

PREPARATION AND CHARACTERIZATION OF PVDF/ENR-50 POLYMER BLEND ELECTROLYTE

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ABSTRACT

The present study is focused on the characterization of polymer electrolyte based on poly(vinylidene fluoride) (PVdF) and epoxidised natural rubber (ENR). Polymer electrolyte film from the blending of PVdF and ENR-50 doped with lithium triflate (LiCF_3SO_3) and N-lithiotrifluoromethane-sulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_3)_2$) are produced through solution casting technique. The best ionic conductivity recorded from the polymer electrolyte which is doped with certain ratio of LiCF_3SO_3 is 1.38×10^{-5} S/cm at room temperature. For the polymer blend doped with $\text{LiN}(\text{CF}_3\text{SO}_3)_2$ the ionic conductivity is 2.69×10^{-5} S/cm at 20°C . Characterizations of these polymer electrolytes were carried out using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). SEM managed to illustrate the different morphologies between the polymer electrolyte films studied. Meanwhile, DSC is employed to determine the glass transition temperature indicating the presence of homogenous and heterogeneous phases in the polymer electrolyte prepared.

INTRODUCTION

Armand et al in their early work had discovered conducting potential of PEO when doped with lithium salts [1]. To date PEO has been the most studied as the host polymer [2-3]. Since the potential of these materials have been realized for commercial exploitation, other polymers such as PAN [4], PVdF [5-6], PMMA [7] and PVC [8-9] had been proposed as a host on electrolyte system. Recently, natural polymer such as chitosan [10-11] had also been studied.

Conventional liquid electrolytes had been extensively studied and their potential has also been proven and discussed elsewhere. However, liquid electrolytes are facing major problems that are to date remain unsolved. For safety and environmental reasons, solid electrolytes are the potential candidates to overcome these problems and soon to replace all liquid based electrolytes for practical electrochemical devices. The advantages of using solid polymer electrolytes are good compatibility with lithium metal, low self-discharge, easy processing, no leakage, elastic relaxation under stress and good electrical conductivity [12]. There are many types of solid electrolyte systems, which include solid crystalline electrolytes, glass electrolytes, molten electrolytes and

polymeric electrolytes. One of the challenges of the polymer electrolytes is to have high conductivity and good mechanical properties.

The original concept of polymer electrolyte is solvent-free electrolyte system. However, electrochemical cells based on this type of materials are currently under development due to their relatively low ionic conductivity especially at room temperature. Many researches had turn to gel and plasticized type electrolytes for commercialization purposes. These systems exhibited relatively high ionic conductivity. In fact, gel electrolyte systems had been developed and tested in electrochemical cells by the industrial community.

In this work, PVdF is blend with ENR-50 to produce thin film electrolyte. This modification is expected to lower the glass transition temperature (T_g) of PVdF. This modification also should lead to such properties as soft elastomeric characteristics at room temperature and good adhesion. Lithium triflate (LiCF_3SO_3) is used to study the conductivity performance of PVdF/ENR-50 film. The ionic conductivity of the electrolyte over the temperature range 293-363 K was investigated as a function of lithium triflate (LiCF_3SO_3) in different ratios.

EXPERIMENTAL

Polyvinyledene fluoride (PVdF, Mw: 534,000) and lithium triflate (LiCF_3SO_3), were purchased from Aldrich and used as received. Epoxidised natural rubber supplied by Guthrie Polymer Sdn. Bhd. Siliau, Negeri Sembilan, Malaysia. Meanwhile, dimethyl formamide (DMF) and tetrahydrofuran (THF) were purchased from Merck and used without further purification.

Polyvinyledene fluoride (PVdF) stock solution was prepared by dissolving the polymer in dimethyl formamide (DMF) by continuous stirring with a magnetic stirrer. The epoxidised natural rubber was cut into grain size and dissolved into tetrahydrofuran (THF) with magnetic stirring. Two of the polymer solutions with ratio 40:60;ENR-50:PVdF were mixed in a beaker. It was left overnight with continuous stirring until complete dissolution of these polymers. The concentration of this polymer blend solution was fixed in all samples preparation.

Appropriate quantities of lithium triflate (LiCF_3SO_3) were dissolved in the polymer blend solution and the solutions were stirred for 24 h at room temperature. The solution was cast into glass petri dishes and the solvent was allowed to evaporate slowly at room temperature. All polymer electrolyte samples were prepared by a solvent casting method. All sample preparations were carried out in glove box due to the hygroscopic nature of compounds. Table 1 report all the samples prepared with the relative weight of the lithium triflate (LiCF_3SO_3) in the polymer electrolyte films.

Table 1: Composition of the samples prepared and relative percentages of LiCF₃SO₃

Sample	PVdF (g)	ENR-50 (g)	LiCF ₃ SO ₃ (g)
PE 1	0.60	0.40	0.05
PE 2	0.60	0.40	0.10
PE 3	0.60	0.40	0.15
PE 4	0.60	0.40	0.20
PE 5	0.60	0.40	0.25

The impedance measurements were carried out on a computer-interfaced Autolab PGSTAT 30 equipment (Eco Chemie B. V., Netherlands) together with frequency response analysis (FRA) system software. Ionic conductivity was determined by using the complex impedance method in the temperature range 293-363 K. The samples were sandwiched between stainless-steel blocking electrodes and placed in a temperature-controlled oven. Impedance measurements were performed for thin films polymer electrolytes about 100 μm in thickness and 3.142 cm² in area. The impedance plots were recorded in the frequency range 1 Hz to 1 MHz. The conductivity was calculated by

$$\sigma = \frac{1}{R_b} \times \frac{\lambda}{A}$$

where R_b is the bulk resistance from AC impedance, A the area of electrode and λ the film thickness.

Scanning Electron Microscopy (SEM) (Philip XL 40) was performed in order to study the morphology of film polymer electrolyte. The resulting film electrolyte polymer was in free-standing nature. Differential Scanning Calorimetry (DSC) (Mettler Toledo DSC 820) was employed for thermal characterization. The temperature scanning was carried out from -50 to 120 °C at a scan rate of 5 °C min⁻¹.

RESULTS AND DISCUSSION

The ionic conductivity value of the film polymer electrolyte was calculated by using the equation $\sigma = l/R_b A$. The electrolyte bulk resistance was given by the intercept on the real axis. Figure 1 showed the ac impedance spectrum of the SS-SPE-SS (SS: stainless-steel; SPE: solid polymer electrolyte) at 293 K. The presence of spike can lead to the further conclusion that the ionic conductivity is mainly the results of ionic conduction. According to Fig. 1, the total conductivity is mainly the result of the ion conduction and the current carriers are ions because of the absence of the high-frequency semicircular portion [13].

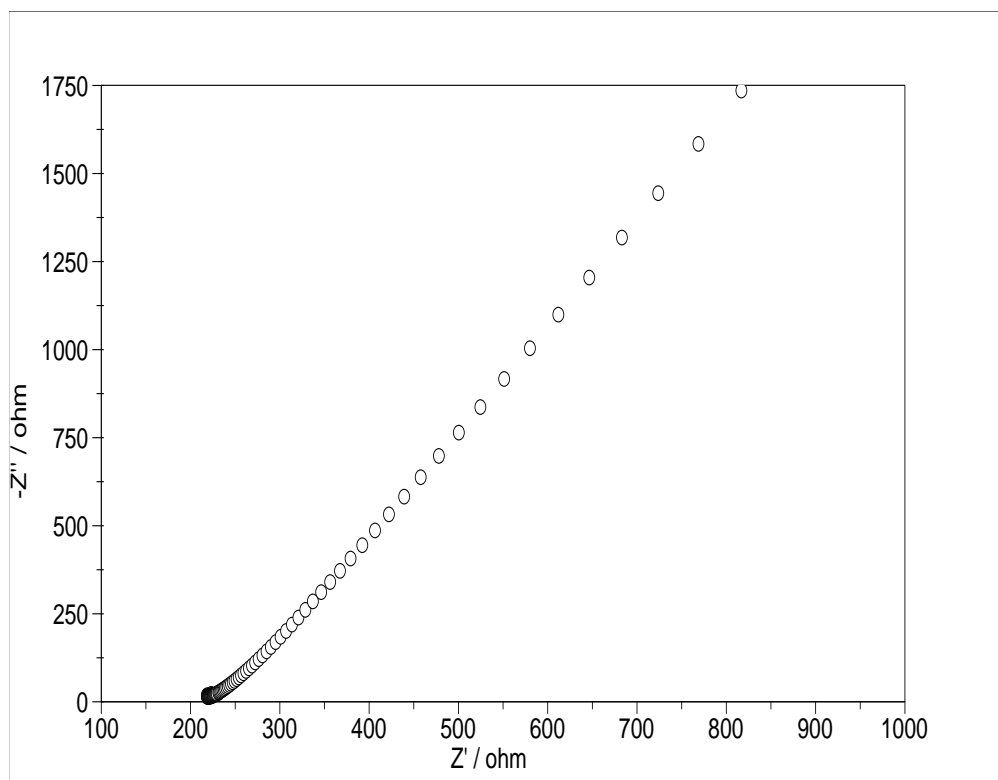


Figure 1: Complex impedance plot of sample PE 4 system at 293 K.

The presence of LiCF_3SO_3 salt helps to increase the conductivity of the polymer electrolyte by three orders of magnitude higher than in their single form. The ionic conductivities for PVdF-ENR-50- LiCF_3SO_3 blend complex containing various compositions of LiCF_3SO_3 were obtained in the temperature range 293-363 K are given in Table 2. From Table 2, it is observed that the conductivity values were increased when the temperature was increased. This can be explained by the free-volume model theory [14]. The ionic conductivity values of the sample are obtained in the order of 10^{-7} to 10^{-4} Scm^{-1} .

Table 2: Ionic conductivities values for PVdF-ENR-50- LiCF_3SO_3 blend complex containing various compositions of LiCF_3SO_3

Sample	σ (S/cm)							
	293 K	303 K	313 K	323 K	333 K	343 K	353 K	363 K
PE 1	7.96E-07	1.10E-06	1.35E-06	1.63E-06	1.91E-06	2.04E-06	2.29E-06	2.57E-06
PE 2	2.24E-06	3.09E-06	3.99E-06	4.58E-06	4.90E-06	5.50E-06	6.02E-06	6.46E-06
PE 3	1.38E-05	1.70E-05	2.29E-05	2.70E-05	3.16E-05	3.39E-05	3.89E-05	4.47E-05
PE 4	2.69E-05	3.98E-05	5.13E-05	6.61E-05	7.59E-05	8.71E-05	1.00E-04	1.17E-04
PE 5	5.50E-06	7.25E-06	8.92E-06	1.05E-05	1.20E-05	1.29E-05	1.38E-05	1.59E-05

It was observed that the maximum conductivity value of the sample PE 4 is $1.17 \times 10^{-4} \text{ Scm}^{-1}$ at 90 °C. The value of $2.69 \times 10^{-5} \text{ Scm}^{-1}$ for the sample PE 4 at 293 K is

comparable with the reported values [14], viz., $1.6 \times 10^{-5} \text{ Scm}^{-1}$ for ENR-50/LiCF₃SO₃ polymer electrolyte. It is also observed that as the temperature increases, the conductivity of the films is also increased. The materials expand and produced local voids that allow species such as motion of ions or polymer segments when temperature is increased. Cations are transferred to the coordinating sites by ion hopping into the same polymer chain or the neighboring polymer chain [15].

The Arrhenius plot shows linearity since the conductivity measurements were performed well below the glass transition temperature. The glass transition temperature of the polymer electrolyte PVdF-ENR-50 obtained is $\sim -243\text{K } ^\circ\text{C}$. Thus, the T_g value for the samples studies is still above the temperature range investigated that the graphs do not deviate from linearity. Arrhenius plots of $1000/T$ versus \log conductivity of different compositions polymer complexes are shown in Figure 2. The data shows that the conductivity can be described by the Arrhenius equation. Both curves of the polymer electrolyte exhibited excellent linearity and seem to obey the Vogel-Tamman-Fulcher (VTF) relation, which describes the transport properties in a matrix [16-17]. As a result, the activation energy of the sample PE 4 was less than the other sample.

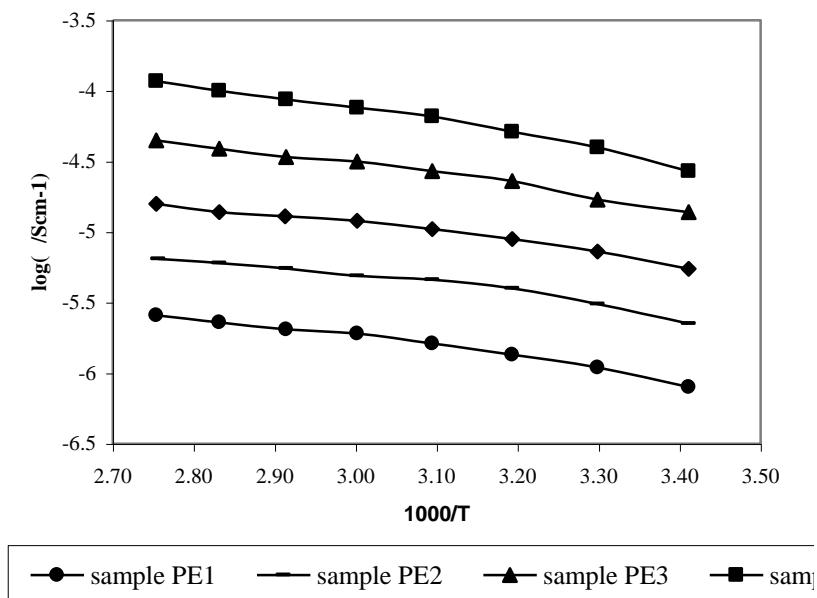


Figure 2: Arrhenius plot of \log conductivity against temperature for polymer complexes.

Scanning Electron Microscopy (SEM) is one of the most versatile and widely used tools for study of surface morphology. SEM micrographs of sample PE 1, sample PE 3 and sample PE 5 are shown in Figure 3.

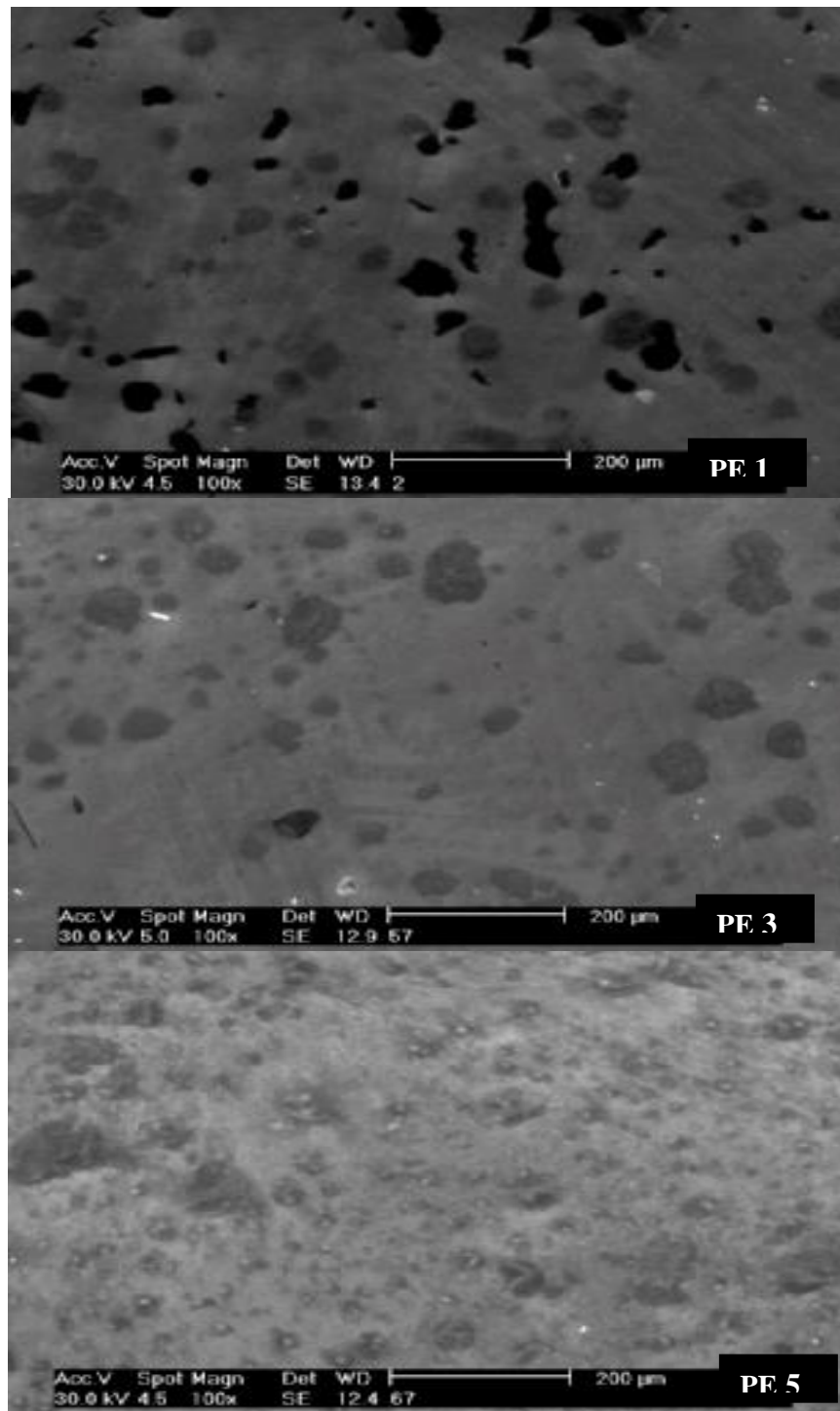


Figure 3: SEM micrograph of sample PE 1, sample PE 3 and sample PE 5

Figure 3 shows the SEM micrographs of the polymer electrolyte based on PVdF/ENR-50/LiCF₃SO₃ with different concentrations of LiCF₃SO₃. The LiCF₃SO₃ salt distributed

uniformly in the polymer matrix. It can be seen that some tiny pores exist between the polymer and salts interfaces. It was attributed to the partial compatibility between the polymer and the salts. The surface morphology of the sample PE 1, sample PE 2 and sample PE 3 showed uneven and rough surface. It exhibited “honeycomb” like structures that are seen to appear from inside the bulk and extends outwards protruding the surface. The roughness of the surface increases with LiCF_3SO_3 content. This might be due to the aggregation of salt which left the bulk polymer solution and appear at the interfaces.

Addition of the salt concentration into the polymer electrolyte system may cause changes in glass transition temperature. For this study, the phase behaviour of PVdF/ENR-50/ LiCF_3SO_3 was investigated using DSC. Figure 4 shows the trend of glass transition temperature of the PVdF/ENR-50 system as a function of the salt concentration. The effect of added salt has markedly increased the T_g values. The decreased in the T_g value above the salt content of 0.20 g might be due to aggregation of salt which compliment SEM results.

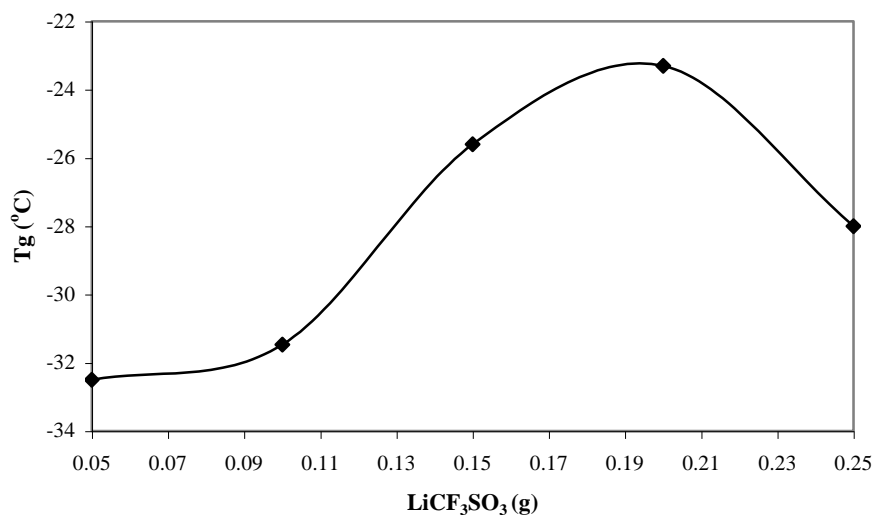


Figure 4: Glass transition temperature as function as a function of salt concentration.

CONCLUSION

The polymer electrolytes based on PVdF/ENR-50/ LiCF_3SO_3 were successfully prepared for different salt concentrations using a solvent casting technique. The ionic properties of the polymer electrolytes based on ENR-50 and PVdF were investigated. The dependence of ionic conductivity on the LiCF_3SO_3 content revealed that viscosity and crystallinity were influencing the ion mobility. The ionic conductivities obtained in the range of 10^{-7} to 10^{-5} Scm^{-1} at 20°C . An optimum concentration of salt was noted after which ‘salting out’ effect could be seen.

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