

Preparation and Characterization of a Solid Polymer Electrolyte PEO-ENR50 (80/20)-LiCF₃SO₃

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ABSTRACT: The preparation and characterization of a polymer electrolyte films containing 80 wt % of poly (ethylene oxide) (PEO) and 20 wt % epoxidized natural rubber (ENR50) complexed with LiCF₃SO₃ has been reported. The ac impedance data showed good conducting properties of the solid polymer electrolyte (SPE) films. The greatest room temperature ionic conductivity of 7.5×10^{-5} S cm⁻¹ was obtained at 25 wt % of LiCF₃SO₃ salt. This result has been supported by differential scanning calorimeter and X-ray diffraction analysis.

Analysis differential scanning calorimetry showed the relative percentage of crystallinity and T_m of PEO decreased with the increasing wt % of LiCF₃SO₃. Analysis with X-ray diffraction suggested that the semicrystalline nature of PEO turned to amorphous due to the presence of LiCF₃SO₃. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 855–859, 2009

Key words: crystallinity; ionic conductivity; PEO/ENR50; solid polymer electrolyte

INTRODUCTION

Solid polymeric electrolyte (SPE)-containing dissolved inorganic salts have received much attention because electrolyte materials are one of the promising candidates for use in solid-state rechargeable lithium batteries and other ionic devices. As such, many polymer electrolyte systems have been developed.^{1–4} SPE possess many advantages over liquid electrolyte in terms of shape, geometry, mechanical strength, and good electrode–electrolyte contact.⁵ Ion-conducting polymer electrolytes were first developed by Fenton et al.⁶ in 1973. They reported that poly (ethylene oxide) (PEO)–salt complexes can exhibit ionic conductivity at room temperature and, since then, there has been substantial research activity towards the development on a various type of SPEs having different combinations of polymer and salts.

PEO (Fig. 1)-based polymer electrolytes have been found to be the best candidates as the electrolyte for lithium polymer batteries in terms of good ionic conductivity, mechanical properties, and electrochemical stability compared with other polyethers, copoly-

mers, or PEO branch.⁷ Furthermore, PEO has a good solubility for many inorganic salts, such as LiClO₄, LiBF₄, and LiCF₃SO₃. However, the disadvantage of this polymer electrolyte is its poor ionic conductivity (10^{-8} to 10^{-7} S cm⁻¹) at ambient operating temperatures.⁸ Conductivity was suggested to result from the hopping of cations between vacant sites inside the PEO helices, paralleling the hopping mechanism of the conventional solid-state ionic conductors.⁹ To enhance the room temperature conductivity of the electrolyte, various modifications have been proposed, such as incorporation of inorganic oxide, ceramic filler, cross linking, blending with different polymers, and plasticizers into conventional electrolyte systems.^{1–8} To improve the ionic conductivity, it is also necessary to preserve the mechanical stability of the electrode–electrolyte interface. Mechanical properties can only be improved by increasing the polymer–solvent ratio, which adversely affects the ionic conductivity of the polymer electrolyte system.

This work proposes PEO complexed with epoxidized natural rubber (ENR50) (Fig. 2) hybrid as a polymer host for polymer electrolyte system to overcome this problem. This is the result of ENR 50, which has distinctive characteristics such as low glass transition temperature (T_g), soft elastomer at room temperature, and good elasticity and adhesion properties.^{1,10,11} However, excessive amounts of ENR50 are sticky and are difficult to peel off from

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Figure 1 Structure of PEO.

the substrate. From our previous work, 20 wt % of ENR50 and 80 wt % of PEO produces a flat, thin, and flexible paper-like film. In the present study, ENR50 complexed with PEO as a polymer host was doped with LiCF_3SO_3 to form solid polymer electrolyte film by use of the solution casting technique.¹² LiCF_3SO_3 was chosen as a doping salt because of its conducting structure (like body center cubic). The anions contribute more to the free volume in the polymer host and will increase the ion mobility.⁵ This polymer electrolyte system displays an interesting enhancement of ionic conductivity and remarkable change in morphology, which reflects a good interaction between lithium salt and polymer host. The electrolyte samples were prepared with different-weight percentages of LiCF_3SO_3 for PEO-ENR50-based polymer electrolyte. Figures 1 and 2 show the structure of PEO and ENR50, respectively.

EXPERIMENTAL

Reagents and electrolyte film preparation

The starting materials are PEO (M_w 6000, Sigma-Aldrich, St. Louis, MO), ENR 50 (Malaysian Rubber Board, Kuala Lumpur, Malaysia), LiCF_3SO_3 (Fluka/Sigma-Aldrich, St. Louis, MO), and tetrahydrofuran (THF; SYSTERM; ChemAR, Kielce, Poland). To prepare the polymer electrolyte film, 80 wt % of PEO (3.2 g) and 20 wt % of ENR50 (1.8 g) (80/20) were dissolved in THF separately and were continuously stirred with a magnetic bar for 24 h. These two solutions were mixed together to obtain a homogenous solution for another 24 h. Various wt % of LiCF_3SO_3 (Fluka, St. Louis, MO) were dissolved separately in THF and mixed together with the mixed solution and stirred efficiently for 12 h to achieve a homogeneous mixture. The solution was cast on a Teflon mould and allowed to evaporate completely at room temperature. Residual solvents were further removed in vacuum oven for 24 h at 60°C. The samples were stored in a desiccator until further use. This procedure will provide mechanically stable, free standing and thickness of flexible films from 190 to 230 μm .

Sample characterizations

The alternate current (ac) impedance measurement was conducted at room temperature using a high-frequency response analyzer (HFRA Solartron 1255, Schlumberger, Paris, France) in the frequency range

of 100 Hz–1 MHz. The electrolyte sample was sandwiched between two stainless-steel, ion blocking electrodes with surface area of 2.011 cm^2 . The bulk resistance (R_b) data were determined from the equivalent circuit analysis by use of frequency response analyzer software. The conductivity values (σ) were calculated from the equation $\sigma = t/(R_b/A)$, where t is the thickness and A is the area of the sample. The ionic conductivity was measured at five different $[\text{O}]/[\text{Li}^+]$ ratios.

Interaction ratio $[\text{O}]/[\text{Li}^+]$ for hybrid polymer can be calculated by using the following formula¹³:

$$[\text{O}]/[\text{Li}^+] = \frac{M_T \times MW_s}{M_s \times \left[\frac{MW_m}{n_m} + \frac{MW_a}{n_a} + \frac{MW_b}{n_b} \right]}$$

where M_T = Total mass (g), MW_s = molecular weight for salt (g mol^{-1}), M_s = mass of salt (g), MW_m = total molecular weight of monomers (g mol^{-1}), MW_a = mass of monomer A (g), MW_b = mass of monomer B (g), n_m = total oxygen atom per repeated unit monomer, n_a = oxygen atom per repeated unit monomer a, and n_b = oxygen atom per repeated unit monomer b.

The thermal measurements were performed by differential scanning calorimetry DSC 8822^e Mettler Toledo model in the temperature range of -60°C to $+150^\circ\text{C}$ at a scanning rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Pure indium and tin were used for temperature and enthalpy calibration of the calorimeter. Approximately 1 to 3 mg of the electrolyte specimens were tested. The X-ray diffraction were carried out at room temperature using Siemens model D5000 (Cu $K\alpha$; $\alpha = 1.5418 \text{ \AA}$) for 2θ values between 15° and 35° to identify the structure of the sample.

RESULTS AND DISCUSSION

The ionic conductivity was measured at five different $[\text{O}]/[\text{Li}^+]$ ratios as shown in Table I, where $[\text{O}]$ is oxygen atoms in both PEO and ENR50. The different value in $[\text{O}]/[\text{Li}^+]$ is because of the difference in the weight percent of the Li salt. The increase in ionic conductivity on departing from the stoichiometric ether oxygen to cation (O/Li) ratio was taken as evidence for this, as the number of vacant sites would increase on increasing the (O/Li) ratio. The ionic conductivity without LiCF_3SO_3 is $2.9 \times 10^{-9} \text{ S cm}^{-1}$, and the value increases to a maximum of $7.5 \times 10^{-5} \text{ S cm}^{-1}$ at 25 wt % of LiCF_3SO_3 salt, as shown

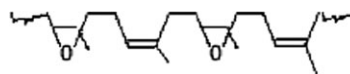


Figure 2 Structure of ENR50.

TABLE I
[O]/[Li⁺] Ratio, Relative Percentage of Crystalline (λ), Melting Temperature (T_m) of PEO-ENR50-LiCF₃SO₃

LiCF ₃ SO ₃ (wt %) to PEO-ENR50 (80/20)	[O]/[Li ⁺]	T_m of PEO (°C)	Relative percentage of crystalline (λ) (%)
Pure PEO	–	68	78.5
Pure ENR	–	–	–
0%	–	65	61.2
5%	17/1	63	48.4
10%	9/1	60	40.5
15%	6/1	57	29.1
20%	4/1	52	24.9
25%	3/1	39	11.9

in Figure 3. It was observed that the conductivity of the electrolyte increases with an increase in LiCF₃SO₃ concentration due to the increasing of the number of conducting species in the electrolyte.¹¹ Cation is transferred to the coordinating sites in the same polymer chain or to the neighboring polymer chain. The segmental motion of the chain promotes the cation transport. The segmental motions are thought to promote ion mobility by making the coordination bonds between cation and polymer.⁹ The optimum value of ionic conductivity shows the maximum and an effective interaction between oxygen atoms and lithium ions in the electrolyte. The interaction was explained by Fourier transform infrared spectroscopy investigated Ramesh et al.¹² and Reddy et al.¹⁴ which shows a coordinate bond that was formed in the complexes between lithium ions and oxygen atoms. The nature of cation (Li⁺) transport similar to that occurs in ionic crystals, where ions jumps into neighboring vacant sites and hence increase the ionic conductivity.¹⁵ This result was

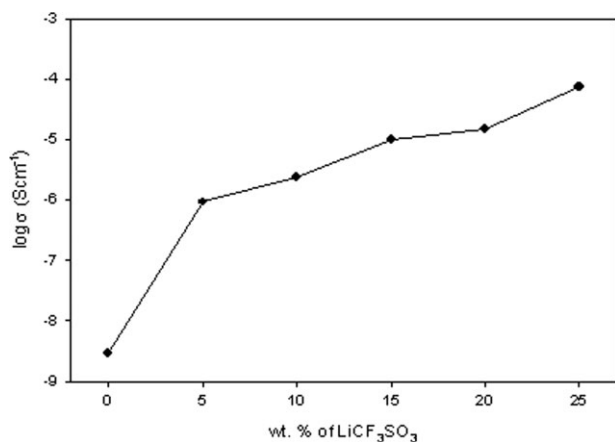


Figure 3 Conductivity as a function of LiCF₃SO₃ concentration of PEO-ENR50-LiCF₃SO₃ electrolytes at room temperature.

slightly greater than that reported in Ramesh et al.¹² obtained from PEO-LiCF₃SO₃ system. This is a result of the presence of ENR50 as a hybrid polymer host for the electrolyte. ENR50 has active oxygen atoms in the epoxy group attached to its main chain. It is assumed that this active oxygen plays a role similar to the ether group in the PEO polymer structure to solvate the Li cation.¹¹ Similar conductivity enhancement has been reported in PEO based polymer electrolyte with inorganic filler.⁵ It shows that without introducing the inorganic filler, the higher ionic conductivity of solid polymer electrolyte can be achieved. As discussed later, the decrease in melting temperature (T_m) and relative percentage of crystalline (λ) of PEO support the conductivity enhancement in the electrolyte system.

Differential scanning calorimetry (DSC) thermographs of PEO, PEO-ENR50, and PEO-ENR50 with various amounts of LiCF₃SO₃ are shown in Figure 4. An endothermic peak was observed at 68°C, which corresponds to the crystalline melting temperature (T_m) of pure PEO. As expected, pure PEO membrane exhibits an endothermic peak at about 64°C because of the well-known crystalline to amorphous transition.⁹ The shift in the melting point can be observed by hybridizing PEO with ENR50 and addition of LiCF₃SO₃ into the electrolyte system. The T_m was reduced from 68°C to 39°C. According to Gray,⁹ above the melting point of pure PEO (65°C), there was an equilibrium between a stoichiometric crystalline phase and a more dilute amorphous phase that was responsible for the ionic conductivity. The curves also indicate a reduction of PEO crystallinity. The relative percentage of crystallinity (λ) of PEO

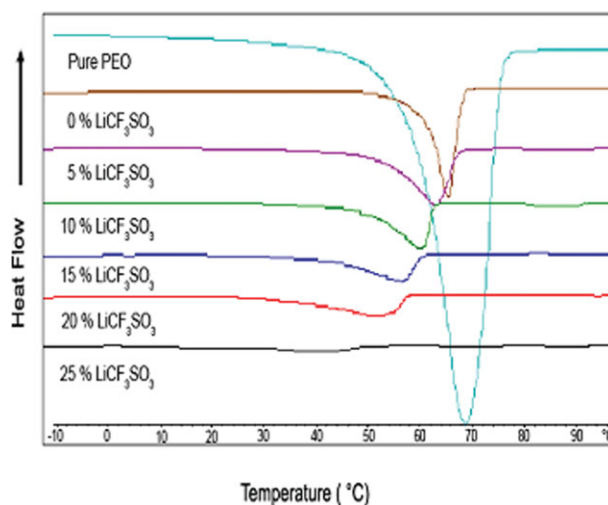


Figure 4 DSC thermographs of the electrolyte with LiCF₃SO₃ of different weight percentage. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

has been calculated by using the equation, $\lambda = (\Delta H_m / \Delta H_m^0) \times 100\%$. Where, ΔH_m is heat of melting given by experimental data, while ΔH_m^0 is heat of melting taken from 100% crystalline PEO reference (213.7 J g^{-1}).¹⁶ The calculated relative percentage of crystallinity (λ) and crystalline melting temperature of PEO are summarized in Table I. Gray⁹ found pure PEO with linear polymer chain and regularity of the $-(\text{CH}_2-\text{CH}_2\text{O})-$ unit allows a high degree of crystallinity around the range of 75–85%. From the experimental data, the relative percentage of crystallinity is still around range, which is 78.5%. Crystallinity decreases with LiCF_3SO_3 content which results in the enhancement of segmental motion and flexibility of PEO host polymer.¹⁷ The observation of reduction of T_m and λ could be attributed to the fact that LiCF_3SO_3 have a permanent dipole moment. Consequently, because of this dipole moment, the former ions interact much more strongly with the polymer chains, thus decreasing its T_m and λ .¹⁸ The complexity of LiCF_3SO_3 anions contributes more to the free volume of the materials. It also suggests that interactions between the polymer host backbone and the lithium salt have affected the dynamic main chain of the polymer electrolyte.² DSC investigations confirmed the reduction of PEO crystallinity with addition of ENR50 and LiCF_3SO_3 and it is supported by the reduced intensities of PEO crystalline peak from X-ray diffraction (XRD) analysis results.

A structural study of solid polymer electrolyte was investigated by XRD. XRD analysis was performed to determine the degree of crystallinity and to observe the glassy nature of the PEO polymer electrolyte. Figure 5 shows the XRD patterns of pure LiCF_3SO_3 , pure PEO, and the electrolyte samples with 0, 5, 10, 15, 20, and 25 wt % of LiCF_3SO_3 . The two prominent peaks of PEO (at $2\theta = 19.2^\circ$ and 23.2°) are present in all the patterns, indicating the presence of pure polymer in all. Some minor peaks of PEO also can be observed at 2θ 15.1° , 26.3° , 26.9° , and 29.5° . LiCF_3SO_3 peaks are seen in none of the polymer-salt complexes, which signifies that the LiCF_3SO_3 solvates very well in PEO-ENR50 matrix. The intensity of the PEO peaks decreases at high salt concentrations. The results show both the decrease in degree of crystallinity and the lamellae size of PEO in the presence of Li salt.⁵ The diffraction peaks of the pure salt are absent in the polymer-salt complexes indicating the absence of pure salt phase in these complexes. For 25 wt % of LiCF_3SO_3 , the intensity of the crystalline peak decreases significantly. This behavior suggests that the semicrystalline structure of PEO change to an amorphous state by the addition of LiCF_3SO_3 .¹⁹ Notice that the PEO crystallinity is not completely reduced by LiCF_3SO_3 , as the diffraction characteristic of crystalline PEO is still

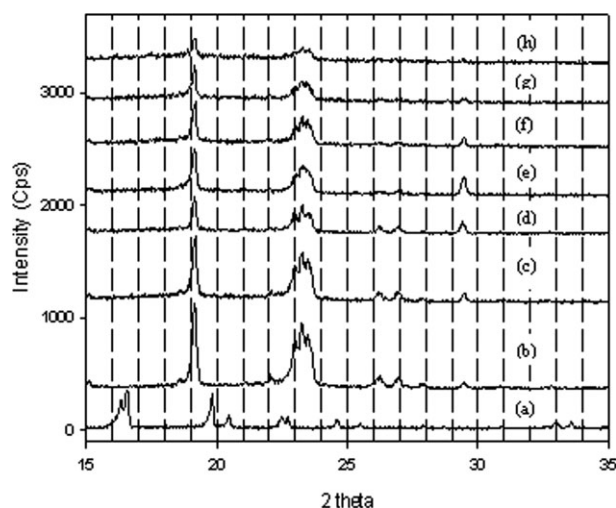


Figure 5 XRD patterns of the electrolyte with different weight percentage of LiCF_3SO_3 . (a) Pure LiCF_3SO_3 , (b) Pure PEO, (c) 0%, (d) 5%, (e) 10%, (f) 15%, (g) 20%, and (h) 25%.

observable as shown in Figure 5(h). The main XRD peaks of PEO are characterized by significant changes in the full width at half maximum (FWHM) with increasing salt concentration. The peak broadening estimated in terms of FWHM has been used to evaluate Scherrer length (l) of main PEO peak where the l was 22.9, 19.6, 21.7, 19.8, 18.9, 16.9, and 9.6 nm for the electrolytes shown in Figure 5(b–h), respectively. It gives a picture of changes in the crystallite size of PEO as polymer host on salt addition with smallest value of 9.6 nm. It is found that the degree of crystallinity decreases as the addition of LiCF_3SO_3 increases. The results suggest that the degree of crystallinity of PEO decreases with the presence of LiCF_3SO_3 with the lowest intensity at 25 wt % of LiCF_3SO_3 .

CONCLUSIONS

A SPE of PEO-ENR50- LiCF_3SO_3 system was prepared by the solution casting technique. The effect of LiCF_3SO_3 salt concentration on ionic conductivity, thermal property, and structure has been investigated. The polymer electrolyte containing 25 wt % of LiCF_3SO_3 produces a free-standing film with optimum conductivity at $7.5 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. DSC analysis showed that the T_m and λ of PEO matrix in PEO-ENR50- LiCF_3SO_3 films decreases with the LiCF_3SO_3 content. XRD analysis suggested that LiCF_3SO_3 has a strong effect on the crystallization of the PEO matrix. In addition of LiCF_3SO_3 into the matrix polymer, the semicrystalline state of the PEO changed to amorphous state with the lowest intensity at 25 wt % of LiCF_3SO_3 . The decrease in PEO matrix crystallinity is an advantageous way in

improving the ionic conductivity of PEO-ENR50-LiCF₃SO₃ system.

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