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The Effect of Cellulose Succinate on Properties of Polymer Electrolyte Membranes Prepared by Blending Cellulose Acetate-Lithium Perchlorate

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ABSTRACT

The effect of cellulose succinate addition towards the characteristics of cellulose acetate-lithium perchlorate polymer electrolyte membranes was studied by the analysis of the functional groups using FTIR (*Fourier Transform Infrared*) spectroscopy measurement, the ionic conductivity analysis utilizing EIS (*Electrochemical Impedance Spectroscopy*) method, mechanical properties characterization by tensile tester measurements, thermal properties analysis by Thermogravimetric Analysis (TGA), morphology analysis utilizing Scanning Electron Microscopy (SEM) and crystallinity analysis by X-Ray Diffraction (XRD) measurements. The addition of cellulose succinate into the cellulose acetate-lithium perchlorate membranes tended to increase the ionic conductivity and thermal stability of membranes, however the mechanical properties of membranes were decreased and the membrane surface morphology changed to become more porous and irregular.

Keywords - cellulose acetate, cellulose succinate, lithium perchlorate**,** polymer electrolyte membranes.

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I. INTRODUCTION

Many cellulose acetate (CA) based polymers have been reported to be used as a polymer electrolyte, such as cellulose acetate (CA)-co-polyethylene oxide blends prepared by the use of gamma irradiation [1], and polyethylene (PE)- on the blended polyvinylidene fluoride (PVDF) and cellulose acetate butyrate (CAB) [2]. CA and its copolymer blends have shown good ionic conductivity and thermal stability. Plasticizing effect of 1-allyl-3-methylimidazolium chloride towards cellulose acetate based polymer electrolyte membranes have good ionic conductivity at room temperature [3]. The cellulose acetate doped with $LiClO_4$ as a biodegradable polymer electrolyte for supercapacitors has the ionic conductivity approximately 4.9 x 10^{-3} Scm^{-1} with lithium salt content of 16% (w/w) at room temperature [4]. However, the mechanical properties of the membranes have not been well elaborated in those reported studies, even though these properties are very important in polymer electrolyte membranes.

In the previous study we have reported the mechanical properties and ionic conductivity measurements in various ratios of lithium perchlorate content in cellulose acetate-based polymer electrolyte membranes [5]. The presence of 10% (w/w) $LiClO_4$ content within cellulose acetate membranes was capable to increase the mechanical properties of the membranes, such as the tensile strength from 19.89 to 43.29 MPa, and the elongation at break from 2.55 to 4.53%. However, the ionic conductivity value of the membrane was still low (1.03×10^{-5} S/cm).

In this study, novel electrolyte polymers with sufficient ionic conductivity and the more comprehensive physical properties has been developed by using modified cellulose-based biodegradable polymers such as cellulose acetate and cellulose succinate to suit the requirements as lithium ion battery polymers by considering the need for practical, safe, and environmentally friendly uses. Blending polymers has attracted the attention of many researchers, due to the possibility of developing new materials from polymer blends [6]. This will encourage dissolution, reduce the crystalline zone and increase the movement capacity of the segments, thus increasing electrical conductivity and mechanical strength [7]. The ionic conductivity of the electrolyte polymer can be increased by blending of two polymers [8].

So far there is no electrolyte polymer prepared from blending between cellulose acetate and cellulose succinate to be applied as lithium ion battery cell application, therefore this blending process is one of novelty in this research. The addition of cellulose succinate into the cellulose acetate is expected to open the membrane pore, therefore the lithium ions transport and their mobility can be faster, and thus the expected ionic conductivity of membranes increases.

II. MATERIALS AND METHODS

2.1 Materials

The materials used in the synthesis of cellulose succinate and its purification were microcrystalline cellulose (Sigma-Aldrich), [BMIM]Cl with purity of 98.0% (HPLC) (Sigma-Aldrich), succinic anhydride synthesis grade (Sigma-Aldrich), isopropanol pro analysis (Merck), and technical acetone.

The materials used in preparation of polymer electrolyte membrane were cellulose acetate (Sigma-Aldrich with average molecular weight of 30,000; 39.8 wt% acetyl content), cellulose succinate synthesis and $LiClO_4$ (Sigma-Aldrich). Tetrahydrofuran (THF) for analysis with purity (GC) of 99.8% were obtained commercially from E-Merck Chem. Co. All materials were used without further purification.

2.2 Synthesis of cellulose succinate

Cellulose and [BMIM]Cl with a ratio of 8.6% (w/w) and succinic anhydride with cellulose-succinic anhydride mole ratio of 1:10 were mixed in a 35 mL reactor tube. Subsequently, the tube containing the reaction mixtures was introduced into CEM® microwave reactor for 30 minutes at 170 °C with a fixed microwave irradiation of 100 W. After completion of reaction, the reaction mixtures were poured into beaker glass containing 20 mL of isopropanol, and the reaction mixtures were stirred at room temperature using magnetic stirrer for 10 minutes, then the reaction mixtures were filtered off and the solid was retained in the filter paper. The solid on the filter paper was washed three times with 20 mL of acetone and twice with 20 mL of isopropanol to remove the residual ionic liquid [BMIM]Cl and succinic anhydride. The washed solid was then dried over hotplate magnetic stirrer (50 ^{o}C, 3 h).

2.3 Preparation of polymer electrolyte membranes

Polymer electrolyte membranes were prepared by mixing cellulose acetate and 10% (w/w) lithium salt ($LiClO_4$) at various concentrations of cellulose succinate 1, 3, 5 % (w/w) using tetrahydrofuran (THF) as solvent. An amount of cellulose acetate, lithium salt and cellulose succinate were dissolved in tetrahydrofuran at a ratio of 1% (w/v) and stirred on the hotplate magnetic stirrer for approximately 3 hours to form homogenous solution. The solution was subsequently poured into a petri dish (10 cm in diameter), and the solvent was evaporated to form thin film and dried for approximately 20 hours.

2.4 Characterizations of polymer electrolyte membranes

2.4.1 Functional group analysis

The polymer electrolyte membranes were analyzed by using FTIR (Prestige 21 Shimadzu) spectroscopy method to determine its functional groups with direct firing method. The membranes were scanned within the wavenumber range of 500 to 4000 cm^{-1}.

2.4.2 Ionic conductivity measurements

The ionic conductivity of the polymer electrolyte membranes has measured by EIS (Electrochemical Impedance Spectroscopy) method. The membranes were cut rectangular approximately with the dimension of 2 cm × 4 cm, and then the membrane was placed between two platinum wire electrodes within the distance of 1.5 cm and 0.4 cm long. The scanning data of impedance was performed within the frequency range between 20 Hz and 2 MHz at 1 V using the equipment of Agilent TM LCR E4980. The impedance data were analyzed using the Zview® software to obtain the resistance value of membranes. The membrane resistance value was taken from the high frequency intercept on the real impedance axis of the Nyquist plot [9]. The ionic conductivity of the membrane was calculated using the following formula:

$$\sigma = \frac{1}{R} . \frac{\sqrt{(d)^2 + (t)^2}}{t.s} \qquad (1)$$

where σ, R, d, t, s, respectively, were ionic conductivity (Scm^{-1}), membrane resistance (ohm), thickness of membrane (cm), distance between two electrodes (1.5 cm), and length of electrode that contacts between membrane and electrode (0.4 cm).

2.4.3 Mechanical strength analysis

The mechanical properties of the polymer electrolyte membranes were measured using tensile tester (Singel Fiber Tensile Tester (Favigraph-Textechno)). Membrane was cut to rectangular with dimension of 4 cm × 3 mm and the membrane thickness was measured using a micrometer, then the membrane was tested with the gauge length of 2 cm, load cell of 10.000 cN, and test speed of 6 mm/min. The mechanical properties of sample were performed by taking the average value of three repeated measurements.

2.4.4 Thermal stability

The thermal stability of the polymer electrolyte membrane was evaluated by Thermogravimetric Analysis (TGA). TGA-studies were carried out using TG/TGA Shimadzu DTG 60 A. Measurements were performed over a temperature range of 25–550 ºC at a heating rate of 10 ºC min^{-1} under the nitrogen atmosphere of 100 mL/min. The thermal stability of the samples was evaluated in terms of decomposition temperature.

2.4.5 Morphology

The morphology of the polymer electrolyte membrane was evaluated using a JEOL JCM-6000 BENCHTOP Scanning Electron Microscopy (SEM), operated at 15 kV. Before the examination, the samples were dried under sputter-coated gold/palladium.

2.4.6 Crystallinity

The crystallinity analysis of the polymer electrolyte membrane was tested with a Rigaku XRD instrument with an Ultra 250D. The membrane samples were cut to a size of 1.5 cm × 1.5 cm and placed over the sample place on the X-Ray instrument, and scanned and then made their diffractograms.

III. RESULTS AND DISSCUSION

3.1 Functional group analysis

Figure 1. showed FTIR spectra of cellulose acetate membrane doped with 10% (% w/w) $LiClO_4$ and 3% (w/w) cellulose succinate content. The presence of the wide absorption peaks of pure cellulose acetate FTIR spectrum at 3485.37 cm^{-1} is due to the presence of moisture in the sample, which was not completely removed [4]. The similar wide absorption peaks shifted to 3508.52 cm^{-1} were also observed in cellulose acetate-$LiClO_4$ (Fig. 1b) and cellulose acetate-$LiClO_4$-cellulose succinate membranes FTIR spectra (Fig. 1c). The absorption peak at wavenumber of 2949.16 cm^{-1} in pure cellulose acetate FTIR spectrum corresponded to the stretching of –CH- of methyl groups (-CH_3), which has been shifted to 2943.37 cm^{-1} in FTIR spectrum of cellulose acetate-$LiClO_4$ and to 2945.30 cm^{-1} in FTIR spectrum of cellulose acetate-$LiClO_4$-cellulose succinate membrane. The carbonyl group (C=O) stretching vibration at 1756.22 cm^{-1} for the pure cellulose acetate has been shifted to 1745.58 cm^{-1} in FTIR spectrum of cellulose acetate-$LiClO_4$ and in cellulose acetate-$LiClO_4$-cellulose succinate membrane. The shifting of these characteristic peaks proves the occurrence of complexation between Li^+ ions and oxygen atoms in polymer backbone chain. The -CH_2- deformation vibration occurred at 1431.18 cm^{-1} for pure cellulose

acetate has been shifted to 1429.25 cm^{-1} for both cellulose acetate-$LiClO_4$ and for cellulose acetate-$LiClO_4$-cellulose succinate membranes. The characteristic peaks of 'C-O-C' anti symmetric stretching vibrations of ester group of pure cellulose acetate at 1240.23 cm^{-1} has been shifted to 1238.30 cm^{-1} in cellulose acetate-$LiClO_4$ membrane. The -C-OH stretching vibration of pure cellulose acetate at wavenumber of 1049.28 cm^{-1} has also been shifted to 1053.13 cm^{-1} for both cellulose acetate-$LiClO_4$ and for cellulose acetate-$LiClO_4$-cellulose succinate membranes.

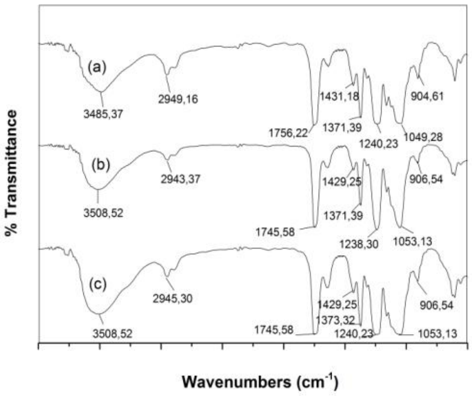

Figure 1. The FTIR spectra of: (a) cellulose acetate; (b) cellulose acetate doped with 10% (w/w) $LiClO_4$ (cellulose acetate-$LiClO_4$) membrane (c) cellulose acetate doped with 10% (w/w) $LiClO_4$ and 3% (w/w) cellulose succinate (cellulose acetate-$LiClO_4$- cellulose succinate) membrane

The presence of the absorption peaks at 904.61 cm^{-1} in pure cellulose acetate could be due to the combination of –C-O- stretching and -CH_2- rocking vibrations that have been shifted to 906.54 cm^{-1} in both cellulose acetate-$LiClO_4$ and for cellulose acetate-$LiClO_4$-cellulose succinate membranes. The symmetric vibration of -ClO^- ion (perchlorate ion) was generally observed at 940 cm^{-1}, which in this study, these peak overlaps with C-O stretching vibration of cellulose acetate, therefore the wavenumber of the same peak at 906.54 cm^{-1} shifted to the lower value. The shifted to the lower value of this wavenumber can be caused by the complexation effect [3].

3.2 Ionic conductivity analysis

The ionic conductivity value of the cellulose acetate-10% (w/w) $LiClO_4$ with the addition of 1%, 3% and 5% (w/w) cellulose was shown in Figure.2. The addition of cellulose succinate causes an increase in the membrane ionic conductivity value, although small, and reaches the optimum value about 1.35×10^{-5} Scm^{-1} at 3% (w/w) cellulose succinate content. The increase in conductivity with the addition of cellulose succinate 3% (w/w) due to the structure of cellulose acetate membranes becomes more amorphous and more open, so that the lithium ion becomes more easily movable. The small increase in ionic conductivity with 1% (w/w) cellulose succinate content is caused by the dispersed cellulose succinate in the cellulose acetate-lithium perchlorate mixture, so that the effect is very small. Furthermore, the addition of a larger cellulose succinate of 5% (w/w) tends to decrease the conductivity, which is likely due to the addition of a larger cellulose succinate, tends to inhibit ion mobility from lithium ions.

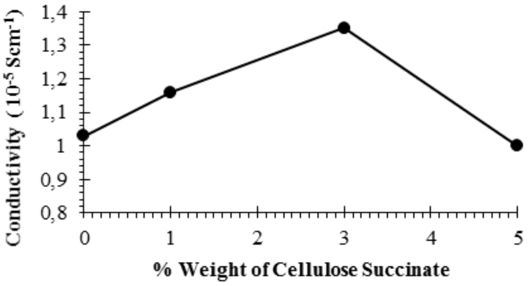

Figure 2. Ionic conductivity of the cellulose acetate-$LiClO_4$ membranes doped with various ratio of cellulose succinate (% w/w)

3.3 Mechanical strength analysis

The mechanical properties of cellulose acetate–10% (w/w) $LiClO_4$ with the addition of 1%, 3% and 5% (w/w) cellulose succinate are shown in Table 1. The tensile strength of the cellulose acetate-lithium perchlorate membrane tends to decrease with the addition of cellulose succinate, and reaches the lowest value at a concentration of 3% (w/w) of 28.03 MPa. This result supports the optimum value of the membrane ionic conductivity at cellulose succinate content of 3% (w/w). The decrease in mechanical strength of the membrane occurred as a result of the increase in amorphous area of the membrane, therefore the membrane tends to be more flexible, and in this condition, can increase ion transport or ion mobility. The addition of larger amount of succinic cellulose by 5% (w/w) tends to raise the tensile strength of the membrane, and this result is compatible with the decreased conductivity value at corresponding concentration. The addition of cellulose succinate more than 3% (w/w) caused the membrane to become more closely packed and denser. The optimum value of tensile strength of cellulose acetate/Li-cellulose succinate membrane was 33.81 MPa at 1% (w/w) of cellulose succinate. The optimum value of tensile strength in this study is still in accordance with the minimum requirements of a polymer electrolyte for lithium batteries (≥30 MPa) [10].

Table 1. Mechanical properties of the cellulose acetate-$LiClO_4$ membranes doped with various ratio of cellulose succinate (in % w/w)

% (w/w) $LiClO_4$	% (w/w) cellulose succinate	Tensile strength (MPa)	Elongation at break (%)	Modulus Young (MPa)
0	0	19.89	2.55	1072.46
10	0	43.29	4.52	1753.69
10	1	33.81	3.43	1885.29
10	3	28.03	2.85	1284.12
10	5	32.745	2.25	2060.02

The elongation at break tends to decrease with the increase in the content ratio of cellulose succinate in the membrane, and reachs the lowest value of 2.25% on the cellulose acetate/Li membrane containing of 5% (w/w) cellulose succinate. However, Young's modulus increases with the increase in the content ratio of cellulose succinate in the membrane and reaches an optimum value of 2060.02 MPa in cellulose acetate-Li membrane with 5% (w/w) of cellulose succinate. This result may be due to a decrease in crystallinity, although the addition of cellulose succinate in the membrane is very small compared to the crystallinity effect of the cellulose succinate structure itself so that the membrane tends to be rigid.

3.4 Thermal stability analysis

The TGA (Thermogravimetric Analysis) curve of 10% LiClO4-cellulose acetate membrane containing cellulose succinate at various ratios was shown in Figure 3. The TGA thermograms showed that the thermal decomposition of cellulose acetate-lithium perchlorate-cellulose succinate membrane consisted of three stages of transition corresponding to the cellulose acetate and cellulose acetate-lithium perchlorate thermal decomposition curves. The addition of cellulose succinate did not change the number of stages in thermal degradation of the membrane. This is likely due to the addition of cellulose succinate only in small amounts. The first stage in thermal degradation of the cellulose acetate-lithium perchlorate-cellulose succinate membrane initially started from room temperature (25 ºC) to ~ 70 ºC indicating the evaporation of volatile matters and/or the evaporation of residual water absorbed. The second stage of thermal degaradation started at varying temperatures over a range of 287-295 ºC and ends at a temperature range of 324-326 ºC, which indicates the major thermal degradation of the cellulose acetate chain. The third stage, which started at 324-326 ºC, and ends at a temperature about at 550 ºC, shows the carbonization of the product to become ash. These three phases correspond to the three transitions suggested by Chatterjee that indicate the thermal degradation of cellulosic material [11].

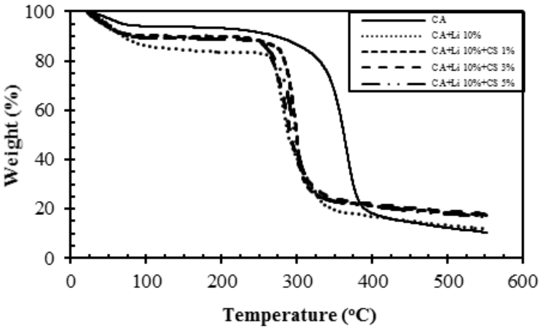

Figure 3. TGA thermograms of the cellulose acetate-$LiClO_4$ membranes doped with various ratio of cellulose succinate (in % w/w)

Table 2. presents the initial degradation temperature (T_{onset}), final degradation temperature (T_{outset}) and weight loss (WL) of the major decomposition of 10% $LiClO_4$ cellulose acetate-litium perchlorate membrane with variation of cellulose succinate concentration. The addition of cellulose succinate to the cellulose acetate-lithium perchlorate membrane tends to increase the membrane's thermal stability compared to the thermal properties of cellulose acetate-lithium perchlorate.

Table 2. The values of the initial temperature (Tonset), end temperature (Toutset) and weight loss (WL) of the main decomposition of the cellulose acetate-$LiClO_4$ membranes doped with various ratio of cellulose succinate (% w/w)

% (w/w) $LiClO_4$	% (w/w) cellulose succinate	T_{onset} (º C)	T_{outset} (º C)	WL (%)
0	0	330	380	74
10	0	265	320	63
10	1	295	324	60
10	3	288	326	65
10	5	287	326	65

3.5 Morphology analysis

The surface morphology and cross-section of the cellulose acetate-lithium perchlorate polymer electrolyte membrane containing various cellulose succinate compositions were depicted in Figures 4. and 5, respectively. The surface morphology of membranes showed the presence of spots/pores derived from the dissolved cellulose succinate in the membrane mixture.

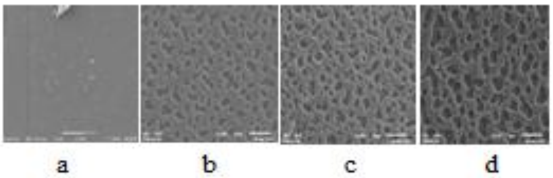

Figure 4. The morphology images (2000×) by SEM of the cellulose acetate-$LiClO_4$ membranes doped with various ratio of cellulose succinate (in % w/w): (a) 0 % (w/w), (b) 1 % (w/w), (c) 3 % (w/w) (d) 5 % (w/w)

The number of pores increased with the increase in cellulose succinate contents within the membrane. The pore size of membranes containing 5% (w/w) of cellulose succinate is noticeably expanded, probably due to the union or the agglomeration of the dispersed cellulose succinate particles. The cross section of the membrane appearead to be more porous and irregular because the content of cellulose succinate in the membrane increased. The results of this cross-sectional morphology analysis were consistent with the increasing in ionic conductivity of membranes by increasing the content of cellulose succinate.

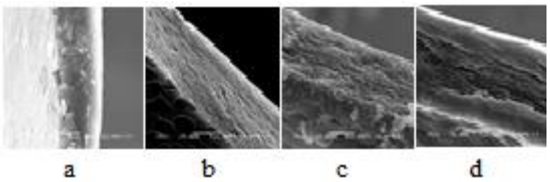

Figure 5. The morphology images (cross-section, 5000×) by SEM of the cellulose acetate-$LiClO_4$ membranes doped with various ratio of cellulose succinate: (a) 0% (w/w), (b) 1% (w/w), (c) 3% (w/w), (d) 5% (w/w)

3.6 Crystallinity analysis

The XRD difractograms of the polymer electrolyte membrane of cellulose acetate-lithium perchlorate-cellulose succinate with various cellulose succinate ratios were presented in Figure 6. The sharp peaks of lithium perchlorate salt occurs at 2θ = 18.39º; 21.19º; 31.58º; 44.28º; 44.37º. However, the XRD pattern did not show the peak intensity associated with lithium salt in the cellulose acetate-$LiClO_4$-cellulose succinate mixture. The diffraction peaks shifted and a new peak appeared on cellulose acetate- $LiClO_4$-cellulose succinate membranes, and these results can confirm the presence of cellulose succinate content in membranes, although in very small amounts.

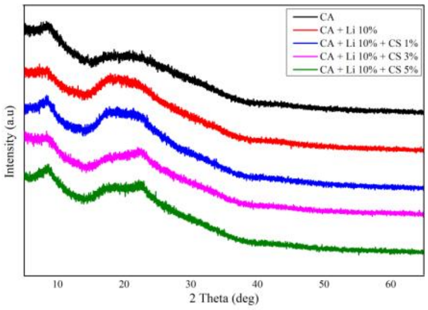

Figure 6. XRD difractograms of the cellulose acetate-$LiClO_4$ membranes doped with various ratios of cellulose succinate (% w/w).

IV. CONCLUSIONS

The addition of the cellulose succinate to the cellulose acetate-lithium perchlorate membrane affect the resulting membrane characteristics. The addition of cellulose succinate into the cellulose acetate-lithium perchlorate membranes caused membranes the ionic conductivity and thermal stability tended to rise, the mechanical properties tended to decrease and membranes morphology tended to change into more porous and irregular form.

The optimum characteristics of cellulose acetate-lithium perchlorate-cellulose succinate membranes were obtained at the cellulose succinate content of 3% (w/w) with ionic conductivity of 1.35×10^{-5} S/cm, the tensile strength of 28.03 MPa, the elongation at break of 2.85%, and thermal stability at 288 ^{o}C. According to the above-mentioned optimum characteristics of the membrane, it can be concluded that this membrane has the potent to be used as polymer electrolyte membrane for lithium ion batteries.

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