

Physico-chemical characteristics of Composites material Based on Sulfonated Cyclone Fibre Cellulose and Benzotriazole

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Abstract – Composites material based on sulfonated cyclone fibre cellulose (SCFC) and benzotriazole (Btri) have been prepared. Cyclone fibre cellulose (CFC) was sulfonated with trimethylsilyl chlorosulfonate (TMSCS), with high degree of sulfonation (150%). The composites material, SCFC-Btri were prepared by doping of benzotriazole in various mole ratios (0.125, 0.25 and 0.5). FTIR spectrum has confirmed the ionic interaction between sulfonic acid from sulfonated cyclone fibre cellulose and benzotriazole units. Thermogravimetric analysis (TGA) showed that the composites material was thermally stable up to 150 °C. The results showed that methanol permeability of the composite material was lower than pristine Nafion112. Activation energy obtained for the materials are 0.106 eV, 0.144 eV and 0.137 eV for SCFC-Btri mole ratios 0.125, 0.25 and 0.5 respectively, composites material was expected to be used as raw material in the fuel cell.

Keyword: Benzotriazole; Sulfonation; Composites material; Cyclone fibre cellulose.

Introduction

Proton conducting membrane for fuel cells based on polymer have been attracting. The polymers used generally are synthetic polymers. However now, research which use natural polymers as proton conducting material have started running such as cellulose. Research on sulfonated cellulose has been reported with sodium periodate oxidizing agent and sulfonating sodium bisulfate (Zhang *et al.*, 2008). Wherein the sulfonate group attached to the C2 and C3, in terms of structure and impact resistance sulfonation at position C2 and C3 will weaken the strength both physically and chemically. Sulfonated cellulose can be obtained without changing the physicochemical properties of cellulose by substitution of proton (H) at position H-C3-OH and H-C2-OH. Sulfonated cellulose without damaging the structure of the ring, will help as a facilitator of proton path way. Previous study have been reported the possibility of the use of cellulose as a natural electroactive polymers (Victoria & Finkenstadt, 2005).

The use of cellulose as a fuel cell membrane materials have been reported such as by adding a dopant ammonium nitrate and polyethylene glycol as a plasticizer (Shuhaimi *et al.*, 2010). Other studies, magnetically responsive bacterial selulosa: synthesis and magnetic studies have been reported (Satish *et al.*, 2010). Previous studies have been reported the manufacture of composite polyelectrolyte membrane of cellulose and methacrylic acid as polymer backbone. Analysis of FTIR, TGA, DSC, and water up take of the membrane, show it has good prospect as proton conducting material which can be applicable in fuel cells (Stanciu *et al.*, 2010).

Benzotriazole is a heterocyclic molecule with melting and boiling points of 100 and 350 °C, respectively. Its proton does not tightly bind to any of the nitrogen atoms but mobile between nitrogen 1 and 3. Therefore, benzotriazole can lose a proton to act as a weak acidity (pK_a 8.2) or accept a proton using the lone pair electrons located on its nitrogen atoms as a very weak basicity ($pK_a < 0$) (Gustian *et al.*, 2012).

Natural materials that can be used as polymers for the manufacture of proton conducting material are widely available in Indonesia. Province of Bengkulu in Indonesia have 83.583 ha of palm plantations. While there are 12 installed capacity of production for the factory unit with a production capacity of 546 tons of fresh fruit bunches (FFB) per hour. Production of 1 ton of fresh fruit bunches per hour will produce about 190 kg of waste cyclone fibre. Sufficient number of waste fibre is support to undertake diversification utilization. Currently fibre is not only used as a boiler fuel in palm oil processing industry but also as natural fertilizer in palm plantations and many are left untapped. Its abundance will continue to increase along with the growth and development of palm plantations in Indonesia (Departemen Pertanian, 2006). Previous studi have been reported, that degree polymerization of cyclone fibre cellulose are 567 repeat unit and it dimensional stability up to 250 °C and soluble in the solvent cupriethylenediamine 5 M (Gustian *et al.*, 2014 a).

In this work, composites material were prepared using sulfonated cyclone fibre cellulose (SCFC) and benzotriazole (Btri). Physico-chemical characteristics of the composites material were studied with FTIR, thermal analyzer, x-ray diffraction, methanol permeability and activation energy.

Materials and Preparation

Cyclone fibre cellulose (CFC from PT. Palm Oil Plantation Bio Nusantara Bengkulu-Indonesia), cupriethylenediamine (CED; Merck, Darmstadt, Germany), trimethylsilyl chlorosulfonate (TMSCS; Sigma-Aldrich, Germany), methanol (Sigma-Aldrich, Steinheim am Albuch, Germany), benzotriazole (BTri; Alfa Aesar, Karlsruhe, Germany), and dimethylformamide (DMF; Merck, Darmstadt, Germany), n-hexane (Merck, Darmstadt, Germany) were used as received.

Cyclone fibre cellulose was soaked in the solvent n-hexane for one night to eliminate palm oil that may remain. Then dried fibres immersed into a solution of 18% sodium hydroxide with heating temperature of 135 °C for 4 h to remove other components such as lignin, fats, waxes. Cyclone fibre cellulose was dissolved in solvent CED at a temperature of 25 °C (Chuan, *et al.*, 2006). TMSCS as sulfonating agent is added into the solution at room temperature; during the sulfonation nitrogen gas flow is maintained. Sulfonation of cyclone fibre cellulose based on mole ratio between cellulose and sulfonation agent used 1:0.25 for 10 h.

The reaction was stopped by adding methanol to obtain sulfonated cellulose. Then it washed with methanol and rinsed with distilled water, evaporated at a pressure of 1 atm and then dried in oven. The degree of sulfonation (DS) of SCFC was determined by acid–base titration with standard NaOH solution. Initially, the SCFC was dissolved in DMF. The solution of polymer was then titrated by an aqueous solution of 0.01 N NaOH, the titration method indicated a sulfonation ratio of 150% [(mol SO₃H/repeat unit) 100%].

Composites material were prepared by blending the sulfonated cellulose and dopant benzotriazole with stoichiometric mole ratio of sulfonated cellulose : dopant; x₁ = 0.125, x₂ = 0.25 and x₃ = 0.5 using DMF solvent. In order to obtain polymer solution, it was stirred for 12 h at room temperature. Furthermore casting on glass plates by pouring the homogeneous solution of polymer and dopant mixtures. The solvent was evaporated slowly at a temperature of 50 °C for 24 h and then transferred to a membrane in the oven for 24 h to evaporate the residual solvent contained in the membrane.

The FTIR spectra of the composites material were characterized using a FTIR spectrometer (Shimadzu IR PRESTIGE-21). Thermal stabilities of the polymer electrolytes were examined by TG analyses with a NETZCH TG 209F3 TGA. Analysis of the glass transition using Mettler Toledo DSC 821 type, analysis were performed with temperature program from -10 °C to 250 °C. Heating rate was 10 °C/min. Used as a purge gas was nitrogen gas with flow rate of 50 ml/min. The X-ray powder diffraction (XRD) analysis was performed using an X-ray diffractometer (Rigaku D-MAX 2200, Japan) with Cu K α (λ = 1.5406 Å) radiation over the range 2 θ between 0° and 80°. The morphology of the material was observed by SEM-type JEOL 7001 FESEM (Tokyo, Japan). The samples were previously coated with gold in a sputtering device.

Activation energy of composites material has been determined by the Semi-empirical Arrhenius equation as follows:

$$\text{Viscosity, } \eta = A_0 e^{-E_a/KT} \quad (1)$$

$$\ln \eta = \ln A_0 - E_a/KT. \quad (2)$$

Methanol permeability determined by using formula as follows (Unal *et al.*, 2008).

$$J = (W \cdot l)/(Mw \cdot A \cdot t). \quad (3)$$

J = methanol permeability as a flux (mol/cm.s).

W = mass losses (g).
l = thickness of the membrane (cm).
A = membrane area (cm²).
t = time (s).

Results and Discussion

Figure 1 shows the FTIR spectra of CFC and SCFC. The difference spectra of sulfonated cellulose and cellulose are evident especially in the region wave numbers around 690 cm⁻¹ which showed absence C-S stretching vibration and near 1310-1200 cm⁻¹ and 1360-1300 cm⁻¹ attributed to symmetric stretching vibration of O = S = O of sulfonate (-SO₃) group. The different types of spectra obtained in the region between the finger print between sulfonated cyclone fibre cellulose and cyclone fibre cellulose. The spectra of cellulose fibre cyclone this study are similar to those reported (Bono *et al.*, 2009).

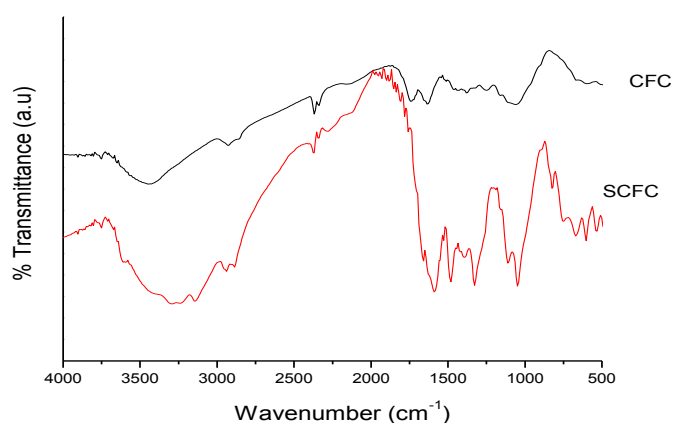


Figure 1. FTIR spectra of CFC and SCFC.

Figure 2 shows FT-IR spectra of the blends and after doping, SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC-Btri-0.5 show C=N and C-N stretching peaks around 1480-1554 cm⁻¹ due to triazole ring (Krishnakumar & Xavier, 2004). The lower intensity of C=N peak comparing to intensity of C-N peak may indicate the ring protonation (Gustian *et al.*, 2013). SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC-Btri-0.5 have two peaks between 3300-3400 cm⁻¹ and one strong peak at 1640 cm⁻¹ due to amine N-H stretching and bending vibrations, respectively (Levchik *et al.*, 1992). Previous studies, protonation of the free nitrogen in triazole ring has been demonstrated around 3100 cm⁻¹ (Gustian *et al.*, 2012). In this case, the peak at 3100 cm⁻¹ region is not sharp. All samples show N=N ring stretching at around 1260 cm⁻¹ and characteristic triazole ring vibration at 1550 cm⁻¹. The peak at wave number 3380 cm⁻¹ associated with the N-H stretching vibration. This research was also supported by previous studies on the formation of supramolecular interactions between sulfonated polysulfone and benzotriazole, hydrogen bonds formed from SO₃H and N acts as a facilitator movement of protons (Gustian *et al.*, 2012).

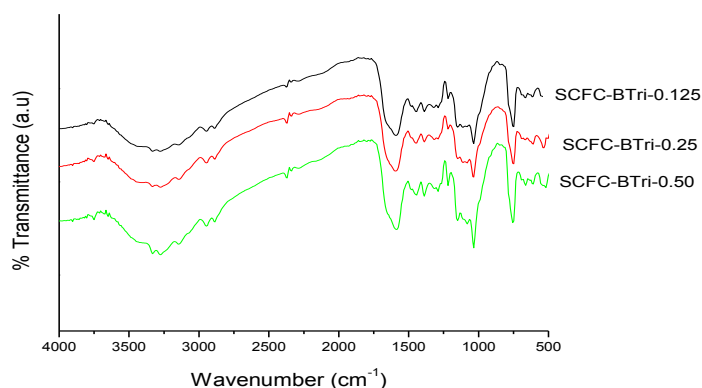


Figure 2. FTIR spectra of the blends SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC-Btri-0.5.

Others research also have reported that the local wave number 3100 cm^{-1} also generated N --- H stretch, indicating the occurrence of protonation on the imidazole ring of poly benzimidazole as a result of the interaction between the hydrogen atoms on the sulfonate group (Oktay *et al.*, 2009). Previous N --- H interaction on the polymer molecule has been reported synthesis of polymer electrolyte membrane based on acid-base complex pair (Gustian *et al.*, 2014 b and Gustian *et al.*, 2016).

Thermal stability of CFC showed in Figure 3, that the CFC has dimensional stability up to $250\text{ }^{\circ}\text{C}$ and degraded at temperatures ranging above $250\text{ }^{\circ}\text{C}$. In the area of 40% by weight of CFC, drastic degradation that occurs around $330\text{ }^{\circ}\text{C}$. Thermogram SCFC still showed thermal stability between $100\text{-}150\text{ }^{\circ}\text{C}$. The greater mole ratio will decreased membrane stability, where the increase in mole ratio of dopant to the polymer will lead to decreased stability the membrane but still above the expected performance. This decrease can be explained as a softening effect of the proton solvent benzotriazol on the composite materials. Privious study have reported about interactions the N--H between sulfonated polysulfone and benzotriazole (Gustian *et al.*, 2012).

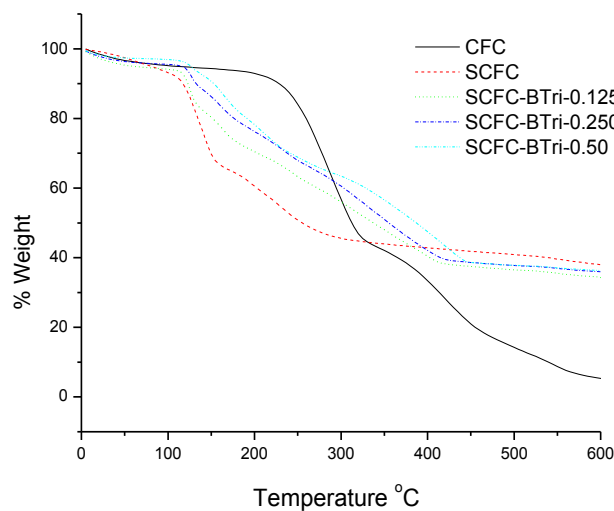


Figure 3. Thermogram of CFC, SCFC, the blends SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC-Btri-0.5.

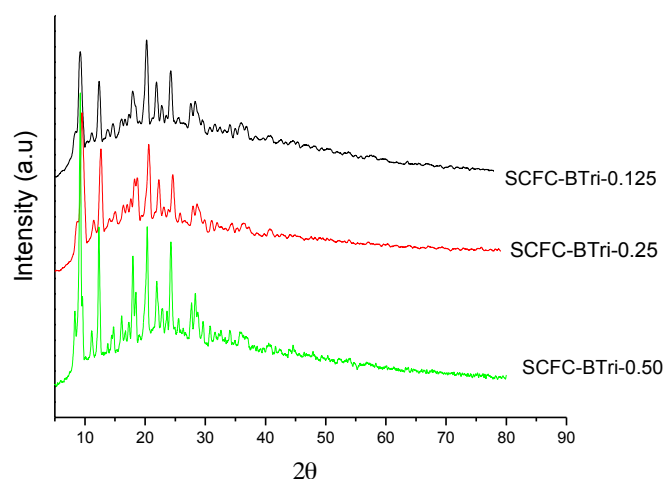


Figure 4. X-ray diffraction patterns of the blends SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC-Btri-0.5.

Figure 4 Shows the X-ray diffraction patterns of the blends SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC Btri-0.5. The X-ray diffraction patterns of the SCFC after the addition of dopants benzotriazole at

various mole ratios were showed that the crystallinity slightly increased in each addition. The blends SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC Btri-0.5 after the addition of the dopant benzotriazole still remains semi-crystalline and showed the existence of an amorphous phase, large amorphous phase raises swamp effect and will inhibit the movement of protons. Meanwhile, in the FTIR studies, suggests that the formation of hydrogen bonds in the polymer as a cause of the formation of a new crystalline character (Bouchet & Siebert, 1999). This fact supports the formation of the blends SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC Btri-0.5.

Figure 5 shows the surface material SCFC, it indicate that the occurrence of intrafibril and fibre morphology still showed that the membrane pores formed between the cellulose intrafibril. After the addition of dopant, the structural morphology of the membrane had changed. The increase of dopant mole ratio made the membrane structure become fragile. The formation of pores with the winding structure and the still formed as a function of the membrane. Relationship between proton conductivity and microstructure polyelectrolyte membrane has been reported (Peckham *et al.*, 2008).

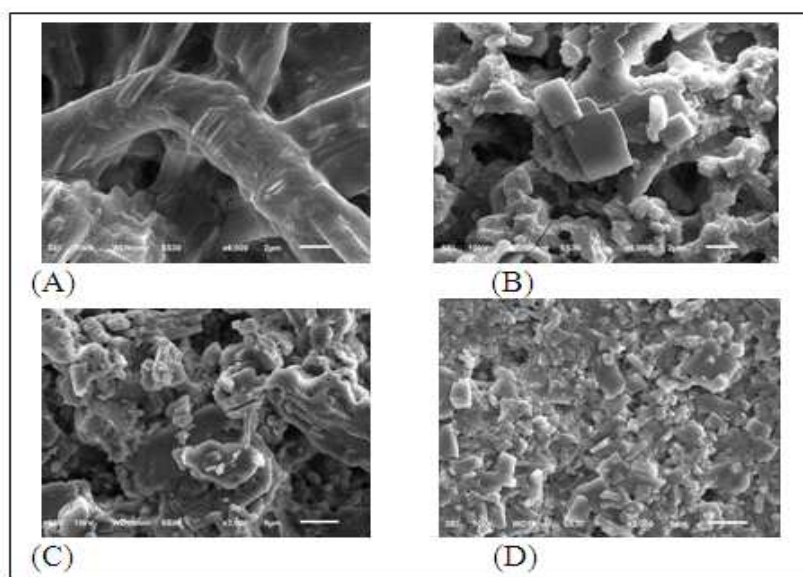


Figure 5. SEM micrographs of (A) SCFC, (B) SCFC-Btri-0.125, (C) SCFC-Btri-0.25 and (D) SCFC-Btri-0.5.

Arrhenius equation for the viscosity of the polymer solution at various temperatures analogue to with the DC conductivity at various temperatures. Activation energy is defined as the minimum energy needed for a particular chemical reaction can occur, sometimes a chemical reaction need a catalyst for the reaction to take place with lower energy supply. In this case as a proton conductor membrane, the activation energy is the minimum energy that must be exceed in order to the movement of protons from the anode to the cathode, resulting in a potential. Table 1. shows activation energy of composites membrane, the activation energy increases with increasing of mole ratio of dopant and declined again to a higher mole ratio which describes the process of relaxation of the polymer chains. This decrease may be due to the plasticity of polymeric material is reduced, so that will affect the mobility of the polymer chains.

Table 1. Activation energy of composites membrane		
N	SCFC:Btri (mole)	Activation energy (eV)
1	SCFC-Btri-0.125	0.106
2	SCFC-Btri-0.25	0.144
3	SCFC-Btri-0.5	0.137

Methanol vapor will experience along the equilibrium with the liquid concentration gradient through the membrane. Mass loss is recorded as a function of time to calculate the methanol permeability.

Problems with the use of a membrane based on methanol in fuel cell, methanol crossover is still a barrier and always found. Especially for portable applications where the current density is lower. Higher crossover methanol fuel with high concentration of the anode side to the cathode side can cause the loss of polarization (Unal *et al.*, 2008).

Table 2. Methanol permeability of composites material SCFC-Btri-0.125, SCFC-Btri-0.25 and SCFC-Btri-0.5

N	Material	Methanol flux (mol/cm.s)
1	SCFC-Btri-0.125	1.7×10^{-9}
2	SCFC-Btri-0.25	1.1×10^{-9}
3	SCFC-Btri-0.5	8.6×10^{-10}
4	Nafion 112*	1.89×10^{-9}

* Unal *et al.*, (2008)

Methanol mass flow of the composites for SCFC-Btri-0.125 has a larger mass flow compared to the other material. Sequentially mass flow of material: SCFC-Btri-0.125 > SCFC-Btri-0.25 > SCFC-Btri-0.5. In Table 2 shows a comparison of methanol permeability composites material SCFC-Btri-0.125, SCFC-Btri-0.25, SCFC-Btri-0.5 and Nafion 112 membrane.

From the methanol flux of composites material were obtained approaching the Nafion 112 membrane and in the same order. While the composite material SCFC-Btri-0.5 even produce methanol flux under the order of the Nafion 112 membrane, in terms of membrane permeability is dense and have the prospect as a proton conducting membrane based on methanol in fuel cell.

Conclusion

We have investigated novel composites material based on sulfonated cyclone fibre cellulose (SCFC) from natural fibre and benzotriazole (Btri) as candidat proton conducting material for fuel cell. The composite material were prepared successfully by impregnation of the protogenic solvents into sulfonated cyclone fibre cellulose. The composites material are thermally stable up to approximately 150°C. From the FTIR studies, it was found that protons are dissociated from the acidic groups and partially protonated triazole units leading to hydrogen bonding network formation for SCFC and Btri. Methanol permeability experiments demonstrated that the composite material have lower methanol permeability compared to pristine Nafion112. Activation energy has been obtained 0.106 eV, 0.144 eV and 0.137 for SCFC-Btri $x_1 = 0.125$, $x_2 = 0.25$ and $x_3 = 0.5$ respectively. From the results of the activation energy were obtained condition that all composite material SCFC-Btri have activation energy is almost similar. Activation energy needed to help initiate that protons move from the anode to the cathode in a fuel cell membrane. These results showed that the insertion of azole units, especially Btri into hydrophilic channels of SCFC resulted in the production of thermally stable material that can be suggested for application as electroactive polymers.

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