Fourier Transform Infrared Spectroscopy (FTIR) of Modified Natural Rubber Electrolyte Containing Sodium Hydroxide

Adam Aidid Mohamad Suhaili[a], Nur Amira Roslan[a], Hazwan Haziq Mohamad Azmi[a], Sharifah Iziuna Sayed Jamaludin[a] Siti Nor Hafiza Mohd Yusoff[b]

[a]*Faculty of Chemical Engineering, Universiti Teknologi MARA Johor Pasir Gudang Campus, Bandar Seri Alam, 81750 Masai, Johor, Malaysia*

[b]*Faculty of Applied Science, Universiti Teknologi MARA Johor Pasir Gudang Campus, Bandar Seri Alam, 81750 Masai, Johor, Malaysia*

Abstract

The solid polymer electrolyte sample has been prepared via contacting Methyl Grafted natural rubber (MG-49) as a polymer host with inorganic salt which is sodium hydroxide, NaOH -salt by using solution casting technique. Using NaOH as the doping salt is a new technique due to the facts that previous researchers prefer to work with lithium perchlorate. This is because of its advantages such as low lattice energy that ease the complexion with the polymer host, high mobility of charge carrier and absence of crystalline complex formation at low salt concentration. In this study, Fourier Transform Infrared Spectroscopy (FTIR) is used to obtain the infrared spectrum by collecting high spectral-resolution data over wide range simultaneously and to observe the interaction and coordination behaviour of chemical bond inside the methyl grafted rubber when contacting with the Na^+ ion from the salt. The coordination of the Na^+ ion from the salt with the polymer host, MG-49 shows a direct proportional relationship as the salt concentration increases, the interaction between the cation of the salt and the anion of the rubber is also increases.

Keywords: FTIR; Methyl-Grafted Natural Rubber; Sodium Hydroxide salt; Solid Polymer Electrolyte; Spectroscopy

1. Introduction

Polymer electrolyte is considered as a new advanced electrochemical application. Polymer electrolyte have many benefits like high in energy density and ion conductivity, solvent-free condition low volatility, stable in structure, light in term of the weight and have a wide electrochemical stability (Ramesh et al., 2007) .

The existence of solid electrolyte maybe unknown to some people where they usually only know about liquid electrolyte. This is due to the fact that liquid electrolyte had been used in many applications since a long time ago. However, being the most common electrolyte used does not make it the ideal electrolyte because liquid electrolyte has a few disadvantages. Some of the disadvantages of liquid electrolyte are leakage, it is hard to transport it from one place to another place and lastly, the electrode will slowly corrode and render the device impractical (Smita, 2011).

Solid polymer electrolyte (SPE) is an ion conducting and solvent free electrolyte which is the enhancement from solid electrolyte. SPE is much more favoured as compared to solid electrolyte due to the facts that SPE have a safer design, superior in density, simpler stacking, flame resistance and a suitable shape in this kind of application (Liang et al., 2015) .

Polymer electrolyte in solid state had contributed great impact in electrochemical industries. From the previous two decades till now, advancement of SPE keeps on pulling in incredible research enthusiasm for the desire of opening new situations for upgraded electrical energy-storage and energy-generation devices (Halim et al., 2017) (Harun et al., 2017) (J.W. Choi et al., 2007) (Karan et al., 2008)

Mostly research and study is about polyethylene electrolyte (PEO) as SPE and limited study on natural rubber as the polymer host has been carried out (Choi et al., 2015) (Harun et al., 2017) (Ramesh et al., 2007) (Sekhon et al., 1995) . Therefore, in this study, elastomer is being used as the polymer host (Mohd et al., 2014).

Elastomers are macromolecular materials which rapidly change into their original shape when distorted by a weak force . Examples of elastomers are natural rubber (NR) and modified NR. Modified NR is better because of its characteristic and properties have improved such as it contain low glass transition temperature T_g , good ionic conductivity, soft elastomer characteristic at room temperature and can act as polymeric solvent (Yusoff, Sim et al. 2015). The chosen modified NR to be studied is poly (methyl methacrylate)-grafted natural rubber which contain 49 wt% poly (methyl methacrylate) of MG-49.

Rather than using NR as the host polymer, modified NR is more preferable. However, research on modified NR based polymer electrolyte is scant (Yusoff et al., 2015) (Chan et al., 2013). Even though the studies on modified NR are scant, some of the studies done by previous researches have proven the effectivity of using modified NR in polymer electrolyte (Ali et al., 2013) (George et al., 2017) (Glasse et al., 2002) . They have showed that the ionic conductivities as well as the dielectric constant increases with increasing of salt content.

Many approaches have used lithium perchlorate ($LiClO_4$) as the salt in their polymer electrolyte (Liang et al., 2015) (Halim et al., 2017) . In this study, sodium hydroxide, NaOH are used as the salt. Modified NR contain oxygen atom which will be a donor atom in polymer host, thus the atom with lone pair will be paired with sodium ion, Na^+ from salt and produce polymer complex.

In this study, modified NR that is MG-49 has been used as the polymer host for SPE and the salt used is sodium hydroxide NaOH. This study focuses on studying the effect of different concentration of salt on the performance of the polymer electrolyte via Fourier- Transform Infrared (FTIR) Spectroscopy.

2. Methodology

2.1 Material

MG-49 was gifted by Green HPSP (M) Sdn Bhd, Petaling Jaya, Malaysia. MG-49 is a modified natural rubber prepared by graft polymerization of poly methyl methacrylate (PMMA) into a natural rubber latex. The number 49 denotes the percentage of PMMA graphed to the rubber elastomer. Therefore, MG-49 has 49 wt% of PMMA and 51 wt% of natural rubber. MG-49 was first purified by dissolution in chloroform and filtered using a piece of nylon cloth before admitting into a rotary evaporator. It is then precipitated with n-hexane and let to dry. The inorganic salt, NaOH was used without any purification or drying.

2.2 Preparation of MG-49/ NaOH Sample

In order to prepare the solid thin film, solution casting method was implemented. MG-49 with different NaOH salt composition; 0wt%, 4wt%, 8wt%, 12wt% and 18wt% were dissolved in acetonitrile, ACN. The solution was stirred for 24 hours at a room temperature at 50 °C so that the polymer and salt are completely dissolved. It was then casted into a Teflon dish carefully to avoid bubbles formation. The solution was left overnight to dry under the fume hood at room temperature. The film formed was then further dried in oven to remove residual solvent at a temperature of 50 °C for 24 hours. Then, vacuum dried again at 25 °C for 24 hours

2.3 Fourier Transform Infrared (FTIR) Spectroscopy

In order to determine the dipole-dipole and ion-dipole interaction of MG-49 and NaOH, FTIR Bruker Model Vertex 80 was used with 32 scans at resolution of 4 cm^{-1} and frequency range of 4000 to 650 cm^{-1}. The chain structure, chemical and physical aspect of the structure can also be determined from the FTIR characterization.

3. Results & Discussion

ATR-FTIR

Fourier-transform infrared spectroscopy (FTIR) technique analysis is used with ATR method to obtain an infrared spectrum of absorption or emission of a copolymer with Germanium crystal. The wavelength spectra range from 650 cm^{-1} to 4000 cm^{-1} are used with the resolution of 4 cm^{-1} and averaging scans of 32 for all sample at room temperature. Figure 1 shows the spectra length of MG-49 rubber with different salt concentration. Meanwhile, table 1 shows the characteristic of absorption and emission of copolymer MG natural rubber.

Table 1: Characteristics of absorption and emission of copolymer MG natural rubber (Harun et al., 2017)

Wavenumber (cm^{-})	Assignment
2962,2916,2852	CH_2 stretching [1]
1728	C=O stretching (corresponding to MG-rubber) [1]
1626-1622	C=C stretching (corresponding to NR) [1]
1445	CH_2 deformation modes [1]
1378-1376	CH_2 wagging [1]
1145 (MG-rubber)	C-O-C stretching mode [1]
834	=C-H out-plane deformation [1]

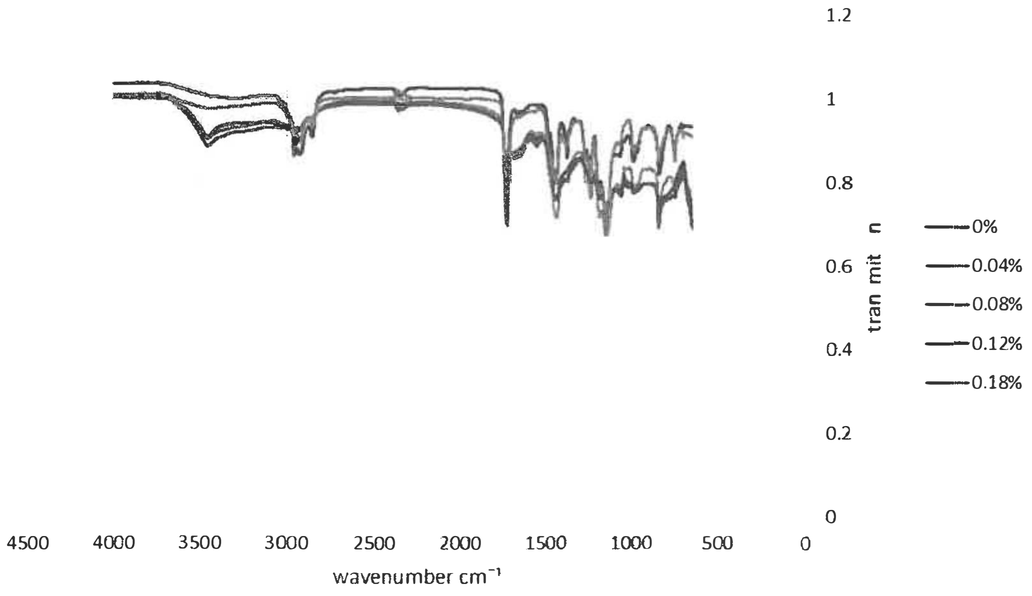

Figure 1 : Spectra length of MG-49 rubber with different salt concentration (a) Y=0.0, (b) Y=0.04 , (c) Y= 0.08, (d) Y=0.12, (e) Y=0.18

In FTIR spectroscopy, the x-axis is used to show wavenumber, in cm^{-1}. The decision to use the wavenumber for infrared spectroscopy as opposed than wavelengths and frequencies was likely done to give a range that has both presence of width to ensure the difference between two peaks is more accurate and reasonable values (Chan et al., 2013). The objective is to effortlessly able to compare values between peaks.

The Na^+ ion from the NaOH salt added to MG-49 backbone to coordinates with the oxygen atoms of the copolymer groups of the MG-49, along these, changing the position of peaks as well as the intensity of the absorption peaks of the polymer polar groups concerned. In order to investigate the reaction between Na^+ and polymer natural rubber, various concentrations of inorganic salt that are Y= 0.00 wt%, 0.04 wt%, 0.08 wt%, 0.12 wt % and 0.18 wt% was added to each 1 gram of natural rubber and characterize by using FTIR.

After addition of inorganic salt into MG-49, it is observed that they have symmetric stretching mode at the carbonyl group, C=O bond. This mode can be observed at range of 1500-2000 cm^{-1}. It was first observed that the symmetric stretching peak with salt concentration, Y= 0.00 absorbs intensely at 1727.77 cm^{-1}. As the salt concentration increases, it is observed that the symmetric stretching peak started to reduce in intensity. The graph also downshifted from 1727.77 to 1726.16 cm^{-1} with increasing salt concentration. The downshifts of the peak is majorly caused by the coordination between Na^+ in the salt with the oxygen atom in the C=O group. The results obtained are in agreement with another previous researcher done by (Chan et al., 2013) (Yusoff et al., 2015)

Wavelength at range 1445 cm^{-1} is to show the peak for CH_2 deformation modes. From Figure 1, it is observed that the CH_2 deformation mode is constantly at the same intensity peak which is at 1445 cm^{-1}. The randomly intensity peak at 1145 to 1446 cm^{-1} is affected by the CH_2 wagging because CH_2 molecule vibrate when contacting with sodium ion.

At wavelength 1146 cm^{-1}, the C-O-C bond will be broadening and reduce the intensity of the peak for salt concentration Y=0.00, 0.04, 0.08 causes by vigorous interaction between sodium ion and the oxygen atom from the C-O-C bond. For the concentration of salt at Y=0.12 and Y=0.18, the peak will slightly increase and becomes narrower. From the curve graph resulting from all sample, we can assume that the crystalline structure phase of MG-49 is conserved along extension of salt with rubber. Absorption bands at v(C-O-C) mode of natural rubber and free anion OH^- are usually joined with the polymer cation interaction as studied by (Harun et al., 2017) .

The appearance of the triplet band come out at 1191cm^{-1}, 1146cm^{-1} and 1038cm^{-1} and the shoulder of this band is at constant peak for every salt concentration and do not shift with addition of salt, while the amorphous phase is reduced in intensity. This show that the intermolecular interaction between MG-49 and salt only happen at amorphous phase. As studied before in a few past researches, results obtained shows an agreement with the results obtained by past researcher. (Chan et al., 2013)

4. Conclusion

Solid polymer electrolyte of the natural rubber MG-49 and the NaOH has been formulated by the solution casting technique which will produce sample of thin film to further characterization of its properties respect to variation of salt concentration. After conducting ATR-FTIR analysis, the results reveal significant behaviour between Na^+ ion from NaOH salt with oxygen atom from natural rubber. It can be concluded that the intermolecular interaction is decreasing at C-O-C stretching mode, however when the salt concentration $Y \geq 0.12$ it turns out that the stretching mode increase, showing that the interaction between inorganic salt and polymer host is greater in that area and has a good conductor characteristic. Meanwhile, the CH_2 mode at amorphous phase has no effect when summation of salt which is supported by the peak intensity constant result extracted from FTIR. No interaction of molecule in amorphous phase and minor interaction at crystalline phase. The result obtained is in agreement with other studies on behaviour of the phase in solid polymer electrolyte. In a nutshell, the natural rubber becomes inelastic, more sturdy and strong interaction at a certain salt concentration with embodiment of salt grafting into the natural rubber backbone. This is proven that when NaOH is contacted with MG-49, an ion-dipole interaction will occur.

sAcknowledgement

The authors would like to thank Faculty of Chemical Engineering, UiTM (MARA) Johor, Pasir Gudang Campus for the facilities provided along the process of completion for our final year project.

References

Ali, A. M. M., Subban, R. H. Y., Bahron, H., Yahya, M. Z. A., & Kamisan, A. S. (2013). Investigation on modified natural rubber gel polymer electrolytes for lithium polymer battery. *Journal of Power Sources, 244*(Supplement C), 636-640.

Choi, B.-R., Park, S.-J., & Kim, S. (2015). Preparation of polyethylene oxide composite electrolytes containing imidazolium cation salt-attached titanium oxides and their conducing behavior. *Journal of Industrial and Engineering Chemistry, 31*(Supplement C), 352-359.

Choi, J.-W., Cheruvally, G., Kim, Y.-H., Kim, J.-K., Manuel, J., Raghavan, P., . . . Song, C. E. (2007). Poly(ethylene oxide)-based polymer electrolyte incorporating room-temperature ionic liquid for lithium batteries. *Solid State Ionics, 178*(19), 1235-1241.

George, G., Sisupal, S. B., Tomy, T., Pottammal, B. A., Kumaran, A., Suvekbala, V., . . . Ragupathy, L. (2017). Thermally conductive thin films derived from defect free graphene-natural rubber latex nanocomposite: Preparation and properties. *Carbon, 119*(Supplement C), 527-534.

Glasse, M. D., Idris, R., Latham, R. J., Linford, R. G., & Schlindwein, W. S. (2002). Polymer electrolytes based on modified natural rubber. *Solid State Ionics, 147*(3), 289-294.

Halim, S. I. A., Chan, C. H., & Winie, T. (2017). *Thermal, Conductivity and Molecular Interaction Studies of Poly(ethylene oxide)/Poly(methyl acrylate) Solid Polymer Electrolytes* (Vol. 371).

Harun, F., Chan, C. H., & Winie, T. (2017). *Influence of molar mass on thermal properties, conductivity and intermolecular interaction of poly(ethylene oxide) solid polymer electrolytes*.

Karan, N. K., Pradhan, D. K., Thomas, R., Natesan, B., & Katiyar, R. S. (2008). Solid polymer electrolytes based on polyethylene oxide and lithium trifluoro- methane sulfonate (PEO–LiCF3SO3): Ionic conductivity and dielectric relaxation. *Solid State Ionics, 179*(19), 689-696.

Liang, B., Tang, S., Jiang, Q., Chen, C., Chen, X., Li, S., & Yan, X. (2015). Preparation and characterization of PEO-PMMA polymer composite electrolytes doped with nano-Al2O3. *Electrochimica Acta, 169*(Supplement C), 334-341.

Ramesh, S., Winie, T., & Arof, A. K. (2007). Investigation of mechanical properties of polyvinyl chloride–polyethylene oxide (PVC–PEO) based polymer electrolytes for lithium polymer cells. *European Polymer Journal, 43*(5), 1963-1968.

Sekhon, S. S., Singh, G., Agnihotry, S. A., & Chandra, S. (1995). Solid polymer electrolytes based on polyethylene oxide-silver thiocyanate. *Solid State Ionics, 80*(1), 37-44.

Smita, M. (2011). Preparation and Characterization of Polymer Electrolyte. Odisha, India: Deaprtment of Physics, National Institue of Technology, Rorkela.

Subban, R. H. Y., Arof, A. K., & Radhakrishna, S. (1996). Polymer batteries with chitosan electrolyte mixed with sodium perchlorate. *Materials Science and Engineering: B, 38*(1), 156-160.

Yusoff, M. S.N.H., Sim, L.H., Chan, C.H., Aziz, S. A. S. S., Mahmud, S.Z., & Hairi, M. H. (2015). Studies on thermal and conductivity of modifeid natural rubber. *Journal of Advamced Research in Materials Science, 12*(1), 1-11.

Chan, C. H., Kammer, H. W., Sim, L.H., Yusoff, M. S. N. H., Hashifudin, A., Winie, T. (2014). Conductivity and dielectric relaxation of Li salt in poly(ethylene oxide) and epoxidized natural rubber polymer electrolytes. *Ionics, 20*, 189-199.