

Effect of Sorbitol Addition to Polymer Solid Electrolytes based on Chitosan

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Solid Polymer Electrolyte (SPE) has great potential in replacing liquid electrolytes. The SPE has many advantages such as high thermal stability, good flexibility, and non-flammable. One of the polymers that can be used is chitosan biopolymer from shrimp skin extraction. Generally, polymers are isolators and have low ionic conductivity, so that modification to the structure of chitosan is needed to increase the ionic conductivity. One way to modify the chitosan structure is by plasticizer addition. In this study the addition of sorbitol plasticizer was carried out with a variation between 0, 20, 40, 60 and 80 (in weight percent) which is called as CA for pure chitosan, CA1, CA2, CA3, CA4 and CA5 respectively. The synthesis of chitosan electrolyte film was prepared by casting method. Then qualitative and quantitative analysis was carried out by using X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS), and mechanical properties. Optimal composition was obtained by 40% (in weight percent) sorbitol addition with a conductivity of $3.74 \times 10^{-5} \text{ S.cm}^{-1}$. XRD measurement shows more amorphous polymers with more sorbitol addition. The sorbitol addition also increases the tensile strength, elongation and Young modulus of film flexibility become 52.3%, and 158.3MPa and 19.8MPa, respectively.

Introduction

Portable technology is dominated by the use of lithium-ion (Li-ion) batteries as energy storage. Li-ions battery can be used repeatedly by recharging process, it has a high energy density, and slowly discharging lost when the device is not used [1]. In these decades, electrolytes are dominated by liquid electrolytes which solution is composed by LiPF_6 dissolved with organic solvents such EC, DMC, and EMC [2]. The problems occur in flammable organic solvents [3]. LiPF_6 also has a low thermal stability below 90°C [4]. When electrochemical reactions are not controlled, the heat in the battery cell will increase continuously and LiPF_6 will produce PF_5 gas which is toxic and flammable. So that the safer and non-toxic materials it will be needed to replace the liquid electrolyte.

Solid Polymer Electrolyte (SPE) is one alternative material that can be used as solid electrolyte in Li-ion battery. SPE has been widely researched and has several advantages, such as: easy to form, good mechanical properties, high cation mobility and also environmentally friendly. In addition, SPE in the battery cell also can act as separator that separate the two electrodes electronically to prevent short-circuit. Chitosan as natural polymer is an appropriate material for SPE, because it is a biodegradable polymer that isolated from crustacean waste and has low price.

However, the ionic conductivity in SPE is still low at room temperature. A simple way to increase the SPE ionic conductivity is by dissolving salt ions and plasticizers.

Many researchers [5-8] have conducted the researches to obtain the high conductivity, amorphous and flexible SPE by salt and plasticizer addition. Especially for chitosan, there are many works have been done to fulfill the requirement as good SPE [9-13].

Based on the previous work, in this research it was used lithium triflate salt as lithium ions source, because this lithium salt is relatively easy to dissociate [14]. The plasticizer used for biopolymers is organic material which has low molecular weight and non-volatile like glycerol, sorbitol and others [15]. Those materials are expected to increase their conductivity without affecting the stability of the polymer [16]. In this research, the sorbitol was chosen as a plasticizer with variations concentration (in weight percent) of 20 to 80 of the chitosan weight.

Experimental

Materials used in this research are chitosan powder (Biotech, Surindo), LiCF_3SO_3 (Aldrich, 99%), sorbitol (Aldrich, 98%), and acetic acid (Merck). The chitosan powder of 2.5 grams was dissolved with 125mL acetic acid and stirred for up to 4 hours called as CA sample. The lithium salt, LiCF_3SO_3 was added to the chitosan solution (in weight percent) as much as 40 which is called as CA1 sample. Furthermore, sorbitol was added with a variation (in a weight percent) of 20, 40, 60 and 80 was noted as CA2, CA3, CA4 and CA5 samples, respectively. The mixture then was stirred until a homogeneous solution formed. The final process, the solution was casted in a petri dish and left at the room temperature until a film formed.

X-ray diffraction measurement was carried out at room temperature using Shimadzu XD-610 with Cu-K α radiation ($\lambda = 1.5418\text{\AA}$), 2θ from 5° to 60° and scan speed of 3° per minute. The impedance measurement is done using HIOKI LCR Hi-Tester Model 3532, Japan. The film was placed between the two electrodes and measured with a range of frequencies from 42Hz to 5MHz. The mechanical properties of electrolyte films were also tested using Universal Testing Machine (UTM) Stograph VGS S-E Toyoseiki based on ASTM D-1822L.

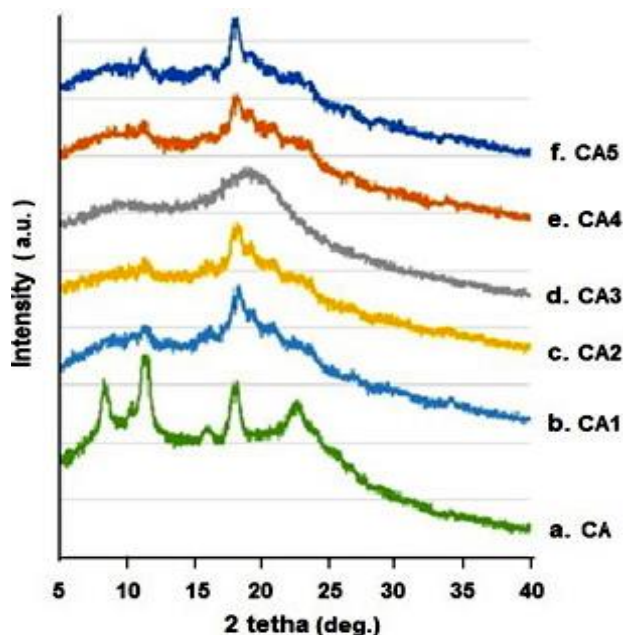


Fig. 1. XRD pattern of (a). Chitosan (CA), (b). Chitosan+ LiCF $_3$ SO $_3$ (CA1), (c). Chitosan+ 20% LiCF $_3$ SO $_3$ (CA2), (d). Chitosan+ 40% LiCF $_3$ SO $_3$ (CA3), (e). Chitosan+ 60% LiCF $_3$ SO $_3$ (CA4), (f). Chitosan+ 80% LiCF $_3$ SO $_3$ (CA5) samples diffraction pattern of the Nd $_{2-x}$ Fe $_x$ O $_3$ samples ($x = 0.5; 1.0$ and 1.2).

Results and discussion

The XRD patterns of the samples were shown in Fig. 1. The XRD patterns show that the addition of lithium salt, LiCF $_3$ SO $_3$ and plasticizers affected the crystallinity of the samples. Based on Fig. 1, the XRD pattern of chitosan (CA) has four sharp peaks at $2\theta = 8.19^\circ, 11.37^\circ, 18.09^\circ$ and 22.74° (Fig. 1(a)). The addition of 20% lithium salt, LiCF $_3$ SO $_3$ (CA1), the XRD peaks only showed two peaks at $2\theta = 11.37^\circ$ and 18.09° , while $2\theta = 8.19^\circ$ and 22.74° was absent and the peak intensity decreased significantly as shown in Fig. 1(b). This condition was the same with XRD pattern in CA2 sample for 20% sorbitol addition as described in Fig. 1(c). The addition of 40% sorbitol (CA3), the XRD pattern was no longer sharp. The peak at $2\theta = 11.37^\circ$ was not visible and the peak at $2\theta = 18.09^\circ$ shifted to $2\theta \approx 20^\circ$. This unsharp and broader peak represents that the particles consisted of a smaller crystallite [15] and for SPE, the broader peak shows that the polymer matrix becomes more amorphous. This composition shows that the addition of sorbitol interfered the interactions of

polymer chains. Consequently, the interaction between molecules inside the materials was also interfered. Furthermore, with the addition of sorbitol concentration to 60% and 80% in CA4 and CA5 samples, respectively, the re-crystallization occurs. This condition is indicated by the appearance of more sharp peaks at $2\theta = 11.37^\circ$ and 18.09° , as shown in Fig. 1(e) and Fig. 1(f).

The narrow and sharp peak indicates the crystallite size [17] become larger, and it means the change in the amorphous chain to become neatly arranged to form lamellae again. This is supported by Rodriguez, *et. al.*, [15] and Casariego, *et. al.*, [18] researches. They assumed that the antiplasticizer effect on saturated sorbitol concentrations could support the rearrangement of the carbohydrate chain in the polymer matrix structure. This occurs because there is a decrease in force against different molecules (adhesion) and a stronger force inter sorbitol molecules (cohesion).

For polymer electrolyte samples, there are relationship between microstructure properties shown in XRD patterns with the conductivity measurement. The more amorphous the sample, the higher conductivity is obtained [19-21].

In Fig. 2 is shown impedance plot of polymer electrolyte chitosan-LiCF $_3$ SO $_3$ -sorbitol with different composition.

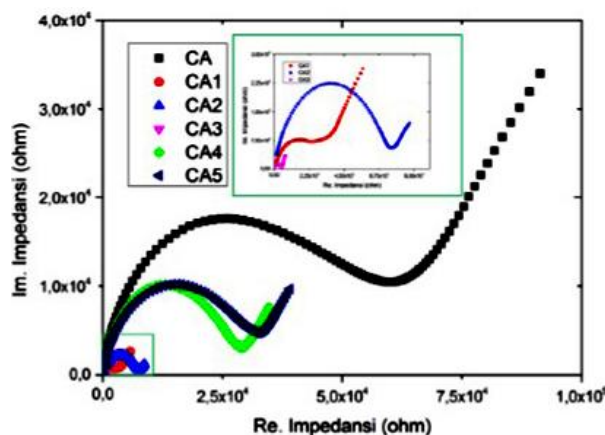


Fig. 2. Cole-Cole plot of chitosan-LiCF $_3$ SO $_3$ -sorbitol

The R_b value is determined by the intersection of semicircle with real impedance (Z_{real}) axis or x axis. The DC conductivity (σ_{DC}) is calculated by using Equation 1.

$$\sigma = \frac{l}{R_b A} \quad (1)$$

where l is the film thickness, A is contact area of electrolyte film with electrode, and R_b is the bulk resistance [22]. The conductivity and bulk resistance values of the polymer electrolyte sample are shown in Table 1. The increasing of samples conductivity could be occurred because of two reasons, (1). The increase in ionic carriers and (2). The free volume in the polymer matrix becomes broader so that the ions could move freely. And the plasticizer addition to polymer electrolyte matrix can make those realized [23].

Table 1. Bulk resistance (R_b) and Conductivity (σ)

Sample	(R_b)	(σ_{dc})
CA	8.36E+04	1.05E-07
CA1	4.13E+03	1.90E-06
CA2	7.77E+03	2.27E-06
CA3	3.28E+02	3.74E-05
CA4	3.14E+04	4.81E-07
CA5	3.30E+04	4.04E-07

AC conductivity is conductivity that is affected by frequency, and this follows Jonscher's law in Equation 2.

$$\sigma(\omega) = \sigma_{DC} + A\omega^n \quad (2)$$

where σ_{DC} is DC conductivity, A is AC conductivity parameter, ω is angular frequency ($2\pi f$), and n is Power Law exponent.

Fig. 3 shows the result of conductivity measurements against frequency for each sample at room temperature. The complex conductivity is DC conductivity which has no effect to frequency increase. This occurs at low frequencies and in high frequencies region there is an increase in conductivity as the frequency increases. Conductivity which has no effect on frequency indicates the transfer of the charge carrier.

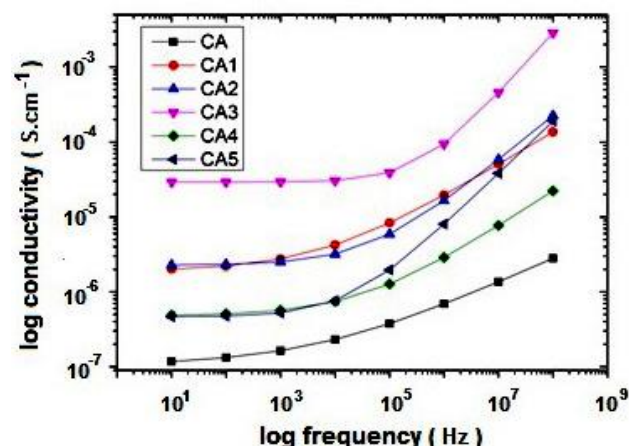


Fig. 3. Curve of conductivity vs frequency resulted.

Conductivity measurement results for CA sample obtained conductivity values of $1.05 \times 10^{-7} \text{ S.cm}^{-1}$. In the CA1 and CA2 samples the conductivity value is not much different which is in the order of $10^{-6} \text{ S.cm}^{-1}$. In CA3 sample, the conductivity value achieved of $3.74 \times 10^{-5} \text{ S.cm}^{-1}$. The polymer film of CA3 sample is the most optimum electrolyte film. This result is corresponding with its XRD measurement stated above The CA3 sample is the most amorphous sample, so that has the highest conductivity value.

The addition of sorbitol can increase the ionic motion space, resulting in conductivity about 2 orders increase. While at high frequencies shows the ion leap conduction mechanism. The hopping rate shows the frequency of plateau region displacement at low frequencies to the dispersion region at high frequencies [24]. **Table 2** is the hopping rate for each sample.

Table 2. Hopping rate for each sample.

Samples	Frequency (Hz)
CA	35.387
CA1	39.732
CA2	288.259
CA3	828.216
CA4	223.132
CA5	72.280

This occurs because of increasing the volume of movement of Li^+ ions. Plasticizer molecules are between polymer chains. The more plasticizer addition, there are more space between the polymer chains. As a result, the working area of the frequency becomes wider so the charge transfer will increase and DC conductivity also increases. Excessive addition of sorbitol causes shrinkage of free space [25]. Therefore, the movement of Li^+ ions becomes inhibited and the hopping rate decreases. It can explain why the conductivity for CA4 and CA5 samples become decrease.

The measurement of tensile strength, elongation, and Young's modulus was used to show the mechanical properties of the SPE produced. **Fig. 4(a)** is a graph of the results of measurements of tensile strength and elongation. Pure chitosan has a tensile strength of 70.56 MPa, while salt added to chitosan the tensile strength decreases to 57.53 MPa. Addition of plasticizer also has a downward trend. The biggest decrease occurred at the concentration of 40% plasticizer having the lowest tensile strength, namely 19.8 MPa. The addition of 60% and 80% plasticizer concentration increases the tensile strength again of 27.49 MPa and 25.03 MPa, respectively. In the elongation chart it can be seen that, the addition of plasticizer concentration causes an increase in the elongation value. Chitosan without salt and plasticizers have elongation of 14.2%. When given salt the film elongation increased to 23.3%. The addition of plasticizer concentration is 40%, 60% and 80% elongation, namely 52.3%, 50.43% and 56.46%. Interesting things are in the composition for CA4 and CA5 samples which are extended along with the increase in tensile strength.

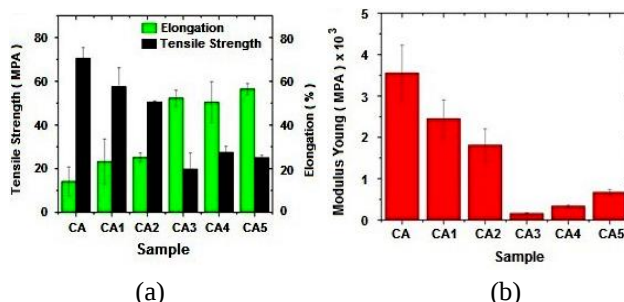


Fig. 4. Mechanical properties for each sample (a). Elongation and Tensile strength (b). Young's Modulus.

There are several stages of changing the elastic shape of the semi-crystalline polymer. The first stages, occurs when withdrawal is an extension of the amorphous part. In the second stage, there was an extension of the amorphous part and stretching of the lamellae in the crystallites. The

occurrence of this stage depends on the combination of the elastic modulus of the amorphous and crystalline parts. Therefore, the elongation and tensile strength which occurred for CA4 and CA5 samples were due to stretching on the crystallites.

Fig. 4(b) shows the modulus value for each sample. Young's modulus measurements are used to determine the level of film stiffness. Large modulus shows a brittle movie. The mechanical tested results (Young's modulus, elongation and tensile strength) indicate that the film CA is the most rigid. Addition of plasticizers can increase flexibility. The addition of plasticizers with 40% sorbitol (CA3) shows films with optimal composition. Due to the addition of sorbitol to the polymer matrix can interfere the polymer chain, so that the interaction of forces between molecules are weakened and increase the ability of polymer chain movements and flexibility [26,16].

Different results were obtained for the addition of sorbitol as much as 60% and 80% in the CA4 and CA5 sample. For those samples the value of tensile strength and film modulus increase. The use of plasticizers has a concentration of limit. This is due to the effect of "antiplasticization". When the concentration used exceeds the limit, the effect given by sorbitol is shrinkage of free space in the polymer matrix [25]. This effect causes disruption in the hydrogen carbohydrate-carbohydrate bond which results in the chains being rearranged, so that interactions between chitosan chains are strengthened [27]. However, the composition of CA4 and CA5 sample has a lower modulus compared to CA and CA2 sample. These results support an increase in elongation and tensile strength in the composition of CA4 and CA5 sample.

Conclusion

The addition of 40% sorbitol plasticizer (for CA3 sample) is the optimal composition. The XRD structure in this composition is a film with the most amorphous structure. The structure changes from semi-crystalline to more amorphous due to the weakening of interaction between polymer chains due to the addition of sorbitol. The ion conductivity in this composition has the highest value of $3.74 \times 10^{-5} \text{ S.cm}^{-1}$, an increase of ~ 2 orders from the film with pure chitosan. This is because the addition of sorbitol gives broader ionic motion space. Thus, ions become easier to move. This composition also has good mechanical properties with tensile strength of 19.8MPa, elongation of 52.3% and modulus Young's of 158.3MPa. This variation composition of the sample shows film more flexible than other compositions.

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Conflicts of interest

Please ensure that a conflict of interest statement is included in your manuscript here. Please note that this statement is required for all

submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

Keywords

Solid polymer electrolyte, chitosan, sorbitol, shrimp skin, LiCF_3SO_3 .

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