

MERCERIZED NATURAL CELLULOSE BASED-SOLID POLYMER ELECTROLYTE

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ABSTRACT. *Cellulosic materials derived from three different types of local wood samples (sawmill woods sawdust, Acacia mangium and belian (Euxideroxilon zwagery) were extracted at atmospheric pressure using organosolv method. In an initial stage, the wood samples were delignified using peroxyacetic acid pulping to remove lignin. Then the pulp was bleached in 0.01 M solution of sodium hydroxide (NaOH) with addition of 4% hydrogen peroxide of absolute dry pulp (ODP). Conversion to alpha-cellulose or mercerized cellulose was achieved by soaking bleached cellulosic materials in 17.5% solution of NaOH for 15 minutes at 25°C. The mercerized cellulose was thoroughly washed with large amount of distilled water until pH of the filtrate reached to natural, then vacuum dried at 60°C. From Scanning electron microscope (SEM) all mercerized woods cellulose were differ in microfibril size with high irregularity observed in sawmill sawdust. Formation of cellulose II was confirmed with X-Ray Diffraction (XRD) and Fourier transform infrared spectroscopy (Ft-IR) analysis. Preparation of solid polymer electrolyte (SPE) membrane was obtained by dissolving dry mercerized cellulose in molten 1-butyl-3-methylimidazolium chloride ([bmim]Cl) in the presence of lithium perchlorate (LiClO₄) to produce a transparent solid gel film. All SPE membranes exhibit conductivity in the range of 3.6×10^{-6} to 5.7×10^{-5} Scm⁻¹ at room temperature. It was also observed that the conductivity of the SPE is affected by the size of cellulose microfibril and type of extraction. It was then further characterized with SEM, XRD, FTIR and TGA.*

KEYWORDS: Wood, Organosolv, Cellulose, mercerized, SPE, conductivity.

INTRODUCTION

Cellulose, a linear polymeric 1,4- β -glucan with the formula $(C_6H_{10}O_5)_n$, is the most abundant natural polymer available on earth. The major source comprises predominantly soft and hard woods, stalks or bamboo (Goring and Timell 1962). In nature, natural or native cellulose mostly combined with lignin and with other polysaccharides, so-called 'hemicelluloses' in the cell wall of woody plants. This cellulose are usually isolated by dissolving the lignin (pulping) and the hemicelluloses via a combined chemical transformation and cleavage, and leaving the cellulose component as a crystalline solid (Klemm et al., 1998). Crystalline regions may contain occasional links or folds in the polymer chain, called "defects". The type and the number of defects vary with the type of cellulose (De Souza et al., 2002). The removal of an amorphous region were achieved by treatment with 17.5% of sodium hydroxide (NaOH) at 25°C (Tappi methods t203). This process is termed as mercerization or conversion to alpha-cellulose. However the degree of crystallinity and crystallite size of the cellulose could be affected (Gümüşkaya et al., 2003) and change the allomorph to new one: cellulose II (Hermans 1949; Nicoll et al., 1954; Krässig 1993) with high concentration of sodium (Gemci, R., 2010).

The major challenge in utilizing cellulose as solid polymer electrolyte (SPE) is the insolubility of cellulose in most common solvents. This issue is solved here by using a room temperature ionic liquid (RTIL) (Welton 1999) 1-butyl,3- methylimidazolium chloride ([bmim]Cl) (Welton 1999), which dissolves up to 25% (wt/wt) of unmodified cellulose by using microwave irradiation (Swatloski et al., 2002). Interestingly the ionic nature of RTIL (Howlett et al., 2004) permits it be used as an electrolyte (Kim et al., 2005). This study was conducted to investigate the potential of mercerized cellulose of woody plant as solid polymer electrolyte (SPE) and to identify some factors that might influence the performance of SPE such as cellulose microfibril lateral size and wood type.

MATERIAL AND METHODS

Cellulose Isolation

Dried wood samples were delignified (1:10 solid to liquid ratio) at 80°C to 90°C for 3 hours in glacial acetic acid/hydrogen peroxide media (H_2O_2/CH_3COOH in mol ratio 0.3) with addition of 5% sulfuric acid (H_2SO_4) as catalyst.

The delignified cellulose was then double bleached at 70°C to 80°C for 45 minutes in 0.01M Sodium Hydroxide (NaOH) containing 4% of hydrogen peroxide, filtered, washed thoroughly with distilled water until pH of the filtrate reached to natural then dried at 60 °C in vacuum drying oven for 3 days. Next, it was further treated with 17.5% of sodium hydroxide (NaOH) solution at 25°C for 15 minutes to remove hemicellulose leave behind alpha-cellulose or mercerized cellulose.

Solid Polymer Electrolyte Casting

For solid polymer electrolyte (SPE) casting, about 10% of mercerized cellulose and varying amount of lithium perchlorate ($LiClO_4$) were dissolved in molten 1-butyl-3-methylimidazolium chloride ([bmim]Cl) at 80°C to 90°C for 30 minutes. The hot solution was solidified slowly by cooling down to room temperature for 3 to 5 days then washed thoroughly with 95% of ethanol.

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The transparent solid gel SPE was measured for its conductivity and characterized with XRD, FTIR and TGA. The detail of the samples of study were displayed in Table 1

Table 1: Summary of the samples used in this study.

Sampel	Mergerized cellulose	SPE
Acacia mangium	AM	SAM
Sawmill wood sawdust	SD	SSD
Belian (<i>Euxideroxilon zwagery</i>)	BL	SBL

Characterizations

Scanning Electron Microscopy (SEM)

JEOL JSM-5610LV Scanning Electron Microscopy (SEM) was used to examine the surface morphology and mechanical shearing on the supramolecular structure of cellulose. Prior to scanning, sample were placed on top of cylindrical sample holder embedded with carbon tape subjected to be silver coated. Upon coated, the sample was transferred onto SEM sample stage to be examined.

X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) was performed with Phillips X'pert MPD diffractometer using $\text{CuK}\alpha$ radiation of wavelength 0.1542 nm, operated at 40 kV and 30 mA. Angular scanning was conducted at 10° to 35° with angular intervals of 0.05° and scan speed of $1^\circ/\text{min}$.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra were taken using PerkinElmer Spectrum 100 FTIR spectrometer equipped with a single horizontal golden Gate ATR cell. To perform FTIR analysis, a small amount sample was placed and pressed on top of the gate and scanned at wavelength between 600 nm to 4000 nm against transmission. Acetone was used to clean the gate prior to analysis.

Electrochemical Impedance Analysis

The impedance of the samples was measured using Solartron 1260 Impedance/gain-phase Analyzer in the frequency range from 0.1 Hz to 100000 Hz at room temperature by sandwiching the electrolyte films between two stainless steel electrodes. Initially, the film samples were cut into a shaped disc with diameter of 16 mm. Conductivity of the electrolytes was calculated using the equation

$$\sigma = \frac{d}{R_b A}$$

where σ is conductivity, and A and d are area and thickness of the electrolyte film, respectively. R_b is the bulk resistance which is derived from the high-frequency intercept on the Cole-Cole plots.

Thermogravimetry (TGA) Analysis

Thermogravimetry analysis was conducted to investigate cellulose temperature tolerance. About 8 to 8.3 mg of sample were placed in sample holder and analyzed in Perkin-Elmer TGA-6 machine. Temperature range selected was 30 °C to 450 °C and nitrogen gas pressure was maintained at 1.8 Ib/in³

RESULT AND DISCUSSION

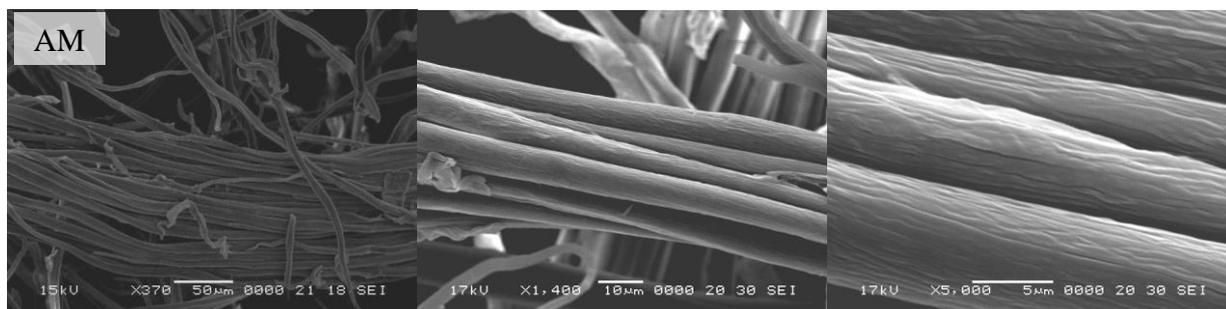
Cellulose Characterization

Morphological Observations

The SEM photos of mercerized wood cellulose are shown in Figure 1. All the image shows a loose network consists of longer microfibril fragment but differ considerably in lateral size. The average microfibrils lateral size of *Acacia mangium* (Fig. 1(AM)) was 5.64 μm in comparison to belian (Fig. 1(BL)) of 13.61 μm. Whereas the distribution in the dimensions of the cellulose isolated from sawdust appeared to be less uniform (Fig. 1(SD)), due to the fact that it consists of various types of woods. At x5000 magnification, microfibril in the outer region of all cellulose microfibril has been exposed. Further more *Acacia mangium* was more affected its microfibril has been released freely and individually than in sawdust and belian. This observation indicates that there is reciprocal relation between microfibril lateral size and sodium hydroxide concentration.

XRD and FTIR Studies

XRD scanning was performed to investigate the structure changes of cellulose after being mercerized. From the XRD profile (Fig. 2) treatment of cellulose with 17.5% of NaOH solution has totally transformed native cellulose or cellulose I to cellulose II (BL, AM, SD). All three wood samples have peaks appeared at diffraction angle of, $2\theta=12.0^\circ$, 20.0° and 21.8° for plane 001, 01(-1) and 002 respectively as these scanning patterns in agreement with the work reported by Dinand et al.,(2002).



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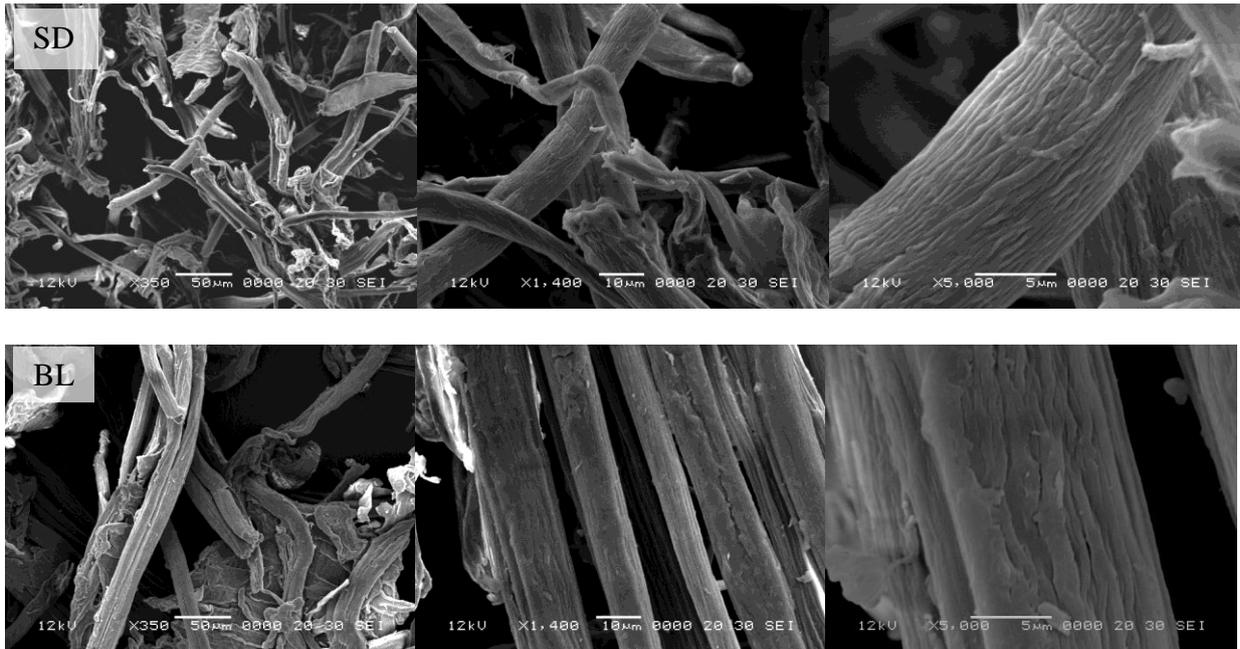


Figure 1. Scanning Electron Micrograph showing the presence of the individual cellulose microfibrils of *Acacia mangium* (AM), sawdust (SD) and belian (BL), at x350, x1400 and x5000 magnifications.

The peak that occurred at $2\theta=20.0^\circ$ being slightly stronger than peak at $2\theta=21.8^\circ$, while the lesser is observed at 12.0° that has $d=7.4\text{\AA}$. This pattern is identified as mercerized cellulose II and was persistently found with native cellulose treated with NaOH solutions at concentration higher than 10% (Dinand et al., 2002).

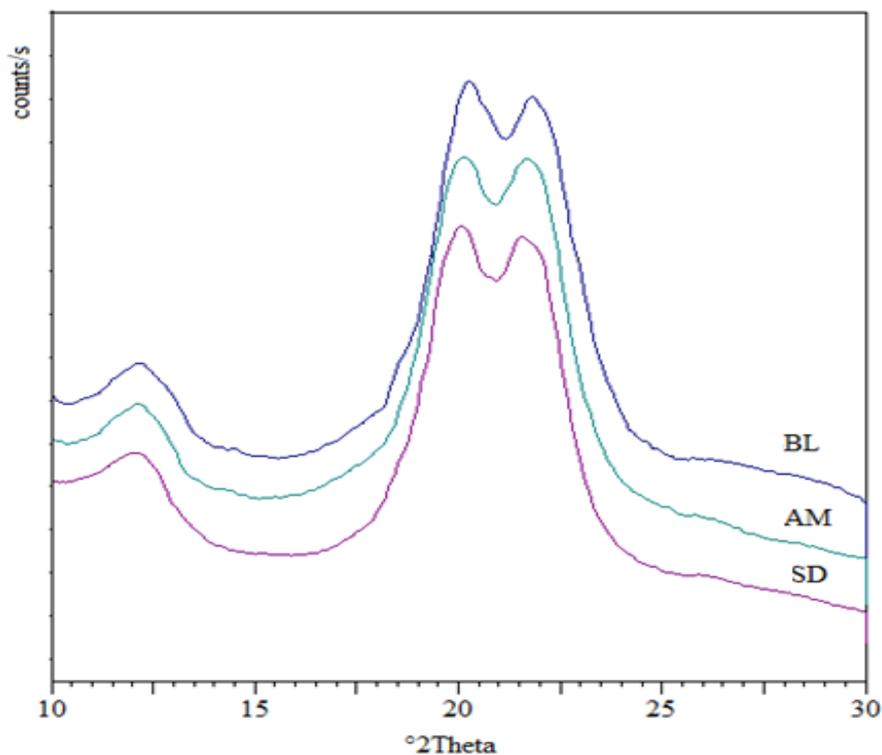


Figure 2 : XRD diffractogram of cellulose treated with 17.5% of NaOH. Belian(BL), *Acacia mangium* (AM) and sawdust (SD).

The structural changes of cellulose I to cellulose II is supported by FT-IR spectra (Fig. 3) in which the existence of peaks at band 3446 cm^{-1} (vibrational stretching hydrogen bonded O-H groups), 2926 cm^{-1} (-C-H stretching), 1368 cm^{-1} (C-H bending), 1261 cm^{-1} and 1226 cm^{-1} (in plane bending of C-O-H at C-6), 1106 cm^{-1} (in plane ring stretching), and 894 cm^{-1} (stretching of C-O-C at β -glycoside bond and C-CH at C-5 and C-6) and 998 cm^{-1} , for belian (BL), Acacia mangium (AM) and Sawdust(SD). All these FTIR characteristics are assigned to cellulose II structure as proposed in many literatures (Kondo dan Sawatari, 1996; Nelson dan O'Connor, 1964; Schwanninger et al., 2004). As for reference, a typical spectrum for cellulose I (Fig. 3(a)) is shown.

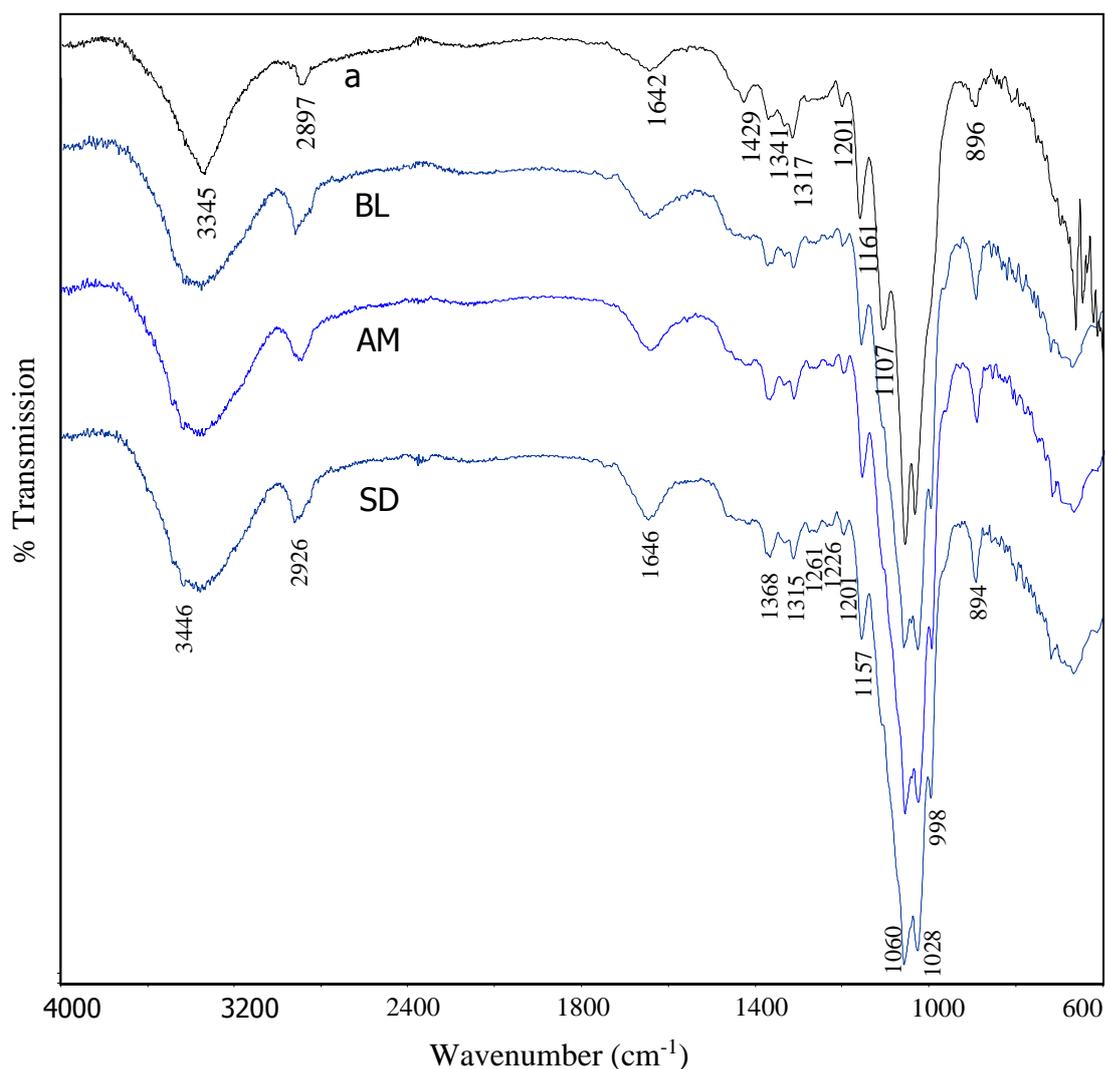


Figure 3. FT-IR spectra cellulose treated with 17.5% of NaOH. Typical spectra for cellulose I (a), belian (BL), Acacia mangium (AM) dan sawdust (SD).

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SPE Characterization

Morphological Observations

Dissolution of 10 % cellulose and 5% LiClO₄ as dopant, in molten [bmim]Cl at 80-90 °C for 30 minutes, has produced a homogeneous viscous gelled material. After gradual solidification by cooling down to room temperature and left untouched for 3 to 5 days, a solid transparent film of SPE is obtained (Fig. 4). Removal of excess [bmim]Cl was done by washing the SPE with 95% of ethanol. In SEM study it was observed that both cellulose and lithium salt were dissolved completely hence a smooth transparent material is obtained. More over it should be noted that Acacia mangium (SAM) produces much clearer and smoother gel material than sawdust(SSD) and belian (SBL), indicating that smaller microfibril lateral size is much easier to dissolved in ionic liquid.

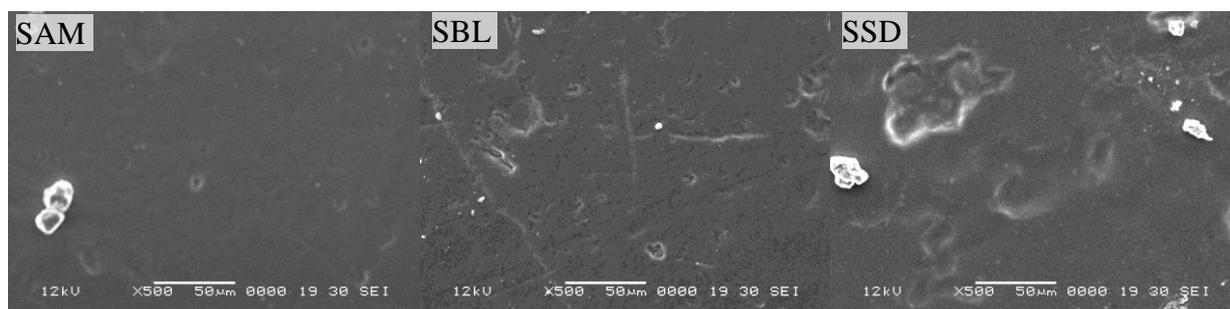


Figure 5. Scanning Electron Micrograph showing the solid gel 10% mercerized cellulose microfibrils of *Acacia mangium* (SAM), sawdust (SSD) and belian (SBL) in [bmim]Cl with addition of 4% LiClO₄

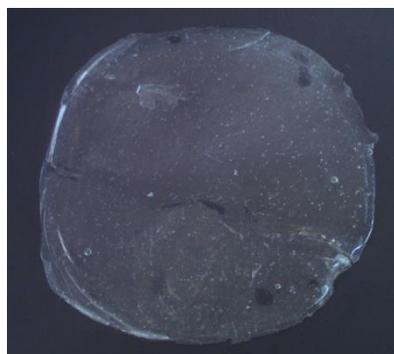


Figure 4. Photo of solid gel 10% mercerized cellulose microfibrils dissolved in [bmim]Cl with addition of 4% LiClO₄

XRD and FTIR Study

In the XRD profile of the SPE, (Fig. 6), the diffraction peaks due to the crystalline structures of the mercerized cellulose (Fig. 6(A)) are not obviously exhibited. Furthermore, the diffraction pattern of all SPE (SBL, SAM and SSD) are identical in shape to figure 6(B) and 6(C). This results indicate that crystalline structure of cellulose polymorph are strongly destroyed in [bmim]Cl and thus, broadening diffraction peaks (Nishino et al., 2004; Kadokawa et al., 2008)).

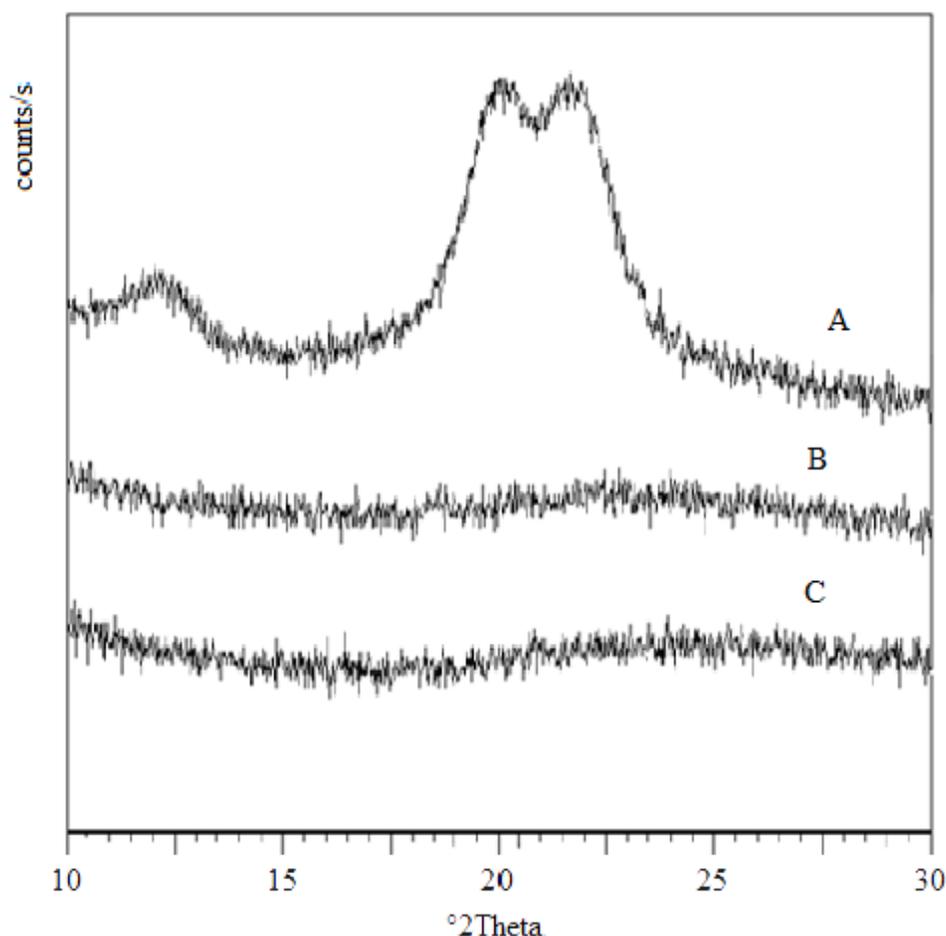


Figure 6. XRD diffractogram mercerized cellulose (A), 10% mercerized cellulose in [bmim]Cl with addition of 4% LiClO₄ (B) and without LiClO₄ (C).

Meanwhile figure 7 depicts FT-IR spectra of SPEs in the range of 600- 4000 cm⁻¹. The spectrum of solid mercerize cellulose (Fig. 7(A)) and cellulose in [bmim]Cl without LiClO₄ (Fig. 7(B)) are also shown as a reference. All SPE (SBL, SAM and SSD) show identical spectrum patterns but differ to cellulose (A) and cellulose in [bmim]Cl (B). Dissolution of cellulose in [bmim]Cl (Fig. 7(B)) has suppressing the some cellulose peaks (Fig. 7(A)) in the range of 890 - 1430 cm⁻¹. Peaks at 894 - 898 cm⁻¹ (stretching of C-O-C of β-glycosidic bonding and C-CH at C-5 and C-6), 1106 -1107 cm⁻¹(glucose ring inplane stretching) and 1315 - 1317 cm⁻¹ (-CH₂ wagging at C-6) of cellulose in [bmim]Cl have been reduced or disappeared. Meanwhile the intensity of peak at 3345-3352 cm⁻¹ (shifted to 3041 cm⁻¹), 1371 cm⁻¹ (shifted to 1365 cm⁻¹) and 1646 cm⁻¹ (shifted to 1648 cm⁻¹) increases. New one weak peak appeared at 1578 cm⁻¹, indicate the

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bending vibration of C-C and C-N for butyl methylimidazolium (Jiang et al., 2006), respectively.

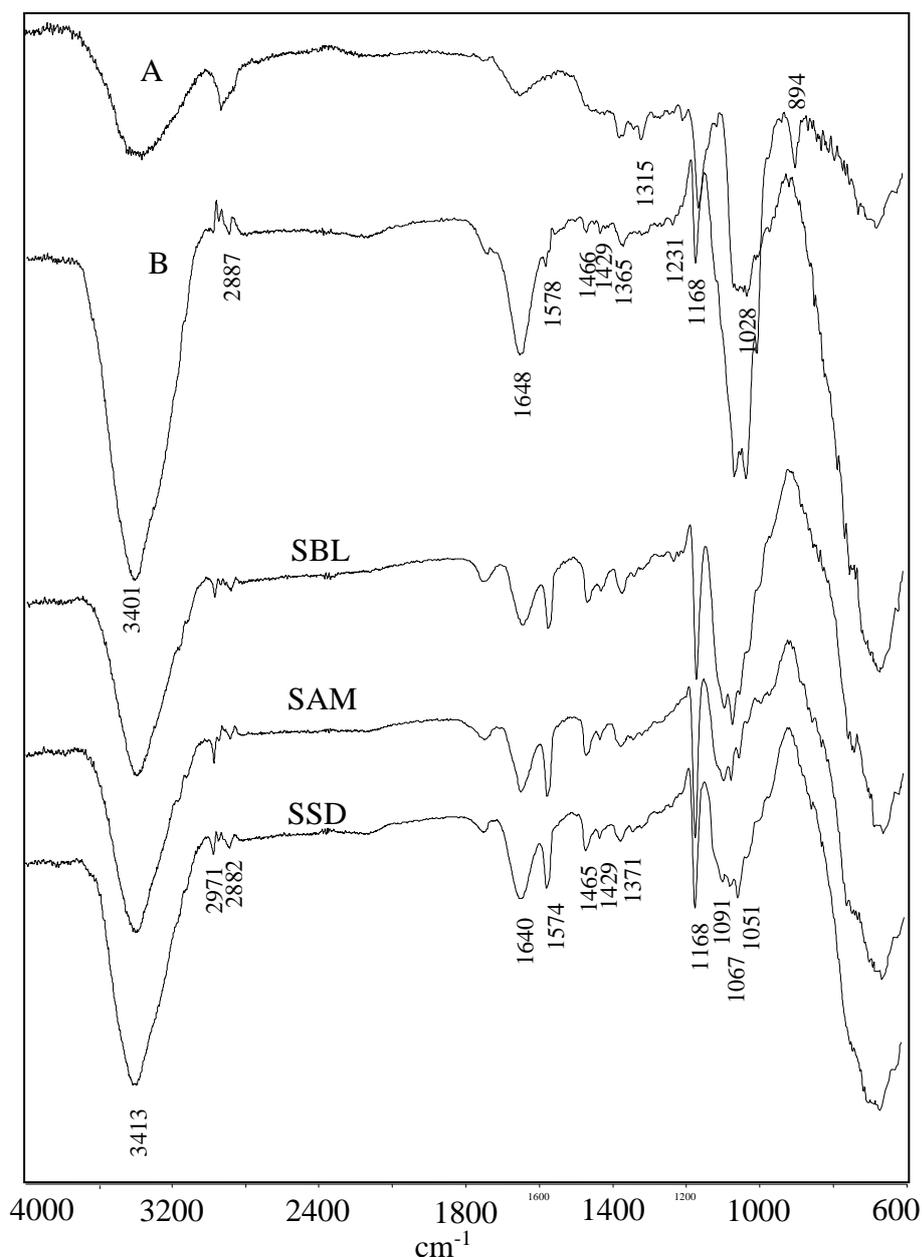


Figure 7 . FT-IR spectra of SPE made of treated with 17.5% of NaOH (SBL, SAM, SSD). Cellulose (A) and 10% cellulose in [bmim]Cl (B)

The intensity at 1574 cm^{-1} also represent the amount of ionic liquids adsorbed in to cellulose surface (Oh et al., 2005; Mahadeva et al., 2009)

When of 5% LiClO_4 is added to cellulose-[bmim]Cl (Fig. 5(SBL, SAM and SSD), peaks at 1574 cm^{-1} and 1465 cm^{-1} (vibration of $-\text{CH}_2-$) increase. However peak that is assigned for stretching vibration hydrogen bonding of O-H group at 3413 cm^{-1} decreased to almost half of the peak intensity of cellulose-[bmim]Cl. The reason for this could be relay on disruption by lithium (Li^+) and perchlorate (ClO_4^-) ions, that lowering the hydrogen bond interaction between cellulose and [bmim]Cl.

Conductivity Study

The aim of this investigation was to arrive at the size of cellulose microfibril which produce high conductivity. Table 2 shows the ionic conductivity of all SPE measured at room temperature, 30°C. The value of bulk resistance, R_b , was calculated in accordance to Nyquist plot in Figure 8. The observed ionic conductivities were in the range of 1.21×10^{-5} to 4.47×10^{-5} Ω/cm . Interestingly, these values were in the range of acceptable ionic conductivity of typical polymer electrolyte i.e. 10^{-5} Ω/cm and above at -20°C to 60°C (Meyer 1998; De Paoli and Gazottib, 2002).

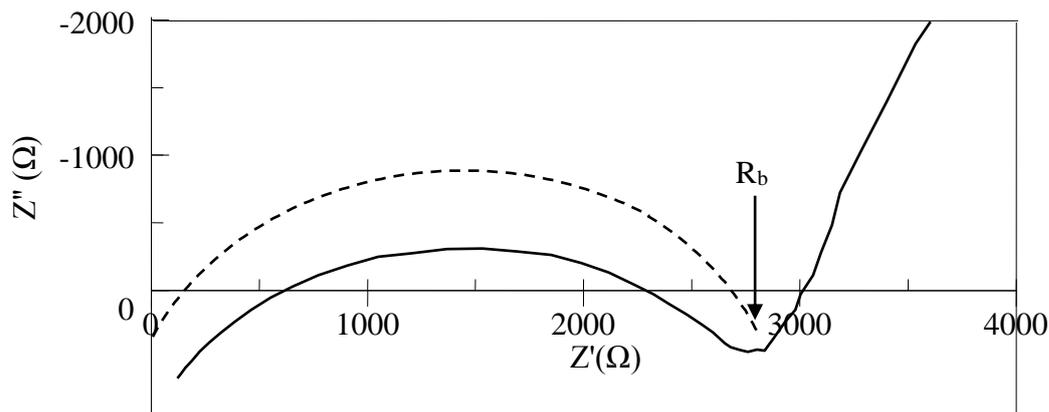


Figure 8: A typical Nyquist plot of SPE. SAM having 5% of LiClO_4 and 10% of cellulose in $[\text{bmim}]\text{Cl}$, measured at 30°C .

We believe the performance of SPE could be increased if the preparation is well optimized. However other parameters such as tensile strength, conductivity over temperature variation and cyclic voltammetry were not tested as this study is only to evaluate the potential of woody plant as SPE. It is also evident that SPE film having cellulose from *Acacia mangium* (SAM) exhibits the higher conductivity (4.47×10^{-5} Ω/cm) than sawdust (SSD) and belian (SBL), at 5% of LiClO_4 , suggest that ionic conductivity could be controlled by cellulose microfibril lateral size. Other factor that may contribute to low conductivity could be attributed to interference of high concentration of sodium ion within cellulose molecule due to formation of stable sodium cellulosate (Gemci, 2010).

Table 2: Ionic conductivity of SPE measure at room temperature.

SPE	Thickness, l/cm	Resistance, R_b (Ω)	σ (Scm^{-1}) $\times 10^{-5}$
SSD	0.151	1679.7	4.47
SAM	0.163	2767.5	2.93
SBL	0.165	6798.8	1.21

Thermogravimetric Analysis (TGA).

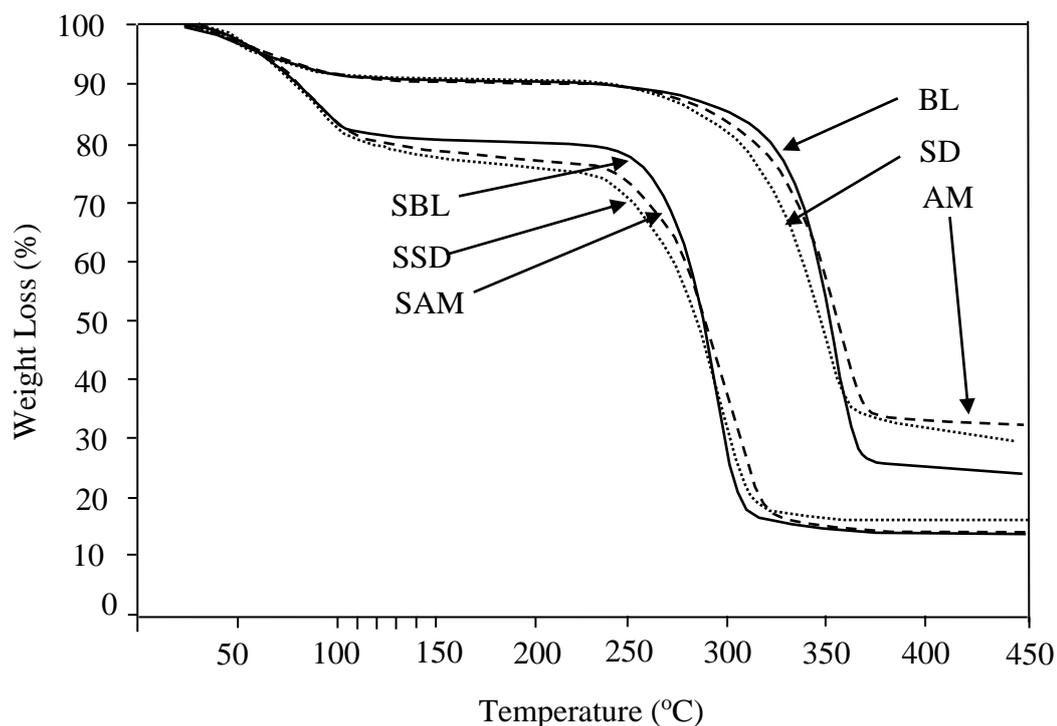


Figure 9. TGA curve of mercerized wood cellulose (BL, SD, AM) and SPE (SBL,SSD,SAM).

TGA curves of mercerized cellulose is found higher than SPE as shown in Fig. 9. At 10% weight loss, the decomposition temperature for BL, SD and AM occurred at 243°C, 247°C and 251°C respectively. While the temperature for 50% decomposition of three cellulosic samples, was observed at 355°C (AM), 353°C (BL) and 350°C for SD, revealed that AM had the highest thermal stability followed by BL and SD. On the other hand, TGA curve of all SPEs (SBL, SAM and SSD) (Fig. 9) exhibits high content of water (18%) that has been evaporated completely at 104°C. An onset weight loss of all SPEs occurred at around 230°C, while at 50% weight loss occurred approximately at 285°C. The difference in the thermal degradation temperatures between mercerized cellulose and SPE also indicates disruption of most of the crystalline regions of cellulose by [bmim]Cl.

CONCLUSION

This study has shown that cellulose of woody plant (*Acacia mangium*, sawmill sawdust and belian) could be utilized as SPE. We have demonstrated that these amorphous SPE are capable of producing ionic conductivity at acceptable level without optimization and exhibiting high temperatures stability. However cellulose microfibril lateral size is found to influence the performance of SPE. Thus, further development will include investigations of suitable cellulose microfibril sizing to increase SPE performance, identification of suitable cellulose extractions, and work to increase SPE mechanical properties such as tensile strength.

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