Characterization nano crystalline cellulose from sugarcane bagasse for reinforcement in polymer composites: Effect of formic acid concentrations

N A S Aprilia, S Mulyati, P N Alam, Karmila and A C Ambarita
Chemical Engineering Departement, Engineering Faculty, University of Syiah Kuala, Banda Aceh, Indonesia

E-mail: sriaprilia@unsyiah.ac.id

Abstract. Nanocellulose from sugarcane bagasse for reinforcement in polymer composites has isolated from formic acid (FA) with different concentration. This research was conducted with three level concentration of FA ei. 15, 30 and 50%. The nanocellulose were successfully prepared with variations of total yields of 66.66, 67.33 and 69.33% respectively with increase of FA concentrations at 6 hours of hidrolysis time. The obtained nanocellulose were characterized by fourier transform infrared (FT-IR) spectroscopy confirmed the introduction of carboxyl goups on the surface of cellulose. The X-ray diffraction (XRD) spectra proved the existence of cellulose, with a highly crystalline of 62.466, 71.033, and 76.296% with increase of FA concentrations. The size of crystallinity of nanocellulose were decreased with increased of FA concentration. The result investigated that size of crystallinity of nano cellulose reduced from 4.37, 4.15 and 3.94 nm.

1. Introduction
The use of agriculture solid waste for reinforcement in polymer composites is one of reduce environment issue. In addition, the use of agricultural waste for various purposes also to increase the added value for the waste itself. The increasing interest in environment-friendly materials has motivated industrial in development and use of biomass for various reinforcement in polymer composites.

Sugarcane bagasse is one of biomass agriculture waste that potential for reinforcement in polymer matrixes because has cellulose content. Many researcher has developed nanocellulose from many bioresources such as kenaf [1], oil palm fronds [2] oil palm tree [3], bagasse pulp [4], dhaincha, corn stalks, rice straw and wheat straw [5], sugarcane bagasse [6-8], Gigantochloa scortechinii [9]. These nanocellulose developed in various method to find out nanocellulose in form of both nano fibril and nano crystalline.

Cellulose found in the main constituent of plant cell wall, is the mayor constituent and is a homopolysaccharide composed of β-1-4 glucopyranose units [10-11]. Many study have extracted nanocellulose from the plant cell wall throught chemical and mechanical treatment. Acid hydrolytic processes are also used to degrade amorphous cellulose in forming cellulose nanofibers. In common processes, cellulose crystallites from cellulosic materials were prepared using acid hydrolysis. During isolation process, the dimention of cellulose is mainly dependent on its origin as well as the preparation methods and condition implemented [12]. The acceptance of acid inside part of the amorphous is easier than in crystalline part due to the more compact strcture of crystals. Acid
hydrolysis allows to break and removal of disorder and part of amorphous in cellulosic fibers, releasing single and well defined crystals in the form of nano crystalline cellulose [7]. Therefore, the extensive properties of nano crystalline cellulose from different bioresources such as mechanical properties, low density, biodegradability are very important for the development of bionanocomposites.

In this study, to extract nano crystalline cellulose from sugarcane bagasse by using formic acid with various concentrations has been investigated. The developed of nano crystalline cellulose by acid hydrolysis having high crystallinity index, supposed to have good surface morphology for polymer reinforcement. The obtained nano crystalline cellulose were characterized using FT-IR and XRD analysis.

2. Experimental

Nano crystalline cellulose extracted from sugarcane bagasse that were collected from seller sugarcane juice of Banda Aceh City, Aceh Province, Indonesia. After drying in sunlight, it was cut in size ± 2 cm, and that the sample wash with dilatated water for 3 times. Bagasse was dried in oven at 60 °C for over night and stored at room temperature.

2.1. Extraction of bleached pulp sugarcane bagasse

Approximately 10 grams of dried sugarcane bagasse was hydrolyzed using 300 ml NaOH 1 M for an hour and 30 minutes at temperature 80 °C. This process is to eliminate lignin content (delignification process). Then the sample was washed by distilled water in a centrifuge for 3 times. After that, added 150 ml of NaOCl 5% for 20 minutes at temperature of 80 °C. Sample washed by distilled water in a centrifuge for several times. The pulp was dried in an oven at 70 °C for 3 hours. This process was prepared base on previously describe methods [6].

2.2. Preparation of nano crystalline cellulose

Isolated nano crystalline cellulose from sugarcane bagasse used FA with ratio between bleaching pulp and FA 1:30. The three variations of FA concentrations were used 15, 30 and 50%. The hydrolysis process was quenched by stirrer at 400 rpm at temperature 90 °C. A colloidal suspension which produced was centrifuged at 4500 rpm for 30 minutes. After that, nano crystalline cellulose was washed with distilled water in the centrifuge as many times. The nano crystalline cellulose was dried in an oven at 70 °C for 3 hours. The percentage of yield was calculated according to Eq. 1 [3].

\[
yield(\%) = \frac{M_1 x M_2}{M_3 x M_o} x 100
\]

Where \( M_o \) is the initial mass of sample, \( M_1 \) is the weight of nano crystalline cellulose finally obtained. \( M_2 \) is the mass of the suspension sample used to get the dry powder. \( M_3 \) is the mass suspension in the final preparation.

2.3. Characterization

2.3.1 Fourier transform infrared spectroscopy (FT-IR) analysis

The FT-IR spectra was used to identify the functional group of nano crystalline cellulose. The analyzed were recorded on Fourier Transform Infrared Spectrometer Shimadzu Prestige 6400. The amount of samples was blended with KBr powder and then pressed into thin pellets. The sample was measured in the wavelength range from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).
2.3.2 X-ray diffraction (XRD) analysis
To determine crystallinity index and crystal size of nano crystalline cellulose were used X-Ray diffraction analyses. XRD analyses were on an X-Ray diffractometer with measurement condition are 40 kV and current 30 mA. The scattering angle range (2θ) was from 10° to 80° with the rate 10°/min. The crystallinity index (CrI) was calculated using the Eq. 2 and crystal size was calculated using Scherrer Eq. 3 [11].

\[ C_r(\%) = \left(1 - \frac{I_{am}}{I_{200}}\right) \times 100 \]  
\[ D = \frac{0.9\lambda}{\beta_{1/2}\cos\theta_{1/2}} \]

Crystallinity index (CrI) was calculated from the maximum peak intensity at lattice diffraction (200) and \(I_{am}\) is the intensity minimum between the 200 and 110 peaks. While for calculating crystal size, K is the Scherrer constant (K = 0.9), \(\lambda\) is the wavelength of X-ray radiation (\(\lambda = 1.5406\ \text{Å}\)) and \(\beta_{1/2}\) is the full width at half-maximum of the Reflection, and \(\theta\) is the Bragg angle.

3. Result and discussion
3.1. Yield of production nano crystalline cellulose
Production of nano crystalline cellulose with acid hydrolysis has investigated with three concentrations of FA and constant of time, acid ratio with fiber and temperature. The obtained yield of nano crystalline cellulose from sugarcane bagasse as concentration function show in Table 1. The basis of the cellulose of sample at 3 grams. The result show that the higher of FA concentration, the greater of the percent yield due to the less dissolved area of amorphous cellulose.

3.2 Functional group nano crystalline cellulose
The FT-IR spectra subjected with various concentrations of FA and cellulose functional group show in Figure 1. The functional group of cellulose could be determine from the wave length at 3247 cm\(^{-1}\) (C-H), 2895 cm\(^{-1}\) (C-H), 1647 cm\(^{-1}\)(N-H), 1369 cm\(^{-1}\) (C-H), 1315 cm\(^{-1}\)(C-O), 1155 cm\(^{-1}\)(C-H), 1055 cm\(^{-1}\), dan 898 cm\(^{-1}\)(C-H), at these wavelengths are typical of cellulose groups.

From Fig. 1 it is clear that the nanoselulose spectrum is similar to the cellulose spectrum, the difference being in the transmittance intensity, meaning that for all three FA concentrations it does not affect the functional group, the similarity of the sample indicated the similar in chemical composition. The deferent sample of cellulose with nano crystalline cellulose, the wavelength appears new peaks at 1714 cm\(^{-1}\) (C ≡ O stretching) and 2360 cm\(^{-1}\) (H-C ≡ O: C-H stretch). From FT-IR spectra are not different nano crystalline cellulose and cellulose. It indicates that there are not new bonds formed during hydrolysis process.

Nuruddin [5] has employed that removed the amophous cellulose on the surface by the acid hydrolysis, therefore, more COH, C-O-C and C-C bonds were exposed, resulting in increased stretching absorbency. Sensitive to crystal structure of the cellulosic part are the wavelength 850-1500 cm\(^{-1}\) (Kumar et al, 2014). Spectral bands at 1420-1430 cm\(^{-1}\) and 893-897 cm\(^{-1}\) are very important to elucidate to the crystal structure of cellulosic material and its (1420/893 cm\(^{-1}\)) spectral ratio and (1375/2900 cm\(^{-1}\)) spectral ratio show index of crystallinity or lateral order index (LOI) and total crystallinity index (TCI), respectively.
3.3 Structure and crystallinity of nano crystalline cellulose

The structure and crystallinity index of isolated cellulose and nano crystalline cellulose were studied using XRD. The XRD patterns of cellulose and nano crystalline cellulose effect of FA concentrations are shown in Figure 2. The crystallinity percentage and crystal size, as calculated from Eq. 1 and Eq. 2, respectively, are summarized in Table 1. In four curves, the peak are observed at $\theta = 15.25^\circ$, $20.29^\circ$ and $22.39^\circ$.

From Table 1 the crystallinity index increase with increasing concentration of FA. It has been reported that the cellulose is partly crystalline and and partly amorphous in molecule structure, meaning that the cellulose chains contains the crystalline regions and amorphous regions [2]. The intensity of the peaks was higher for nano crystalline cellulose, showing that nano crystalline cellulose are more crystalline. On the other hand, there is a decrease of diffraction intensities in the amorphous region [5]. The higher crystallinity is associated with the higher tensile strength of nano crystalline cellulose [3, 13]. When the amorphous regions that hold the crystalline parts dissolve during acid hydrolysis, single crystals are released and the crystallininity increase [1].

The size of crystallite of nano crystalline cellulose decrease with increasing of acid concentrations. From Table 1 show that size crystalline of cellulose higher than nano crystalline cellulose. The loose structure of celluloses favored alteration in the crystal size and that the degradation of smaller crystals as well as the growth of defective crystal was responsable for increasing the crystallite size [1].

Table 1. Yield, crystallinity and size of crystalline for sugarcane bagasse of nano crystalline cellulose

| Concentration of FA (%) | Yield (%) | Crystallinity (%) | Size of crystalline (nm) |
|-------------------------|-----------|-------------------|-------------------------|
| Cellulose               | -         | 44.030            | 4.55                    |
| FA-15%                  | 66.66     | 62.644            | 4.37                    |
| FA-30%                  | 67.33     | 71.033            | 4.15                    |
| FA-50%                  | 69.33     | 76.296            | 3.94                    |
4. Conclusion
Nano crystalline cellulose was prepared from sugarcane bagasse with acid hydrolysis. The three level various FA concentrations has investigated. Functional group of the cellulose and nano crystalline cellulose shown the similarity pattern. It was indicated that no new bonds formed during acid hydrolysis. The crystalline index increase with increasing acid concentrations. But, for size of crystallite nano cellulose decrease when increasing of acid concentration. The higher crystalline index and the smaller the size of crystal of nano crystalline cellulose will be effect for good properties (tensile strength) of nano crystalline cellulose as reinforcement in polymer biocomposites.

Acknowledgment
The authors would like to thank The Research Institutes and Community Service University of Syiah Kuala and Directorate of Research and Community Service and Directorate General of Research and Development, Ministry of Research, Technology and Higher Education who have funded this research in accordance with the Research Contract No. 105/SP2H/LT/DPRM/IV/2017, April 03, 2017.

References
[1] Aprilia N A S, Davoudpour Y, Zulqarnain W, Abdul Khalil H P S, Hazwan C H, Hossain C I, Dungani R, Fezree H M, Zaidon A and Mohammad Haafiz M K 2016 Bioresour. p3875-3889
[2] Owalabi A W T, Arniza G, Daud W W and Alkharkhi A F M 2016 Bioresour. 11 3013
[3] Karim Md. Z, Ali Md. E, Chowdury Z Z and Hamid S B A 2016 Bioresour. 11 3840
[4] Du H, Liu C, Mu X, Gong W, Lv D, Hong Y, Si C and Li B 2016 Cellulose 1 20
[5] Nuruddin M, Chowdhury A, Haque S A, Rahman M, Farhad S F, Jahan M S and Quaiyyum A 2011 Cellulose Chem. Technol. 45 347
[6] Apprilia N A S, Ambarita A C, Karmila, Armando M A and Guswaru F Y 2017 Oriental J. Phys. Sci. 2 1
[7] Kumar A, Negi Y S, Choudhary V and Bhardwaj N K 2014 J. Mater. Phys. Chem. 2 1
[8] Saele K, Yingkamhaeng N, Nimchua T and Sukyai P The 26th Annual Meeting of the Thai Society for Biotechnology and International Conference. 26-29 November 2014 Thailand
[9] Saurabh C K, Mustapha A, Mohd. Masri A, Owolabi A F, Syakir M I, Dungani R, Paridah M T,
Jawaid M and Abdul Khalil H P S 2016 *J. Nanomater.* 1

[10] Lee S-Y, Mohan D J, Kang I-A, Doh G-H, Lee S and Han O 2009 *Fiber Polym.* 10 77

[11] He W, Jiang S, Zhang Q and Pan M 2013 *Bioresour.* 8 5678

[12] Hamid S B A, Chowdhury Z Z, Karim Md Z and Ali Md E 2016 *Bioresour.* 11 3840

[13] Zhou Y M, Fin S Y, Zheng L M and Zhan H Y 2012 *eXPRESS Polym. Lett.* 6 744