

Properties of ENR-50 Based Electrolyte System (Sifat Sistem Elektrolit Berasaskan ENR-50)

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ABSTRACT

In this work, epoxidized natural rubber 50 (ENR-50) has been used as a host polymer for the preparation of electrolyte system. Attenuated total reflection-fourier transform infrared spectroscopic analyses showed the presence of lithium salt-ENR interactions. The glass transition temperature displayed an increasing trend with the increase in salt concentration indicating that the ionic conductivity was not influenced by segmental motion of the ENR-50 chains. The increase in glass transition temperature with the addition of salt was due to the formation of transient cross-linking between ENR-50 chains via the coordinated interaction between ENR-50 chains and salt. The highest room temperature ionic conductivity obtained was in the order of $10^{-5} \text{ S cm}^{-1}$ for the film containing 50 wt% of lithium salt. The ionic conductivity of this electrolyte system increased with increasing temperature and obeyed the Vogel-Tamman-Fulcher behavior. The increase in ionic conductivity of the electrolyte system with salt concentration could also be correlated to the charge carriers concentration and/or migration rate of charge carriers.

Keywords: Activation energy; conductivity; ENR-50; VTF

ABSTRAK

Dalam kajian ini, getah asli terepoksi 50 (ENR-50) digunakan sebagai polimer perumah untuk penyediaan sistem elektrolit. Analisis menggunakan spektroskopi inframerah menunjukkan terdapat interaksi garam litium dengan ENR. Suhu peralihan kaca meningkat dengan penambahan kepekatan garam yang menunjukkan bahawa kekonduksian ion tidak dipengaruhi oleh pergerakan segmen rantai ENR-50 itu. Kenaikan suhu peralihan kaca dengan penambahan garam mungkin disebabkan oleh pembentukan hubungan silang sementara rantai ENR-50 melalui interaksi antara rantai ENR-50 dan garam. Kekonduksian ion tertinggi yang diperolehi adalah dalam tertib $10^{-5} \text{ S sm}^{-1}$ bagi filem yang mengandungi 50% berat garam litium. Kekonduksian ion bagi sistem elektrolit ini meningkat dengan penambahan suhu dan mematuhi perlakuan Vogel-Tamman-Fulcher. Penambahan kekonduksian ion bagi sistem elektrolit ini dengan kepekatan garam juga boleh dihubungkan dengan kepekatan pembawa cas dan/atau kadar pemindahan cas.

Kata kunci: ENR-50; kekonduksian; tenaga pengaktifan; VTF

INTRODUCTION

Modification of natural rubber to epoxidized natural rubber diversifies the potential application of natural rubber. One of its applications is for the development of polymer electrolytes. The epoxy group in ENR provides an effective conduction path of carrier ions. The use of this polymer in polymer electrolytes may yield flexible films with good adhesive property and high ionic conductivity (Idris et al. 2001).

Investigations of ENR based polymer electrolytes have been reported by a few groups of researchers. The polymer electrolytes were developed employing ENR as the host polymer or by blending the ENR with other polymers added with various type of lithium salts and plasticizers (Glasse et al. 2002; Idris et al. 2001, 2007; Kim et al. 2004; Mohamed et al. 2008; Razali & Wan Siti Nor 2007).

Even though many studies have been done on ENR based polymer electrolytes, the conduction mechanism of the ENR-salt systems is still not fully understood. Thus, the objective of the present study was to investigate

systematically the properties of ENR-50 doped with lithium imide (LiTFSI) in order to explain its conductivity behavior. The interactions of the constituents and the glass transition temperature of the electrolyte were investigated by attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR) and differential scanning calorimetry (DSC), respectively. The ionic conductivity was determined using a.c. impedance spectroscopic technique. The data of this study may add new knowledge about ENR based polymer electrolytes for future efforts in enhancing the properties of ENR-50 based electrolytes.

MATERIALS PREPARATION AND CHARACTERIZATION

ENR-50 was supplied by the Rubber Research Institute Malaysia. Tetrahydrofuran and lithium imide salt were purchased from R&M Chemicals and Aldrich, respectively. Polymer electrolyte films were prepared by solution casting method. In order to prepare the electrolyte films, ENR-50 was first cut into small pieces and then dissolved

in tetrahydrofuran. When homogeneous solution was formed, LiTFSI of desired amount was added. After a day of stirring, the viscous homogeneous solution formed was cast into Teflon petri dishes and left for slow drying at room temperature to form electrolyte films. The films were further dried in a vacuum oven for 48 h at 40°C to remove residual solvent. Finally, the films were kept in a dry sample container until further use.

ATR-FTIR spectra were recorded using Perkin Elmer Spectrum 400 with a resolution of 2 cm^{-1} in a range from 4000 to 450 cm^{-1} to investigate the polymer-salt interactions. Mettler Toledo DSC 822 equipment was employed to find glass transition temperature. The data were recorded from -65°C to +120°C in nitrogen atmosphere at a scan rate of 10°C min^{-1} . Impedances of the electrolyte films were measured over a frequency range from 100 Hz to 1 MHz using a HIOKI 3532-50 hi tester analyzer. Impedance measurements were done at temperatures ranging from 30 to 80°C. For the impedance measurement, the films were sandwiched between two stainless steel electrodes.

RESULTS AND DISCUSSION

ATR-FTIR spectra were recorded in the transmittance mode. The ATR-FTIR spectra of pure ENR-50 and (ENR-50)-LiTFSI electrolyte films were presented in Figure 1. Figure 1 shows the spectra in spectral range from 1200 to 1500 cm^{-1} . For pure ENR-50, the focus was on C-O-C band located at 1255 cm^{-1} which corresponded to the symmetrical ring stretching of the epoxide group (Gan & Hamid 1997). Other characteristic bands were also observed at 1449 (C-H deformation of $-\text{CH}_2-$) and 1378 cm^{-1} (C-H deformation of $-\text{CH}_3$).

From Figure 1, it can be seen that the C-O-C band at 1255 cm^{-1} disappeared after addition of lithium salt. Other bands, i.e. the bands at 1378 and 1449 cm^{-1} , shifted to higher wavenumbers in the ENR-50-salt systems.

Figures 2(a) and 2(b) show the ATR-FTIR spectra for LiTFSI and (ENR-50)-LiTFSI electrolyte films. From these spectra, S-N stretching was found at 740 cm^{-1} , a combination of C-S and S-N stretching is located at 789 cm^{-1} , S=O bonding at 1053 cm^{-1} and C-SO₂-N bonding at 1137, 1335 and 1355 cm^{-1} (Ramesh & Chien Lu 2008). It is observed that the bands of S-N stretching, C-S and S-N stretching and S=O shifted to a higher wavenumbers in the salted ENR system. Meanwhile the bands of C-SO₂-N bonding at 1137, 1335 and 1355 cm^{-1} shifted to lower wavenumbers in the salted ENR systems. The disappearance, shifting and changes in intensity of the bands in the spectra shown in Figures 1 and 2 suggest that interactions have occurred between the ENR-50 and LiTFSI forming (ENR-50)-LiTFSI complex.

The DSC traces of the pure ENR-50 and (ENR-50)-LiTFSI electrolyte films are shown in Figure 3. The pure ENR-50 shows a phase transition at -22°C, which is known as glass transition temperature, T_g . The values of T_g for (ENR-50)-LiTFSI are found to be higher compared with the pure ENR-50 film. The variation of T_g with LiTFSI content is

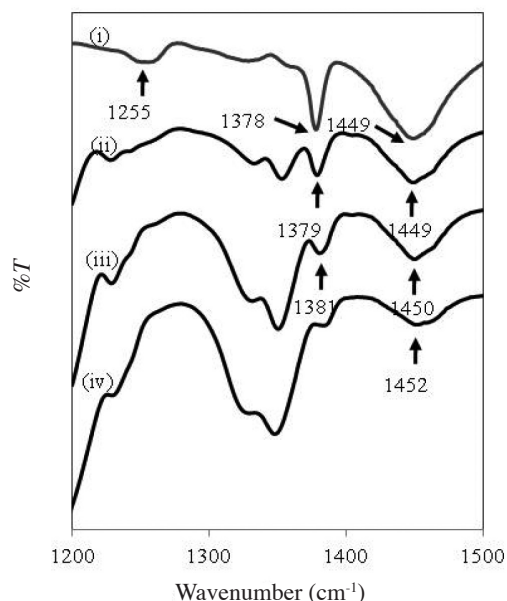


FIGURE 1. ATR-FTIR spectra of (i) pure ENR-50, (ii) ENR-50 with 10 wt%, (iii) ENR-50 with 30 wt% and (iv) ENR-50 with 50 wt% of LiTFSI in the range from 1,200 to 1,500 cm^{-1}

shown in Figure 4. The figure shows the T_g increases with the increase in salt concentration. The increase in T_g with the addition of salt was due to an increase in formation of transient cross-linking between the ENR-50 chains and salt (Kim et al. 2003). The increase in the formation of transient cross-linking leads to an increase in the ENR-50 network stiffness which in turns increased T_g value.

Ionic conductivity measurement was done using a.c. impedance spectroscopic technique. Bulk resistance,

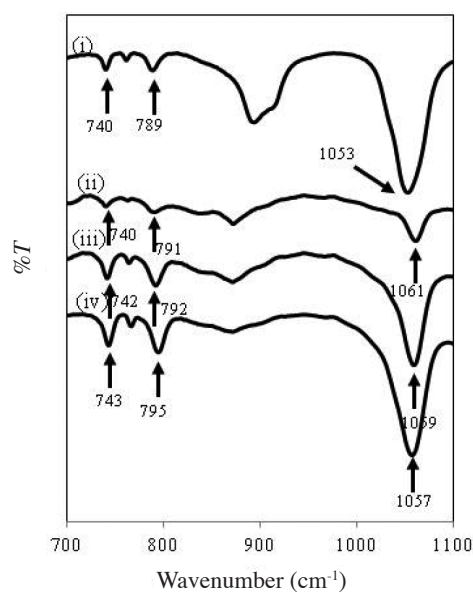


FIGURE 2(a). Transmission spectra of (i) lithium imide salt, (ii) ENR-50 with 10 wt%, (iii) ENR-50 with 30 wt% and (iv) ENR-50 with 50 wt% of LiTFSI in the range from 700 to 1100 cm^{-1}

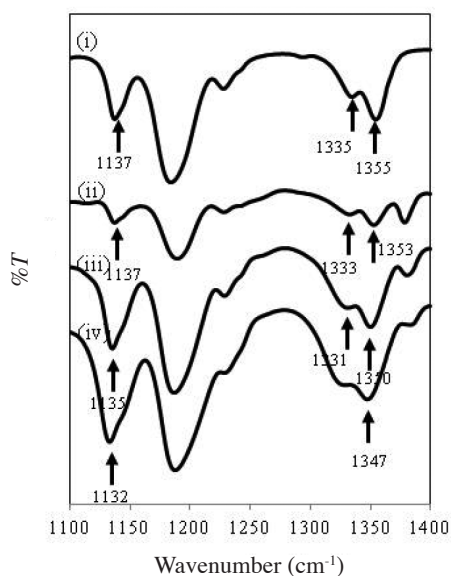


FIGURE 2(b). Transmission spectra of (i) lithium imide salt, (ii) ENR-50 with 10 wt%, (iii) ENR-50 with 30 wt% and (iv) ENR-50 with 50 wt% of LiTFSI in the range from 1100 to 1400 cm^{-1}

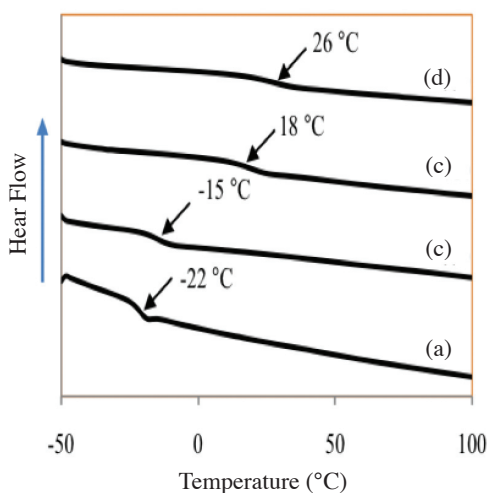


FIGURE 3. DSC curves of (a) pure ENR-50, and ENR-50 doped with (b) 10 wt%, (c) 30 wt%, and (d) 50 wt% of LiTFSI

R_b of the films was determined from impedance plots. The electrolyte conductivity, σ was calculated from the equation, $\sigma = t/AR_b$ where t and A are the thickness and the electrode area, respectively. Figure 5 shows the relationship between the conductivity of (ENR-50)-LiTFSI electrolyte and LiTFSI concentration at room temperature. It is observed that the conductivity increases with the concentration of LiTFSI. The maximum ionic conductivity of $3.53 \times 10^{-5} \text{ S cm}^{-1}$ was obtained at 50 wt% of LiTFSI. The impedance study was not done on films with salt concentration greater than 50 wt%. This is because the films were inhomogeneous and 'salting out' effect could also be seen on the surface of the films.

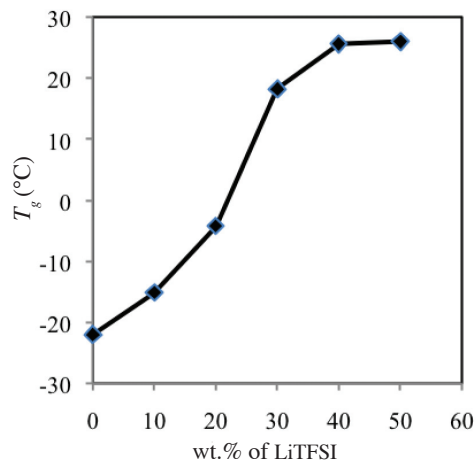


FIGURE 4. Variation of T_g as a function of salt concentration

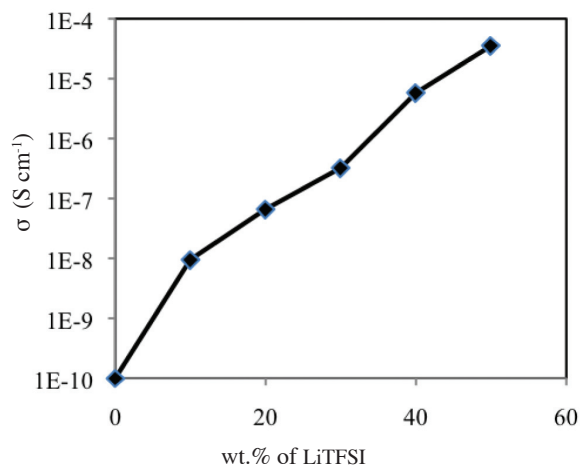


FIGURE 5. Conductivity against wt% of LiTFSI at room temperature

The σ -salt concentration trend contradicts the T_g -salt concentration trend. One would expect the conductivity to decrease when the T_g increases since there is less segmental motion. This apparent contradiction can be explained in terms of cross-linking that formed between the ENR-50 chains and lithium salt as mentioned earlier. In this system, the cross-links are well separated in space and can move with respect to each other to a certain extent thereby contributing to ionic conductivity (Subban 2004). The ionic conductivity may also be contributed by the anions which interact weakly with the polymer (Johansson et al. 1995).

The temperature dependent ionic conductivity plots are presented in Figure 6. The conductivity is found to increase with the increase in temperature and obeys the Vogel-Tamman-Fulcher (VTF) relation:

$$\sigma(T) = AT^{-1/2} \exp [-B/R(T - T_0)] \quad (1)$$

where R is the universal gas constant, T is the absolute temperature and T_0 is a temperature related to T_g . A and

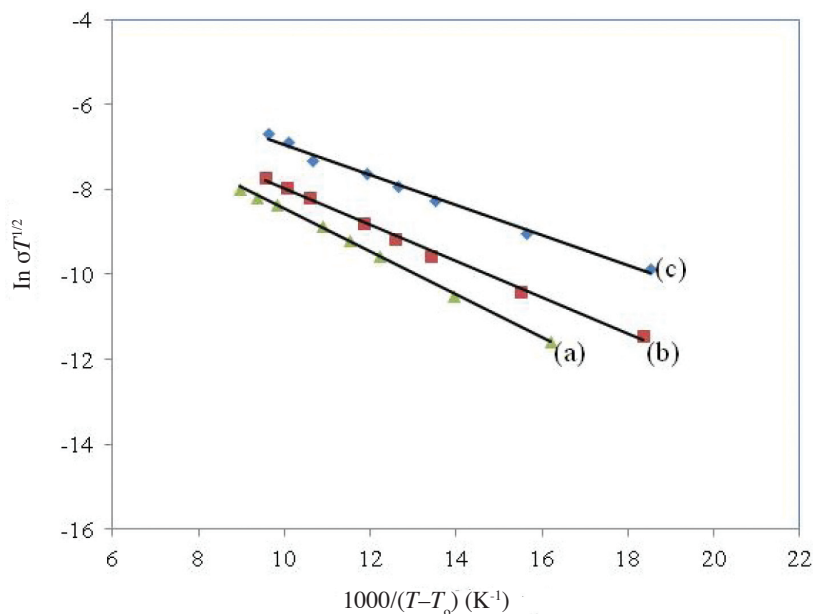


FIGURE 6. VTF plots for films of ENR-50 added with (a) 30 wt%, (b) 40 wt% and (c) 50 wt% of LiTFSI

TABLE I. Ionic conductivity and conduction activation energy values for (ENR-50)-LiTFSI electrolyte films

wt. % of LiTFSI	σ (S cm ⁻¹)	B (kJ mol ⁻¹)
30	3.22×10^{-7}	4.17
40	5.78×10^{-6}	3.56
50	3.53×10^{-5}	2.94

B are constants related to the number of charge carriers and the conduction activation energy, respectively. The increase in conductivity with temperature may be due to an increase in number of charge carriers due to greater dissociation of salts (Rajendran et al. 2003). In addition, it can also be explained in terms of free volume concept (Kim et al. 1996). According to this concept, as the temperature increases, the host polymer expands and the free volume around its chains is also increased, thus a sufficiently large void is created locally into which the charge carriers may jump, which in turn enhances the conductivity. Table 1 summarizes the conduction activation energy, B that was determined from the slope of VTF plots. The highest conducting material was found to exhibit the lowest activation energy. This implied that the energy required for the ion transport was small. Ahmad et al. (2007), reported the activation energy values of the same order of magnitude for their PVC-ENR-LiClO₄ electrolyte films.

CONCLUSION

The effect of salt concentration of (ENR-50)-LiTFSI electrolyte film on the glass transition temperature and ionic conductivity values were studied. The increase in T_g with increase in salt concentration was due to the formation

of transient cross-linking between polymer and salt. The temperature dependence conductivity plots showed the VTF behavior. This indicated that at temperatures higher than the T_g , the charge carrier transport mechanism was governed by the motion of polymeric chains. The conductivity of the ENR-50-LiTFSI electrolyte increased with the increase in LiTFSI. The increase in ionic conductivity was correlated to the concentration of charge carriers and/or the migration rate of charge carriers.

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