

CHARACTERIZATION OF PLASTICISED AND NON PLASTICISED EPOXIDISED NATURAL RUBBER BASED POLYMER ELECTROLYTE SYSTEMS

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ABSTRACT

Lithium polymer electrolyte film consists of epoxidized natural rubber (ENR50) and lithium imide, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ salt was prepared by solvent casting technique. Lithium imide was employed for interaction with ether oxygen of epoxidized rubber to improve ionic conductivity value at ambient temperature. The electrolyte compositions consist of various salt concentrations express in molar ratios calculated based on oxygen to lithium denoted as O/Li; ~ 64:1, 23:1, 13:1, 9:1 and 3:1 respectively were studied. Polymer electrolytes made from ENR rubber formed free-standing films with thickness range 100-200 μm were obtained. Plasticizer-added sample containing salt has shown optimal ionic conductivity $10^{-3} \text{ S cm}^{-1}$ with compositional molar ratio O/Li~ 9:1 at room temperature. The trend of thermal behavior indicates that single transition glass temperature (T_g) for all systems. T_g values has increased for ENR50- $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ system whereas addition of EC/PC has reduced their values dramatically.

INTRODUCTION

Researchers in the field of solid-state science have devoted their effort to seek appropriate polymer electrolyte for their applications in electrochemical devices particularly in lithium-ion polymer battery. There will be criteria need to be filled by polymer electrolytes in order to fulfil specific performance requirements. These include high ionic conductivity, thermal, chemically and electrochemically stable. The right combination of components and compatible each other will contribute to the successful formation of polymer electrolyte system. The most preferred polymer host to solvate lithium ion is highly amorphous polymer containing co-ordinating site with much lower tendency to crystallisation as well as low glass transition temperature[1]. The development of polymer gel electrolytes has rapidly progressed using thermoplastic polymer hosts for practical application usage [2]. The conductivity of the polymer gel electrolytes is comparable to that of conventional liquid electrolyte being used in secondary batteries [3]. In parallel to the above described approach this paper will discuss a novel modified natural rubber polymer electrolyte as an alternative to conventional poly(ethylene oxide) to act as polymer host for lithium ion conducting polymer electrolyte. Modified natural rubber has desirable properties suitable for making polymer electrolytes. These include low glass transition temperature, soft-elastomer characteristic at room temperature and good adhesion properties to solid substrates. Rubbery films can result in flat, thin, flexible and leakage-free, which

provide suitable support structure for electrolyte active species to couple with electrodes for lithium-ion batteries. It also gives excellent contact between the electrolytic layer and electrode. Polymer electrolyte is critically dependent on this junction [4]. This paper reports the investigation of non plasticized and plasticized ENR based solvent cast polymer electrolyte films and its effect on ionic conductivities and thermal properties.

EXPERIMENTAL DETAILS

Epoxidized natural rubber (M_w 250,000) was supplied by Lembaga Getah Malaysia under abbreviated name ENR-50. Prior to experimental requirement the ENR rubber was masticated into two-roll mill with seven passes. Lithium imide, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (Aldrich product, purity 99.8%) was used as received without further purification. Ethylene carbonate, EC (Aldrich product with purity, 99.8%) and propylene carbonate, PC (Aldrich product with purity, 99.8%) were used as received

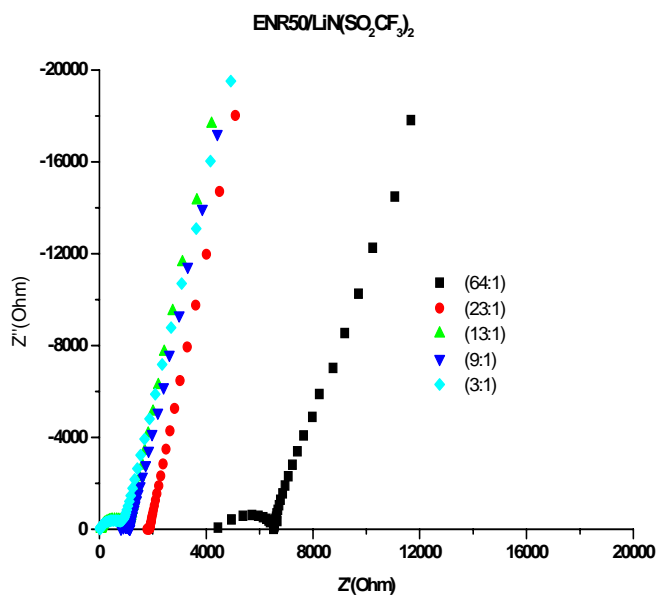
Preparation of polymer electrolytes

The masticated ENR rubber was cut into grain size and dissolved into tetrahydrofuran with efficient magnetic stirring. The viscous solution of ENR rubber was formed after 24 h continuous stirring. Then lithium triflate salt was added into the solution. The solution of the ENR rubber mixed with was cast into Teflon mould and left for evaporation process. Rubbery polymer electrolyte film of ENR rubber was obtained after the THF solvent evaporated off. The final films were further dried under vacuum oven for 48 h to remove residual solvent. Then, the films were kept in desiccator until further use for characterisation. In the case of plasticised polymer electrolytes were obtained by dissolving the appropriate amount of polymers, lithium salt and plasticiser in tetrahydrofuran (J.T Baker, no further purification). Similar procedure was applied for casting process to obtain the films.

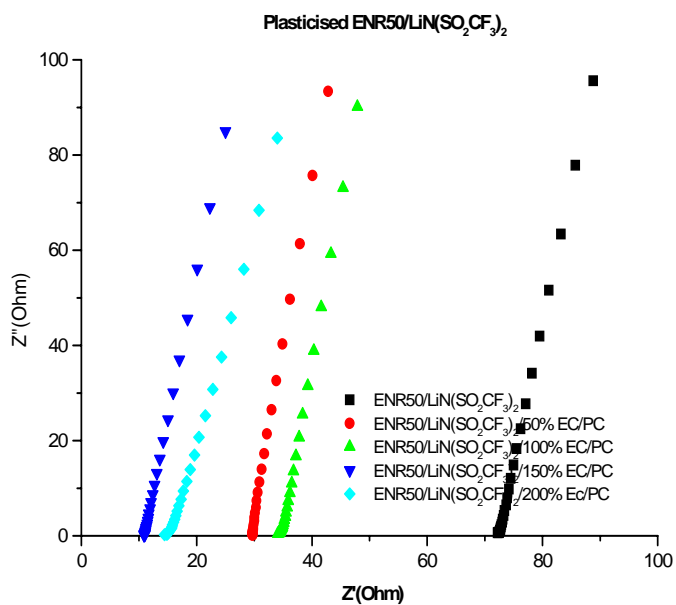
Ionic conductivity measurements at room temperature were conducted using a Solartron 1255 impedance analyser coupled to a computer installed with Z-plot software for data handling in the test frequency range of 0.1 Hz to 75 kHz. For room- temperature conductivity measurements the thickness of the sample was measured with a micrometer screw gauge. ENR film test samples were mounted between two disc-shaped stainless steel electrodes in a Teflon test cell which was self-constructed in the laboratory.

Thermal data were obtained from differential scanning calorimetry (DSC) recorded in a Mettler TA4000 instrument, which was run under liquid nitrogen atmosphere. ENR film samples were loaded in aluminium pan and sealed. They were placed in a module compartment, which was set to heating and cooling in temperature range of -100 to 250°C at scan rate of $10^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION



(a)



(b)

Figure 1: (a) Impedance plots of non plasticized and (b) plasticized of ENR50/LiN(SO₂CF₃)₂ samples at frequency range 0.1 Hz to 75 kHz

The masticated ENR-50 rubber, lithium imide and EC/PC were mixed in tetrahydrofuran solvent and produced faint yellowish viscous solutions upon stirring after 24h. Translucent and robust polymer electrolyte films were obtained from the solution after casting process in the glass mould. Elsewhere reported that some research workers used ultraviolet radiation polymerisation and thermal polymerisation techniques [5] to produce solid polymer electrolytes with lithium ion-conducting behaviour. The approach for this work using simple solvent casting method was conducted throughout the experiments for ENR electrolytes. The findings show similar ion-conductive properties compared with the above said techniques. The typical impedance plots of the polymer electrolyte systems studied at room temperature are illustrated in figure 1. The frequency response from ENR $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ samples in the blocking electrodes has produced the arc at the high frequency region, which represents the bulk electrolyte impedance. It follows up with a slanting line slightly away from the origin indicates that diffusion impedance at the electrode/electrolyte interface occurred at low frequency. The bulk resistance, R_b obtained from the intercept on the real axis. The area (A) and known thickness l of the electrolyte film give the estimated ionic conductivities of the electrolyte systems. The ionic conductivity of the ENR based electrolyte system is calculated using equation below;

$$\sigma = l/AR, \quad (1)$$

The results of the ionic conductivities of polymer electrolytes produced ENR systems were summarised in Table 1 and 2. It shows the variation of ionic conductivity values for different ENR50/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ complexes expressed in the mole ratio EO:Li at room temperature. Ionic conductivity $4.6 \times 10^{-5} \text{ S cm}^{-1}$ was obtained for ENR50/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ system with salt concentration relative to ENR polymer (EO:Li=9:1). The series of EC/PC plasticizer-added ENR50 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ systems with salt concentration ratio EO:Li (9:1) show much higher conductivity than non plasticized one. The highest conductivity value $2.6 \times 10^{-3} \text{ S cm}^{-1}$ was obtained for EC/PC (150 weight percent) added into the ENR/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ system. This result is in agreement with the work reported by K.M. Abraham et al [6]. It suggests that ionic conduction mostly occur in the plasticized polymer electrolyte system. This data generate information on the mass transport of solvated molecules via segmental dynamics in the network ENR50 polymer electrolyte phases. This has been shown in figure 2 and 3 the shift of the impedance spectra toward a low resistance intercept. The ionic conductivity values $10^{-4} - 10^{-3} \text{ S cm}^{-1}$ were obtained for the EC/PC electrolyte added sample whereas non- plasticized one at 10^{-7} to $10^{-5} \text{ S cm}^{-1}$ at room temperature. The rationale of using epoxidized natural rubber, which contains polar epoxy group in the polymer chain acts as coordinating site for Li ion. It can be suggested that the ionic conductivity is assumed to occur by Lewis acid-base interaction between the Li^+ ions and the oxygen atoms in the epoxy bond situated at ENR polymer chain.

The cation is significant species, which play a key role for the battery function since it is responsible for the exchange of the electric charge between the electrodes. The behaviour of this ion moves through the electrolyte will be a decisive factor for the

efficiency and practicality of the entire system. In ENR polymer electrolyte material, lithium ion in principal has possibilities to coordinate with anion, the plasticiser or the polymer chain. As a result of the interaction an effect of electrolyte local structures and change in film morphology occurs. In this work lithium imide salt is chosen for ENR to avoid ion-ion and ion-cluster as being pointed above because the $\text{LiN}(\text{SO}_2\text{CF}_3)$ has the lowest association tendency among lithium salts[7]. In the present case the small and light Li ion would be expected to move rapidly in the ENR polymer than considerably heavier larger $\text{N}(\text{SO}_2\text{CF}_3)$ anion, provided there is no strong interaction between the species as being mention earlier. It also relates to cation mobility within amorphous polymer chain promoted by its segmental motion couple with plasticiser, which create an increase in the free volume of the system.

Table 1: T_g and conductivity data of ENR50/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ systems

Sample	ENR50/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$		
	Conductivity (S cm^{-1})	EO/ Li^+	T_g (° C)
43E50 001S 1	5.6×10^{-7}	64:1	- 28.17
43E50 002S1	2.2×10^{-5}	23:1	- 22.58
43E50 003S1	2.3×10^{-5}	13:1	- 21.09
43E50 004S1	4.6×10^{-5}	9:1	-17.66
43E50 005S1	3.8×10^{-5}	3:1	-20.58

Table 2: T_g and conductivity data of various plasticised ENR50/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ systems

Sample	ENR50/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$			T_g (° C)
	Conductivity (S cm^{-1})	EO/Li	EC+PC (wt. %)	
43E50 001S2	5.8×10^{-4}	9:1	50	-34.02
43E50 002S2	8.4×10^{-4}	9:1	100	- 40.61
43E50 003S2	2.6×10^{-3}	9:1	150	- 44.41
43E50 004S2	1.1×10^{-3}	9:1	200	- 46.81
43E50 005S2	4.6×10^{-5}	9:1	-	- 17.66

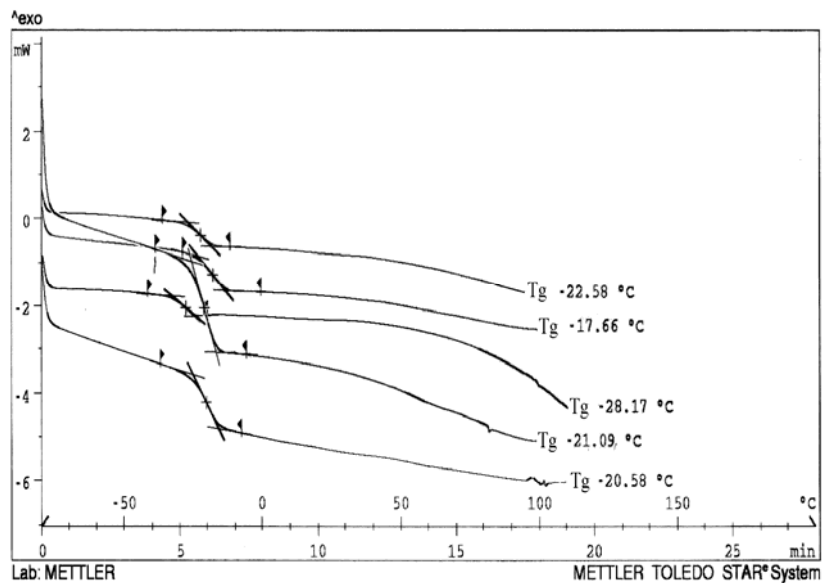


Figure 2: DSC traces of non-plasticised ENR50 /LiN(CF₃SO₂)₂ system

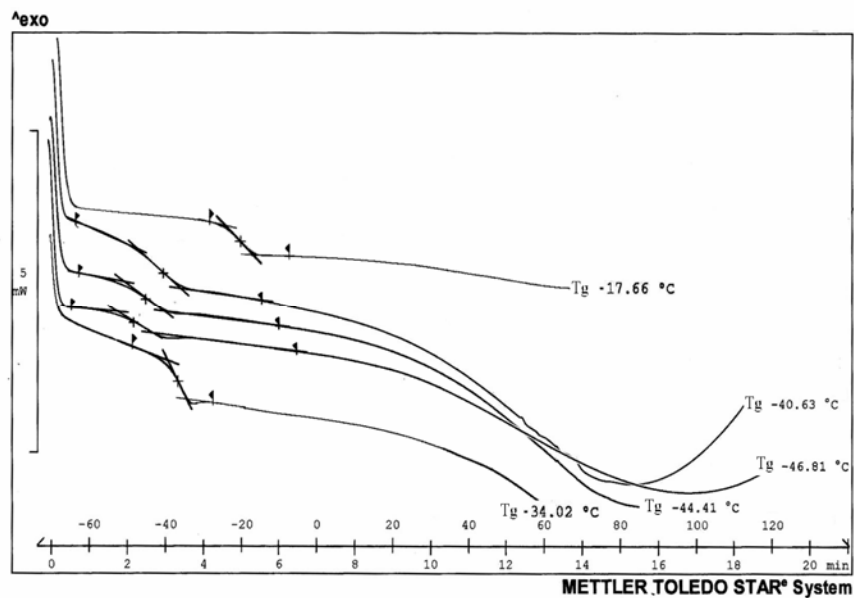


Figure 3: DSC traces of ENR50 /LiN(CF₃SO₂)₂/EC/PC system

The presence of high amount lithium imide salt at the EO:Li ratio (3:1) into the system contributes to increasing the T_g of the polymer host to a higher temperature. For control sample the T_g of ENR-50 rubber – 24°C . Figure 2 and 3 show thermal data using DSC method for the ENR50/LiN(CF₃SO₂)₂ polymer electrolyte systems. The addition of LiN(SO₂CF₃)₂ salt displayed a single glass transition temperature and increasing the values between -17.66 and -22.58°C . However T_g at -28.17°C also appear from the DSC data, which is lower than control sample. In contrast to this incorporating of EC/PC into ENR system has reduced the glass transition temperature in the range values -34.02 to 46.81°C .

The optimal amount of LiN(CF₃SO₂)₂ salt was found to be moderate concentration for the ENR50/LiN(CF₃SO₂)₂ series experiment as being shown in Figure 4. It was observed the increase of ionic conductivity of the ENR50 electrolytes with increasing lithium salt concentrations and appreciable increase of the T_g values. In the series of EC/PC plasticisers-added ENR50/LiN(CF₃SO₂)₂ compositions with constant salt concentration ratio EO:Li (9:1) show much higher conductivity than non plasticised one. Figure 5 illustrates the relationship of glass transition temperature with ionic conductivity of plasticised and non plasticised ENR50 polymer electrolyte system.

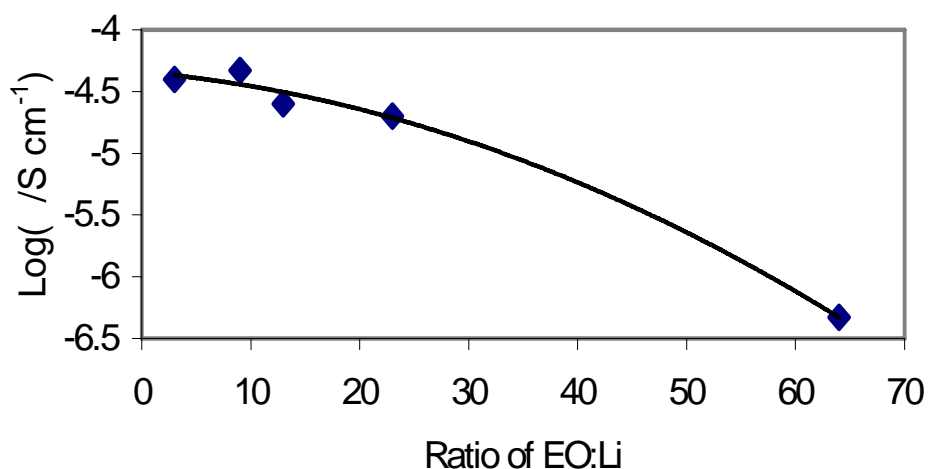


Figure 4: Ionic conductivity versus ratio of EO: Li for ENR50 /LiN(CF₃SO₂)₂

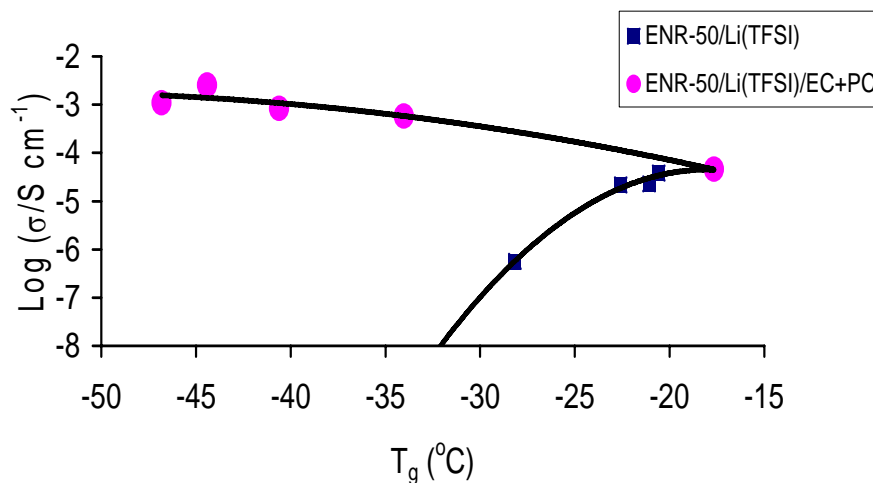


Figure 5: Ionic conductivity against T_g 's for non plasticised and plasticised ENR50 /LiN(CF₃SO₂)₂ system

Results indicate that plasticising salt has an effect on the conduction process of the non plasticised samples and further improved by incorporation of plasticiser to higher conductivity values. The plasticising lithium imide salt, LiN(SO₂CF₃)₂ has an effect to the local ENR50 rubber chain reorganisation, which is amorphous by its own nature. Plasticiser-added ENR polymer electrolytes can thus offer an interesting option compared to other several reported electrolyte systems [8,9,10] for room temperature in rechargeable lithium-ion polymer batteries

CONCLUSIONS

Ionic conductivities and thermal properties of plasticised and non plasticised ENR50/LiN(CF₃SO₂)₂ systems in correlation with the polymer-salt mixtures were investigated. The ionic conductivity attained is lower for non plasticised ENR50/LiN(CF₃SO₂)₂ systems compared to plasticised ENR50/LiN(CF₃SO₂)₂ polymer electrolytes. The highest ionic conductivity $2.6 \times 10^{-3} \text{ S cm}^{-1}$ was obtained for plasticised ENR50/LiN(CF₃SO₂)₂ polymer electrolytes at room temperature. Thermal behaviour by the phase transition showed a reduction of glass transition temperature for plasticised ENR50/LiN(CF₃SO₂)₂ polymer electrolytes but higher T_g values at elevated lithium salt concentration for non plasticised ENR electrolyte systems

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