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# Solid polymeric electrolyte of poly(ethylene)oxide-50% epoxidized natural rubber-lithium triflate (PEO-ENR50-$LiCF_3SO_3$)

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## ABSTRACT

**A solid polymer electrolyte (SPE) films consisting of polyethylene oxide (PEO), 50% epoxidized natural rubber (ENR50) and $LiCF_3SO_3$ with various compositions of PEO-ENR50 and various weight percentage of $LiCF_3SO_3$ were prepared by solution casting technique. The polymer electrolyte films were characterized using DSC, XRD and AC impedance spectroscopy. The SPE with the PEO-ENR50 composition of 70-30 shows the highest conductivity of $4.2 \times 10^{-5}$ $Scm^{-1}$ at the 15 wt.% of $LiCF_3SO_3$ compared with the other composition of PEO/ENR50. This composition was then chosen to investigate the effect of $LiCF_3SO_3$ on the thermal property, structure and conductivity of the electrolyte. The highest room temperature conductivity of $1.4 \times 10^{-4}$ $Scm^{-1}$ was achieved at 20 wt.% of $LiCF_3SO_3$. The conductivity result is supported by the DSC and XRD analysis which showed the semi- crystalline nature of PEO turning to amorphous state due to the increase in $LiCF_3SO_3$ content.**

**Keywords:** A. Polymers; C. Differential Scanning Calorimetry (DSC); C. X-Ray Diffraction; D. Electrical Conductivity; D. Electrical Properties

## 1. INTRODUCTION

Main application of polymer electrolytes lies in electrochemical device such as display, sensor, electrochemical window, super-capacitor, rechargeable battery and photoelectrochemical cell. However, the main attention of many solid state researchers is the development of secondary lithium batteries [1-4]. Ionic conducting polymer electrolytes were first suggested by Fenton *et al.* in 1973 [5], who reported that PEO-salt complexes are capable of exhibiting ionic conductivity and subsequently substantial activities were directed towards the development of a wide variety of solid polymer electrolytes using different combinations of polymer and salt. The most reported and extensively studied polymer host for solid polymer electrolyte is PEO [6-12]. This is due to a high electrochemical stability of PEO in comparison with other polyethers, copolymers or PEO branched polymers [9]. Besides, PEO has a good solubility for many salts such as LiTFSI, $Li_2SO_4$, $NH_4ClO_4$ and $LiCF_3SO_3$. Even though PEO has a good electrochemical stability, PEO exists in semi-crystalline state at room temperature and does not have an excellent contact with the electrodes.

Solid polymer electrolytes (SPE) for lithium batteries have many advantages over its counterpart liquid electrolyte, such as mechanical stability and processing flexibility. However, the conductivity at room temperature is usually too low to be utilized in ionic device. There are various techniques that can be employed to enhance the conductivity of SPE at room temperature. The recent technique developed for solid polymer electrolytes is the dispersion of nanosize inorganic ceramic filler particles such as $Al_2O_3$, $SiO_2$, $TiO_2$, $SnO_2$, ZnO and ZrO in the electrolyte systems [6-10]. Propylene carbonate (PC), ethylene carbonate (EC) and dibutyl phthalate (DBP) are also used as plasticizers for conventional polymer electrolyte systems [11-13]. An alternative to ceramic fillers or plasticizers is to employ a complexing polymer such as modified natural rubber. This is due to their distinctive characteristics such as low glass transition temperature, soft elastomeric characteristic at room temperature, good elasticity and adhesion that makes them a suitable candidate as a filler for polymeric electrolyte systems [1,11,12]. **Figure 1** shows the structure of ENR50 dimmer.

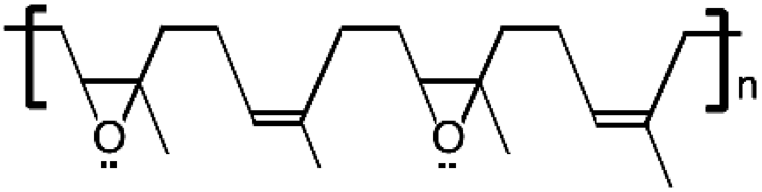

**Figure 1.** Structure of ENR50 dimmer.

This work describes the effect of ENR50 content on the conductivity of PEO-ENR50-$LiCF_3SO_3$ electrolyte at the fixed concentration of the $LiCF_3SO_3$ salt. The PEO-ENR50 composition that gave the highest room temperature conductivity was chosen to study the effect of the salt content on the conductivity of the electrolyte. The blended polymer of PEO-ENR50 as a polymer host was doped with $LiCF_3SO_3$ using the solution casting technique [14] to obtain a solid polymeric electrolyte film. This work also reports the effect of $LiCF_3SO_3$ content on thermal property and structure of the electrolyte fixed at PEO-ENR50 composition of 70/30.

## 2. EXPERIMENTAL

### 2.1. Sample Preparation

The SPE films were prepared by means of the solution-cast technique using a single solvent of THF. The host materials, poly(ethylene oxide) (PEO) ($M_W$ = 600,000) was obtained from Sigma Aldrich, while 50% epoxidized natural rubber (ENR50) ($M_W$= 592,487) was supplied by Malaysian Rubber Board. The required amounts of PEO and ENR50 were dissolved in tetrahydrofuran (THF) that was obtained from SYSTERM ChemAR. Lithium triflate ($LiCF_3SO_3$), obtained from Fluka was used as the doping salt. All the materials were used without further purification. Subsequently, the desired amounts of PEO-ENR50 and various weight percentage of $LiCF_3SO_3$ were dissolved separately in THF, mixed together and stirred efficiently for 24 hours in order to achieve a homogeneous mixture. The solutions obtained was cast on a teflon mould and was allowed to evaporate completely at room temperature to produce an electrolyte film. Then, the film was dried in a vacuum oven at 60°C for 24 hours to remove the residual solvent. This procedure provided a mechanically stable, free standing and flexible films with the thickness ranging from 150 to 250 µm. The preparation of SPE was carried out in an atmosphere environment at room temperature [12,14].

### 2.2. Sample Characterizations

The AC impedance measurement was carried out at room temperature using a high frequency response analyzer (HFRA Solartron 1256, Schlumberger) in the frequency range of 100 Hz-1 MHz with 30 mV amplitude. The electrolyte was sandwiched between the stainless steel ion-blocking electrodes with a surface contact area of 2.0 $cm^2$. The bulk resistance, ($R_b$) of the electrolyte was determined from the equivalent circuit analysis assisted with Z-View software. The conductivity, (σ) have been calculated from the equation $\sigma = (1/R_b)(t/A)$, where t is the film thickness and A is the active area of the electrode. The thermal property measurement was conducted using a differential scanning calorimeter model 8822$^e$ Mettler Toledo from -60°C and + 150°C at a scanning rate of 10°C $min^{-1}$ under nitrogen atmosphere. Previously, a pure indium and tin were used for temperature and enthalpy calibrations for DSC measurements. Approximately, 1 to 3 mg of the electrolyte film specimen was used for each DSC measurement. The X-ray diffraction technique was performed on the electrolyte films at room temperature using a Siemens model D5000 (Cu-K$\alpha$; $\alpha$ = 1.5418 Å). The diffraction angle, $2\theta$ was 10° to 45° using a step size of 0.025° to determine the crystallinity of the electrolyte samples. The Scherrer length was then automatically calculated by evaluation (EVA) software.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of ENR50 Content on Conductivity of PEO- ENR50-$LiCF_3SO_3$ Electrolyte

The freestanding electrolyte films of PEO-ENR50-$LiCF_3SO_3$ have been produced by using solution casting technique. **Table 1** shows the conductivity the electrolyte with various compositions of PEO-ENR50 at the fixed concentration of $LiCF_3SO_3$ (15 wt.%). The percentage by weight of ENR50 was chosen up to 30% since after this level, the electrolyte became a gel electrolyte and was not a free standing film. It made the electrolyte film

**Table 1.** Room temperature conductivity for various composition of PEO-ENR50 at 15 wt.% $LiCF_3SO_3$.

| Composition | Ionic conductivity ($Scm^{-1}$) |
|---|---|
| 100-0 | $2.1 \times 10^{-6}$ |
| 90-10 | $4.1 \times 10^{-6}$ |
| 80-20 | $1.0 \times 10^{-5}$ |
| 70-30 | $4.2 \times 10^{-5}$ |

was difficult to peel off from the mould. From **Table 1**, the conductivity of the electrolyte without ENR50 was $2.1 \times 10^{-6}$ $Scm^{-1}$. The conductivity was found to increase with the increasing percentage of ENR50 in the polymer host. The highest room temperature conductivity of $4.2 \times 10^{-5}$ $Scm^{-1}$ was achieved at 70-30 composition of PEO- ENR50. This observation shows that the ENR50 content affected the conductivity of the electrolyte. It shows that the elastomeric characteristic of ENR50 reduced the glassy nature of PEO. This condition will enhance the segmental motion of the polymer host. The effect of segmental flexibility is responsible for the formation of free volume which enhances the ionic conductivity. The strong adhesive property can give an efficient contact between the electrodes in electrochemical contacts [12]. This behavior can be seen in the electrolyte system which is due to a good elasticity and adhesion property of ENR50. Razali *et al.* [12] reported that ENR50-LiTf with 100% wt. of EC/PC gave ionic conductivity of $4.0 \times 10^{-5}$ $Scm^{-1}$ at room temperature. This conductivity value was almost similar with our electrolyte system for 70-30 composition without any plasticizer. It shows that with the absence of a costly plasticizer, the conductivity of the electrolyte has been improved by blending PEO with ENR50. In addition, this electrolyte system produced a low cost and an environmental friendly electrolyte. Besides, the use of PC and EC can corrode the lithium metal electrode in electrochemical cell [16]. Glasse *et al.* [11] reported the incorporation of PEO with ENR50 can reduce the sticky property of ENR50 and made the film could be peeled off easily from the mould.

### 3.2. Effect of $LiCF_3SO_3$ Salt on Thermal Property, Structure and Conductivity of PEO-ENR50-$LiCF_3SO_3$ Electrolyte

The effect of $LiCF_3SO_3$ salt on the above properties of a PEO-ENR50-$LiCF_3SO_3$ electrolyte was investigated by choosing the electrolyte with the 70-30 composition of PEO-ENR50. This is because this composition has shown the best performance in term of ionic conductivity as compared with the other compositions of PEO-ENR50. The electrolytes were prepared by varying the percentage by weight of $LiCF_3SO_3$ from 5% to 25% at 5% interval. In order to investigate the effect of the salt content on the thermal property of the electrolyte such as melting point, DSC measurement was performed on the prepared electrolyte samples. **Figure 2** shows the DSC thermographs for all samples. The sharp endothermic peak observed at 68°C, corresponds to the crystalline melting temperature ($T_m$) of the pure PEO [15]. The endothermic peak for pure PEO showed the transition from 68°C to 60°C by addition of 5 wt.% of the salt. The $T_m$ value decreases dramatically to 49°C with addition of 20 wt.% of the salt. This observation shows the reduction in $T_m$ value by addition of the salt. The endothermic curves also indicate a reduction of PEO crystallinity. The relative percentage of crystallinity ($\lambda$) of PEO has been calculated by using the relation, $\lambda = (\Delta H_m/\Delta H_m^o) \text{ x } 100\%$, where, $\Delta H_m$ is the melting enthalpy estimated experimentally and $\Delta H_m^o$ used as referenced is the melting enthalpy for 100% crystalline PEO (213.7 $Jg^{-1}$) [16]. The calculated values of $\lambda$ are summarized in **Table 2.** The crystallinity degree of the electrolyte decreases with the wt.% of the salt which causes an increase in the amorphous phase. The polymeric chain in the amorphous phase is more flexible, which results in the enhancement of segmental motion of the polymer [17]. The $T_m$ and $\lambda$ values obtained from this work for polymer electrolyte based on PEO closely agree with the values reported in literature [8,18]. The reduction of $T_m$ and $\lambda$ suggest that the interaction between the polymer host backbone and $LiCF_3SO_3$ affects the dynamic main chain of the polymer. This will promote the amorphous phase which is ex-

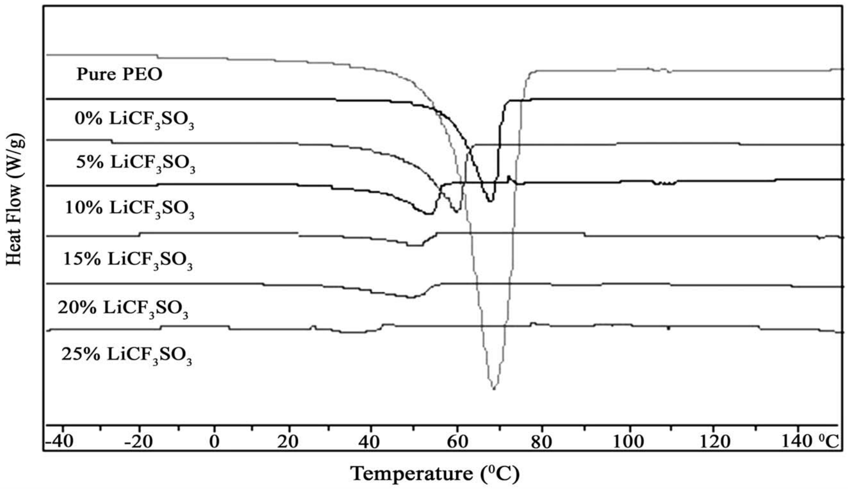

**Figure 2.** DSC thermograms of PEO,PEO-ENR50 (70-30) with different wt.% $LiCF_3SO_3$.

**Table 2.** O/Li mole ratio, crystallinity, ($\lambda$) and melting temperature, ($T_m$) of PEO-ENR50-$LiCF_3SO_3$ electrolyte.

| $LiCF_3SO_3$ (wt%) to PEO/ENR50 (70/30) | O/Li | $T_m$ of PEO (°C) | Relative percentage of crystalline phase ($\lambda$) (%) |
|---|---|---|---|
| Pure PEO | - | 68 | 78.5 |
| Pure ENR | - | - | |
| 0% | 0/1 | 67 | 49.9 |
| 5% | 16/1 | 60 | 35.9 |
| 10% | 8/1 | 53 | 31.6 |
| 15% | 5/1 | 50 | 24.5 |
| 20% | 4/1 | 49 | 19.1 |
| 25% | 3/1 | - | - |

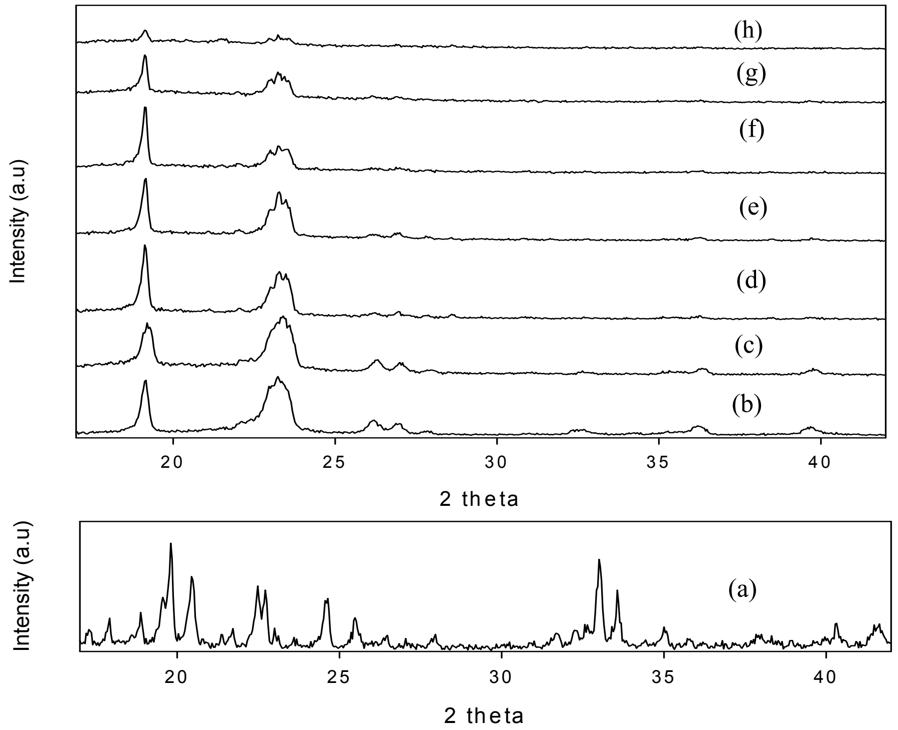

**Figure 3.** XRD patterns of PEO-ENR50 (70/30) with $LiCF_3SO_3$ with different weight ratios (a) Pure salt (b) Pure PEO (c) 0% (d) 5% (e) 10% (f) 15% (g) 20% (h) 25%.

pected to favour ion transport, thus enhancing the electrolyte conductivity [2]. DSC investigation confirmed that PEO crystallinity is reduced with the addition of ENR50 and the salt which has a plasticizing effect on the polymeric chain.

The structure of the electrolyte samples was investigated by XRD analysis. The XRD pattern of the electrolyte samples with various concentrations of $LiCF_3SO_3$, and that for pure PEO and pure $LiCF_3SO_3$ salt are shown in **Figure 3**. The indexing of the two PEO peaks are reported to be (120) at 19.5° and (032) + (112) at 23.5° of the monoclinic system [19]. The characteristic diffraction peaks of crystalline PEO are apparent between $2\theta = 15° – 40°$ [3,20]. The two prominent peaks for PEO at $2\theta$ = 19.2° and 23.2° are present in all patterns, indicating the presence of pure polymer. Nevertheless, the patterns show that the intensities of the prominent peaks decrease and become broader with the increasing wt.% of $LiCF_3SO_3$. The broadening of sharp peaks of PEO could be due to the disruption of the PEO crystalline structure by $LiCF_3SO_3$ and indicates that the complexation has taken place in the amorphous phase [10]. These results confirm both the decrease in degree of crystallinity and the lamellae size of PEO with the presence of plasticizing $LiCF_3SO_3$ [15]. The $LiCF_3SO_3$ peaks are not seen in any of the polymer-salt complexes and this signifies that $LiCF_3SO_3$ solvates very well in PEO-ENR50 matrix, resulting in the absence of pure salt phase in the complexes. The main XRD peaks of PEO are characterized by significant changes in the full width at half maximum (FWHM) with the increasing salt concentration. The peak broadening estimated in terms of FWHM has been used to evaluate the Scherrer length ($l$)

of main PEO peak which was 22.90, 18.20, 18.12, 18.07, 15.84, 12.51 and 8.14 nm for the electrolytes shown in **Figure 3(b)-3(h)**, respectively. The length was automatically calculated using evaluation (EVA) software with the formula ($l$) = [0.9$\lambda$]/[B$\cos\theta_B$] where $\lambda$ is the wavelength of the X-rays used and B is FWHM in radians [21]. The $l$ of main PEO peak was 22.9 nm. This value was decreased to 18.20 nm when PEO was blended with ENR50 and become 8.14 nm at 20 wt.% of LiCF$_3$SO$_3$. The Scherrer length characterizes the crystallite size of PEO and it gives a picture of changes in the PEO crystallinity as a polymer host upon the salt addition. These results suggested that the degree of crystallinity of PEO decreases with the LiCF$_3$SO$_3$ content.

The ionic conductivity measurement was carried out with the aim to observe the effect of LiCF$_3$SO$_3$ addition on the ionic conductivity of the electrolyte. The AC spectra for two of the PEO-ENR50-LiCF$_3$S0$_3$ electrolyte films are shown in **Figure 4** in form of Cole-Cole plot. The high frequency semicircle gives the information about the bulk properties of the electrolyte, such as bulk resistance (R$_b$) and bulk capacitance (C$_b$) which arises from the migration of lithium ions and the dielectric polarization of the electrolyte film, respectively. In the low frequency response region, the appearance of a non vertical spike is attributed to the additional capacitance and resistance, arising from dielectric relaxation and ion trapping in PEO-ENR50-LiCF$_3$SO$_3$ electrolyte [13]. At room temperature, the conductivity of the electrolyte without LiCF$_3$SO$_3$ is 1.5 × $10^{-9}$ Scm$^{-1}$. The ionic conductivity increases rapidly by two orders of magnitude with addition of 5 wt.% of LiCF$_3$SO$_3$ as Li$^+$ charge carriers were added to the system. It was observed that the conductivity increases gradually as the wt.% of LiCF$_3$SO$_3$ increases to 20 wt.% of LiCF$_3$SO$_3$ and began to decrease at 25 wt.% of LiCF3SO$_3$. The maxi

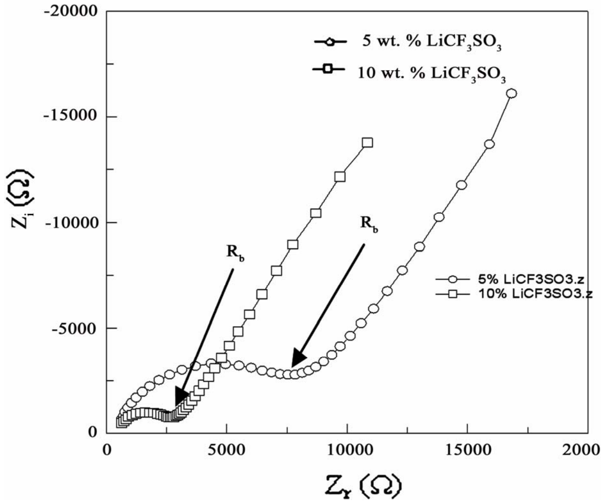

**Figure 4.** Cole-cole plot for two PEO-ENR50 (70/30)-LiCF$_3$SO$_3$ electrolytes.

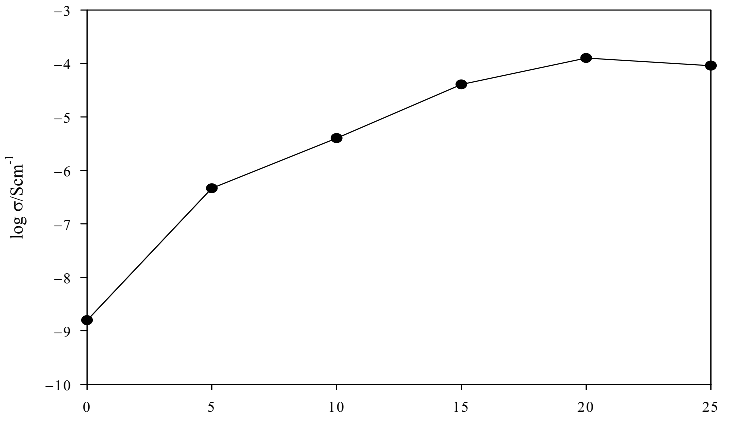

**Figure 5.** Room temperature conductivity of PEO-ENR50 (70/30)-LiCF$_3$SO$_3$ electrolyte a function of LiCF$_3$SO$_3$ concentration.

mum conductivity of 1.4 × 10-4 $Scm^{-1}$ was achieved at 20 wt.% of LiCF3$SO_3$ as presented in **Figure 5**. An additional factor that favoured the salt dissociation was that the salt with a large monovalent anions such as $LiCF_3SO_3$ has a low lattice energy and as a result, it will easily dissolve in polyether [15]. The conductivity is reduced after the maximum value due to an ever-increasing number of transient crosslink in the system, thus reducing the chain mobility. Besides, the formation of immobile aggregated species will contribute to the fall in conductivity.

The conductivity increases with the lithium salt concentration due to the increase in charge carrier density and also due to the plasticizing affects of the $LiCF_3SO_3$ which decreases PEO crystallinity, thus increasing the pathway for the polymer segmental motion [21]. Ramesh *et al.* [14] reported that the highest conductivity achieved for PEO-$LiCF_3SO_3$ electrolyte was 1.1 × $10^{-6}$ $Scm^{-1}$ at room temperature. However, the result is slightly lower than the ionic conductivity obtained from this work. In conclusion, the electrolyte based on PEO blended with modified natural rubber possess higher ionic conductivity than conventional PEO-based electrolytes at ambient temperature [11,12]. This result is due to the molecular structure of ENR50. In term of molecular structure of the polymer, ENR50 has active oxygen in the epoxy group attached to the main chain as shown in **Figure 1**. It is assumed that the ENR50 oxygen atom takes a role similar to the ether group in the PEO polymer structure and provide co-ordination sites for $Li^+$ ion conduction [1,11,12]. Glasse *et al.* [11] reported a gel electrolyte of PEO-ENR-LiTf-EC/PC and found the highest conductivity around $10^{-4}$ $Scm^{-1}$ at the fixed salt concentration. This value was also in the range of the electrolyte with 20 wt.% of $LiCF_3SO_3$. It shows that the conductivity was influenced by the salt concentration. However, the excessive of salt will increase the transient crosslink in the electrolyte, thus reducing its chain mobility. This observation also shows without using the EC/PC, high room temperature conductivity can be achieved for solid electrolyte system by increasing the wt.% of salt. The increase in ionic conductivity with the wt.% of $LiCF_3SO_3$ clearly suggests that the major contribution to the conductivity enhancement is associated with structural modification. This can be observed by the increase in amorphous phase with Li salt content as observed from the DSC and XRD results. According to Chandra & Chandra [20], there is a correlation between Scherrer length and conductivity. As the crystallite size decreases, the ionic conductivity increases. Hence, it can be proven that the conductivity of our electrolyte is greatly influenced by the wt.% of $LiCF_3SO_3$ through a consequential change in the crystallite size of the host matrix.

## 4. CONCLUSIONS

A solid polymeric electrolyte of PEO-ENR50-$LiCF_3SO_3$ has been successfully prepared by solution casting technique. The effect of ENR50 content on the conductivity of the electrolyte was found to increase with the weight percentage of ENR50. The highest room temperature conductivity of 4.2 × $10^{-5}$ $Scm^{-1}$ was achieved at 70-30 composition of PEO-ENR50 host and at 15 wt.% $LiCF_3SO_3$ salt. The effect of the salt content on the thermal property, structure and conductivity of the electrolyte was investigated for the electrolyte with 70-30 composition of PEO-ENR50. The maximum room temperature conductivity was 1.4 × $10^{-4}$ $Scm^{-1}$ corresponding to 20 wt.% of $LiCF_3SO_3$. This result was supported by the lowest relative percentage of crystalline phase and the decrease in crystalline melting temperature of the electrolyte. Also, XRD analysis showed that the semi-crystalline of the electrolyte became more amorphous with the increase in $LiCF_3SO_3$ content.

## 5. ACKNOWLEDGEMENT

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