

Surface Modification of Cellulose from Sugarcane Bagasse Using Soybean Oil to Increase the Hydrophobicity

Abdillah Hisyam¹, Lisman Suryanegara², Tun Tedja Irawadi¹, Yudhi Dwi Kurniawan²

¹ Department of Chemistry, Bogor Agricultural University, Bogor 16680, Indonesia

² Research Center For Biomaterials, Indonesia Institute of Sciences, Bogor 16911, Indonesia

Email: abdillahhisyam@gmail.com

Abstract. Cellulose fibers from sugarcane bagasse were bleached and modified by soybean oil in order to increase the hydrophobicity. The modified cellulose prepared by mixing cellulose fibers with soybean oil in various quantity and ethanol as a solvent. The process was mixed using ultrasonic for 3 minutes and then was dried using oven at 110 °C for 60 minutes. Identification of the infrared spectrum confirmed that cellulose modified by 0,35 g and 0,5 g soybean oil generates signals carbonyl functional group at wavenumber 1750 cm⁻¹. The XRD patterns indicated that degree of crystallinity from modified cellulose did not change significantly. In addition, the wettability test showed that the modified cellulose hard to dispersed in water solvent.

1. Introduction

Sugarcane bagasse is a byproduct in the manufacture of sugar from sugarcane stems. Sugarcane bagasse is generated during manufacture of sugar when sugarcane is squeezed by the squeezer machine at the sugar factory. This process results 5% sugar, 90% sugarcane bagasse and water [7]. Sugarcane bagasse containing 40-50% cellulose, 25-35% hemicellulose composed of xylose, arabinose, galactose, glucose and mannose, and the rest of lignin as well as some minerals, wax, and other compounds [6]. The amount of cellulose content in sugarcane bagasse make sugarcane bagasse as a source of cellulose which is quite abundant.

Cellulose is widely used in many fields, such as coating, membrane, pharmaceuticals and foodstuffs [3]. This caused the cellulose has several advantages, such as the source is abundant in nature, requiring a low cost, easily biodegradable, and have a high tensile modulus [1]. High tensile modulus of cellulose can be used as reinforcement in polymer. Suryanegara *et al.* (2009) utilized the cellulose fibers as a reinforcing material in the polymer of polylactic acid. Polylactic acid reinforced by cellulose fiber increased tensile strength and stiffness. However, cellulose has some shortcomings, such as tend to clumps and is hydrophilic [5]. Therefore, to use cellulose widespread need to do chemical modification of the cellulose surface fibers.

Chemical modification of cellulose surfaces in this study will be conducted using soybean oil. Soybean oil is a vegetable oil containing triglycerides. Vegetable oil triglyceride containing 3 acyl chains with various lengths and degrees of saturation that is connected to the main chain glycerol. Cellulose surface being covered completely by the hydrophobic triglycerides lead to increased hydrophobicity on the surface of cellulose. Increasing the hydrophobicity of the cellulose surface can expand the application, such as stain resistant product, raincoat, water repellent outdoors gear [2], and improved compatibility with the polymer to form a composite [4]. Therefore, this study aims to modified the surface cellulose using soybean oil to improve the hydrophobicity.

2. Experimental

2.1. Materials

Sugarcane bagasse was obtained from Sugar Group Company, Inc, Indonesia. Glacial acetic acid, sodium chlorite 25%, potassium hydroxide, benzene, acetone, dichloromethane, soybean oil, and ethanol were used for isolation of cellulose and modification of cellulose.

2.2. Cellulose Isolation from Sugarcane Bagasse (Sun et al. 2004)

The dried sugarcane bagasse weighed 10 grams. Afterwards, sugarcane bagasse put in a baker containing 600 mL distilled water. As much as 0,8 mL glacial acetic acid and 16 ml sodium chlorite 25% were added to beaker respectively. Subsequently, the mixture was put into a waterbath at 80 °C for 5 h. Every hour, glacial acetic acid and sodium chlorite were added to the mix with same amount. After that, the mixture was filtered using distilled water until the filtrate does not yellow. The residue obtained then soaked in 500 mL of 6% potassium hydroxide for 12 h. Then, the residue was filtered and rinsed with distilled water until no remaining potassium hydroxide. Subsequently, the residue was soaked again in 500 mL potassium hydroxide 6% but was assisted by heating in a waterbath at 80 °C for 2 h. Finally, the residue was filtered and rinsed using distilled water until there is no remaining potassium hydroxide.

2.3. Modification of Cellulose Using Soybean Oil

Cellulose/water suspension of 6 wt% was prepared by ultraturax with a speed of 6000 rpm for 75 minutes. After that, water was removed by centrifugation. Cellulose was stirred in ethanol with the ratio of 1:100 (w/v) for 15 minutes. The process was repeated four times in order to replace water to ethanol.

As much as 0,196 g soybean oil was mixed with 4,7 mL ethanol with stirring. Then, 0,5 g (wet based) cellulose was added to the soybean oil-ethanol mixture and stirred ultrasonic at full power (400 W) for 3 minutes. After the mixture dry at room temperature, sample was stored in an oven at 110 °C for 60 minutes. After that, the product is washed with ethanol for 3 times using a centrifuge and then dried at room temperature. The process was also done for 0,35 g and 0,5 g soybean oil.

2.4. Characterization

Unmodified and modified cellulose spectrum are measured by FTIR spectrophotometer (IRPrestige 21 Shimadzu, Japan).

The structur of unmodified and modified cellulose were analyzed by using X-ray diffractometer (Maxima, Shimadzu, Japan) with Cu K α radiation at 40 kV and 30 mA and also scanning from 5° to 40°. The X-ray diffraction patterns were record at a speed of 2° min⁻¹.

Wettability test was used to characterize hydrophobicity of the modified cellulose. 5 mg of sample was mixed with two immiscible solvents (water and dichloromethane) in a vial.

3. Results and discussion

The chemical composition of sugarcane bagasse and sugarcane bagasse cellulose are presented in Table 1. Percentages of cellulose, hemicellulose, lignin and ashes were calculated on a dry weight basis.

Table 1. Chemical composition of sugarcane bagasse and sugarcane bagasse cellulose

Composition	Content (%)	Content (%)*	Content (%) **
Ash	3,3	1,9	20,9
Hemicellulose	62,8	41,7	24,5
Alfa cellulose	37,2	51,8	35,2
Lignin	26,1	6,7	22,2

* bleached cellulose

** sugarcane bagasse chemical components based on Rezende *et al.* (2011)

Surface modification of cellulose made by mixing cellulose with soybean oil and ethanol as a solvent. the reaction is assisted by ultrasound. Ultrasonic waves increase the kinetic energy of each reagent so that the course of the reaction will be faster, here is a transesterification reaction that occurs between the cellulose and soybean oil.

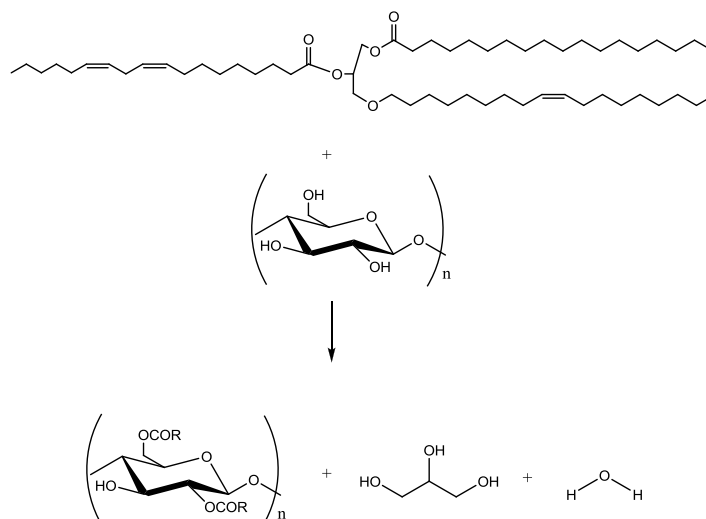


Figure. 1. Transesterification reaction between cellulose and triglyceride

Byproduct in the form of water and glycerol will be dissolved into ethanol so as not to interfere the resulting product. Heating used oven at 110 °C aims to eliminate the ethanol containing water and glycerol. Transesterification reaction run equilibrium, so that the resulting water will make the reaction turned and produce cellulose and triglyceride back. Therefore, water needs to be removed so that transesterification reactions can occur perfectly.

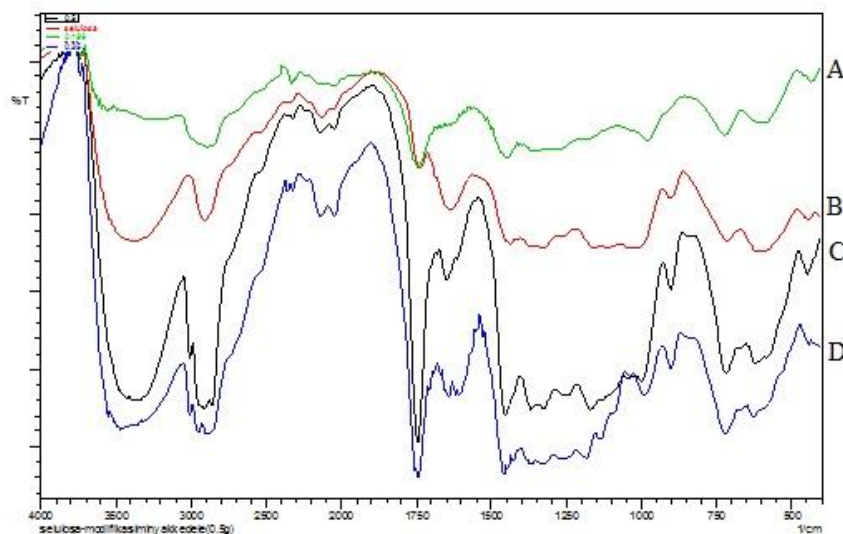


Figure. 2. FTIR spectrum of cellulose (B) and cellulose modified soybean oil 0,196 g (A), 0,35 g (D), and 0,5 g (C)

Fig. 2 showed the FTIR spectra of cellulose and cellulose modified soybean oil 0,196 g, 0,35 g, and 0,5 g. New peak emerge at wavenumber 1745 cm⁻¹ in the spectrum of cellulose modified soybean 0,35 g and 0,5 g. However, the addition of soybean oil 0,196 g did not showed new peak in the wavenumber. This showed that the addition of 0,196 g soybean oil was not enough to modify cellulose. Peak at wavenumber 1745 cm⁻¹ is a signal to the strain of the ester carbonyl and this is an evidence of esterification. Furthermore, peak at wavenumber 2800-2950 cm⁻¹ showed the C-H band from aliphatic acid chain.

The hydrophobicity was characterized using wettability test. Sample was mixed into two immiscible solvent (water and dichloromethane). The result showed that unmodified cellulose was well to dispersed in water solvent. on the other hand, cellulose modified soybean oil with various quantities were hard to dispersed in water solvent (Figure 3). This alteration indicated that the hydrophobicity of cellulose had increased.

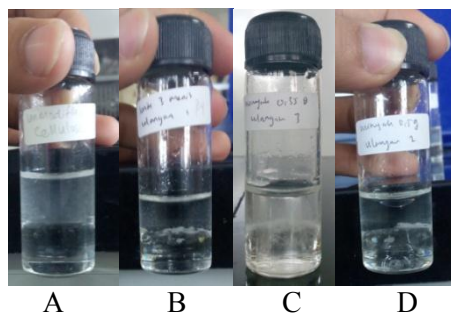


Figure 3. Wettability test of cellulose (A) and cellulose modified soybean oil 0,196 g (B), 0,35 g (C), and 0,5 g (D)

The XRD patterns of cellulose and cellulose modified soybean oil 0,196 g, 0,35 g, and 0,5 g were given in Fig. 4. In general, the X-ray diffractograms of the modified cellulose showed a progressive decrease and broadening in the intensities of the signals. Eventhough, cellulose modified soybean oil 0,196 g and 0,5 g has almost similar degree of crystallinity with cellulose, which is very important when modified celluloses are used as reinforcement for composite application.

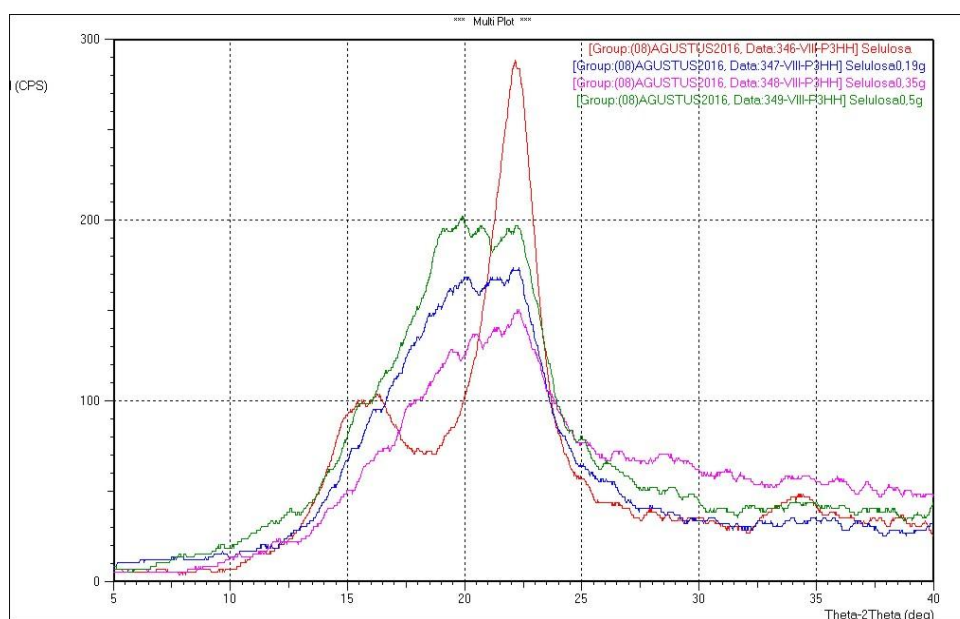


Figure 4. The XRD patterns of cellulose and cellulose modified soybean oil 0,196 g, 0,35 g, and 0,5 g

4. Conclusion

The polarity of cellulose could be modified by mixing with soybean oil an dheatin at 110 °C. After the modification, cellulose displayed a higher hydrophobicity. Cellulose modification does not change the degree of crystallinity of cellulose, so that can be used as reinforcement in composite application.

Acknowledgements

The authors are grateful to Research Center For Biomaterials Indonesia Institute of Sciences for financial support and PT Sugar Group Company, Indonesia for giving sugarcane bagasse.

References

- [1] Cerqueira EF, Baptista CARP, Mulinari DR. 2011. Mechanical Behaviour of Polypropylene Reinforced Sugarcane Bagasse Fibers Composites. *Procedia Engineering*. 10:2046-2051.
- [2] Dankovich TA and Hsieh. 2007. Surface Modification of Cellulose With Plant Triglycerides for Hydrophobicity. *Cellulose*. 14:469-480. Doi:10.1007/s10570-007-9132-1.
- [3] Klemm D, Kramer F, Moritz S, Lindstrom T, Ankerfors M, Gray D, Dorris A. Nanocelluloses: a new family of natur-based materials [review]. *Green Nanomaterials*. Doi:10.1002/anie.201001273.
- [4] Mulinari DR, Voorwald HJC, Cioffi MOH, Rocha GJ, Pinto da Silva MLC. 2010. Surface Modification of Sugarcane Bagasse Cellulose and Its Effect on Mechanical and Water

- Absorption Properties of Sugarcane Bagasse Cellulose/HDPE Composites. *BioResources*. 5(2):661-671.
- [5] Mulinari DR, Voorwald HJC, Cioffi MOH, Lucia da Silva M, Gouva da Cruz T, Saron C. 2009. Sugarcane Bagasse Cellulose/HDPE Composites Obtained by Extrusion. *Composites Science and Technology*. 69:214-219.
- [6] Rezende CA, Aparecida de Lima M, Maziero Priscila, Ribeiro deAzevedo E, Garcia Wanius, Polikarpov Igor. 2011. Chemical and Morphological Characterization of Sugarcane Bagasse Submitted to A Delignification Process for Enhanced Enzymatic Digestibility. *Biotechnology for Biofuels*. 4(54): 1-18.
- [7] Sun JX, Sun XF, Zhao H, Sun RC. 2004. Isolation and Characterization of Cellulose from Sugarcane Bagasse. *Polymer Degradation and Stability*. 84:331-339.
- [8] Supriyadi A. 2002. *Rendemen Tebu Liku-Liku Permasalahannya*. Yogyakarta(ID): Kanisius.
- [9] Suryanegara L, Nakagito AN, Yano H. 2009. The Effect of Crystallization of PLA on The Thermal and Mechanical Properties of Microfibrillated Cellulose-Reinforced PLA Composites. *Composites Science and Technology*. 69:1187-1192.