

EFFECTS OF IONIC LIQUIDS ON THE CONDUCTIVITY OF METHYL GRAFTED NATURAL RUBBER BASED POLYMER ELECTROLYTES

Norizah Abd. Karim^{1*}, Razali Idris², and Nafisah Osman³

¹Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^{2,3}Faculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia

ABSTRACT

Solid polymer electrolytes composed of Poly(methylmethacrylate) (PMMA) grafted natural rubber (MG49) host polymer, lithium perchlorate and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, ionic liquid were prepared using solvent casting technique. Different concentrations of ionic liquids (2, 5 and 10 weight percent) were added into polymer host with fixed lithium perchlorate salt (10 wt percent) to produce polymer films with thicknesses range 0.2-0.5 mm in reproducible formed. Electrolyte samples were characterized using FTIR and Impedance Complex measurement techniques. The FTIR peaks have shown the interaction between lithium ions from the perchlorate salt and the oxygen atoms in the structure of the PMMA-g-NR polymer host. Room temperature conductivity measurements for the electrolyte samples were conducted using frequency in the range of 42 Hz- 1 MHz. Incorporation of ionic liquid to the systems yielded mechanically stable film and increased ionic conductivity up to 10^{-4} - 10^{-3} Scm^{-1} at room temperature.

Modified natural rubber such as poly(methylmethacrylate) (PMMA) grafted natural rubber (PMM-g-NR) or commercially known as MG-49 rubber was identified to be one of the potential candidate for solid polymer electrolyte in various electrochemical device applications such as dye sensitized solar cells, sensors and electrochromic device and so forth. The lone pair electron of the oxygen atom from MMA monomer is expected to forms a coordination bond with the cation from ionic salts, resulting in the formation of polymer-complexes [1-2]. However, PMMA grafted natural rubber with lithium salt at room temperature has achieved an optimal ionic conductivity of 10^{-4} S cm^{-1} at room temperature [2]. One of the possibilities to increase the conductivity of PMMA grafted natural rubber is incorporating of ionic liquid. Recently, ionic liquid or room temperature ionic liquid (RTILs) are receiving great attention as ion source or additives in solid polymer electrolyte systems (SPEs) due to their interesting characteristics such as high ionic conductivity, non-volatility, non-flammability, wide electrochemical window and so forth [3]. RTILs are molten salts at room temperature. They are composed of a large asymmetrical cation and weakly coordinating inorganic or organic anion. The advantages of RTILs such as high thermal stability up to 200 to 300°C and non-flammability are suitable to be employed in electrochemical devices such as electrochromic windows and solar cells for the outdoor applications. Several approaches employing RTILs were reported to produce high conductivity in polymer electrolyte systems. Among other reasons have increased the number of charge carriers for ionic transport [4]. Furthermore the utilization of ionic liquid is creating free volume in the long entanglement of polymer main-chains for the movement of ions. This will make the ions move freely, resulting in increase of the conductivity. Hence, in this study, the effect of different concentration of ionic liquid on ionic conductivity of the electrolyte system was investigated. The addition of ionic liquid into the methyl grafted natural rubber based polymer electrolyte has improved with expected ionic conductivity $\sim 10^{-3}$ Scm^{-1} at room temperature.

Poly(methylmethacrylate) (PMMA) grafted natural rubber or MG-49 was supplied by Malaysian Rubber Board (MRB). Tetrahydrofuran, THF (FISCHER SCIENTIFIC), Lithium Perchlorate (ClLiO_4) (FLUKA) and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide Mw: 447.42 g/mol (MERCK) were used without further purification. About 1.5 gram of MG49 was dissolved in 90ml tetrahydrofuran (THF) solvent in a closed bottle for about 24 h. Then 10 weight percent of lithium perchlorate salt was added into the solution and stirred for another 8 hours. Then, the ionic liquid was added into the mixtures of ionic salt and rubber in different compositions ranging 2, 5 and 10 wt percent. The mixture solution was further stirred until 8 h at ambient temperature in the argon filled glove-box. After finished stirring, the solution was transferred and cast into a Teflon mould. It was left for solvent evaporation process and kept in a glove-box until a thin rubbery film formed. Then, the thin film was left in a glove-box to remove remaining solvent and further tests. The sample was characterized

using Fourier Transform Infrared (FTIR). The ATR-FTIR spectra were scanned using a Perkin-Elmer Spectrum-One spectrometer in the range of 4000-500 cm^{-1} . The ionic conductivity measurement was conducted using Impedance Analyser (HIOKI 3532-50 LCR Hi TESTER) in the frequency range of 42Hz- 1MHz at ambient temperature. Round shaped film samples were cut and sandwiched between two stainless steel blocking electrodes and mounted in the test cell. The ionic conductivity values were calculated from the bulk electrolyte resistance value (R_b) of Cole-Cole plots data. The impedance spectra measurements were analysed using the Z-man software.

FT-IR Spectroscopy technique is utilized as a tool to observe the vibration energies of covalent bonds in the polymer host and the interactions that occur in the polymer-salt complexes. Due to the fact that each type of bond has a different natural frequency of vibration, the identification of the absorption peak in the vibration portion of the infra red region gives a specific type of bonding. The main region of interest includes the oxygen atoms of the carbonyl group, (C=O) stretch (1750-1730 cm^{-1} from MG49 rubber. K.Kumutha and Y.alias reported that peaks due to oxygen group in PMMA grafted natural rubber (MG49) could be observed in, C=O symmetrical stretching at 1730 cm^{-1} [1]. According to the literature, the oxygen atom in the structure of the polymer host acts as electron donor atom and form a coordinate or dative bond with the lithium ions from doping salts to form a polymer-salt complex. Figure 1 shows the FT-IR spectrum of the symmetrical stretching of the carbonyl group. With the addition of lithium salts and ionic liquid in the system, the intensity of the (C=O) of the MMA peak was reduced and shifted to 1735 cm^{-1} [5]. Figure 2 suggests the assymetric deformation of the MMA group from (O-CH₃) of 1455 cm^{-1} in the MG49 rubber to 1460 cm^{-1} with the addition of lithium salts and ionic liquids. The peak shift confirms the interaction between lithium ions from the doping salt and the oxygen atoms in the structure of the polymer host. The reduction with broadening of intensity and peak shift indicates that the remaining vibration frequency between C-O-CH₃ bonding was disturbed by the interaction between lithium ions and the oxygen atoms. This is because a new bond was formed between the lithium ions from the doping salt and the oxygen atoms in the structure of the polymer host, also known as a coordinate or dative bond, which led to the formation of polymer-salt complexes [5-9]. The symmetric stretching of polyisoprene in the rubber chain of (C=C) at 1604 cm^{-1} showed no changes in term of both the peak shift and intensity of the vibration for each type of concentration. This signifies that there was no interaction with the non-polar group in the polymer chain [10].

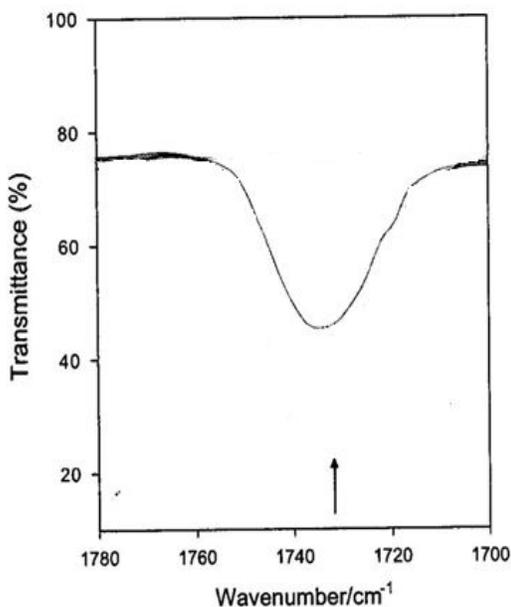


Figure 1. FT-IR Spectrum of the symmetrical stretching of the carbonyl groups

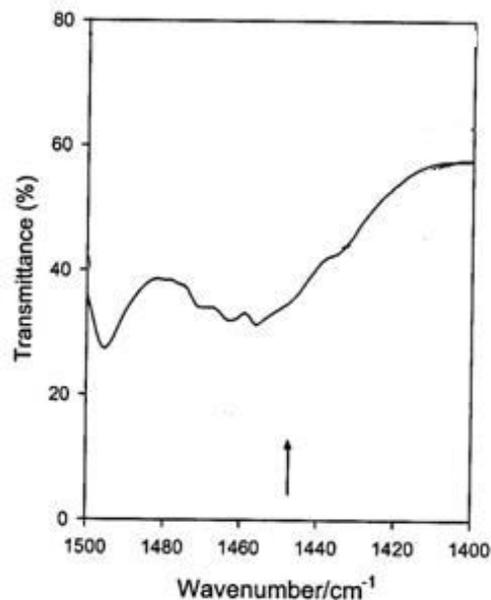


Figure 2. FT-IR Spectrum of the asymmetrical deformation of MMA monomer

Figure 3 displays the results of impedance plot for MG 49 based electrolyte with fixed amount of lithium perchlorate and various percentages of ionic liquid added. Table 1 shows the MG 49 based electrolyte films exhibited with the ionic conductivity of $10^{-4} - 10^{-3} \text{ S cm}^{-1}$ at room temperature. The conductivity of solid polymer

electrolyte film for sample incorporated with 2 weight percent ionic liquid is $3.1 \times 10^{-4} \text{ S cm}^{-1}$, whereas electrolyte film containing 5 wt percent of ionic liquid is $1.6 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. However, the highest conductivity is the electrolyte film with 10 weight percent of ionic liquid which is $2.1 \times 10^{-3} \text{ S cm}^{-1}$. This is attributed to the higher percentage of ionic liquid which believed to provide free volume for the movement of ions in the entangle polymer chains. Ionic liquid also serves as both as the charge carrier and a plasticizer [3, 11]. This is in agreement with Kang and co-workers which reported that the incorporation of ionic liquids 1-butyl-3-methylimidazolium nitrate (BMINO₃) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄) into poly (2-ethyl-2oxaline) (POZ) –silver nitrate (AgNO₃) –based polymer electrolyte system increased the amount of free ions [4, 12]. This phenomenon is attributed to the interaction between the imidazolium cation (BMI⁺) and the NO₃⁻ from salt which weakened the attractive force between Ag⁺ and NO₃⁻. However, the mechanism on how highly concentrated ionic liquid effect and increase the conductivity is not fully understood at the present time.

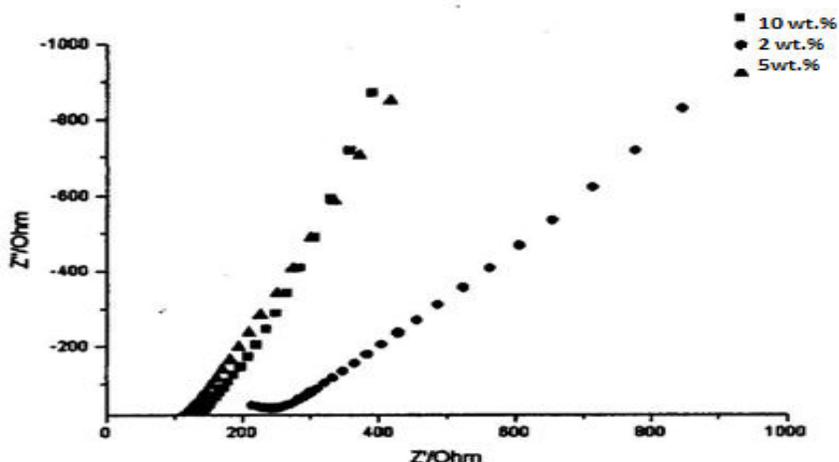


Figure 3. Impedance plots of PMMA-g-NR (MG-49) based electrolyte films with different wt percent of ionic liquid.

Table 1. Compositions of PMMA-grafted-natural rubber (MG49) based polymer electrolytes and ionic conductivities with different wt percent of added ionic liquid.

Reference of PMMA-g-NR based electrolyte film	Percentage of ionic liquid (wt. %) in PMMA-g-NR+LiClO ₄	Conductivity of PMMA-g-NR+LiClO ₄ +IL / S cm ⁻¹
MG-49/SPE-1/A	2	3.1×10^{-4}
MG-49/SPE-1/B	5	1.6×10^{-3}
MG-49/SPE-1/C	10	2.1×10^{-3}

PMMA-g-NR Poly (methyl methacrylate) grafted natural rubber or MG-49

LiClO₄ (Lithium Perchlorate)

IL-Ionic liquid (1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide

SPE (Solid polymer electrolyte)

Solid polymer electrolytes employing PMMA grafted natural rubber (MG 49), lithium perchlorate and ionic liquid were prepared using solvent cast technique. The FTIR peaks shift have shown the interaction between lithium perchlorate ions from the doping salt and the oxygen atoms in the structure of the PMMA-grafted-natural rubber polymer host. With the addition of lithium salts and ionic liquid in the system, the intensity of the (C=O) of the MMA peak was reduced and shifted to 1735cm^{-1} . Impedance data showed that with addition of ionic liquids has improved their conductivity at room temperature. The optimum ionic conductivity of the solid electrolyte film

containing 10 wt percent of ionic liquid, 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide and ionic salt was $10^{-3} \text{ S cm}^{-1}$ at room temperature. This was due to the effect of ionic liquids which can increase the number of charge carriers for ionic transport. Incorporation of ionic liquid is creating free volume in the long entanglement polymer chains of PMMA-g-natural rubber has increased the amorphous phase for the movement of ions. Thus it is preferred dominant phase in polymer for the ions to move freely, resulting in the increase of the ionic conductivity at room temperature.

REFERENCES

- [1] Kumutha, K., Alias, Y., (2006). *Spectrochim. Acta A*. 64, 442.
- [2] Ali, A.M.M., Subban, R.H.Y., Bahron, H., Winie, T., Latif, F., Yahya, M.Z.Y., (2008). *Ionics* 14, 491.
- [3] Sim, L. N., Majid, S. R., Arof, A. K., (2014). *Electrochimica Acta*. Accepted Manuscript.
- [4] Lewandowski, A., Swiderska, A., (2004). *Solid State Ionics*. 169, 21.
- [5] Su'ait, M. S., Ahmad, A., Hamzah, H., Rahman, M. Y. A., (2011). *Electrochimica Acta*. 57, 123-131
- [6] Yahya, M.Z.A., Arof, A.K., (2003). *European Polymer Journal*. 39, 897-902.
- [7] Rajendran, S., Sivakumar, M., Subadewi, R., (2004). *Material Letter*. 58, 641-649
- [8] Ahmad, A., Low, S. P., Almakhzoom, F. S. A., Rahman, M. Y. A., (2012). *Advance materials Res*. 501, 44-88
- [9] Chen, H. W., Lin, T. P., Chang, F. C., (2002). *Polymer*. 43, 5281
- [10] Su'ait, M.S., Ahmad, A., Hamzah, H., Rahman, M. Y. A., (2009). *Journal of Physics, D: Applied Physics*. 42, 55410.
- [11] Loupy, A., Tchoudar, B., (1991). *Salts Effects in Organic and Organic Metallic Chemistry*, VCH Publishing, New York.
- [12] Kang, S. W. Char, K., Kim, J. H., Kim, C. K., Kang, Y. S., (2006). *Chem. Material*. 18, 1789