

Polymer electrolytes based on modified natural rubber for use in rechargeable lithium batteries

Razali Idris, M.D. Glasse, R.J. Latham*, R.G. Linford, W.S. Schlindwein

Solid State Research Centre, Faculty of Applied Sciences, De Montfort University, The Gateway, Leicester, LE1 9BH, UK

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Abstract

Modified natural rubber (NR) polymer hosts having low transition glass temperatures have been investigated. Three types of modified NR, namely 25% epoxidised NR (ENR-25), 50% ENR (ENR-50) and polymethyl methacrylate grafted NR (MG-49) were employed. Results are reported for ionic conductivity and thermal properties for both unplasticised and plasticised polymer electrolyte systems. The samples were in the form of free standing films with the thickness 0.2–0.5 mm and mixtures of ethylene carbonate (EC) and propylene carbonate (PC) were used as plasticisers. Unplasticised modified NR based systems exhibit ionic conductivities in 10^{-6} – 10^{-5} S cm⁻¹ range at ambient temperatures. Incorporating 50–100% of EC/PC by weight to the systems yielded mechanically stable films and ionic conductivities in 10^{-4} – 10^{-3} S cm⁻¹ range at ambient temperature. The thermal event of the systems has displayed an increasing trend of transition glass temperature at elevated salt concentration whereas incorporation of EC and PC into the systems leads to marked reduction in their T_g values. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidised natural rubber; Plasticiser; Poly(methyl methacrylate)-grafted natural rubber; Polymer electrolytes

1. Introduction

Polymers are used widely for automotive components, electronic kits, toy products, building panels, etc. In addition to this growing list is the utilisation of polymeric materials as a solid medium to replace the liquid counterpart as the component of electrochemical devices such as displays, sensors, electrochromic windows, supercapacitors and rechargeable batteries. In particular there has been interest regarding the use of polymeric materials for polymer gel electrolyte systems in solid polymer batteries [1–3]. These systems have shown improved ionic conductivities over previous conventional solid polymer electrolyte systems [4,5]. In order to enhance room temperature conductivity, various types of gel polymer electrolytes have been developed and a variety of polymer hosts have been proposed as matrices for plasticised or gel polymer electrolyte systems.

These polymer hosts can be classified into a few main groups. The first group consists of thermoplastic polymer hosts such as polyacrylonitrile (PAN) [6–8], poly(ethylene oxide) (PEO) [9], poly(methyl methacrylate) (PMMA) [10,11], poly(vinylchloride) (PVC) [12], polyurethane

(PU) [13] and polyvinylidene fluoride (PVDF) [14,15]. The second group includes network polymer hosts prepared by crosslinking reactions of acrylate or methacrylate monomers having low molecular weight [16]. The third group consists of mixtures of the polymer hosts mentioned above [17] and the fourth group comprises synthetic elastomeric host matrices of poly(acrylonitrile-cobutadiene) (NBR)/poly(styrene-co-butadiene) (SBR) rubbers [18]. The main drawback of these systems is their poor mechanical properties at low polymer concentrations, i.e. in the ‘gel’ state. Mechanical properties can be improved only by increasing the polymer–solvent ratio, which adversely affects the conductivity. This paper presents the initial findings of modified natural rubber (NR) elastomers as matrices for ionic conductors for potential use in lithium batteries.

Diversification of the traditional uses of NR can be achieved by changing the properties of the base polymer through chemical modification. There appears to be no data in the literature for the use of polar modified NR based polymer electrolytes in lithium battery applications. To date the material has not been explored as a potential candidate for polymer electrolytes in electrochemical device applications. Modified NR has desirable properties making it suitable for use in polymer electrolytes. These include low glass transition temperature, T_g , soft elastomer characteristics at room temperature and good elasticity. Suitable

* Corresponding author.

elasticity can result in flat, thin and flexible paper-like batteries. It also gives excellent contact between an electrolytic layer and an electrode in batteries. In other words, if an elastomer can act a polymeric 'solvent', a higher conductivity is expected in elastomeric matrices compared with glassy or crystalline states of polymers. Two suitably modified NRs have been considered in this study. They are PMMA grafted NR (Heveplus MG-49) and epoxidised NR (ENR). This study reports the results of ionic conductivity and thermal analysis measurements performed on the non-plasticised and plasticised modified NR based polymer electrolyte systems.

2. Experimental

2.1. Sample preparation

2.1.1. MG-49 based polymer electrolyte system

All polymer electrolyte samples were prepared by a solvent casting method. The procedures involved the following steps. The first step was casting of MG-49 latex supplied by Green HPSP Co., Malaysia to obtain a dry rubber film. Then the MG dried rubber film was sliced into grain size. About 4 wt.% MG-49 polymer solution was prepared by dissolving it in 25 cm³ stoppered flask, containing toluene with efficient magnetic stirring. It was left overnight with continuous stirring until there was complete dissolution of polymer into clear viscous solution. A lithium trifluoromethanesulfonate (LiCF₃SO₃) salt solution of tetrahydrofuran (THF) was prepared separately. Then, these two solutions were mixed together to obtain a homogenous solution. The solutions were cast onto glass ring mould with Teflon substrate underneath and the solvent was allowed to evaporate in a fume cupboard at room temperature. A free standing film was obtained when the solvent had evaporated off. Residual solvent was further removed in a vacuum oven for 48 h at 50°C. The samples were stored in a desiccator until further use.

2.1.2. ENR based polymer electrolyte system

The masticated ENR supplied by the Tun Abdul Razak Rubber Research Centre, London was used as polymer host for this system. The ENR rubber was received as masticated sheet after it was passed into the two-roll mill machine about six times. The supplier carried out the mastication process. The masticated ENR was cut into grain size and dissolved into THF with efficient magnetic stirring. A viscous solution of ENR rubber was formed after it was left overnight with continuous stirring. Then, lithium salt was added to the solution. The THF solution of ENR rubber mixed with lithium salt was cast into glass ring mould on a Teflon substrate. A similar procedure was repeated for the plasticised system. A free-standing 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 a desiccator until further use.

2.2. Conductivity measurements

Disk-shaped film samples were sandwiched between two stainless steel blocking electrodes and mounted in the test cell. The samples between the electrodes in the cell were pressed at constant pressure to maintain good interfacial contact. A Solartron 1250 frequency response analyser and 1286 electrochemical interface were used to measure the impedance of electrolyte films over the frequency range from 0.1 Hz to 65 kHz. The ionic conductivity was calculated from the bulk electrolyte resistance value (R_b).

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) (Perkin–Elmer DSC-4) was employed for thermal characterisation of the polymer gel electrolyte systems over temperature of –80 to +30°C range in a nitrogen atmosphere. Samples were rapidly cooled to –80 and heated to 30°C at a scan rate 10°C min⁻¹. This allows observation of any salt precipitation phenomena and determination of transition glass temperature.

3. Results and discussion

Polymer gel films have been produced from three types of modified NR by casting from solvent-based viscous solutions. They are namely masticated 25% ENR (ENR-25), masticated 50% ENR (ENR-50) and 49% methyl methacrylate grafted NR (MG-49). Tables 1–6 summarise results for different compositions for both plasticised and non-plasticised films.

Lithium salt contents in ENR-25 and ENR-50 based electrolyte systems are expressed in terms of O/Li ratio. On the other hand for MG-49 based electrolyte systems, the contents of lithium are based on weight percent.

3.1. Ionic conductivity

3.1.1. Unplasticised modified natural rubber based electrolyte systems

The variation of the ionic conductivity, σ , of the modified NR based gels is shown in Fig. 1. It indicates that at a fixed polymer concentration the conductivity of the gel increases as the salt concentration is increased.

Ionic conductivities in 10⁻⁶–10⁻⁴ S cm⁻¹ range are possible. The ionic conductivity is 6.2 × 10⁻⁵ S cm⁻¹ at room temperature when the salt content is 20 wt.% and is 1.8 × 10⁻⁴ S cm⁻¹ at 60 wt.% salt content. It was observed that further increase in salt concentration results in an abrupt increase in conductivity values. The reason for the particular conductivity behaviour of highly concentrated

Table 1
Properties of ENR-25 systems with salts

Sample	Composition		Electrical properties	Thermal behaviour
	ENR-25/LiCF ₃ SO ₃ (w/w)	O/Li	Conductivity (S cm ⁻¹)	T _g (°C)
ENR-25/S1s	100/2	27	6.9 × 10 ⁻⁶	-27
ENR-25/S2s	100/5	11	1.6 × 10 ⁻⁵	-40
ENR-25/S3s	100/10	5	1.8 × 10 ⁻⁵	-32
ENR-25/S4s	100/15	4	1.4 × 10 ⁻⁵	-30
ENR-25/S5s	100/20	3	6.2 × 10 ⁻⁵	-37
ENR-25/S6s	100/60	1	1.8 × 10 ⁻⁴	-25
ENR-25/C	100/0		2.1 × 10 ⁻⁷	-41

Table 2
Properties of ENR-25 systems with plasticisers

Sample	Composition		Electrical properties	Thermal behaviour
	ENR-25/LiCF ₃ SO ₃ /EC + PC	O/Li	Conductivity (S cm ⁻¹)	T _g (°C)
ENR-25/1p	100/5/25	8/1	3.7 × 10 ⁻⁵	-41
ENR-25/2p	100/5/50	10/1	5.1 × 10 ⁻⁵	-42
ENR25/3p	100/5/100	13/1	1.8 × 10 ⁻⁴	-42
ENR-25/4p	100/5/200	20/1	2.9 × 10 ⁻⁴	-43
ENR-25/5c	100/5	11/1	1.6 × 10 ⁻⁵	-40

(ENR-25)-LiCF₃SO₃ electrolytes is not fully understood at this present time. The (ENR-25)-LiCF₃SO₃ system containing 20 wt.% of salt corresponds to a mole ratio O/Li ~ 5/1. Among the three types of modified NR, ENR-25 shows the highest conductivity at room temperature. Overall the conductivities of doped modified NR based electrolytes have

shown higher conductivity than conventional polyethylene oxide (PEO) based electrolyte at ambient temperature. In terms of the polymer molecular structure, ENR-25 and ENR-50 have an active oxygen in the epoxy group attached to their main chain. It is assumed that the ENR oxygen atom takes a role similar to the ether group in the PEO polymer

Table 3
Properties of ENR-50 systems with salts

Sample	Composition		Electrical properties	Thermal behaviour
	ENR-50/LiCF ₃ SO ₃	O/Li	Conductivity (S cm ⁻¹)	T _g (°C)
ENR-50/1	100/2	26/1	5.0 × 10 ⁻⁶	-22
ENR-50/2	100/5	10/1	2.0 × 10 ⁻⁵	-22
ENR-50/3	100/10	5/1	1.6 × 10 ⁻⁵	-17
ENR-50/4	100/15	3/1	1.9 × 10 ⁻⁵	-17
ENR-50/5	100/20	3/1	2.3 × 10 ⁻⁵	-13
ENR-50/6	100/60	1/1	1.0 × 10 ⁻⁴	-19
ENR-50/C	100/0		3.1 × 10 ⁻⁶	-21

Table 4
Properties of ENR-50 systems with plasticisers

Sample	Composition		Electrical properties	Thermal behaviour
	ENR-50/LiCF ₃ SO ₃ /EC + PC	O/Li	Conductivity (S cm ⁻¹)	T _g (°C)
ENR-50/1p	100/5/25	11/1	3.3 × 10 ⁻⁵	-37
ENR-50/2p	100/5/50	14/1	3.5 × 10 ⁻⁵	-37
ENR-50/3p	100/5/100	18/1	4.0 × 10 ⁻⁵	-31
ENR-50/4p	100/5/200	27/1	1.3 × 10 ⁻⁴	-35
ENR-50/5c	100/5/0	20/1	2.0 × 10 ⁻⁵	-21

Table 5
Properties of MG-49 systems with salts

Sample	Composition	Electrical properties	Thermal behaviour
	MG-49/LiCF ₃ SO ₃ (w/w)	Conductivity (S cm ⁻¹)	T _g (°C)
MG-49/S1	100/2	4.0 × 10 ⁻⁶	-62
MG-49/S2	100/5	4.1 × 10 ⁻⁶	-67
MG-49/S3	100/10	5.9 × 10 ⁻⁶	-62
MG-49/S4	100/15	6.1 × 10 ⁻⁶	-63
MG-49/S5	100/20	3.7 × 10 ⁻⁵	-59
MG-49/S6	100/60	2.5 × 10 ⁻⁵	-63
MG-49/C	100/0	2.8 × 10 ⁻⁶	-61

Table 6
Properties of MG-49 systems with plasticisers^a

Sample	Composition	Electrical properties	Thermal behaviour
	MG-49/SALT/EC + PC	Conductivity (S cm ⁻¹)	T _g (°C)
MG-49/P1	100/5/25	6.0 × 10 ⁻⁵	-
MG-49/P2	100/5/50	1.8 × 10 ⁻⁴	-68
MG-49/P3	100/5/100	3.2 × 10 ⁻⁴	-
MG-49/P4	100/5/200	4.3 × 10 ⁻⁴	-
MG-49/5c	100/5	4.1 × 10 ⁻⁶	-61

^a MG-49/P1, MG-49/P3 and MG-49/P4-DSC traces exhibit peculiarities; absence of noticeable phase-transitions.

structure and that Li cation solvation in ENR occurs due to the formation of coordination bond with the oxygen of the polar epoxy group ENR.

However, in the case of MG-49 rubber, there is a carbonyl group grafted in the main chain of NR to interact with the Li cation to form a complex. The formation of the complex and the ionic conduction mechanism in these systems is not clearly understood at this stage. The impedance plots exhibited by these gels are shown in Fig. 2.

3.1.2. Plasticised modified natural rubber systems

The masticated rubbers and the other electrolyte components, namely the lithium salt solution in the mixtures of ethylene carbonate (EC) and propylene carbonate (PC), mixed very well in the THF solvent overnight and formed

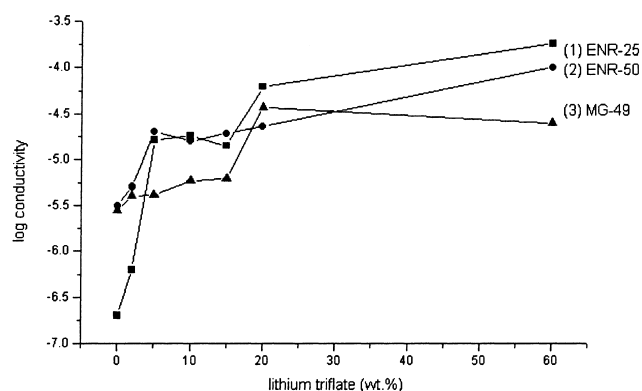


Fig. 1. Conductivity as a function of salt concentration for modified NR based systems.

viscous homogenous solutions. The viscous homogeneous solutions were cast onto glass ring with Teflon substrate underneath. The resultant cast films were slightly sticky and difficult to peel off from the substrate. Unusually the films bonded strongly to the Teflon substrate. However, they were stripped off under treatment by liquid nitrogen. The films were immediately transferred into the vacuum oven for further removal of solvent and moisture. From the DSC traces it was found that the morphology of the film is not affected by the treatment of liquid nitrogen. The details of thermal history of these films will be discussed in the later part of this section.

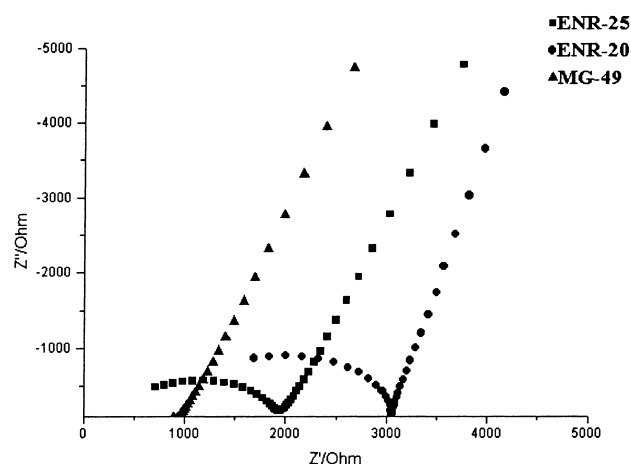


Fig. 2. Impedance plots of salt-doped modified NR based gel electrolyte.

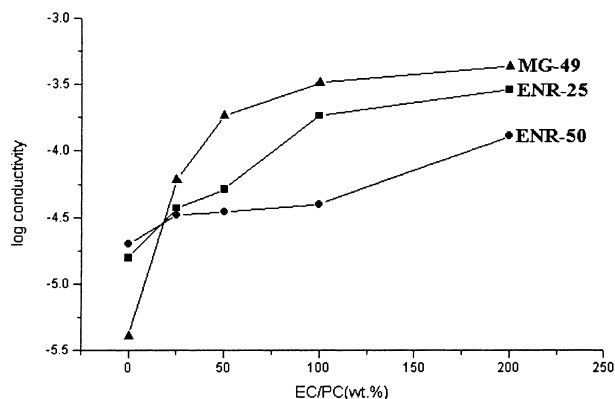


Fig. 3. Conductivity as a function of EC/PC for modified NR based systems.

The strong adhesive property may be significant for efficient contact with the electrodes in electrochemical cell systems. This is one of the promising features discovered in this study. Fig. 3 shows the conductivity of plasticised modified NR based polymer electrolyte films as a function of EC/PC ratio. Typical impedance plots are shown in Fig. 4.

The data illustrate the evidence for the major role of the liquid electrolyte in the ionic conductivity of the gel electrolytes. Tables 2, 4 and 6 show results for all modified NR based film samples containing 5% lithium triflate salt with various weight percent ratios of EC/PC. The conductivity value of the plasticised ENR-25 system is $5.1 \times 10^{-5} \text{ S cm}^{-1}$ at ambient temperature when the liquid electrolyte content is 50 wt.% and reaches $1.8 \times 10^{-4} \text{ S cm}^{-1}$ at 100 wt.% liquid electrolytes. It was observed that the modified NR based film has the ability to uptake a high loading of polar low molecular weight organic solvent. The polymer electrolyte films with ionic conductivities in the order $10^{-4} \text{ S cm}^{-1}$ still retain their rubbery characteristic in spite of the presence of a large amount of absorbed electrolyte solution.

These findings were compared with the study of Matsumoto [18], who studied elastomeric-based materials using

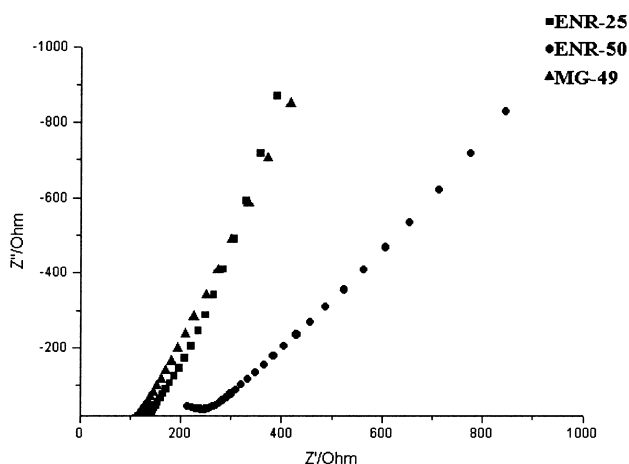


Fig. 4. Impedance plots of plasticised modified NR based gel electrolytes.

synthetic rubber as the polymer host. It was reported that an ionic conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ was obtained by swelling a polymer electrolyte system with electrolyte solvent. In this study a different material and approach has been used but the conductivity trend mimics the above systems. It is suggested that the polarity of the both materials is one of the key factors to attain high ionic conductivity. It was reported that only polymers possessing high dipole moments are suitable candidates. Taking this into consideration, modified NR have fulfilled the above criteria in making a polymer electrolyte for potential use in lithium batteries. Many of the recent studies on gel electrolytes have been also reported employing polar matrices such as diacrylates, acrylonitrile-methyl methacrylate-styrene terpolymer [3,5].

3.2. Differential scanning calorimetry

The presence of more than one phase in the polymer electrolyte system complicates analysis of the transport property data. For this reason, it is desirable to investigate the thermal properties prior to study. Addition of salt and plasticiser into the polymer electrolyte system may cause changes in glass transition temperature. For this study, the phase behaviour of ENR polymer- LiCF_3SO_3 , ENR polymer- LiCF_3SO_3 -EC/PC with O/Li ratios ranging between 57/1 and 5/1 were investigated using DSC. Films made from modified NR- LiCF_3SO_3 solutions appeared homogenous and fully amorphous at room temperature, and no melting transitions were observed between -80 and $+30^\circ\text{C}$. The ENR-25, ENR-50 and MG-49 types of modified NR doped with lithium triflate in this study exhibited a single T_g in the DSC experiments. This indicates that no microphase separation occurs in this system.

Fig. 5 shows the trend of glass transition temperature of the modified NR based systems as a function of the salt concentration. The traces show an increase of glass transition temperatures (T_g s) for the three types of modified NR based polymer electrolyte systems. The concentration of salt added to the polymer at O/Li ratio ranged from 27/1 to 1/1 for the ENR-25 series (see Table 1). The T_g of control ENR-25, is -43°C and that of $(\text{ENR-25})_3(\text{LiCF}_3\text{SO}_3)$ is -25°C .

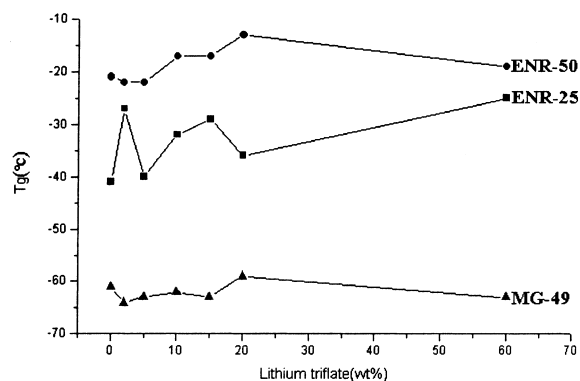


Fig. 5. Glass transition temperature as a function of salt concentration for modified NR based systems.

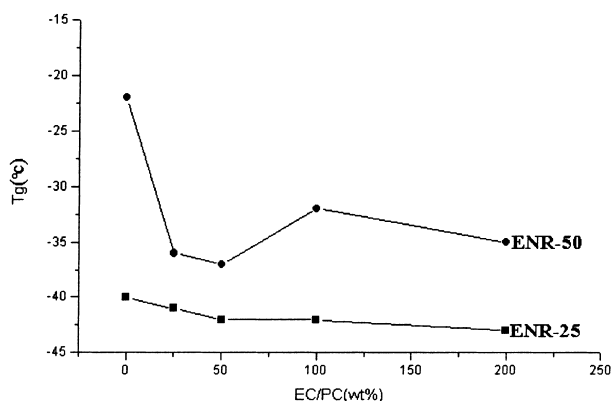


Fig. 6. Glass transition temperature as a function of EC/PC for plasticised ENR systems.

Thus, the effect of added salt has markedly increased the T_g value as in the case with the conventional PEO electrolytes.

As seen in Fig. 3, the increase of chain flexibility can assist ion transport to raise the ionic conductivity of the plasticised complex. It was observed that plasticised system showed higher conductivity in comparison to the salt-doped system. In the plasticised ENR-25 series the gel system prepared at O/Li = 8/1 to 11/1, with incorporation of various EC/PC ratios has retained its T_g value in the vicinity of -43°C . For the ENR-50 series the gels have been prepared at O/Li ratio ranging from 51/1 to 5/1. In these systems the initial T_g of ENR-50 is -22°C . The addition of 20% lithium triflate salt increases the T_g of (ENR-50)₇(LiCF₃SO₃) complex (see Table 3) to -13°C . In contrast to this, the T_g of (ENR-50)₇(LiCF₃SO₃)(EC/PC) complex was -37°C . The plasticising solvents have reduced the T_g value dramatically (Fig. 6).

However, in the case of MG-49 series, the gel systems show inconsistency of their T_g values (see Table 5). The transition glass temperature of MG-49 rubber recorded by DSC is -62°C . The T_g value is higher in comparison to that of the above two types modified rubbers.

T_g is found, in general, to increase with increasing salt concentration. This indicates that a complex has formed between the rubber polymer and the lithium salt. The ionic mobility is closely related to the relaxation modes of the polymer host. This can be observed through the increase in T_g of polymeric systems as salt concentration is increased. But a lowering of T_g values is observed as a result of incorporating plasticisers or solvents into the modified NR matrices. It is believed that the compatibility of the rubber and the solvent determines the optimum uptake of electrolyte species in the composition.

4. Conclusion

Modified NR based electrolytes incorporating lithium triflate salt (LiCF₃SO₃) are potential polymer electrolytes. In addition, mixtures of EC and PC enhance their ionic conductivities at room temperature. The electrolytes using

polymer hosts of modified NR containing LiCF₃SO₃ salt and plasticiser had composition regions suitable for free standing films.

The majority of the salt-doped polymer electrolyte systems have ionic conductivities about $10^{-5} \text{ S cm}^{-1}$ at room temperature. It was found that plasticising modified NR with EC/PC/LiCF₃SO₃ salt solution significantly increased their ionic conductivity. Addition of 100 wt.% of EC/PC (1:1) into the salt-doped polymer system has considerably increased an average ionic conductivity by almost twofold in magnitude. The ionic conductivities obtained in 10^{-4} – $10^{-3} \text{ S cm}^{-1}$ range at room temperature. The DSC traces of the salt-doped polymer electrolytes displayed a single and increasing trend of transition glass (T_g) temperatures when increasing amount of salt concentration was introduced into the polymer matrix. However the incorporation of EC/PC into the system has resulted in a marked reduction in their T_g values.

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