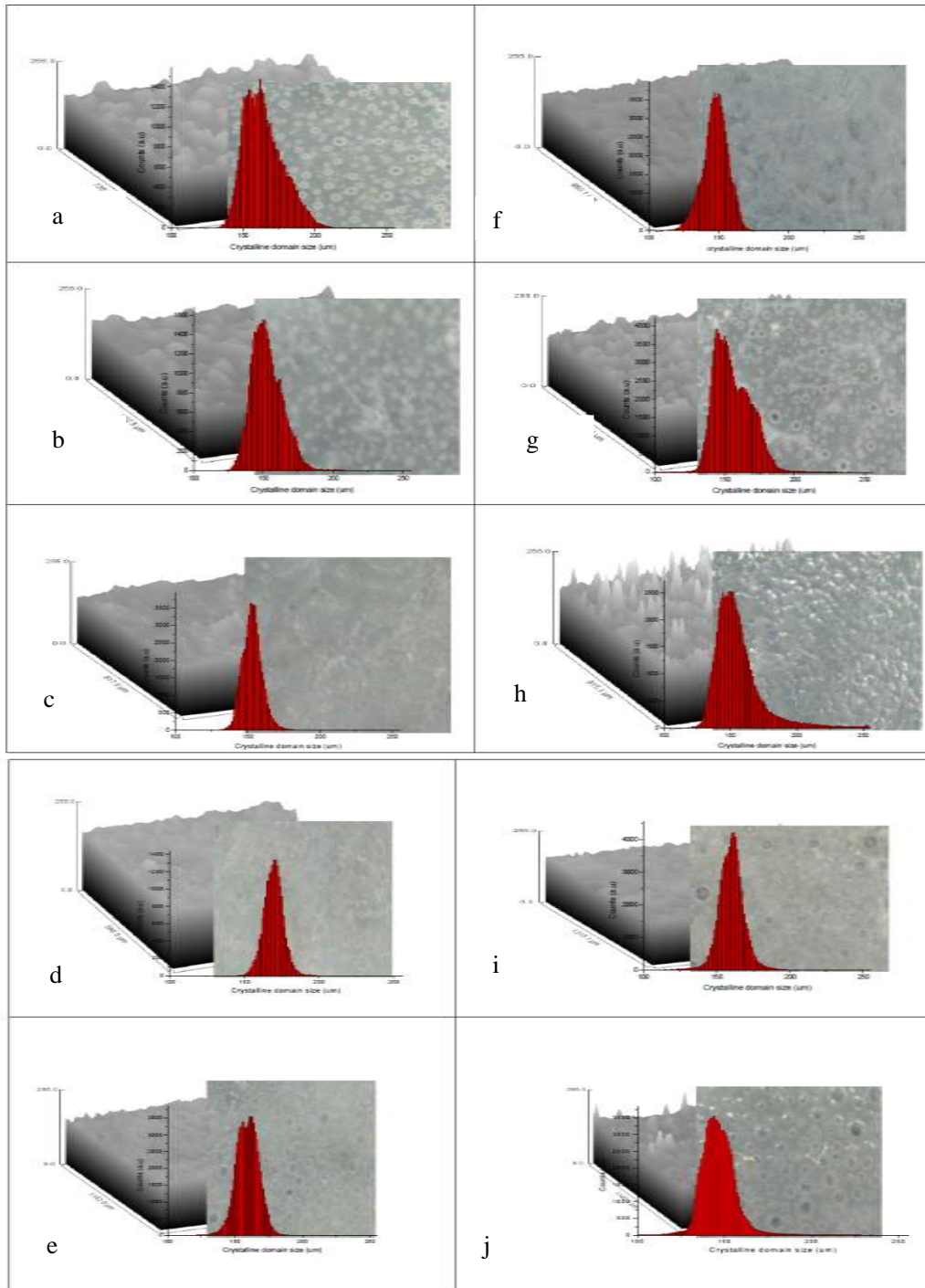


Fig. 2. Optical micrograph, surface topography and Histogram of particle distribution for (a) PEO/EG/ 5% salt (b) PEO/EG/ 10% salt (c) PEO/EG/ 15% salt (d) PEO/EG/ 20% salt (e) PEO/EG/ 25% salt (f) PEO/ 5% salt (g) PEO/ 10% salt (h) PEO/15% salt (i) PEO/ 20% salt (j) PEO/ 25% salt

Ethylene glycol [CH₂ (OH).CH₂OH] each containing 5-25% of Mg(CH₃COO)₂ salts given in Figs. 3(a-e) and 4(a-e) respectively, were

recorded periodically to find out if the Mg(CH₃COO)₂ salts were embedded in the PEO matrix and chemically bonded to polymer chains.

In this work, the significant absorptions observed below 800 cm^{-1} represent metallic bond with oxygen and those above 800 cm^{-1} represent both metallic and metal oxide bonds with hydrogen and hydroxyl groups. The FTIR spectra display broad bands at 3392.69 cm^{-1} - 3905.98 cm^{-1} , which are believed to be associated with the stretching vibrations of hydrogen bonded surface water molecules and hydroxyl groups reflecting the additivity of PEO and Ethylene glycol [$\text{CH}_2(\text{OH})\cdot\text{CH}_2\text{OH}$]. It is also noticed that the hydroxyl stretching bands became much broader with increasing $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ salts content. This strongly supports the idea that a hydrogen bonding can form between either oxygen atoms of PEO and hydroxyl groups of $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ salts. The asymmetric stretching vibrations occurring in the range 2777.59 cm^{-1} - 2924.18 cm^{-1} represent the characteristic band of Aldehyde groups.

The bands occurring at 2166.13 cm^{-1} - 2364.81 cm^{-1} represent the triple carbon bond of the $\text{C}\equiv\text{C}$

stretching vibrations. In addition, the bands at 1060.88 cm^{-1} - 1149.61 cm^{-1} are associated with C-OH bending vibrations of the secondary alcohols. The shift to higher frequencies may be attributed to additional bonding of these groups with metallic compounds. The band at 1599.04 cm^{-1} - 1967.46 cm^{-1} is associated with both C=O conjugated and non-conjugated stretching vibration implying the existence of carbonyl absorptions. The changes observed in the vibration frequency of $\nu\text{C}=\text{O}$ in the SPEs indicate that the incorporation of the $\text{Mg}(\text{CH}_3\text{COO})_2$ salts has great influence on the vibration frequency of $\nu\text{C}=\text{O}$. The bands at 1315.50 cm^{-1} - 1458.23 cm^{-1} are associated with the bonding of MgO with ethylenic groups. The characteristic band of PEO was observed at 823.63 cm^{-1} - 960.58 cm^{-1} due to the C-O-C bending vibration occurring in the range 1263.42 cm^{-1} - 1280.78 cm^{-1} . The changes in the C-O-C band in the spectrum; suggest that hydrogen bonding is the underlying mechanism in the interaction.

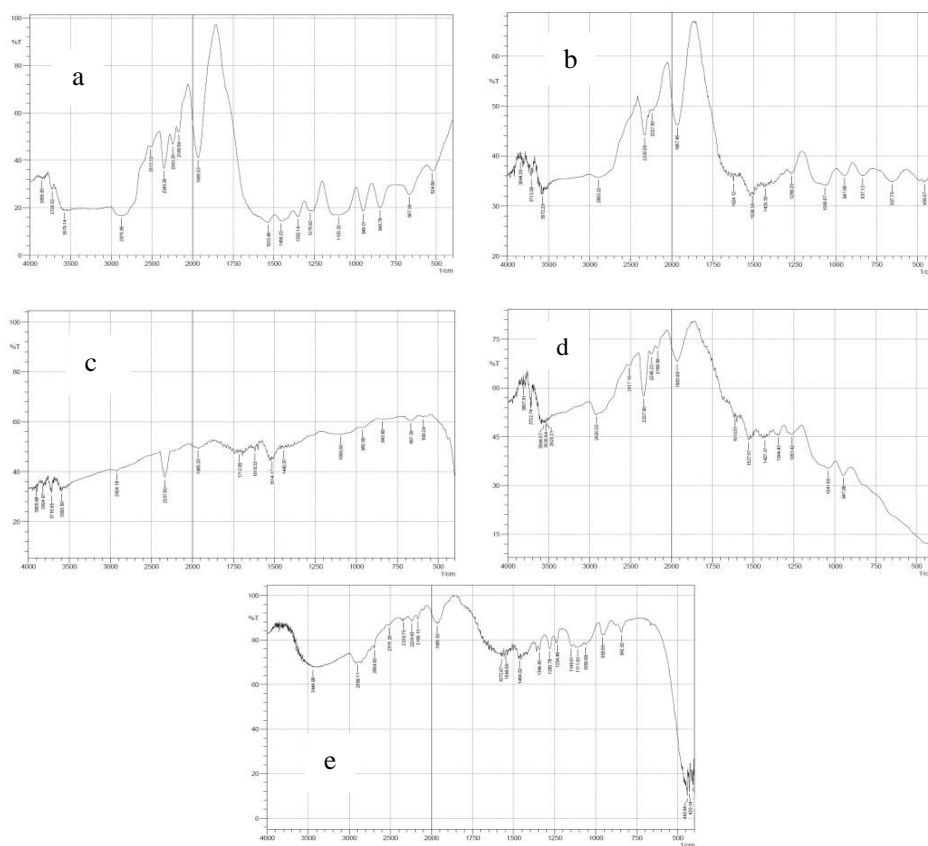


Fig. 3. FTIR Spectra for the SPEs containing (a) PEO/EG/5% salt (b) PEO/EG/10% salt (c) PEO/EG/15% salt (d) PEO/EG/20% salt (e) PEO/25% salt

In addition, hydrogen bonding has a strong influence on the dispersoid (in our case the $-OH$ of $Mg(CH_3COO)_2 \cdot 4H_2O$ salts) and the absorption maxima of stretching vibration shifts toward higher frequencies. Finally, the out of plane bending vibrations appearing at 823.63 cm^{-1} – 960.58 cm^{-1} are due to slight transformation in the ethylenic groups as a result of oxidation and hydrolysis.

In the present study, the likely mobile species are protonic and the total transference number was evaluated using equation (1) above. The calculated values of t_{ion} for the two batches of SPEs ranges from 0.74 to 0.98 where the SPE containing 15% $Mg(CH_3COO)_2 \cdot 4H_2O$ salts has the highest value. From these values, it is obvious that PEO- $Mg(CH_3COO)_2$ Solid Polymer Electrolytes (SPEs) are essentially ionic materials. The quality of the values is limited due to uncertainty in the measurement of initial current due to quick onset of polarisation [1]. The temperature dependence of the conductivity (i.e.

$\ln\sigma$ versus $1/T$ and σ versus $1/T$ plots) for the SPEs containing Ethylene glycol $[CH_2(OH).CH_2OH]$ are presented in Figs. 5 and 6 while that for the SPE containing 15% salt without Ethylene glycol $[CH_2(OH).CH_2OH]$ is presented in Fig. 7. The addition of Ethylene glycol $[CH_2(OH).CH_2OH]$ as a plasticizer enhances the conductivity after T_m , in each of the five compositions shown in Figs. 5 and 6; this may be attributed to phase transition from semicrystalline to amorphous phase as a result of plasticization whereas the batch without plasticizer did not show any conductivity except for the sample containing 15% $Mg(CH_3COO)_2 \cdot 4H_2O$ salts. Thus, for both batches, there exists continuous decrease in conductivity with temperature due to the size of mobile species and the values for the sample are presented in Table 1 near the phase transition. The calculated values for activation energy obtained from the Arrhenius plots and the ionic conductivity at 338K for the SPEs are given in Table 1.

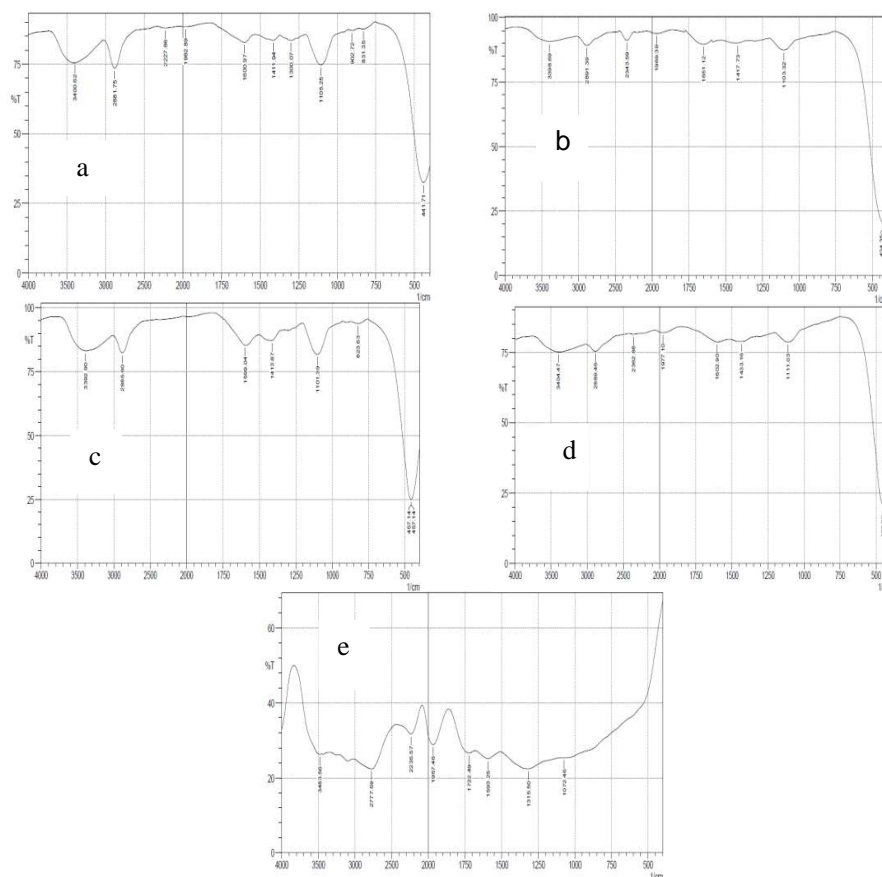


Fig. 4. FTIR Spectra for the SPEs containing (f) PEO/5% salt (g) PEO/10% salt (h) PEO/15% salt (i) PEO/20% salt (j) PEO/25% salt

The activation energies for the SPEs range from 1.23×10^{-3} eV to 1.97×10^{-3} eV where the sample containing 15% salt has the lowest activation energy. The reduction in activation energy

leading to higher conductivity may be due to smoother morphologies of the films upon addition of Ethylene glycol [$\text{CH}_2(\text{OH})\text{CH}_2\text{OH}$].

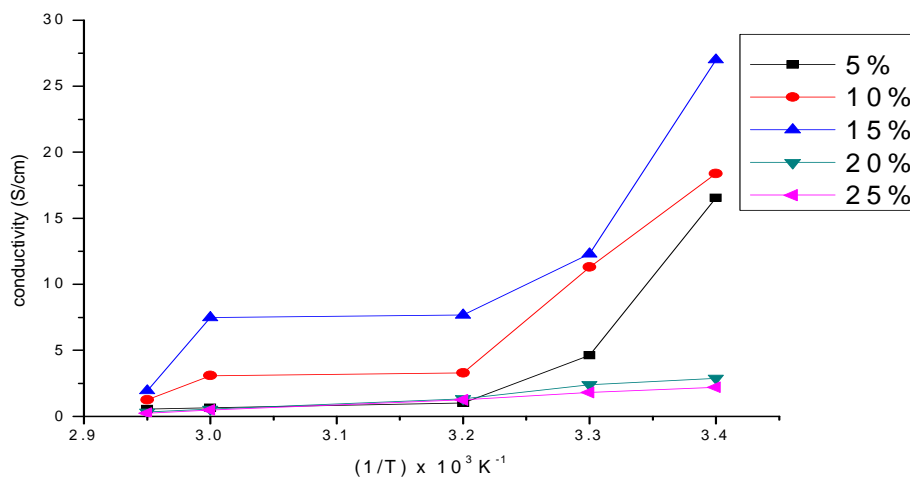


Fig. 5. Variation of conductivity with temperature for the SPEs containing 5% -25% $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with ethylene glycol

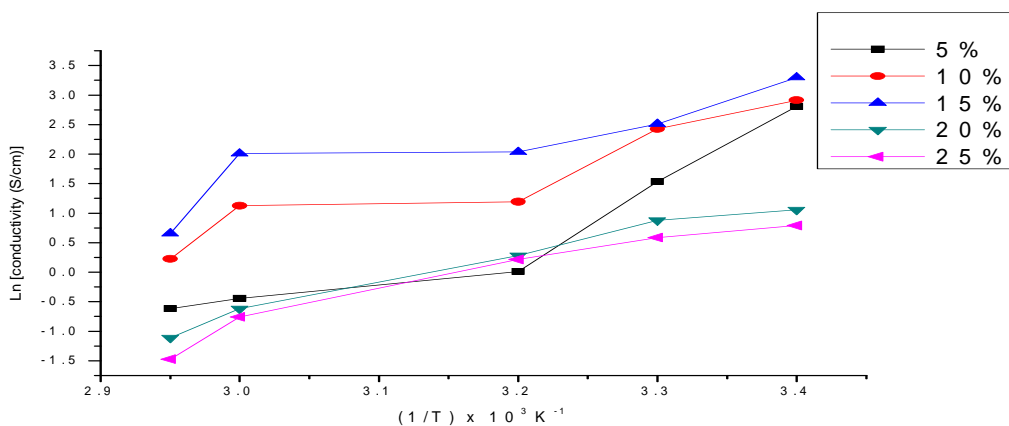


Fig. 6. Variation of Ln conductivity with temperature for the SPEs containing 5% -25% $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with ethylene glycol

Table 1. Transport properties for SPEs containing 5%- 25% $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts with ethylene glycol

Salt con. (%)	Cond. (S/cm) @338K ($\times 10^{-2}$)	Transference number	Activation energy (eV) ($\times 10^{-3}$)
5	5.4	0.88	1.97
10	12.5	0.91	1.45
15	19.3	0.98	1.23
20	3.3	0.77	1.33
25	2.3	0.74	1.34

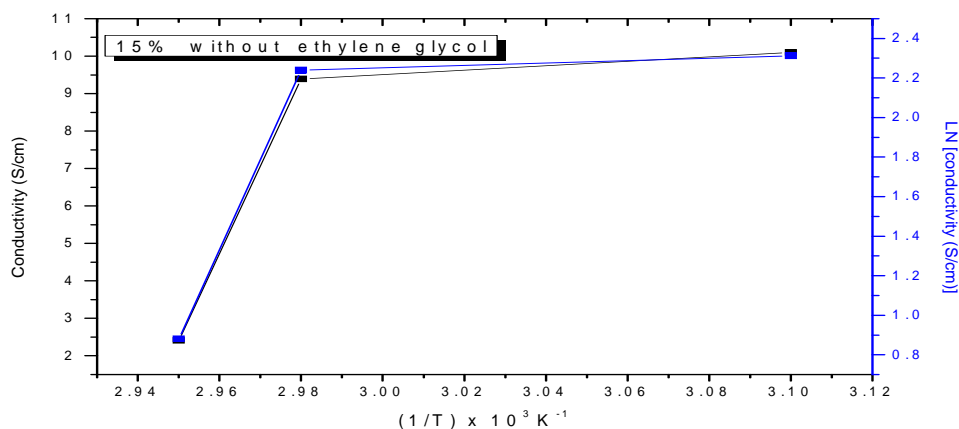


Fig. 7. Variation of conductivity and Ln conductivity with temperature for the SPEs containing 15% $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ without ethylene glycol

4. CONCLUSION

The use of low molecular weight Ethylene glycol $[\text{CH}_2(\text{OH})\cdot\text{CH}_2\text{OH}]$ as a new type of plasticizer in addition to the versatility of PEO have been exploited for the development of (PEO)/ $\text{Mg}(\text{CH}_3\text{COO})_2$ solid polymer electrolytes. The morphological characteristics and transport properties of the developed SPEs were examined employing Optical Microscopy, FTIR and dc conductivity. The FTIR spectroscopy revealed the existence of strong interfacial interaction between PEO and $\text{Mg}(\text{CH}_3\text{COO})_2$ as the pristine polymer matrix are uniformly interspersed with $\text{Mg}(\text{CH}_3\text{COO})_2$ salts showing strong absorption bands for the polymer and the $\text{Mg}(\text{CH}_3\text{COO})_2$ salts. Thus, the significant absorptions observed below 800 cm^{-1} represent metallic bond with oxygen and those above 800 cm^{-1} represent both metallic and metal oxide bonds with hydrogen and hydroxyl groups. Observation with optical microscope also revealed that the crystallinity of the pristine PEO decreases with increase in percentage weight of $\text{Mg}(\text{CH}_3\text{COO})_2$ salts. Finally, polarisation and conductivity studies confirmed that the transference number and ionic conductivity were found to increase with increase in $\text{Mg}(\text{CH}_3\text{COO})_2$ salts content up to 15% and above this, a decrease in the conductivity was observed. However, a maximum conductivity of $19.3 \times 10^{-2}\text{ S/cm}$ and transference number of 0.98 was observed for sample containing 15 wt% $\text{Mg}(\text{CH}_3\text{COO})_2$ salts at 338 K. The temperature dependence of ionic conductivity of the SPEs seems to follow an Arrhenius-type, thermally

activated process with activation energies reducing with addition of Ethylene glycol $[\text{CH}_2(\text{OH})\cdot\text{CH}_2\text{OH}]$.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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