Effect of Metal Salts on Ionic Conductivity of Waste Cooking Oil Based Polyurethane Solid Polymer Electrolyte

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Abstract. The constant quest for green material to replace petroleum leads to utilization of waste cooking oil (WCO) as sustainable raw material to prepare polyurethane solid polymer electrolyte (SPE). In this study, pre-treated WCO was converted into polyol via epoxidation and hydroxylation reaction which aimed to introduce hydroxyl group on double bonds of free fatty acids in WCO. Then, WCO-based polyol was combined with 4,4-diphenylmethane diisocyanate to produce polyurethane (PU) as polymer host and 30 wt% metal salt was added to obtain SPE. Three types of metal salts were chosen to be incorporated in the SPE; lithium chloride (LiCl), lithium perchlorate (LiClO3) and sodium chloride (NaCl). The SPE films were prepared using solvent casting method and characterized using Fourier transform infrared (FTIR) spectroscopy, electrochemical impedance spectroscopy (EIS), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). FTIR spectra showed the presence of urethane linkage to verify that polyurethane has been successfully synthesized. EIS revealed the highest ionic conductivity value achieved at 3.02 x 10^-5 S/cm for SPE with 30 wt% LiCl. The results showed the significance of metal salts cation and anion size on performance of SPE.

1. Introduction
In 1970s, Peter Wright and Michael Armand introduced the first new class of solid ionic conductors that led to the development of solid polymer electrolyte (SPE). SPE defined as solid ion conductors formed by dissolving salt in high molecular weight polymer [1]. SPE had gained substantial attention due to their advantages over liquid electrolyte especially in terms of thermal and mechanical stability as well as safety. These advantages make SPE widely applied in electrochemical devices such as batteries, fuel cells, solar cells supercapacitors and chemical sensors [2].

Polyurethane (PU) is one of the promising polymer host used in SPE. PU is a block copolymer that contains soft and hard segments made up of isocyanate and polyol. The soft segment will act as solvent to solvate cations while the hard segment give the mechanical stability to the PU structure [1,3]. Polyol is a polyether or polyester compound containing many hydroxyl groups. Polyol is conventionally prepared from petroleum. Due to constant increase in price and depletion in supply, preparation of polyols from vegetable oils has been the subject of many studies as a greener and more sustainable option. Castor oil, palm oil, soybean oil and rapeseed oil are the examples of vegetable oil that had been used [4-6].

Recently, the vegetable oil has been replaced with waste cooking oil (WCO) as raw material for polyurethane because it is cheaper and has organic structure almost similar to vegetable oil and contains
high free fatty acid content [7]. However, studies on WCO-based PU as ion conductive solid are still very limited [8-10].

In this study, epoxidation and hydroxylation processes was used to synthesize WCO based polyol and reacted with 4,4-diphenylmethane diisocyanate (MDI) to form polyurethane and 30 wt% metal salts was added. Three types of metal salts; lithium chloride (LiCl), lithium perchlorate (LiClO₃) and sodium chloride (NaCl), chosen as charge carriers and their effect on ionic conductivity of WCO-based polyurethane SPE was observed.

2. Experimental

2.1. Collection and pre-treatment of waste cooking oil

Waste cooking oil (WCO) sample was collected from a restaurant located at Bandar Pusat Jengka, Pahang. Pre-treatment of WCO was carried out to remove food particles and water. The pre-treatment process involved filtration followed by heating for two hours at 95-125°C [7]. The sample was characterized using FTIR spectroscopy.

2.2. Synthesis of waste cooking oil based polyol

WCO based polyol was synthesized using one-pot epoxidation and hydroxylation reaction. 40 g of pretreated WCO and 5 g of formic acid were stirred in a three-necked round bottom flask equipped with a thermometer, magnetic stirrer bar and water condenser. Then, the flask was immersed in ice bath to reduce temperature to 10 °C - 15 °C and 80 g of 35% hydrogen peroxide was added drop wise with continuous stirring. Next, temperature was raised to 50 °C and reaction was continued for 5 hours and the mixture was then allowed to cool down to room temperature. Afterwards, 50 ml of distilled water was added followed by 5 ml of 11.6 M concentrated HCl. Temperature of the mixture increased gradually to 80 °C and reaction was continued for another 5 hr before allowing it to cool down at room temperature. Then, the product obtained was extracted in petroleum ether and the ether layer was washed away with aqueous sodium carbonate, followed by distilled water and sodium chloride solution. Finally, the ether was removed over rotary evaporator at 80 °C to obtain the WCO-based polyol. The polyol obtained was characterized using FTIR to confirm the formation of hydroxyl groups [4].

2.3. Production of polyurethane solid polymer electrolyte

In this study, the solution casting method was used to prepare SPE. Initially, waste cooking oil based polyol, 2,4-MDI, ethylene carbonate (EC) as plasticizer and metal salts were separately dissolved in acetone at room temperature. Then, MDI was added into polyol drop-wise followed by appropriate amount of metal salt and EC. WCO-based polyol to MDI ratio of 20:80 (NCO: OH) was used in this study. The mixture was stirred for more than an hour until homogenization and then it was casted onto a petri dish. The solvent was slowly evaporated in a fume hood at room temperature for 24 h [3]. The compositions of the SPE films prepared are shown in Table 1. The film produced were observed using FTIR, TGA, EIS and DSC.

| Sample     | MDI | Polyol | LiClO₃ | LiCl | NaCl | EC |
|------------|-----|--------|--------|------|------|----|
| PU-SPE 1   | 20  | 80     | 30%    | 0    | 0    | 10%|
| PU-SPE 2   | 20  | 80     | 0      | 30%  | 0    | 10%|
| PU-SPE 3   | 20  | 80     | 0      | 0    | 30%  | 10%|

2.4. Characterizations

FTIR spectra were recorded using Spectrum 100, Perkin Elmer, in the range of 450-4000 cm⁻¹. Thermal stability was analyzed using Netzsch DSC model 214 Polyma with heating temperature from 20 °C to 250 °C at scanning rate of 10 °C /min under nitrogen atmosphere. Approximately 3 mg of the film samples were used for each measurement. The T₆ of the sample was taken at mid-point of the endothermic peak using STARE software. The crystallinity of the sample was determined by using XRD model D-5000 Siemen. The data was collected for diffraction angle 2θ ranging from 5 to 60° at the rate
of 0.04 s\(^{-1}\). The ionic conductivity was analyzed by EIS equipped with high frequency resonance analyzer (HFRA; Solartron 1260, Schlumberger), with applied frequencies ranging from 1 MHz to 0.1 Hz at the voltage of 1000 mV. The measurement was taken at room temperature using 1 cm\(^2\) of SPE film sample that was sandwiched between two stainless steel block electrodes.

3. Results and Discussion

3.1. Waste cooking oil based polyol

FTIR spectra in Figure 1 shows the presence of hydroxyl (O-H) stretching peak at 3482.99 cm\(^{-1}\). The presence of hydroxyl group indicated the successful formation of the polyester polyol in the WCO-based polyol using epoxidation and hydroxylation reaction. In addition, the carbonyl group (C=O) was observed at 1742.71 cm\(^{-1}\) confirmed the presence of ester group in the WCO-based polyol.

![Figure 1 FTIR spectra of waste cooking oil and waste cooking oil based polyol](image)

3.2. Waste cooking oil based polyurethane solid polymer electrolyte

Using WCO-based polyol, polyurethane solid polymer electrolyte (PU SPE) film was synthesized by incorporating three different types of metal salts. Ethylene carbonate (EC) as plasticizer was added to enhance the ionic conductivity of the polymer electrolytes [11].

Figure 2 presents the FTIR spectra of PU SPE with different type of metal salts. The FTIR analysis was conducted to observe the coordination and the interaction of the metal salts with polyurethane structure [1]. The peaks at ~1511 and ~3350 cm\(^{-1}\) refer to N-H vibration (-NH-C=O-) and the peaks at area ~1740 cm\(^{-1}\) confirm the presence of carbonyl group ester (C=O). The presence of the amine and carbonyl peaks indicates the conversion of monomers to urethane [12]. The band of C=O is shifted to lower wavenumber from 1741.53 to 1740.19 cm\(^{-1}\) at the time of addition of lithium and sodium chloride salts. It is due to the coordination of lithium and sodium ions with the carbonyl oxygen atoms and indicates the strong intermolecular interaction between the ions and electron donor atoms in the polymer matrix [12]. The effect observed for lithium salts is related with their anion structure. The anion size for perchlorate (ClO\(_4\)^-) ion is bigger than chloride (Cl\(^-\)) ion. Previous study shows that the LiClO\(_4\) have much
stronger interaction compared to LiCl and the salts with large size anions had low lattice energies and require less solvation [13].

![Figure 2 FTIR spectra of waste cooking oil-based polyurethane solid polymer electrolyte](image)

In this study, the thermal stability is affected by the addition of cation and anion metal salts. Figure 3 shows the thermogravimetric curves for PU SPE with different type of metal salts. The thermal degradation stages (Td) of PU SPE containing ethylene carbonate (EC) and different type of metal salts were observed at four temperature regions; 25-110 °C, 150-230 °C, 240-370 °C and 370-520 °C. Table 2 lists the degradation temperatures and the percentage of weight loss. From the diagrams, it was observed that PU SPE with lithium perchlorate (LiClO₄) salt started the thermal degradation first at temperature of 25.74°C followed by PU-SPE with lithium chloride (LiCl) and sodium chloride (NaCl). The analysis shows the degradation of soft segments and hard segments. From the table, Td₁ indicate the degradation of soft segment and water at temperature range 25-110°C. At Td₂, the degradation of the hard segment of the urethane linkages occurred. The third step of the thermal degradation, Td₃, refer to the release of free isocyanate and last step of thermal degradation, Td₄, referred to breakage of the ester linkages [13].

| Sample      | Percentage of Weight Loss (wt. %) |
|-------------|-----------------------------------|
|             | Td₁ 25-110°C | Td₂ 150-230°C | Td₃ 240-370°C | Td₄ 370-520°C |
| PU-SPE LiClO₄ | 11.6          | 14.5           | 20.0           | 54.5           |
| PU-SPE LiCl  | 9.9           | 21.2           | 26.1           | 70.3           |
| PU-SPE NaCl  | 6.4           | 13.6           | 25.9           | 50.7           |
Figure 3 Thermogravimetric curves of waste cooking oil-based polyurethane solid polymer electrolyte

The ionic conductivity was calculated by using the formula of \( \sigma = \frac{l}{R_bA} \), where \( l \) is the thickness of the film, \( A \) is the surface area and \( R_b \) is bulk resistance value that can be observed from the intercept of the impedance plot. Table 3 shows the ionic conductivity value based on different types of metal salts. The higher the concentration of the salt, the higher the ionic conductivity [3]. In this study, 30 wt. % of salt was used in order to achieve higher ionic conductivity value. It can be seen in Table 3 that PU-LiCl has the highest ionic conductivity followed by PU-LiClO_4 and PU-NaCl. An increase in the ionic conductivity is due to the interaction between the ions with the chemical group in the PU chains. PU-LiCl has the highest conductivity because of the dissociation of the salt in the polymer matrix. The Li^+ and Cl^- moved through the polymer matrix that created a flow of charges, with the help of the PU segments. The free mobile ions present in the polymer may increase the amorphous structure of the polymer host; making migration of ion easier [3]. Compared to PU-NaCl, the conductivity for PU-LiCl is greater because of the size of cations. Lithium ions have smaller size of cation as compared to sodium ion. Smaller cations have higher conductivity because of the greater mobility of the cation [12].

Table 3 Ionic conductivity value of PU-SPE with different type of metal salts

| Sample   | Ionic conductivity value (S/cm) |
|----------|-------------------------------|
| PU-LiCl  | 3.02×10^{-5}                 |
| PU-LiClO_4 | 9.00×10^{-7}               |
| PU-NaCl  | 2.34×10^{-8}                 |

Differential scanning calorimetry (DSC) analysis was carried out to determine the glass transition temperature of the synthesized polyurethane and polymer electrolytes. The glass transition temperature \( T_g \) gave information about the polymer chain dynamics and it plays a vital role in ionic conduction [14]. The DSC analysis can be related with the EIS analysis. Table 4 shows the value of the \( T_g \) for PU SPE with each type of metal salts. In the amorphous phase of SPE, the cation conduction is supported by the polymer segmental chain motion, while the anion moves in the created free space [14]. Based on
the results, PU-LiClO$_4$ gave higher $T_g$ value as compared to PU-LiCl followed by PU-NaCl. An electrolyte with low $T_g$ indicate fast ionic conduction [12]. Therefore, between PU-LiCl and PU-NaCl electrolytes, the ionic conductivity of PU-LiCl is higher than PU-NaCl. In PU-LiCl and PU-LiClO$_4$ electrolyte, the $T_g$ recorded explained the isolation of hydrogen bonds in the urethane soft segment which may contribute to the segmental motion of the polymer. The lithium cations were present as free ions and may act as transient crosslinkers between polyurethane chains segment by the coordinated interaction between ester oxygen and lithium cations, resulting in increase in $T_g$ [3].

| Table 4 Glass transition temperature ($T_g$) for PU-LiCl, PU-LiClO$_4$ and PU-NaCl |
|---------------------------------|---------------------------------|
| Sample                         | Glass transition temperature (°C) |
| PU-LiCl                        | 157.4                           |
| PU-LiClO$_4$                   | 164.2                           |
| PU-NaCl                        | 148.3                           |

4. Conclusions
In this study, the waste cooking oil-based polyol was successfully synthesized by one-pot epoxidation and hydroxylation process. By using the polyol, polyurethane (PU) film for solid polymer electrolyte (SPE) was successfully synthesized by solution casting method. Three kinds of metal salts with different cation and anion size were used to prepare the polyurethane-solid polymer electrolyte (PU-SPE). The metal salts are lithium perchlorate (LiClO$_4$), lithium chloride (LiCl) and sodium chloride (NaCl). From the analysis and chemical reaction, it can be concluded that the structure of the cation and anion of the metal salts affect the chemical interaction, thermal stability and ionic conductivity of the PU electrolytes. It was related with the ability of the cation and anion dissociation of metal salts in the PU as well as the interaction capability between the ion and the PU segments. The FTIR analysis proved the occurrence of chemical interaction between segmented PU and lithium ion as well as sodium ion to form a coordinate bond and subsequently forming polymer-salt complexes. EIS reveals the highest ionic conductivity value achieved at 3.02 x 10$^{-5}$ S/cm for SPE with LiCl. These results indicated that the waste cooking oil-based PU posed potential for the application as host in polymer electrolytes.

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References
[1] Mustapa, S R, Aung M M, Ahmad A, Mansor A and Khoon L T 2016 Electrochimica Acta 222 293
[2] Wong C S, Badri K H, Ataollahi N, Law K P, Su M S and Hassan N I 2014 International Journal of Chemical and Molecular Engineering 8 1168–75
[3] Daud, F N, Ahmad, A and Badri, K H 2014 International Journal of Polymer Science 1-5
[4] Akintayo, C O, Akintayo, E T, Thomas Z and Babalola, B M 2013 3 984–993
[5] Ali, A, Yusoh, K and Hasany, S F 2014 Journal of Nanomaterials 2014
[6] Sun, L J, Yao, C, Zheng, H F and Lin, J 2012 Chinese Chemical Letters 23 919-922
[7] Ferraro L G, Alvarenga F B S, Gelfuso M V and Thomazini D 2014 Materials Science Forum 775 351-356.
[8] W Salleh, SM Tahir, NS Mohamed Polymer Bulletin 75 (1), 109-120
[9] Enderus N F and Tahir S M 2017 IOP Conference Series: Materials Science and Engineering 271 012062
[10] Huzaizi R M, Tahir S M and Mahbhor K M 2017 AIP Conference Proceedings 1901 090002
[11] Su‘ait, M S, Ahmad, A, Badri, K H, Mohamed, N S, Rahman, M Y A, Ricardo, C L A and Scardi, P 2014 International Journal of Hydrogen Energy 39 3005-3017
[12] Ibrahim, S, Ahmad, A and Mohamed, N S 2015 Polymers 7 747-759
[13] Wang, S and Min, K 2010 Polymer 51 2621-2628
[14] Boschin, A and Johansson, P 2015 Electrochimica Acta 175 124-133