The Effects of Monosaccharides on The Physico-Electrochemical Properties of Chitosan Based Solid Polymer Electrolytes (SPEs)

(Kesan Monosakarida terhadap Sifat Fiziko-Elektrokimia bagi Elektrolit Polimer Pepejal Berasaskan Kitosan (SPEs))

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ABSTRACT

Monosaccharides have shown their potential as plasticizers in solid polymer electrolytes (SPEs) due to the presence of numerous hydroxyl (OH) functioning groups. Glucose and fructose were used in this study. The effect of monosaccharides on physico-electrochemical properties of solid polymer electrolytes based on chitosan have been studied. Chitosan-based polymer electrolytes have been successfully plasticized using a solution-casting technique at six different weight percentages (0-30 wt.%). The result shows that 15 wt.% was the highest ionic conductivity achieved by both chitosan-glucose (CG) and chitosan-fructose (CF) systems. Lithium transference number (T_{Li}^{+}) analysis showed that CF had a high number of lithium ions compared to the CG system, with values of 0.26 and 0.14, respectively. In addition, Linear Sweep Voltammetry (LSV) analysis shows that the electrochemical stability for the CG system was 2.98 V compared to 3.20 V for the CF system. This discovery demonstrates that monosaccharides have the potential to be used as plasticizers due to the presence of several oxygen atoms in the structure, which act as a coordination site for cation interaction and can also improve the ion mobility and ionic conductivity of chitosan-based solid polymer electrolytes.

Keywords: Chitosan; ionic conductivity; monosaccharides; plasticizer; polymer electrolyte

ABSTRAK

Monosakarida menunjukkan potensi sebagai bahan pemplastik dalam aplikasi elektrolit polimer pepejal disebabkan oleh kehadiran kumpulan berfungsi hidroksil (OH) yang banyak. Kehadiran kumpulan hidroksil yang mempunyai pasangan elektron terpencil ini mampu bertindak sebagai tapak aktif untuk berinteraksi dengan kation dan dalam kajian ini, glukosa dan fruktosa telah dipilih. Kesan monosakarida sebagai bahan pemplastik berasaskan kitosan terhadap sifat fiziko-elektrokimia telah dikaji. Elektrolit polimer pepejal berasaskan kitosan telah berjaya dihasilkan dengan menggunakan teknik pengacuan larutan dengan menggunakan peratusan monosakarida yang berbeza (0-30 bt. %). Hasil kajian mendapati nilai kekonduksian tertinggi dicapai pada 15 bt. % bagi sistem kitosan-glukosa (CG) dan kitosan-fruktosa (CF). Analisis nombor pengangkutan litium menunjukkan sistem CF mempunyai bilangan ion litium yang tinggi berbanding sistem CG dengan nilai masing-masing 0.26 dan 0.14. Selain itu, analisis LSV menunjukkan elektrolit polimer pepejal berasaskan kitosan ini memberikan kestabilan elektrokimia sehingga 2.98 V bagi sistem CG dan 3.20 V bagi sistem CF. Keputusan kajian yang diperoleh ini menunjukkan monosakarida berpotensi untuk digunakan sebagai bahan pemplastik kerana kehadiran beberapa atom oksigen dalam struktur monosakarida yang bertindak sebagai tapak aktif untuk berinteraksi dengan kation yang seterusnya dapat meningkatkan mobiliti ion dan kekonduksian ion elektrolit polimer pepejal berasaskan kitosan.

Kata kunci: Bahan pemplastik; elektrolit polimer; kekonduksian ion; kitosan; monosakrida

INTRODUCTION

Chitosan has been documented as a host polymer for solid polymer electrolyte (SPE) due to the presence of free amino groups and hydroxyl groups on the polymer backbone, which is important in the process of dissolving inorganic salts within the polymer host (Aziz et al. 2019, 2018; Seng 2018). The reported ionic conductivity of chitosan-salts based SPE is in the range of 10^{-8} - 10^{-4} S/cm (Ali et al.

2005; Fauzi et al. 2014; Sudaryanto et al. 2016). It has been used in a variety of electrochemical applications, including batteries, and the resulting performance is influenced by a variety of factors, including the number of free mobile lithium ions. The battery-based chitosan-LiTFSI film can achieve 50 cycles with a voltage plateau near 3.5 V using a $LiFePO_4$ electrode according to Taib and Idris (2014). They measured a discharge capacity of approximately 160 mAh/g and a lithium transference number of 0.119. Meanwhile, Ding et al. (2019) observed that a composite gel electrolyte (CGE) made by combining bacterial cellulose (BC) and $Li_3xLa_{2/3-x}TiO_3$ nanowires (LLTO NWs) has a higher lithium-ion transference number than Taib and Idris. Their research was able to achieve a discharge capacity of around 160 mAh/g over more than 100 cycles with a lithium transference number of 0.88. The Lithium Transport Number (TN_{Li}^+) is thus critical for the electrochemical performance. The incorporation of plasticizers such as ethylene glycol (EG), ethylene carbonate (EC), propylene carbonate (PC), glycerol, and oleic acid (OA) into chitosan have been reported to increase the lithium transference number (Asnawi et al. 2020; Mishra et al. 2019; Saadiah et al. 2021). A plasticizer is a low molecular weight material that is commonly used as an additive in the polymer industry as it improves the flexibility and processability of the polymers. Its low molecular weight allows it to fill the intermolecular spaces between the polymer chains and reduces the intermolecular forces among the polymers, resulting in decreased rigidity of the polymers three-dimensional structure and enhanced deformation ability, without rupturing the polymer system (Moeini et al. 2021; Vieira et al. 2011).

The incorporation of plasticizer into a polymer system will reduce the crystallinity and increase the amorphous state of the electrolyte, thus increasing the mobility of ions and leading to higher ionic conductivity (Arof et al. 2001). Besides that, the presence of electronegative atoms on the plasticizer can also act as a coordination site for cation interaction, which will further help in increasing ionic conductivity (Rahman et al. 2011). Young-Tae and Eugene (2002) discovered that the use of plasticizer increased the transference numbers of lithium. They show that the electrolyte containing poly (ethylene glycol dimethyl) ether (PG) has a higher lithium transference number (0.516) than the unplasticized electrolyte (0.487). Chitra et al. (2019) also reported that the lithium transference number of an *i*-carrageenan/$LiClO_4$/succinonitrile (SN) system was slightly higher (0.58) than that of an *i*-carrageenan/$LiClO_4$ system (0.56).

In this study, glucose and fructose, well-known monosaccharides that have several oxygen atoms, were selected as plasticizers. Monosaccharides is a water-soluble crystalline compound that contain one or more hydroxyl group and one carbonyl group. There are three types of monosaccharides: glucose, fructose, and galactose. However, only glucose and fructose were used in this investigation since galactose belongs to the same functional group as glucose, which is aldehydes. To the best of our knowledge, no research has been done on the incorporation of monosaccharides as plasticizer in SPE based on chitosan, despite the fact that it meets all of the good criteria to be used as plasticizer. Nur Hani (2018) has reported the use of monosaccharides as a plasticizer in lithium iodide liquid electrolyte systems. She discovered that at room temperature, the system without monosaccharides has an ionic conductivity of 2.38 mS/cm, whereas the system with monosaccharides has an ionic conductivity of 5.94 mS/cm for glucose and 5.55 mS/cm for fructose. This shows that monosaccharides help in the enhancement of ionic conductivity. Zhoa et al. (2013) which studied the limiting molar conductivity for $MnSO_4$-saccharide (D-glucose, D-galactose, and D-fructose)-water solution, reported that the association constant (K_a) value increases with the increase of saccharide molality. These indicated that saccharides could promote the association of $MnSO_4$ in aqueous solutions. Additionally, according to the research done by Liao et al. (2001) and Fuchs and Kaatze (2001), the dielectric constant (ε_r) of glucose and fructose in the water at 25 °C was 74.3 and 74.4, respectively. This is comparable with the ε_r of ethylene carbonate reported by Ralph and Ernesh (1957), which was 80.5. Plasticizer with high ε_r improved salt dissociation that will increase the number of ionic species which in turn enhance the ionic conductivity (Shukur et al. 2019).

According to Yang et al. (2015), moisture has serious destructive aftermath on battery performance as it affects the capacity and cycle life of the battery. Based on research done by Mellor and Naumovski (2016), sugar itself has been preferably used in food preservation due to its ability to limit water activity in food. The addition of a large amount of sugar will withdraw water molecules out of the food cells effectively, thus lowering the food's water activity. Meanwhile, according to studies by Edelman et al. (2015) and Kisiliak and Livney (2017), the hydration number of sugars is essentially influenced by the orientations of hydroxyl groups, where the equatorial hydroxyls are significantly more hydrated than the axial ones. Based on research done by Nur Hani (2018), the hydroxyl groups on carbons 2 and 4 of the glucose

structure are in the equatorial position, while the hydroxyl groups in the fructose structure at C2 are equatorial and hydroxyl group on C4 are axial. However, serious precautions such as the use of glove box and desiccator have been considered throughout the experiments to avoid the formation of moisture.

Thus, in this present work, the effects of the weight percentage of glucose and fructose as plasticizers on the electrochemical properties of chitosan-based solid polymer electrolyte are studied. Although glucose and fructose share the same chemical formula ($C_6H_{12}O_6$), they are different in structural and stereochemical terms, as they have a different type of carbonyl group (aldehyde in glucose and ketone in fructose). Therefore, this research will also determine the effects of carbonyl functional group type on the electrochemical properties of a solid polymer electrolyte based on chitosan.

MATERIALS AND METHODS

MATERIALS

Chitosan powder was obtained from CHITO-CHEM (Malaysia) Sdn Bhd. The degree deacetylation and molecular weight of chitosan powder was 89.25% and 6.12×10^7 g/mol. Other materials used included acetic acid (R&M Chemicals, 99%), D-glucose (Systerm, 99.5%), D-fructose (Systerm, 99%) and Lithium nitrate, $LiNO_3$ (Systerm, 99%).

PREPARATION OF SOLID POLYMER ELECTROLYTE FILM

Plasticized polymer electrolyte based on chitosan was prepared by solution-casting techniques. Initially, the chitosan powder was mixed with a 1% acetic acid solution and stirred for 24 h. The amount of glucose used was varied from 0-30 wt.% and then the solution mixed and stirred continuously for 24 h to obtain a homogenous mixture. After that, 30 wt.% of $LiNO_3$ salt was added into the mixture and stirred for another 24 h. The solution was then poured into a petri dish and left to dry in the fume hood until a solid polymer electrolyte film was formed. The film was peeled carefully from the petri dish and stored in a desiccator for continuous drying. The samples were designated as CGX, where X is the range of glucose concentration. The preparation of the polymer electrolyte film was then repeated with fructose, and the samples were designated as CFX, where X is the range of fructose concentration. The monosaccharides intake procedure was performed in a glove box since it is air sensitive.

CONDUCTIVITY MEASUREMENT OF SOLID POLYMER ELECTROLYTE

Electrochemical Impedance Spectroscopy (EIS) is used to measure the electrochemical properties of solid polymer electrolytes. Here, measurements were conducted using a HIOKI 3532 LCR Hi-Tester that was connected to a computer under a controlled atmosphere. The prepared film was cut into several small discs with a 16 mm diameter. The average thickness was measured using a digital mechanical micrometre. Then, the films were assembled on the holder with stainless steel electrodes under spring pressure. The measurements were made at a frequency ranging from 50 Hz to 5 MHz, with an amplitude of 10 mV at room temperature. The resistance of the polymer electrolyte R_b was then extracted from the impedance spectra using Z-view software. For temperature dependence conductivity, the measurements were conducted at the same frequency, but the temperatures were different, ranging from 30 °C to 110 °C (303 to 383 K). Then the values of polymer specific conductivity (σ) were calculated using the equation below:

$$\sigma = \frac{t}{R_b \, A} \qquad (1)$$

where σ is conductivity; t is the film thickness in cm; R_b is the bulk resistance in unit ohms (Ω); and A is the cross-sectional area in cm^2.

For temperature-dependent conductivity, the activation energy was calculated using the Arrhenius equation. This explains the relationship between direct current conductivity and temperature, as shown in the following equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (2)$$

where σ is pre-exponential factor; E_a is activation energy; k is Boltzmann's constant; and T is temperature in Kelvin (K). The conversion of the above Arrhenius equation into linear form (log σ versus 1000/T) enables the value of activation energy to be obtained from the slope of the plot.

The ionic mobility of cations (μ_+) and anions (μ_-) for electrolyte systems were calculated using equations (3) and (4). In these equations, μ_+ and μ_- represent the relative values of the mobility theory of cations and anions in an aqueous state, while μ represent the sum mobility obtained from the ionic conductivity graph gradient. The value of the diffusion coefficient (D) for cations and anions was then calculated using equation (5),

where k is Boltzmann's constant, T is the temperature (K), Q is the ionic charge, and μ is the ionic mobility value obtained from equations (3) and (4).

$$\mu_+ = \left[\frac{\mu_+ \text{ (aq)}}{\mu_+ + \mu_-}\right] \times \mu \qquad (3)$$

$$\mu_- = \left[\frac{\mu_- \text{ (aq)}}{\mu_+ + \mu_-}\right] \times \mu \qquad (4)$$

$$D = \left[\frac{kT}{Q}\right] \times \mu \qquad (5)$$

DIELECTRIC AND MODULUS ANALYSIS

Dielectric parameters, including the dielectric constant (ε_r), were calculated from EIS impedance data using the following equations:

$$\varepsilon_r = \frac{Z_i}{\omega\, C_0 (Z_r^2 + Z_i^2)} \qquad (6)$$

where Z_i and Z_r are the imaginary and real parts of complex permittivity, respectively, ω is angular frequency (f) in Hertz (Hz) where $\omega = 2\,\pi\,f$. C_0 or free volume capacitance is obtained by following formula:

$$C_0 = \frac{\varepsilon_0 A}{t} \qquad (7)$$

where ε_0 is the free volume permittivity which is 8.854×10^{12} F/m, A is the area of electrolyte and t is the thickness of the sample.

Modulus parameters, consisting of real modulus (M_r) and imaginary modulus (M_i), were calculated from EIS impedance data using the following equations:

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \qquad (8)$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r^2 + \varepsilon_i^2)} \qquad (9)$$

where:

$$\varepsilon_i = \frac{Z_r}{\omega\, C_0 (Z_r^2 + Z_i^2)} \qquad (10)$$

where ε_i are the dielectric loss, that can be obtained from dielectric analysis. The dielectric loss tangent (tan δ) is given by the expression:

$$\tan \delta = \frac{\varepsilon_i}{\varepsilon_r} \qquad (11)$$

The relaxation time (t_r) can be express as:

$$t_r = \frac{1}{\omega} \qquad (12)$$

LITHIUM TRANSFERENCE NUMBER $(T_{Li}{}^+)$

The lithium transference number $(T_{Li}{}^+)$ was measured to evaluate the contribution of lithium ions towards the conductivity of solid polymer electrolyte (SPE), measured by assembling the film with two lithium electrodes (Li/SPE/Li). Chronoamperometry measurement was conducted to determine the values of initial and steady-state current by applying voltage at 10 mV towards the sample. Meanwhile, impedance spectroscopy with a frequency of 1 Hz to 1 MHz was conducted to determine the values of resistance before and after potentiostatic measurement (Ghosh et al. 2010). The formula to calculate the value of $T_{Li}{}^+$ was as follows by applying the Bruce and Vincent method:

$$T_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0((\Delta V - I_{ss} R_{ss})} \qquad (13)$$

where ΔV is applied voltage; I_{ss} is steady-state current; I_0 is initial current; R_0 and R_{ss} are resistance before and after chronoamperometry measurement, respectively.

LINEAR SWEEP VOLTAMMETRY (LSV)

Linear sweep voltammetry (LSV) was used to determine the stability of an electrochemical electrolyte. Each sample was cut to a suitable size and assembled with two stainless steel electrodes (SS/SPE/SS). The LSV measurement was recorded at a scan rate of 0.01 V/s in the potential range of -6V to 6V at room temperature.

X-RAY DIFFRACTION (XRD)

The crystallinity of chitosan based SPE was measured using XRD. The changes of the XRD peak were recorded in Siemen D 5000 Diffractometer with parameters set as radiation Cu-Kα ($\lambda = 1.54060$ Å) towards refraction angle (2θ) range from 3° to 60° at room temperature with the scan rate of 2θ/min.

RESULT AND DISCUSSION

IONIC CONDUCTIVITY

Figure 1 depicts the room temperature ionic conductivity of a polymer electrolyte incorporated with monosaccharides. The slightly increased of ionic conductivity can be observed upon the addition of glucose and fructose compared to chitosan-salt system (0 wt.%). The increase in conductivity demonstrates

that the presence of glucose and fructose weakens the Coulombic force between the cation and anion of $LiNO_3$, thereby encouraging salt dissociation and increasing ionic conductivity. Furthermore, as shown in Table 1, the mobility of anions and cations in solid polymer electrolyte based on chitosan increased with the addition of 15 wt.% monosaccharides. This also suggests that the addition of monosaccharides created a new pathway for ions to move through.

Although the incorporation of monosaccharides can enhance the ionic conductivity of the system, it has been discovered that with the addition of 20 to 30 wt.%, the value of ionic conductivity for CG and CF systems decreased. The increase in weight of the plasticizer will still increases the number of $LiNO_3$ ion that are dissociate in the electrolyte system. This has caused saturation in the system that resulting in less space for free-moving ions to move within the polymer matrix, thus limiting the movement of free ions in the polymer chains which also decrease the ionic conductivity (Azli et al. 2015; Najwi et al. 2018; Rahman et al. 2011; Raphael et al. 2012; Yahya et al. 2003).
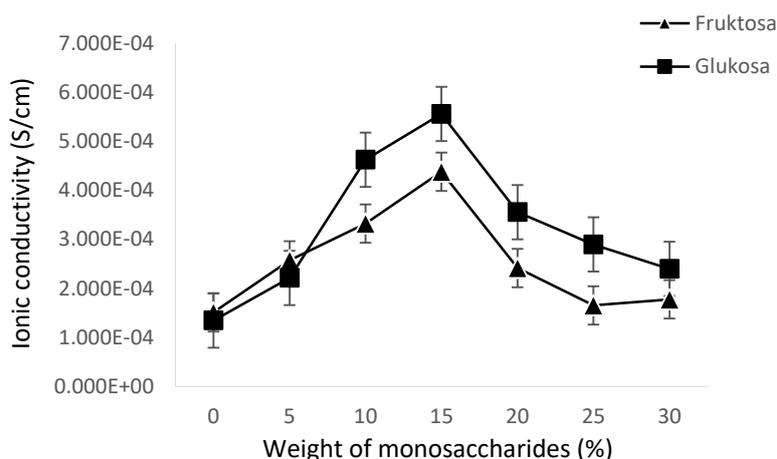
FIGURE 1. The ionic conductivity for CG and CF systems

TABLE 1. Ionic mobility and diffusion coefficient for chitosan-$LiNO_3$ (Chit0), chitosan-glucose (CG) and chitosan-fructose (CF) system

Type of monosaccharides	Ionic mobility ($cm^{-2} V^{-1} s^{-1}$)		Diffusion coefficient ($cm^{-2} s^{-1}$)	
	Cation	Anion	Cation	Anion
Chit0	8.39	1.55	3.45	6.38
CG		1.43	3.13	5.78
CF	4.87	8.98	1.97	3.63

The influence of the functional group on ionic conductivity can be seen at 5 wt.%, as the ionic conductivity achieved by CF was slightly higher than that of CG. The presence of ketone in the fructose structure, which has a high basicity, accounts for this. Strong basicity, according to Dou et al. (2019), aids in the dissociation of salts. This increased the number of charge carriers and improves the ionic conductivity of electrolyte. However, as the weight percentages increased from 10 wt.% up to 15 wt.%, the ionic conductivity of CG was higher than CF. This is due to the fact, that the diffraction peak of CG at 11.7° and 18.1° is not visible in Figure 2, indicating that the crystallinity of the system has decreased. The reduction or loss of diffraction peak proves that the amorphous content of SPEs is increasing. This led to the increased of free space in the system that led to higher conductivity in CG15 system (Azli et al. 2015; Sahli et al. 2017; Yahya & Arof 2003).
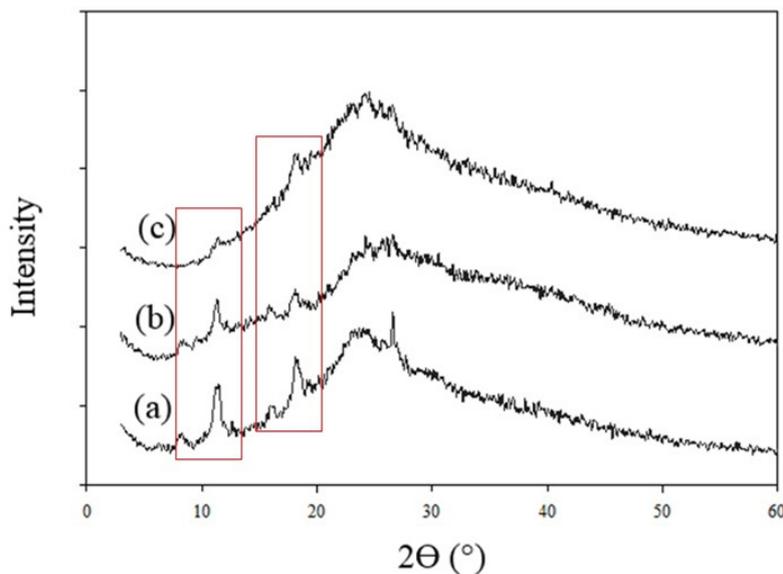
FIGURE 2. XRD pattern of (a) Chit0, (b) CF15, and (c) CG15

DIELECTRIC ANALYSIS

Plots of the dielectric constant (ε_r) and real modulus (M_r) at different frequencies for both type of monosaccharides at room temperatures are shown in Figure 3. Figure 3(a) depicts the frequency dependent real part of dielectric permittivity for both type of plasticizers, and both plots show that ε_r decreases as frequency increases. The increase in ε_r at the lower frequency side was due to the aligned of free charges on the electrode-electrolyte interface, whereas the decrease in ε_r at higher frequency was caused by the ions that were unable to diffuse in the direction of the field (Azli et al. 2015; Najwi et al. 2018; Osman et al. 2011; Raphael et al. 2012; Salman et al. 2018).

Aziz et al. (2018) reported that higher ε_r resulted in a higher number density of carriers and ion mobility, as well as enhanced ionic conductivity. It is also noted that with the addition of glucose and fructose from 5 to 15 wt.%, the value of ε_r increased. The incorporation of both monosaccharides in the polymer systems increased the localization of charge carriers, including Li$^+$ ions. This supported the highest ionic conductivity achieved at these weight percentages for both monosaccharides and demonstrated the salt dissociation abilities of glucose and fructose (Yahya et al. 2003). Besides that, the strong basicity of ketone in the structure of fructose compared to aldehyde in the structure of glucose has directly influenced the dissociation as it can be observed that ε_r for CF15 is higher compared to CG15 systems

with value of 1853752 and 258323. However, as the concentration increase by more than 15 wt.%, the ε_r decreased. This demonstrates that as the concentration of monosaccharides increased, the amounts of free charges decreased. This may be due to the re-association of the dissociated free mobile ions (Pawlicka et al. 2019).

Figure 3(b) shows the frequency dependence of the real part (M_r) of the electric modulus for chitosan-monosaccharides polymer electrolytes. From the modulus spectrum, it is observed that the M_r part for both polymer electrolytes systems increase with an increase in frequency. This is due to the presence of electrode polarization (EP) phenomena at higher frequencies. The presence of an EP has caused ion accumulation to occur, and this has allowed the sample's ability to keep the charge measured. Besides, it can also be observed that at lower frequency regions, both M_r plots reach zero due to the association of capacitance value with electrode polarization. Based on Pawlick et al. (2019) and Tan et al. (2018), the resonance peaks were expected in the high frequency region. However, the peak cannot be observed in this study as the frequency range is beyond the limitations of the equipment.

Figure 4 depicts the effects of monosaccharides weight on loss tangent (tan δ) at room temperature. The maximum peak obtained in these tan δ plots represents the relaxation peaks of the dielectric relaxation process, which can be seen with the addition of the monosaccharides weight. It can be observed that the

(a)

(b)
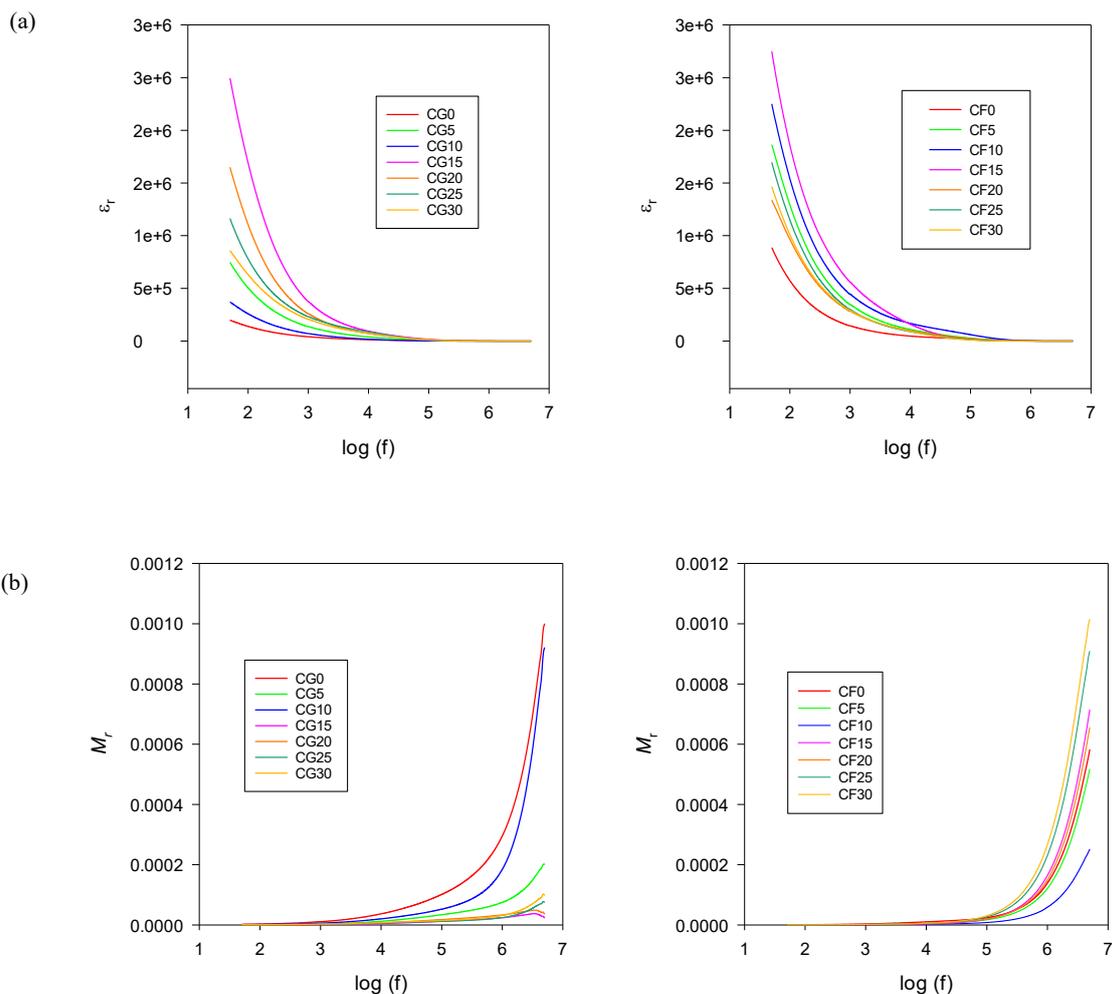
FIGURE 3. Plot of (a) dielectric constant (ε_r) and (b) real modulus (M_r) of CG and
CF systems at room temperature

addition of both monosaccharides into the system has shifted the relaxation peak to a higher frequency. This may be due to the rising proportion of amorphous material and the presence of dipole relaxation (Hadi et al. 2020). Research done by Shukur (2015) observed the appearance of a peak that represented the α peak at a higher frequency, with the β peak at a lower frequency. Here, α and β relaxation are described as mechanisms in the crystalline and amorphous phases, respectively. In Figure 4, it is noticeable that the relaxation peak for both glucose and fructose systems for all concentrations (0-30 wt.%) appeared on the high-frequency side. This shows that there is a possibility that the orientation of polar groups in the backbone of polymers is supported by the XRD data.

When compared to the Chit0 system (5.76 10^{-5} s), the CG and CF systems have lower t_r values of 1.6 10^{-5} and 1.95 10^{-4} s, respectively. According to Ramly et al. (2011), adding plasticizer to the SPE system increases ionic conductivity was contributed by the fast segmental movement of the polymer and the increase in the number of charge carriers, where these two factors led to the decrease in relaxation time. This indicates that the presence of glucose and fructose improves the ionic conductivity of SPE based on chitosan due to increases in the ion mobility value and number of carrier ions.

TEMPERATURE DEPENDENCE IONIC CONDUCTIVITY

Temperature-dependent ionic conductivity was conducted to study the effect of temperature on the mechanism of
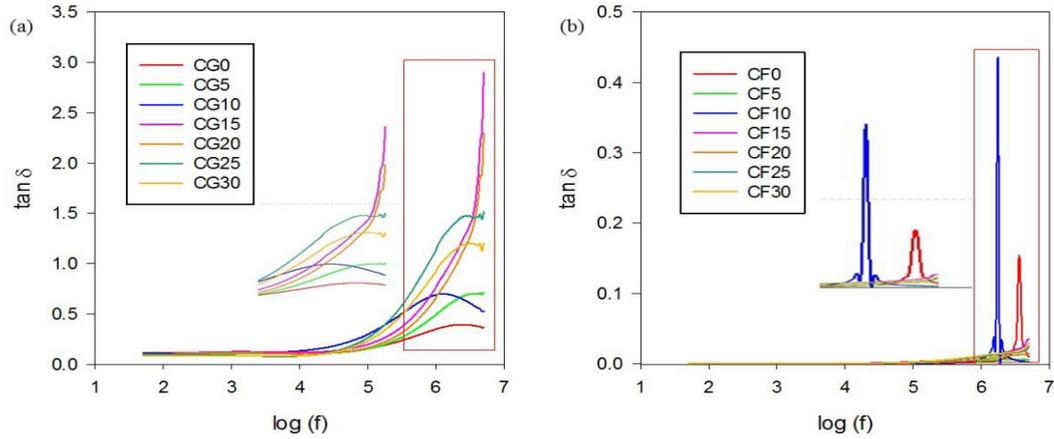
FIGURE 4. Loss tangent (tan δ) at room temperature of (a) CG and (b) CF systems with different weight percentage

ion movement in chitosan based SPEs. The comparisons of conductivity for both monosaccharides, with a temperature range from 303 to 383 K, are shown in Figure 5. The plot showed that the ionic conductivity for both CF15 and CG15 increased as the temperature was increased.

Even though monosaccharides have a proclivity to form new intermolecular associations with water due to the presence of hydroxyl groups, there is no significant change in ionic conductivity as temperature is increased. This situation demonstrated that moisture does not strongly affect ionic conductivity (Wang et al. 2003). The conductivities at highest temperature (383 K) for both the CF15 and CG15 systems were 5.55×10^{-3} and 1.95×10^{-3} S/cm, respectively. The increasing ionic conductivity with increasing temperature can be attributed to an increase in the number of ions and/or an increase in the mobility of the ions.
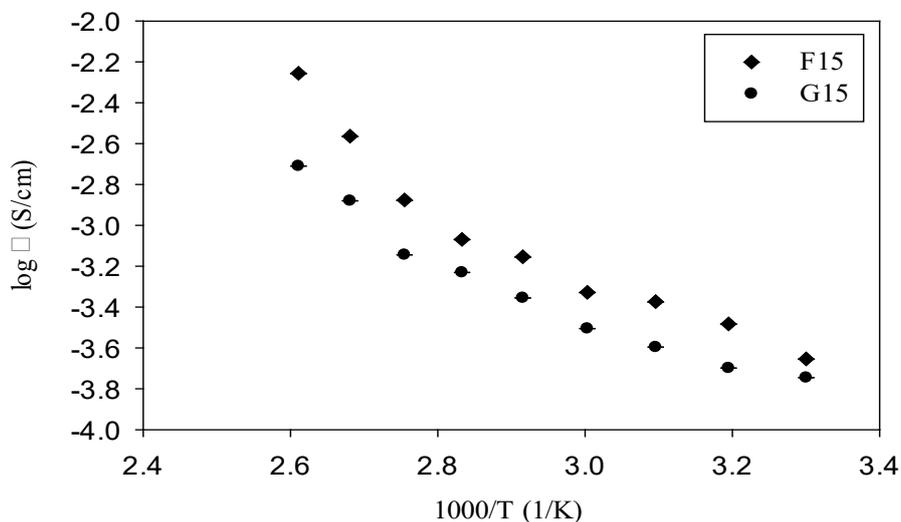
FIGURE 5. The temperature dependence of ionic conductivity for CG15 and CF15 with temperature ranges from 303 K to 383 K

Temperature-dependent conductivity also enables the determination of activation energy (E_a) which can be defined as the minimum energy required to move the ion along the polymer chain and can be obtained from the slope of the plot. Notably, biopolymer electrolytes with lower values of activation energy are necessary for

practical applications (Samsudin & Isa 2014). Based on the calculations, the E_a for CG15 (0.13 eV) was lower than for CF15 (0.16 eV). The lower value of E_a represents how the ion is easier to move along the polymer chain (Francis et al. 2016). Ahmad et al. (2012) also showed that electrolytes with a lower value of E_a lead to rapid ion movement in the system and thus elevated ionic conductivity.

LITHIUM TRANSFERENCE NUMBER (T_{Li}^+)

Table 2 shows the lithium transference number (T_{Li}^+) for Chit0, CG15, and CF15. Based on the calculations of

T_{Li}^+, the values obtained for CG15 and CF15 were 0.14 and 0.26, respectively. This is higher compared to Chit0 with only 0.02. This demonstrated that monosaccharides could improve ion dissociation and capable to act as plasticizers. Meanwhile, T_{Li}^+ data showed that CF15 was higher compared to CG15. This shows that there is more free mobile lithium ion in the CF system. The presence of a high basicity functional group in the fructose system greatly increases the mobility of ions as it helps salts dissociate. This can be proved by the ionic mobility of cations for the CF system being higher than the CG system with 4.87×10^{-1} and 7.75×10^{-1} cm^{-2} V^{-1} s^{-1} (Table 1).

TABLE 2. Lithium transference number (T_{Li}^+) for chitosan-LiNO$_3$ (Chit0), chitosan-glucose (CG15) and chitosan-fructose (CF15)

Samples	T_{Li}^+
Chit0	0.02
CG15	0.14
CF15	0.26

LINEAR SWEEP VOLTAMMETRY (LSV)

The electrochemical stability of the polymer electrolyte system containing 15 wt.% monosaccharides has been studied using the LSV technique and the voltammogram is shown in Figure 6, which focuses on the decomposition voltage. In this work, it can be observed that the decomposition voltage for sample CF15 is around 3.20 V and 2.98 V for CG15. This is due to the number of freely moving ions in the CF15 system, as shown in lithium transference number analysis, causing resistance to the SPEs before decomposition takes place. The value obtained is higher compared to the value of chemical stability achieved for the Chit0

system reported by Mobarak et al. (2015), which only achieves a chemical stability value of 3.00 V except for CG15. Furthermore, Sampathkumar et al. (2019) reported that the decomposition voltage of a polymer electrolyte based on tamarind seed polysaccharide (TPS) doped with lithium perchlorate and plasticized with ethylene carbonate (EC) has a decomposition voltage of 2.98 V, which is lower than the result obtained in this work. Therefore, this indicates that chitosan-based solid polymer electrolyte systems with the addition of monosaccharides, especially fructose, are suitable for use in electrochemical cell applications as the decomposition voltage values produced in this work are higher than the solid electrolyte values ever produced and fabricated.
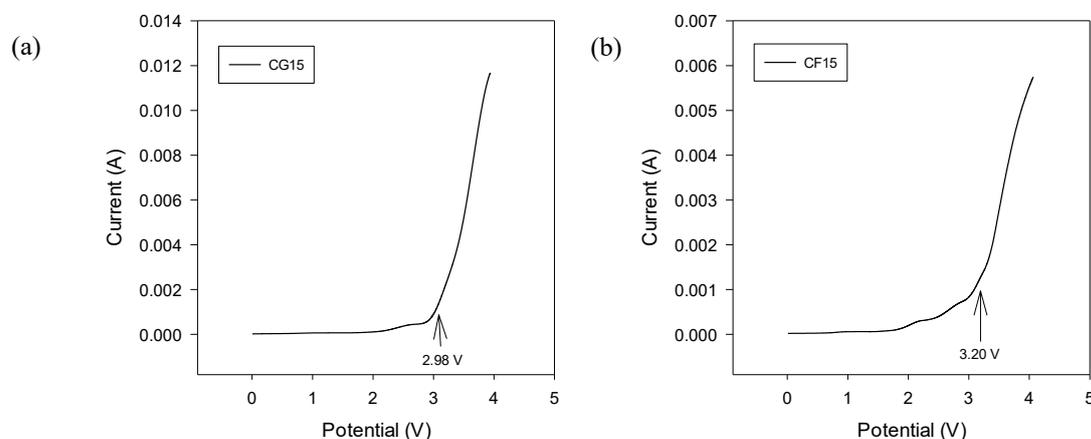
FIGURE 6. LSV voltammogram for (a) CG15 and (b) CG15 system

Conclusion

SPEs based on chitosan and plasticizer with 0-30 wt.% of monosaccharides were successfully prepared by using the solution casting method. The addition of both monosaccharides in electrolyte polymer applications led to an improvement in the ionic conductivity. The incorporation of monosaccharides improved the dielectric properties of the polymer electrolytes, as CG15 and CF15 obtained the highest ε_r. Although the ionic conductivity obtained in this study shows that the CG system is slightly higher than the CF system, the LSV and T_{Li}^+ analysis shows that the effect of the CF system in chitosan based SPE was better than the CG system. The results of the present work prove the ability of monosaccharides to act as alternative plasticizers for solid polymer electrolyte applications.

Acknowledgements

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