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EFFECTS OF ENR ON MORPHOLOGY, CHEMICAL INTERACTION AND CONDUCTIVITY OF PEO-$LiCF_3SO_3$ SOLID POLYMER ELECTROLYTE

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ABSTRACT

The effects of Epoxidized Natural Rubber (ENR) in the PEO doped $LiCF_3SO_3$ solid polymer electrolyte (SPE) were investigated. These films were prepared by a solution casting technique and characterized by Field Emission Scanning Electron Microscopy (FESEM) to determine the surface morphology, while the presence of the complexes was investigated by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy. Electrochemical Impedance Spectroscopy (EIS) was conducted to obtain ionic conductivity. SEM analysis showed that, the rough surface morphology of SPE became smoother with addition of ENR and salt while ATR-FTIR spectroscopy analysis confirmed the polymer salt complex formation. The interaction occurred between the salt and ether group of polymer host where the triple peaks of ether group in PEO merged and formed one strong peak at 1096 cm^{-1}. The incorporation of ENR is found to increase the conductivity of the system. The highest conductivity achieved was 4.67×10^{-5} S/cm at room temperature when 25 wt. % of $LiCF_3SO_3$ was added into the PEO blend containing 10% ENR. The ionic conduction mechanism for both with and without ENR electrolytes comply with the Arrhenius rule which the ion transport in these materials is thermally assisted.

INTRODUCTION

Ionic conducting polymer electrolytes were first suggested by Fenton and Wright in 1973 [1]. They found that the ionic conductivity of polymer-based electrolyte of PEO-NaSCN system could achieve 10^{-5} Scm^{-1} at room temperature. However, the technological significance especially in developmental usage of electrochemical was only appreciated after the publication of Andrews in 1978 [2]. To date, polymer electrolytes are the main concern of researches due to its ability for new types of electrical power generation and storage systems such as displays, sensors, electrochemical windows, supercapacitors, and rechargeable batteries. Several types of

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polymer such as poly(methyl methacrylate) (PMMA), poly(vinyl chloride; PVC), poly(vinylidene fluoride; PVDF), and poly(ethylene oxide; PEO) have been studied to see their potential as a polymer-based electrolyte [3, 4].

PEO based polymeric electrolytes as polymer ionic conductors are the most extensively studied due to its electrochemical stability, good solubility with many salts, and beneficial structure in supporting fast ionic transport [4].Unfortunately, a high crystalline phase concentration limits the conductivity of PEO-based electrolyte. Various techniques have been developed to reduce the crystallinity of PEO and enhance the ionic conductivity at room temperature. The most common technique is to add plasticizers such as propylene carbonate (PC), ethylene carbonate (EC), and dibutyl phthalate (DBP) [5–7]. However, incorporation of plasticizers will promote deterioration of the electrolytes' mechanical properties and increases its reactivity towards the lithium metal anode. The recent technique developed for solid polymer electrolyte is the dispersion of nano-size inorganic ceramic filler particles such as Al_2O_3, SiO_2, TiO_2, SnO_2, ZnO, and ZrO into the system [4, 8–10]. An alternative to plasticizers and ceramic fillers is to blend it with complex polymer such as modified natural rubber. This is because of their distinctive characteristics such as low glass transition temperature, soft elastomeric characteristics at room temperature, good elasticity, and adhesion that make them a suitable candidate as a polymer host for polymeric electrolyte systems [3, 6]. The good elasticity and adhesion properties of modified natural rubber will provide an efficient contact between the electrodes in electrochemical contacts [6]. Furthermore, modified natural rubber such as 50% epoxidized natural rubber (ENR50) have a polar group in their epoxy ring that will provide coordination sites for Li^+ conduction. In addition, the usage of modified natural rubber will produce SPE that is both low in cost and environmentally friendly. From our previous work, 20 wt.% of ENR50 with 80 wt.% of PEO and 30 wt.% of ENR50 with 70 wt.% of PEO produces a flat, thin, and flexible paper-like film. The characterizations of a SPE of PEO-ENR50 (80/20) and (70/30) have been discussed earlier in [11, 12].

In the present study, the effect of ENR 50 (10%) on morphology, chemical interaction and conductivity of a PEO with various wt.% of $LiCF_3SO_3$ will be discussed. The polymer electrolyte film was prepared by solution casting technique. These polymer electrolytes were characterized by field emission scanning electron microscope (FESEM), reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and electrical impedance spectroscopy (EIS).

EXPERIMENTAL METHOD

Reagent and electrolyte film preparation

The starting materials are PEO (M_w 600 000, Sigma Aldrich, St. Louis, MO, USA), ENR50 (Malaysian Rubber Board, Kuala Lumpur, Malaysia), $LiCF_3SO_3$ (Fluka/Sigma-Aldrich, St. Louis, MO, USA), and tetrahydofuran (THF; SYSTERM; ChemAR, Kielce, Poland). To prepare the polymer electrolyte film, PEO and ENR50 were dissolved in THF separately and were continuously stirred with magnetic bar for 24

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hours. These two solutions were mixed and continuously stirred for another 24 hours to obtain homogenous solution. Various wt.% of $LiCF_3SO_3$ (5 to 25 wt.%) were dissolved separately in THF and mixed with the blended PEO-ENR50 and stirred efficiently for 12 hours to achieve a homogenous mixture. The solution was then casted on a Teflon mold and allowed to evaporate completely in a fumed hood at room temperature to produce a film. The film then was kept in a vacuum oven at 60 °C for 24 hours to remove the residual solvent. Samples were stored in a desiccator until further usage. This procedure provided mechanically stable, free-standing, and flexible films of thickness from 150 to 250 μm. The preparation of SPE was done in an open atmosphere condition at room temperature.

Sample characterization

The morphology of the samples was characterized by FESEM model (SUPRA 55VP, ZEISS) with ×3,000 magnification at 25 kV electron beam. FESEM analysis was done at the fractured with gold sputtered-coated film. ATR-FTIR analysis was carried out using PerkinElmer Spectrum 2000 in the range of wave numbers 4,000 to 400 cm^{-1} with scanning resolution of 4 cm^{-1}. This analysis was conducted to see the functional group and interaction that occur between polymer-based and lithium salt. The alternate current (AC) impedance measurement was carried out using high frequency response analyzer (HFRA; Solartron 1255, Schlumberger) combined with electrochemical interface (SI 1,286) in the frequency range of 1 MHz with 30 mV amplitude. The polymer electrolyte was sandwiched between the stainless steel ion-blocking electrodes with a surface contact area of 2.0 cm^2. The bulk resistance (R_b) was determined from the equivalent circuit analysis by using the analyzer software. The conductivity values (σ) have been calculated from the equation

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

where t is the film thickness and A is the active area of the electrode. The EIS analysis was conducted at room temperature and temperature range of 298 K to 333 K.

RESULTS AND DISCUSSION

Surface Morphology

FESEM micrographs of pure PEO, pure ENR50, blended PEO-ENR50, and PEO-ENR50 with various wt.% of $LiCF_3SO_3$ are shown in Figure 1. It can be seen from Figure 1 that pure PEO shows a rough surface morphology with a lot of rumples. It shows the presence of crystalline phase in PEO [13]. Figure 1 shows the surface morphology of pure ENR50. It shows a smooth surface morphology of ENR50 due to the fully amorphous nature of natural rubber. When the PEO was blended with 10% ENR50, the surface morphology of PEO changes from rough to almost smooth, and the reductions of rumples are also found in Figure 1. It shows ENR50 coated the rumples of PEO, making the surface morphology of PEO to become smoother than pure PEO. The semicrystalline nature of PEO is reduced by ENR50, as evidenced by the reduction of rumples. The homogeneity of PEO-ENR50 can be seen as no phase separation can be observed. The improvement of surface morphology can be seen as addition of salt into

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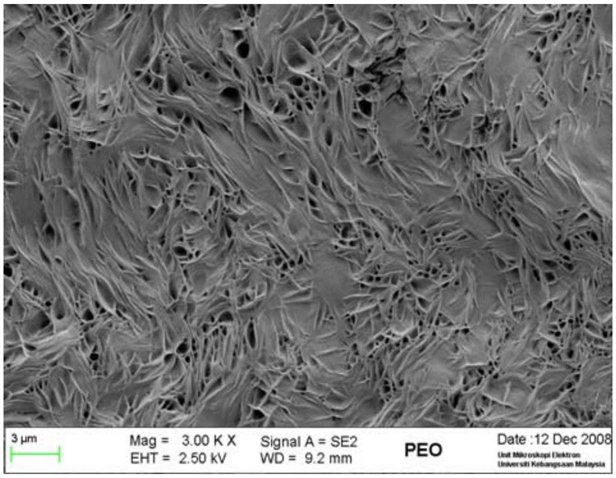
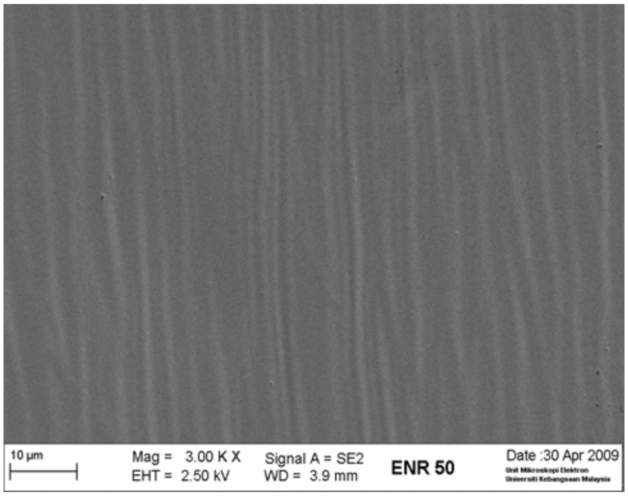
PEO and blended PEO:ENR 50 (90:10) as shown in Figure 2d and 2e. The rumples of PEO are decreased, and the rough surface changed into a smooth surface due to the addition of salt. The smooth morphology is closely related to the reduction of PEO crystallinity in presence of salt [14]. The reduction of PEO crystallinity arises from random distribution and dissociation of salt which may introduce the topological disorder in the electrolyte. The reduction of crystallinity will produced more amorphous phase in the system. The amorphous phase makes the electrolyte more flexible, resulting in increase of the segmental motion of the polymer. However, it can be seen that the surface morphology of blended PEO:ENR 50 with salt is smoother than PEO based polymer electrolyte. It shows that the existence of ENR 50 improve the surface morphology of the polymer electrolyte. Furthermore, the smooth surface morphology indicates that salt was completely dissolved in the matrix. It suggests the existence of interaction between salt and polymer host.

(a)



(b)



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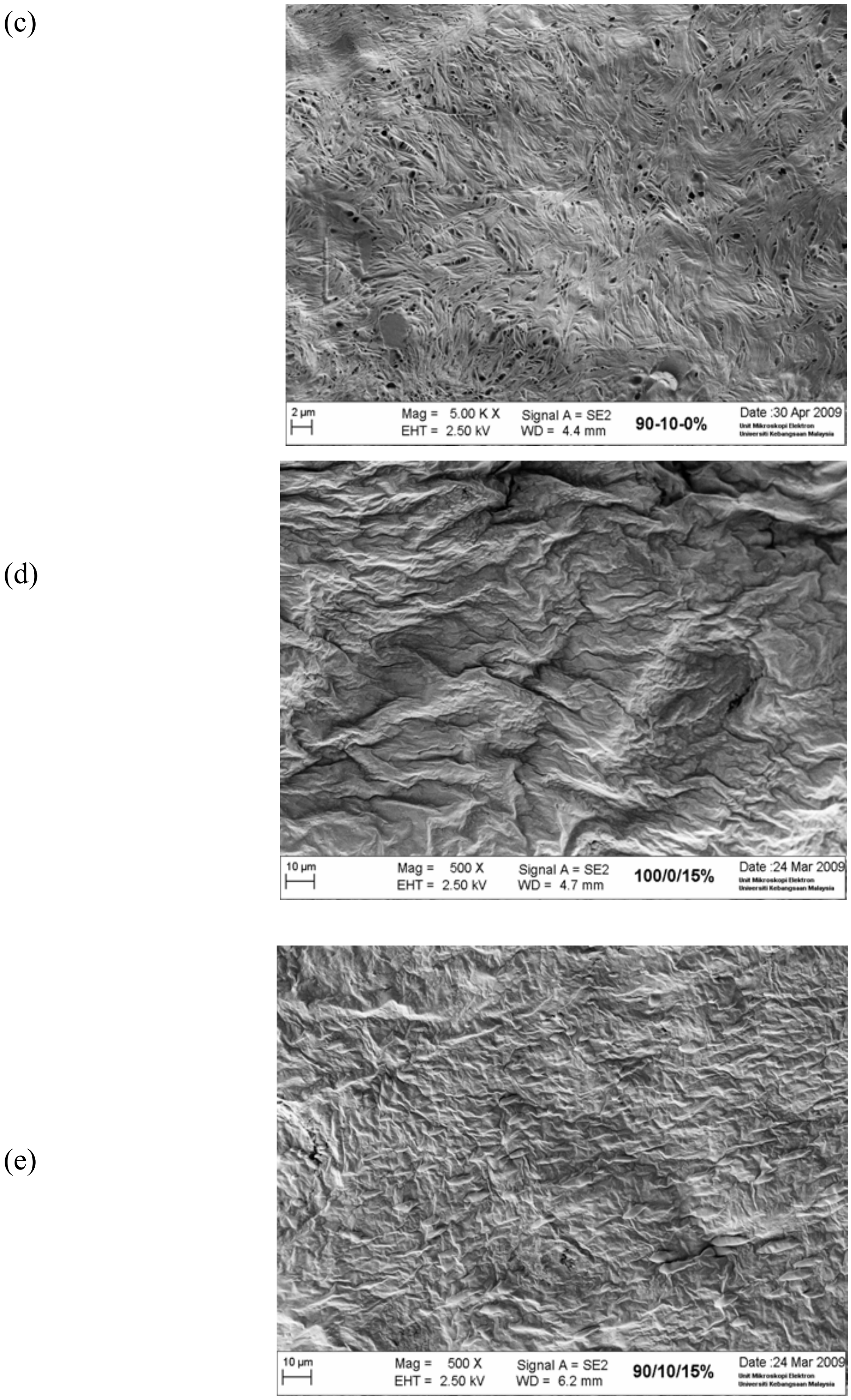

Figure 1 : (a) FESEM micrographs for pure PEO, (b) pure ENR50, (c) PEO:ENR50 (90:10), (d) PEO with 15 wt.% of $LiCF_3SO_3$, (e) PEO:ENR50 (90:10) with 15 wt.% $LiCF_3SO_3$

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FTIR Analysis

Figure 2 represents the FTIR spectra for pure $LiCF_3SO_3$, pure PEO, pure ENR50, PEO and PEO:ENR 50 (90:10) with 15 wt.% $LiCF_3SO_3$. The semicrystalline phase of PEO is confirmed by the presence of triplet peak of C-O-C stretching [15, 16]. C-O-C stretching can be found at 1,145, 1,095, and 1059 cm^{-1} vibrations with maximum peak at 1095 cm^{-1}. For pure ENR50, the band for C-O-C stretching is located at 1,017 cm^{-1} while C=C stretching band at 1588 cm^{-1}. For blended of PEO-ENR 50, it was observed that the triplet peak of PEO C-O-C stretching slightly shifted to 1,146, 1,100, and 1,060 cm^{-1}. Besides, one of the split in the CH_2 wagging mode, in the pure PEO at 1,360 cm^{-1} and C-O-C stretching from the epoxide ring were disappeared. These observations show the existence of intermolecular interaction between oxygen from the epoxide ring and methylene group from the PEO [17]. The characteristic band regions of ether group in PEO and ENR50 are the main focus in the detection of ionic interaction. These regions show interesting changes because if the cations were coordinated with the ether oxygen, changes in the ether oxygen vibrational modes are expected to be observed [18]. The oxygen atom at the C-O-C functional group carries lone pairs of electron, which are donated to Li^+ in the formation of complexes with the lithium salt [3, 18]. The region of C-O-C was showed in Fig. 2 (in box (i)). From the spectra, the maximum of triplet peak C-O-C band (1,100 cm^{-1}) for the polymer host became wide and broad as addition of $LiCF_3SO_3$ in PEO and PEO:ENR 50. Meanwhile, the two minor peaks of triplet peak C-O-C band at 1,045 and 1,060 cm^{-1} almost disappeared because both peaks is combine into their corresponding peaks. This observation shows that the C-O-C band is strongly affected by cation complexation. The complexations that occur at C-O-C group were through dative bond formation between the Li^+ from the doping salt and the lone pairs of the oxygen atom from the polymer host [3, 18]. Furthermore, the broadening of peaks also indicates a reduction of PEO crystallinity [16]. On the other hand, the peak of SO_3 symmetric stretching from the triflate anion at 1,045 cm^{-1} shifted to lower wave number in the complexes which is at 1,030 cm^{-1} in both PEO and PEO:ENR 50. The complexation that occurred at the C-O-C effects the region of vibration assigned to the methylene (CH_2) units. In the region of 1,300 – 1,150 cm^{-1}, CH_2 twisting mode was observed at 1,241 and 1,279 cm^{-1} as shown in box (ii). The characteristic of salt can also be observed at this region. The vibrational frequencies of several functional groups presence in triflate anion can be used to show ion dissociation and the interactions of salt in the complexes. The asymmetric stretching of SO_3 mode is located at 1,292 and 1,252 cm^{-1} and the symmetric stretching of CF_3 at 1,189 cm^{-1}. These bands have merged to form a small shoulder and a broad band centered at 1,252 cm^{-1} as addition of 15 wt.% of salt into polymer host. These changes suggest that the environment of the CF_3 and SO_3 vibrational mode has change as a result of complexation with PEO-ENR50 [19].

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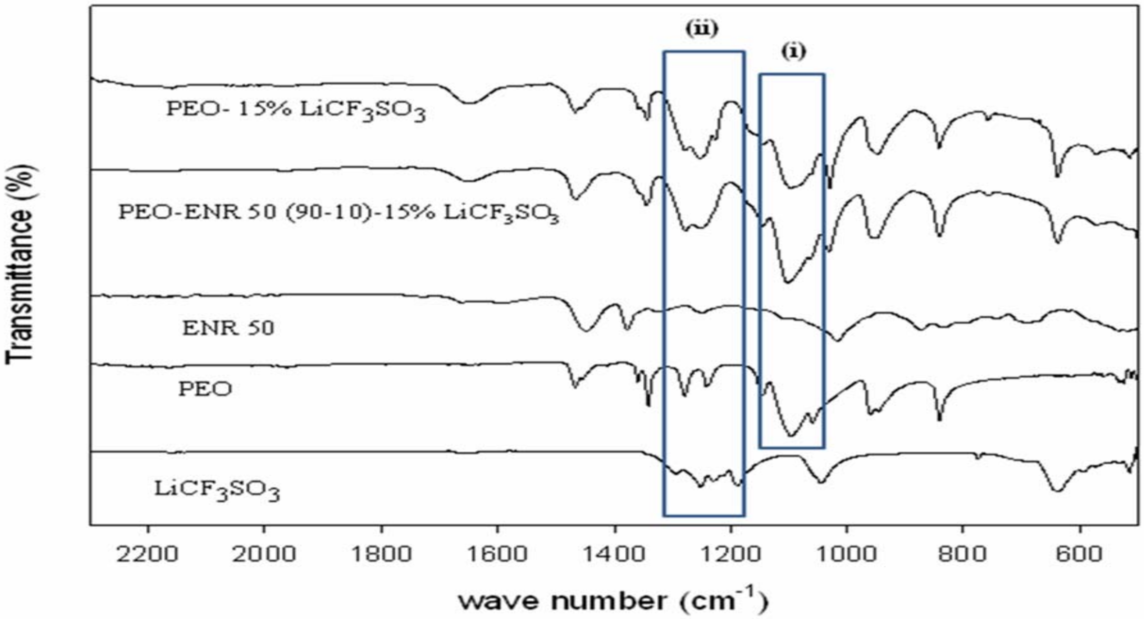

Figure 2: FTIR spectra for $LiCF_3SO_3$, PEO, ENR 50 and PEO and PEO-ENR 50 with 15 wt.% of $LiCF_3SO_3$

Ionic conductivity

The ionic conductivity measurements were carried out with the aim to observe the effect of $LiCF_3SO_3$ addition on the electrical property of the PEO and PEO-ENR 50 based electrolyte system. The ionic conductivity without $LiCF_3SO_3$ for PEO and PEO-ENR 50 based polymer electrolyte is 1.75×10^{-9} and 1.84×10^{-9} S/cm respectively. It was observed that the ionic conductivity increase by increasing the wt. % of $LiCF_3SO_3$ in both PEO and PEO-ENR 50 based polymer electrolyte. This is due to the increasing of the conducting species in the electrolyte. The increase in ionic conductivity with the addition of salt is attributed to a reduction of crystallinity of polymer electrolyte. Overall, the ionic conductivity of PEO-ENR 50 based polymer electrolyte is slightly higher than PEO based polymer electrolyte in all concentration of $LiCF_3SO_3$ salt as shown in figure 3. This is due to the effect of blended PEO with ENR50. In terms of molecular structure of the polymer, ENR50 has an active oxygen in the epoxy group attached to the main chain [5]. It is assumed that the ENR50 oxygen atom plays a role similar to the ether group in the PEO polymer structure which provides coordination sites for Li^+ conduction and will produce a great number of charge carriers for ionic transport [3, 5, 6]. Besides, ENR 50 may have played the role of a plasticizer to reduce the viscosity of the PEO chains hence increasing the chain mobility.

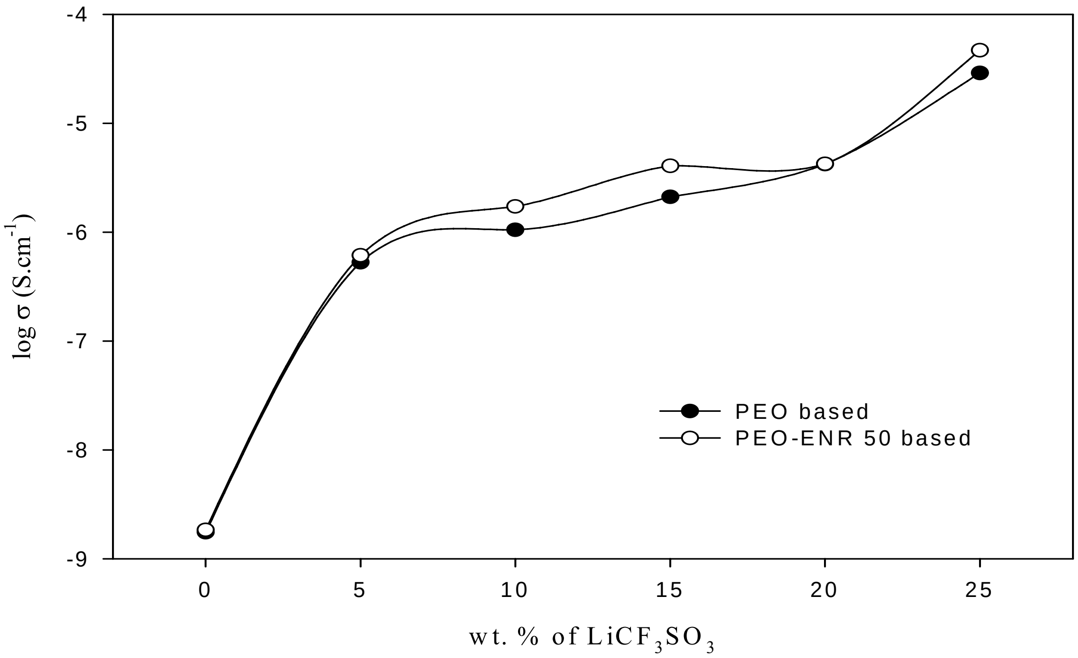

Figure 3: Ionic conductivity at room temperature for PEO and PEO:ENR 50 with various wt.% of $LiCF_3SO_3$ salt

Figure 4 shows the plot of ionic conductivity (log σ) versus the inverse absolute temperature for the PEO and PEO-ENR50 with 25 wt.% $LiCF_3SO_3$. The measurements were carried out from 298 K to 333 K. The plot exhibits a straight line indicating that this system obeyed the Arrhenius rule which the ionic conductivity increases with temperature. It shows the electrolyte was thermally assisted. Therefore, as temperature was increased, the number of free lithium ions was also increased. Hence, it increases the conductivity of the electrolyte. The increase in the ionic mobility and the segmental motion will also enhance the transport of ions in the polymer blend [3, 20]. The ionic conductivity can be expressed as $\sigma = \sigma_o \exp [-E_a / kT]$ where, σ_o is the conductivity pre-exponential factor, E_a is the activation energy, and k is the Boltzmann constant. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be evaluated by linear fitting to the plot [3, 21]. Therefore, it can be suggested that the value of E_a is due to the energy that is required to provide a conductive condition for the migration of ions. The E_a for PEO based polymer electrolyte is 0.73 eV and the pre-exponential factor is 5.1×10^7 $S.cm^{-1}$ with the regression line of 0.993. The Ea for the PEO-ENR 50 based polymer electrolyte is 0.58 eV and the pre-exponential factor is 2.6×10^6 $S.cm^{-1}$ with the regression line of 0.992. It can be concluded that the energy required to dissociate cations from anions in the PEO-ENR 50 based polymer electrolyte is smaller than the PEO based polymer electrolyte. From the value of pre-exponential factor, it indicated

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that the mobility of charge carrier of PEO-ENR 50 based is smaller than PEO based polymer electrolyte.

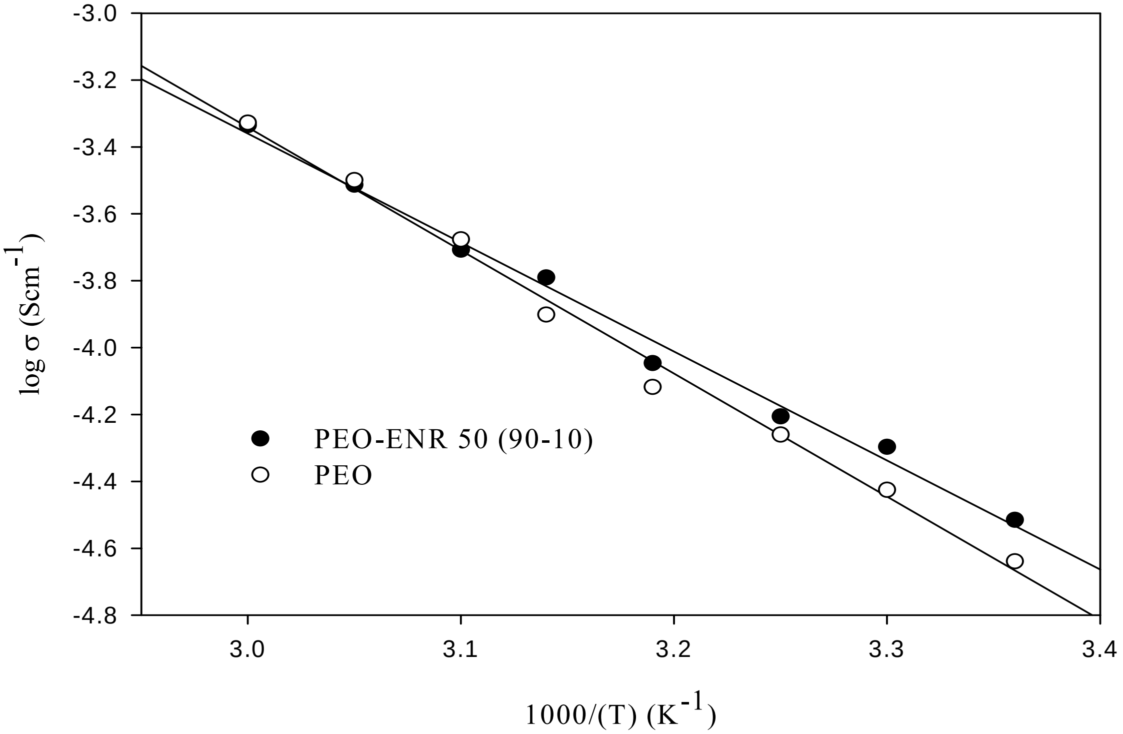

Figure 4: Arrhenius plot for the electrolyte with PEO and PEO:ENR 50 composition at 25 wt.% of $LiCF_3SO_3$

CONCLUSION

A solid polymeric electrolyte of PEO- $LiCF_3SO_3$ and PEO:ENR50-$LiCF_3SO_3$ has been prepared by solution casting technique. The effect of ENR 50 and $LiCF_3SO_3$ salt on the morphology, chemical interaction, and conductivity of PEO-ENR50 based polymer electrolyte was investigated by FESEM, FTIR, and AC impedance spectroscopy. The FESEM results showed a rough surface of pure PEO becomes smooth due to the blended with ENR 50 and addition of salt that also showed the reduction of PEO crystallinity. The interaction between polymer host and lithium salt was confirmed by ATR-FTIR analysis. The triple peak of C-O-C stretching was combined to form a wide and broad peak centered at 1,096 cm^{-1} when salt was introduced to the electrolyte system. From the impedance analysis, the ionic conductivity of PEO:ENR 50 based polymer electrolyte is higher than PEO based polymer electrolyte. The ionic conductivity was found to increase with the wt.% of salt and reached the maximum value at 25 wt.% of $LiCF_3SO_3$ for both PEO and PEO:ENR 50 based polymer

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electrolyte. The temperature dependence on conductivity implies with the Arrhenius rule.

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