

STRUCTURAL, MORPHOLOGICAL AND ELECTRICAL PROPERTIES OF CORN STARCH BASED SOLID POLYMER ELECTROLYTES

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Abstract: Solid polymer electrolytes (SPEs) based on corn starch and various compositions of sodium bisulphite (NaHSO_3) were prepared by a solution casting technique. The Fourier transform infrared spectroscopy (FTIR) spectra results confirmed that there was interaction between corn starch and NaHSO_3 with the presence of peaks. Moreover, XRD studies showed that the structure modification of corn starch has improved based on its amorphous properties. The SEM observations showed that the surface of SPE films had formed a porous and branch morphology. The presence of 5 wt.% NaHSO_3 content within the corn starch matrix can improve the mechanical properties of the films from 0.26 MPa to 2.11 MPa of tensile strength and from 5.7% to 16.1% for elongation at break. Meanwhile, Young's modulus was observed in the range of between 1.6×10^{-2} and 2.6×10^{-2} MPa. The highest ionic conductivity of $2.22 \times 10^{-4} \text{ Scm}^{-1}$ was obtained by the composition ratio of 15 wt.% NaHSO_3 at room temperature. The non-destructive impedance spectroscopy was used to determine the ionic transport parameters in SPE films. The transport properties analysis showed that ionic conductivity is related to diffusion coefficient (D) of mobile ions and its mobility (μ). Results showed that the prepared SPE films have potential to be applied in electrical device applications.

Keywords: Solution casting technique, sodium bisulfite, conductivity, physical analyses.

Introduction

An electrolyte consists of free ions and acts as a medium for transferring ion charges between pairs of electrodes. It can be categorised into a few types, some of them are liquid and solid electrolytes. However, a few obstacles which may limit performance are faced by the liquid electrolytes, for example, difficulty for storage and packaging, highly corrosive between separator and electrodes and cause leakage of harmful solvent (Chong *et al.*, 2018; Misenan & Khiar, 2018). To overcome this problem, solid polymer electrolytes (SPE) was introduced.

Research is mostly focused on solid polymer electrolyte as compared to liquid electrolyte because it is safer since there is no volatile liquid, easier to shape, lightweight and ease of processability (Shukur *et al.*, 2013; Deraman *et al.*, 2013; Babu & Kumar, 2015; Ngai *et al.*, 2016; Hassan & Azimi, 2019). In addition, polymer electrolytes are widely studied due to their various applications in solid state and

electrochemical devices, such as batteries, fuel cells, supercapacitors, electrochromic devices and sensory systems (Ramesh *et al.*, 2010; Buraidah & Arof, 2011; Rama Mohan *et al.*, 2011; Shahrudin & Ahmad, 2016; Aziz *et al.*, 2017). Starch was chosen in this study because it is naturally formed and bonded with many linear amyloses and branched amylopectin with a glycosidic bond (Vernon-Carter *et al.*, 2017). Furthermore, starch is low cost, abundant in nature and a renewable raw material (Teoh *et al.*, 2014; Mohan *et al.*, 2016 & Khan *et al.*, 2017; Fuzlin *et al.*, 2020). So, it is believed that the sources will stay available to be used in a long term. Besides, starch was reported to form mechanically stable films when added with proper ionic dopants. However, starch based SPEs show relatively low ionic conductivity. To improve this challenge, several attempts can be done to enhance conductivity, such as a mixed salt system, blending of polymer (Aziz *et al.*, 2020), plasticising (Isotton *et al.*, 2015) and the addition of ceramic fillers (Klongkan

& Pumchusak, 2015; Sudhakar & Selvakumar, 2012; Misenan *et al.*, 2018).

One of the alternatives that can be done to increase the ionic conductivity of SPEs is by adding the lithium salts into the polymer (Omar & Ahmad, 2016). There are some concerns about the usage of lithium elements in applications for electrochemical devices because the characteristics of raw lithium materials are not safe to the environment and pricey as compared to sodium (Vignooraban *et al.*, 2017; Sundaramahalingam *et al.*, 2018). In this work sodium based-electrolytes were chosen to overcome this challenge. The selection of sodium salts as a dopant was due to its properties such as low toxicity, natural abundance, lightweight and high electrochemical potential (Ahmad *et al.*, 2013 & Othman *et al.*, 2017). It is also possible to be applied in a battery system as it can exhibit chemical properties similar to lithium. The main objective of the present work is to develop a polymer electrolyte system with different ratios of NaHSO₃. Besides, the addition of glycerine in the electrolyte is to improve the film fragility caused by higher intermolecular forces. Therefore, the samples will be characterised using Fourier transform infrared spectroscopy (FTIR), X-Ray diffractometer (XRD), scanning electron microscope (SEM), tensile analyser and electrochemical impedance spectroscopy (EIS) to understand the interactions between the polymer host and dopant salts.

Materials

Experimental

Solid polymer electrolytes were prepared using a solution casting method. The corn starch (Sigma-Aldrich) with linear formula C₆H₁₀O₅, sodium bisulphite (NaHSO₃) was obtained from Aldrich with 96% purity. Then, two different solvents were used, which were distilled water and glycerine with 100% and 96% purity. These aforementioned materials were used as a polymer host, salt and ionic liquid, respectively.

Sample Preparation

1 g of corn starch and different masses of sodium bisulphite (NaHSO₃) were weighed. First, NaHSO₃ was stirred into 0.6 ml of glycerine and 20 ml of distilled water until there was no residue left. Next, the corn starch was stirred in the mixed solution until it turned homogenous at the temperature of 60°C – 70°C. The common method, used to prepare the solid polymer electrolyte (SPE), is called solution casting technique (Hassan *et al.*, 2018; Mejenom *et al.*, 2018). Then, the homogenous solutions were cast into petri dishes and left to dry naturally at room temperature to form electrolyte films. For further drying, the samples were kept in a desiccator that was filled with silica gel. The amount (in weight percentage, wt.%) of sodium bisulphite used is listed in Table 1, which was calculated by using the following equation;

$$wt.\% = \frac{x}{x + y} \times 100 \quad (1)$$

Where, x is the amount of salt in gram (g), y is the amount of corn starch and weight percentage is the varying values in percentage for salt as a dopant. Therefore, the preparation steps are summarised in Figure 1.

Characterization

The physical nature of the SPE films was observed with the naked eyes and recorded by using a mobile camera with 5× magnification and eight MP.

Fourier transform infrared spectroscopy (FTIR) test was used to confirm the interaction between corn starch and NaHSO₃ by using a Thermo Nicolet Avatar 380 FTIR spectrometer. It is attached with a germanium crystal of an attenuated total reflection (ATR) accessory. The SPE films were tested at a resolution of 8 cm⁻¹ within a frequency range of 400 cm⁻¹ to 4000 cm⁻¹ at room temperature. The infrared light was passed through the samples and a graph was plotted.

X - ray diffraction method was used to analyse the amorphous or crystalline nature

Table 1: The various ratios of corn starch and NaHSO₃ powders

Samples	Corn Starch (g)	Ionic Salt (wt.%)	Ionic Salt (g)	Solvents (ml)	
				Distilled Water	Glycerine
Pure	1	0	0	20	0.6
5	1	5	0.053	20	0.6
10	1	10	0.111	20	0.6
15	1	15	0.177	20	0.6
20	1	20	0.250	20	0.6
25	1	25	0.333	20	0.6
30	1	30	0.429	20	0.6
35	1	35	0.538	20	0.6
40	1	40	0.667	20	0.6

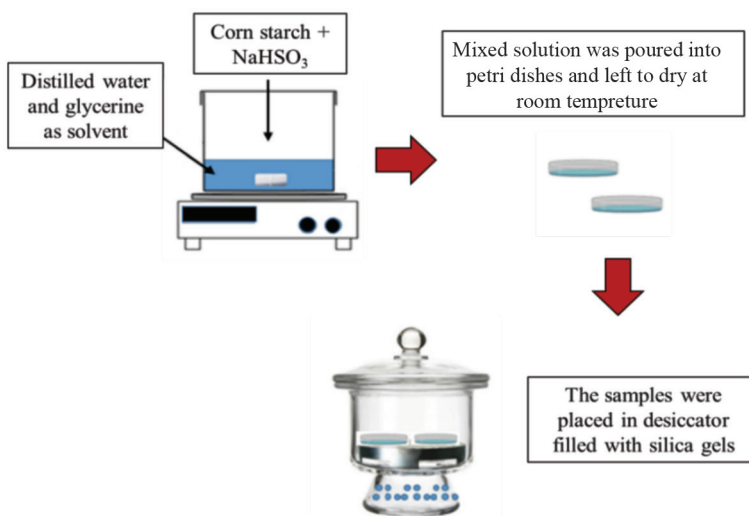


Figure 1: The overall SPE preparation process

of samples. The films used were cut into appropriate size (1.00 cm × 1.00 cm) and placed in the specimen holder. It was performed using a MiniFlex II diffractometer with CuK α radiation in the range of 10° to 80°, with step size of 5°/min of the prepared samples.

The morphology of the prepared samples was studied by using Scanning Electron Microscopy (SEM) at an acceleration potential of 20 kV at room temperature. Images were captured by JEOL JSM-6350LA with ×350, ×750 and ×1000 scanning magnifications. The

samples were placed on specimen tubs with double cellophane and coated prior to further observation.

The mechanical strength of SPE films was examined by using the Shimadzu Ez-500NLX tensile tester machine. The samples were cut into a dimension of 3.00 cm × 1.00 cm and tested at a rate of 10 mm/min. The evaluation of mechanical properties of prepared films was performed by taking the average measurement values.

Electrical Impedance Spectroscopy (EIS) was used to determine electrical properties of the films. Impedance analysis was measured at room temperature by using HIOKI 3532-50 LCR Hi-Tester, which was connected to a computer over a frequency range of 50 Hz to 1 MHz. The samples were cut and sandwiched between two stainless-steel blocking electrodes. The thickness of the films was measured by using a digital micrometer screw gauge. The value of bulk resistance (R_b) was obtained from the plotted graph of the imaginary impedance (Z_i) versus the real impedance (Z_r), known as the Cole-Cole plot as shown in Figure 2. The samples' conductivity was calculated by using Equation 2;

$$\sigma = \frac{l}{R_b A} \quad (2)$$

Where, σ is the ionic conductivity in (Scm^{-1}), l is the thickness of the samples (cm), A is the surface area of the blocking electrodes (cm^2) and R_b is the value of bulk resistance in ohm.

Results and Discussions

The physical nature of SPE films had changed, which corresponded to the additional amount of salt. It can be seen that the SPE films were changed into translucent with the addition of NaHSO_3 (5 wt.%, 15 wt.% and 25 wt.%). Moreover, the changes in film properties may have altered its structure and morphology. Figure 3 shows the selected images of corn starch- NaHSO_3 complex with varying amounts of salt.

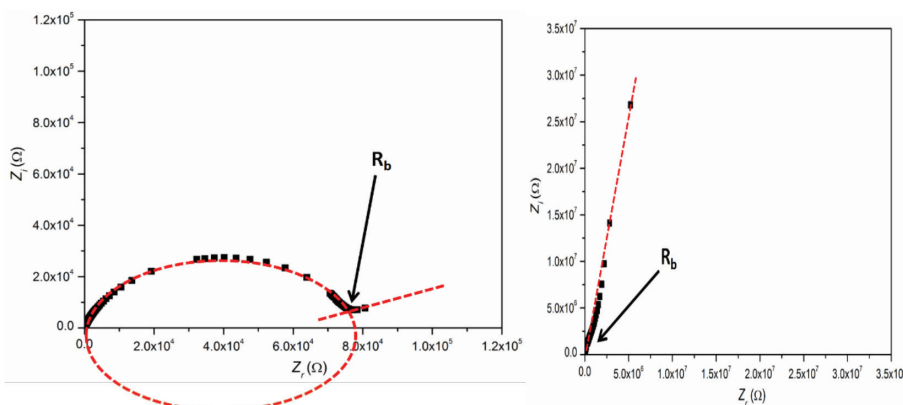


Figure 2: The values of bulk resistance are determined

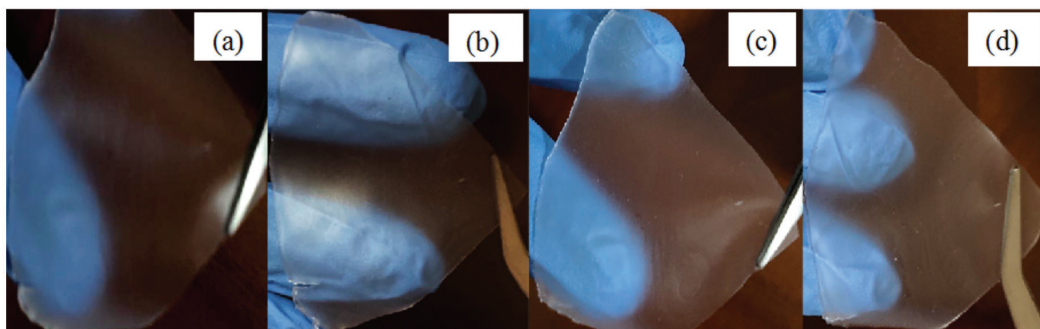


Figure 3: The images of selected corn starch- NaHSO_3 SPE films for (a) corn starch film (b) 5 wt.% of NaHSO_3 , (c) 15 wt.% of NaHSO_3 and (d) 25 wt.% of NaHSO_3

The FTIR spectra were used as a tool to find the nature of functional groups that existed between corn starch and NaHSO_3 through the formation of new peaks. Figure 4 shows that the FTIR spectrum for corn starch, sodium bisulphite and varying ratios of NaHSO_3 salt composition in the SPE films. From Figure 4, the glycosidic linkage band peaks of pure corn starch appeared at 921 cm^{-1} . It was observed that the peak was shifted to 926 cm^{-1} after adding NaHSO_3 to the polymer. This may happen due to the interaction between cation from sodium salt with an oxygen atom in C-O-C group of the polymer host (Shukur, 2015). Besides, according to Shahrudin and Ahmad (2017), the oxygen atom in corn starch has lone pair of electrons located at C-O-C groups. Hence, to prove that the complexation happens between corn starch and Na^+ ions at C-O-C band, it will be analyzed by shifting of wavenumbers. The peaks of corn starch appeared at 1019 cm^{-1} for CO stretching and an -OH band was shown at 1397 cm^{-1} . The absorption peak for corn starch was at 1655 cm^{-1} which was attributed to hydroxyl groups (-OH bending). This was attributed to water existence in the starch molecules. The other peak at 2935 cm^{-1} corresponded to the methyl group (- CH_2 stretching vibration). Meanwhile, the broad absorption of the corn starch at 3306 cm^{-1} indicated the stretching of intermolecular hydrogen bonds of hydroxyl groups (-OH). As

mentioned by Teoh *et al.* (2012), the strong and wide absorption in the hydroxyl region indicated several -OH groups in starch. With the addition of 5 wt.% – 15 wt.% NaHSO_3 , the hydroxyl band was shifted to 3327 cm^{-1} . The shift to a higher value of wavenumber can be caused by the complexation effect (Ramesh *et al.*, 2012). As the salt content increased, more cations were available to interact with the oxygen atom of hydroxyl, and thus increased the ionic conductivity. However, for the sample with 20 wt.% – 40 wt.% of NaHSO_3 content showed that the hydroxyl band peak had shifted to 3336 cm^{-1} , which was significant to the occurrence of ions recombination to form neutral ion pairs. Formation of neutral ion pairs in the electrolyte can decrease the ionic conductivity which results from the reduction in charge carriers in the electrolyte (Mason *et al.*, 2010). The characteristic bands of NaHSO_3 salt disappeared in the spectra of a complex polymer. This might happen due to interruption of the initial order of polymer structure.

From the spectrum of pure NaHSO_3 , absorption peaks at 971 cm^{-1} were assigned as S-O deformation to the NaHSO_3 . Then, the bands appeared at 1059 cm^{-1} and 1148 cm^{-1} as expected belong to SO_3 stretching. While, peak at 3159 cm^{-1} was attributed to -OH stretching. Overall, it can be said that these effects were generally caused by the intermolecular interactions

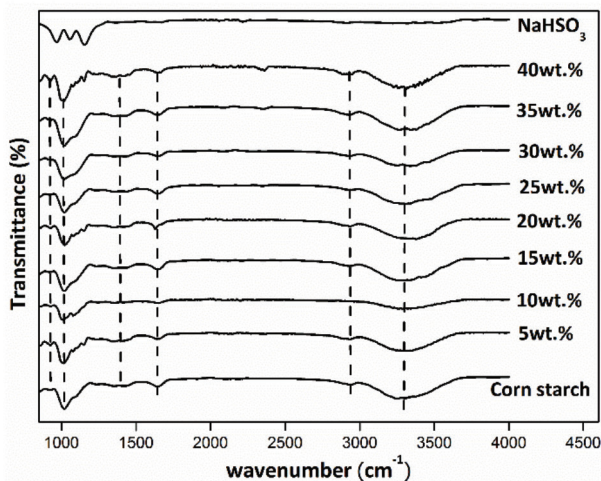


Figure 4: The FTIR spectra of corn starch and corn starch- NaHSO_3 SPE films

between polymer and salt. All corresponding bands are summarised in Table 2.

The structural characteristics of pure corn starch (NaHSO_3) and corn starch ($-\text{NaHSO}_3$) complex system, which were evaluated through X - Ray diffraction method, are shown in Figure 5. It can be noticed that the diffraction pattern for corn starch appeared as a broad peak at 15° to 28° , confirming the non-ordered structure. In other words, the peak of polymers corresponded to the amorphous nature (Hassan *et al.*, 2018).

According to Lian *et al.* (2018), the starch grains were restructured with the addition of glycerine. It can be said that the crystallinity of corn starch was reduced and tended to appear in highly amorphous condition. Then, XRD patterns of NaHSO_3 were visible at peaks of $2\theta = 21.5^\circ, 22.7^\circ, 23.5^\circ, 25.6^\circ, 29.6^\circ, 31.9^\circ, 33.8^\circ, 37.9^\circ, 46.6^\circ, 47.9^\circ$ and 52.9° . The presence of sharp peaks for NaHSO_3 showed the dominance of the crystalline phase in polymer electrolyte (Mohan *et al.*, 2005). According to Hodge *et*

Table 2: The functional groups and references of corn starch- NaHSO_3 films

Sample	Wavenumber (cm^{-1})	Functional Group	References
Corn starch	921	(C-O-C) band regions	Shukur, 2015
	1019	(C-O stretching)	Hassan & Ting, 2018; Ning <i>et al.</i> , 2009
	1397	(-OH bending vibration)	Hassan & Ting, 2018
	1655	Hydroxyl (-OH bending)	Shahrudin & Ahmad, 2016
	2935	Methyl ($-\text{CH}_2$ stretching vibration)	Hassan & Ting, 2018
	3306	Hydroxyl (-OH stretching)	Tang <i>et al.</i> , 2008; Yusof <i>et al.</i> , 2014; Hassan & Ting, 2018
NaHSO_3	971	S-O deformation	Priyanto <i>et al.</i> , 2018
	1059, 1148	(SO_3 stretching)	Sahli & Ali, 2012; Malathi <i>et al.</i> , 2010
	3159	-OH stretching	Mobarak <i>et al.</i> , 2013

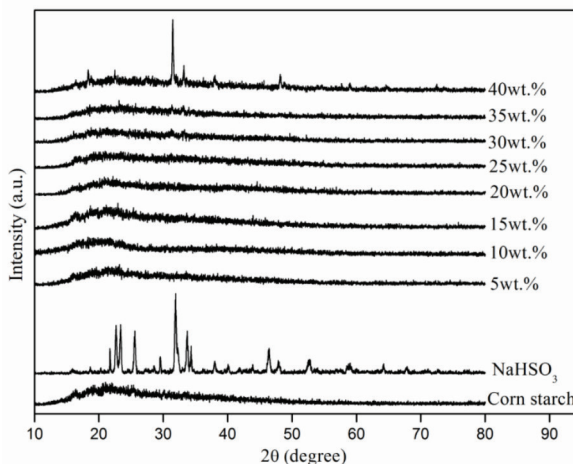
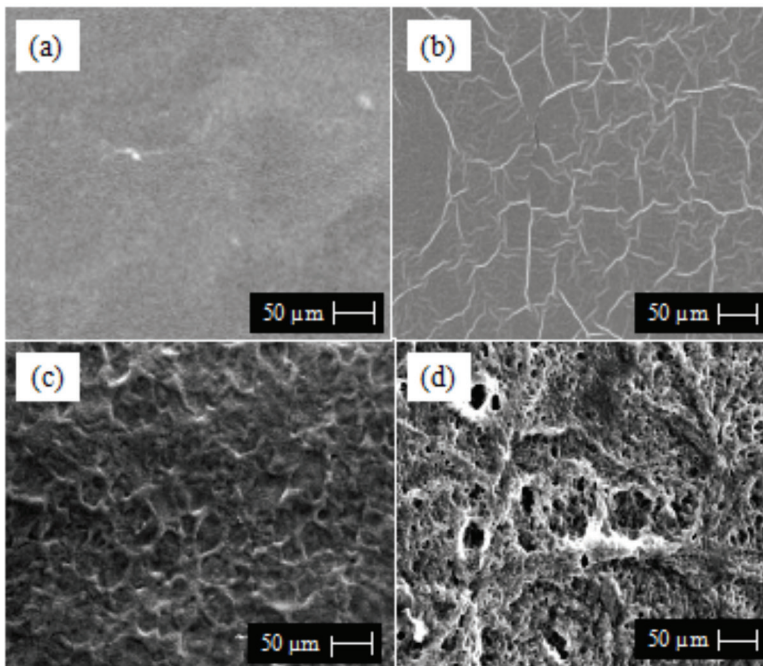


Figure 5: XRD patterns for corn starch, NaHSO_3 and corn starch- NaHSO_3 complex films

al. (1996), intensity of the peaks would also be related to the degree of crystallinity. As can be seen, the addition of NaHSO_3 up to 35 wt.% in the polymer system would not alter much of the peak values as compared to the amorphous state. This was because the complete dissolution of salt happened in the polymer matrix. Therefore, the XRD studies confirmed that complexation occurred in the polymer matrix of amorphous state and would influence the ionic conductivity of SPE films (Osman *et al.*, 2010). Meanwhile, several peaks which appeared at 31.5° , 33.1° , 37.8° and 48.1° corresponded to NaHSO_3 for SPE sample which contained 40 wt.% of NaHSO_3 . This also implied that there was no solvate of salts by the polymer, which might contribute to the association of ions. Therefore, it reduced the number of freely mobile ions and led to a decrease in conductivity.

SEM is a common method used to understand the components that are compatible in the polymer electrolytes through the perception of interfaces and phase separations (Zang *et al.*, 2004). Figure 6 shows the morphologies of the corn starch and NaHSO_3 complexed with corn starch polymer electrolyte. Corn starch image

(Figure 6a) shows the smooth and homogenous surface without any impurities. The absence of pores or any internal structure on the corn starch surface represents the structural integrity of the polymer matrix (Domene-Lopez *et al.*, 2019), which could give better tensile strength. Upon addition of 5 wt.% NaHSO_3 (Figure 6b), the image of the root structure was seen. It clearly showed that the introduction of NaHSO_3 played an important role in the morphology and particle distribution in the SPE films. Then, the surface area of SPE films in Figure 6c, which contains 10 wt.% of NaHSO_3 , is surrounded with bay shapes and some small pores. After that, when 15 wt.% of NaHSO_3 was added, the sample in Figure 6d shows branch structures with an increase in the number and size of pores. The sample with 20 wt.% of NaHSO_3 (Figure 6e) showed the branch structures with some pores that were present in certain areas. The root image with some foreign particles was seen in SPE films with 25 wt.% of NaHSO_3 (Figure 6f). Besides, it also showed a smoother surface morphology which represented the lowering crystallinity of corn starch. Next, for Figure 6g - 6i (30 to 40 wt.% of NaHSO_3), the quantity and estimated



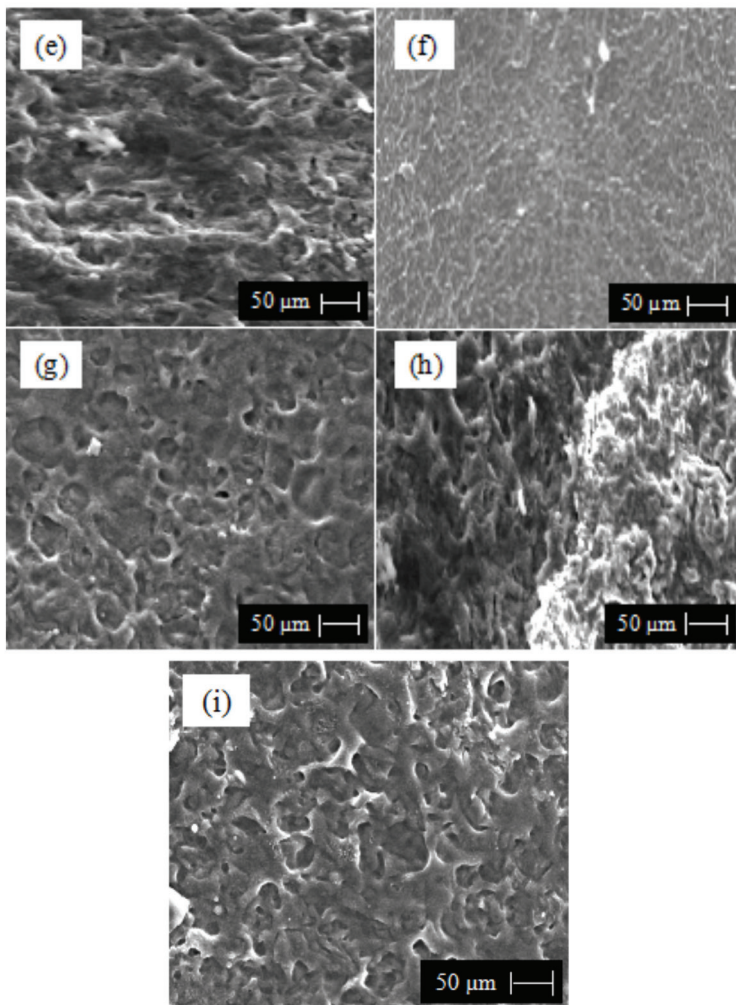


Figure 6: SEM images for (a) corn starch film, (b) 5 wt.% of NaHSO_3 , (c) 10 wt.% of NaHSO_3 , (d) 15 wt.% of NaHSO_3 , (e) 20 wt.% of NaHSO_3 , (f) 25 wt.% of NaHSO_3 , (g) 30 wt.% of NaHSO_3 , (h) 35 wt.% of NaHSO_3 , (i) 40 wt.% of NaHSO_3

diameter of the pore structure was smaller than the previous sample with some connecting branches. Generally, it can be said that the disorderly structure will limit the penetration of the ions in an electrolyte (Dou *et al.*, 2011); hence, a decrease in conductivity would happen. In addition, the formation of pores would help to increase the ionic conductivity as it can facilitate easier ion penetration.

Mechanical properties of SPE films are important to determine their ability to resist force before fracture. The mechanical property

values are included tensile strength and Young's modulus, as shown in Figure 7, while the thickness and SPE samples are tabulated in Table 3. The tensile strength increased with increase in the NaHSO_3 ratios in polymer electrolyte, and reached the maximum value at 5 wt.% of NaHSO_3 with a value of 2.11 MPa. However, a higher addition of NaHSO_3 tended to decrease the tensile strength of membranes. This happened because the polymer membrane became more brittle because the high content of NaHSO_3 can interrupt the intermolecular

interactions between polymer and salt. Then, Young's modulus tended to decrease after it reached the highest value at 5 wt.% of NaHSO₃, with a value of 2.6×10^{-2} MPa. These results might be caused by the increase in SPE films' amorphicity and flexibility. However, SPE film's mechanical strength at 5 wt.% was opposed to the SEM morphology and ionic conductivity value. This is believed to be due to internal structure showing an ordered arrangement (root structure) as crystalline, resulting in lower conductivity value. After the drying process, SPE films' thickness was recorded in the range of 0.101 mm to 0.256 mm. According to Chai *et al.*, (2018), the thickness of SPE films was influenced by the volume of polymer electrolytes poured into petri dishes

and the time taken for samples to dry. It can be observed from the results that the thickness of SPE films was not constant. Generally, the content of amylose and amylopectin in starch can influence the performance of a polymer. The decrease of ionic conductivity at 20 wt.% until 40 wt.% of NaHSO₃, may be due to the lower amylose content in starch, which has bigger crystalline domains. This was because the conductivity was related to crystallinity or amorphous phase of SPE films.

The determination of ionic conductivity is considered as one of the vital aspects of electrolyte that should be addressed. Through polymer electrolyte literature, there are two mobile ions that can be considered, namely cation

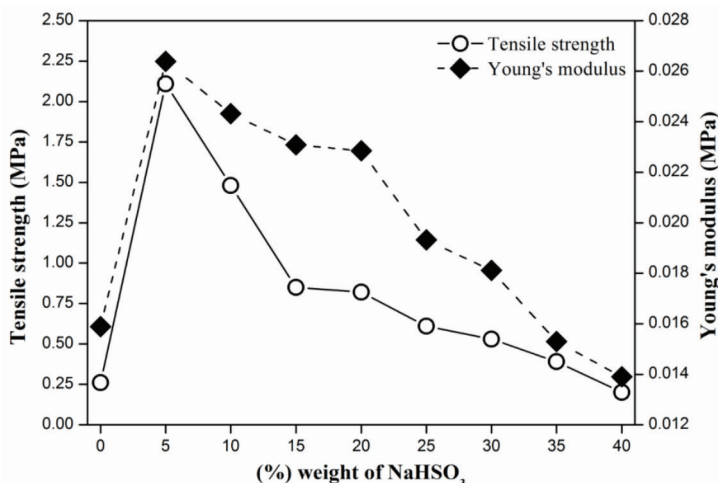


Figure 7: Mechanical properties of SPE films

Table 3. The mechanical properties of corn starch complex with NaHSO₃

Samples	Thickness (mm)
Pure corn starch	0.104
5wt. %	0.101
10wt. %	0.169
15wt. %	0.174
20wt. %	0.133
25wt. %	0.251
30wt. %	0.185
35wt. %	0.293
40wt. %	0.256

and anion that may influence the conductivity through their mobility and density. The trend of ionic conductivity of corn starch versus weight percentage of NaHSO_3 is shown in Figure 8. It can be observed that the conductivity of pure corn starch was $1.1 \times 10^{-6} \text{ Scm}^{-1}$. The addition of 5 wt.% of NaHSO_3 increased conductivity to $7.65 \times 10^{-6} \text{ Scm}^{-1}$. The rise in conductivity was due to the fact that the addition of salt promotes more mobile ions into the polymer membrane. Then, it continued to increase until the highest conductivity was achieved at 15 wt.% of NaHSO_3 , with value of $2.22 \times 10^{-4} \text{ Scm}^{-1}$. The rise in conductivity as the salt content increased was attributable to the increasing number of density ions and increased the amorphousness of polymer; hence, reduced the energy barriers which improved the mobility of the ions (Sahli & Ali, 2012). Further addition of salt (25 wt.% until 40 wt.%) in polymer electrolyte would decrease the conductivity values until $6.98 \times 10^{-6} \text{ Scm}^{-1}$. This happened because the distance between dissociated ions may become too close and increase the possibility for them to recombine and form neutral ion pairs that do not contribute towards conductivity. Therefore, the decrease in ion concentrations as well as the mobility will lead to a drop in conductivity (Hassan & Ahmad, 2016).

For further confirmation of conductivity results, the non-destructive EIS technique was employed to study the transport properties of SPE films. A previous study showed that the diffusion coefficient (D) and mobility of ions (μ) influenced the conductivity (Awang *et al.*, 2020). It can be seen that the highest conducting electrolyte (15 wt.% of NaHSO_3) had the D and μ which were $2.41 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $9.39 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}$, respectively. According to Khanmirzaei and Ramesh. (2013), these results indicated that the conductivity increased with the increase in those parameters. It can be concluded that the increase in salt concentration will increase the number density of ions, and thus contributed to the increase in conductivity.

Conclusion

In summary, ions conducting corn starch solid polymer electrolyte films containing NaHSO_3 salt were prepared using a solution casting technique. The effects of salts on the host polymer can be seen with the presence of SPE films in amorphous state and complexation occurred between the particles, which was shown by using XRD and FTIR analyses. The changes in the surface texture of SPE films significantly modified the morphology of the films and the mechanical properties of samples were improved by adding NaHSO_3 in

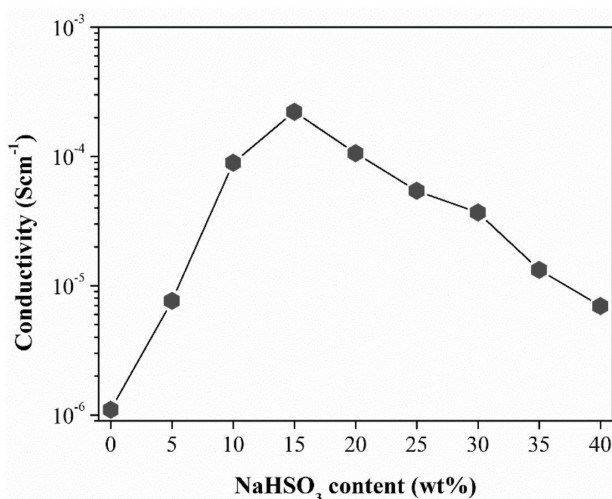


Figure 8: Ionic conductivity of the corn starch doped with various ratio of NaHSO_3 (in wt.%)

the polymer membrane. Lastly, the 15 wt.% of corn starch-NaHSO₃ exhibited the highest ionic conductivity at room temperature with a value of $2.22 \times 10^{-4} \text{ Scm}^{-1}$. The highest conducting electrolyte has the mobility and number density of ions $2.41 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $9.39 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1}$ s, respectively. It may be concluded that the present SPE has potential to be used as an electrolyte for application in sodium ion batteries.

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