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Temperature Effect of Crystalinity in Cellulose Nanocrystal from Oil Palm Empty Fruit Bunch (OPEFB) using Sonication-Hydrothermal Methods

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ABSTRACT

Production of cellulose nanocrystals (CNCs) from cellulose of oil palm empty fruit bunches (OPEFB) have been done. The delignification of OPEFB was mixed with 17,5% NaOH and carried out in the three-neck flask with refluxed for 2 hour at 80^{o}C. Further the suspension was bleached with NaOCl 2% for 1 hour at 70^{o}C. Then, to produce CNCs, Cellulose was firstly sonicated for 30 minutes at 40^{o}C. After that cellulose was hydrolized at hydrothermal reactor for 0,1,2,3,4,5 hours at 110 and 120^{o}C respectively. After filtration and washing, CNCs was analyzed by X-Ray Diffraction and the result shows that the grade of the highest CNCs crystalinity at consentration of HCl 2 M at a temperature of 110^{o}C with reaction time of 2 hours is equal to 75.87%. It can be concluded that sonication-hydrothermal can increase the grade of crystalinity of cellulose nanocrystal.

Key word: delignification, hydrolysis, cellulose, CNCs, crystalinity

INTRODUCTION

Oil palm empty fruit bunches (OPEFB) contains 44.4% cellulose and 30.9% hemicellulose. High levels of cellulose at this polysaccharides has potentially processed into cellulose nanocrystal [1]. Cellulose is unbranched polymer of glucose linked through beta 1,4 or 1,4 beta glucosidase. In nature, cellulose are arranged in the form of cellulose fibrils that consists of multiple cellulose molecules that linked with glucosidic bond. These fibrils form a crystal structure that is packed by lignin [2].

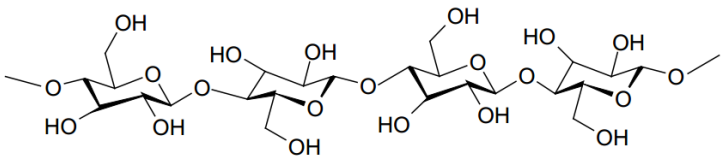

Figure 1. Cellulose structure [1].

Cellulose nanocrystal is a crystalline regions derived from cellulose. General method normally use is acid hydrolisis. Amorphous region is more easily attached with acid than crystalline regions. Therefore under controlled condition, in assuming there is no amorphous

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region while the crystalline regions remain, as illustrated in Fig.2. These assumption have been shown by X-ray diffraction, which indicates that the acid treatment gives the same size as the original crystal cellulose [3].

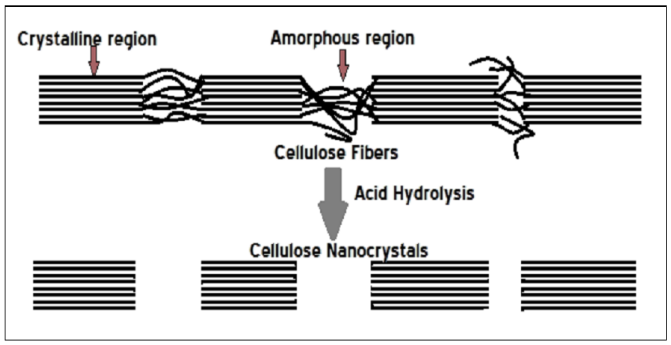

Figure 2. Acid hydrolisis illustration[4].

The general method for extracting cellulose nanocrystals is hydrolysis of sulphuric acid, that followed by fragmentation and neutralization to produce crystalline cellulose [5-8]. Unfortunately, yield obtained is less than 35%, degradation of crystalline cellulose chains and the resulting product shows thermal stability with low degradation temperature maximum (Tmax) of 250 ^{o}C [9-11]. To prevent further fabrication, they use some melting techniques as injection molding, mixing twin-screw and extrusion. Degradation can be derived from reaction of dehydration caused by sulphate group (SO_4^{2-}) remaining in the cellulose nanocrystal. Although the sulphuric groups can be removed by dialysis or desulphation, it is very complicated and time-consuming, and particularly difficult to avoid particle aggregation [5],[12-14]. Therefore, the selection of the proper chemical materials of hydrolysis to prevent aggregation and produce a high crystallinity is an important consideration.

As alternatives to strong sulfuric acid, several mineral acids of low concentration such as hydrochloric acid and organic acids (maleic acid) were utilized under ultrasonic or microwave irradiation can prevent aggregation and degradation of CNCs [13,15,16]. It has been reported that the CNCs produced through hydrochloric acid hydrolysis exhibited high thermal stability, but their aqueous suspensions tended to flocculation, and only a low yield of 20 % can be achieved [14,17]. Filson and Dawson-Andoh shortened the preparation period of CNCs by utilizing high-power ultrasonic irradiation, but only 2–5 % yield was obtained [12]. They also obtained a yield of 38.2 % by introducing endoglucanase enzyme and microwave heating [12]. Tang reported a yield of 50.04% by applying a cation exchange resin hydrolysis method. However, the removal of cation exchange resin by post treatment and repetitive centrifugations is very time-consuming [16].

Yu also reported that the high yield of CNCs caused by utilization of weak acid with lower process time under hydrothermal condition, which acid can penetrate rapidly into inner layer of cellulose tissue and hydrolyze amorphous region of cellulose chains. Whereas, crystalline regions of cellulose is more resistant with hydrolysis weak acid because of hydrogen bonding strength between nearby cellulose molecules compared amorphous regions which is less compact [8].

In ultrasonic system both crystalline and amorphous regions are equally hit continuously. But crystalinity of cellulose only decreased approximately 11%. Continuously hit caused damage of particles and then decompose into CNCs as shown in Figure 3 [18].

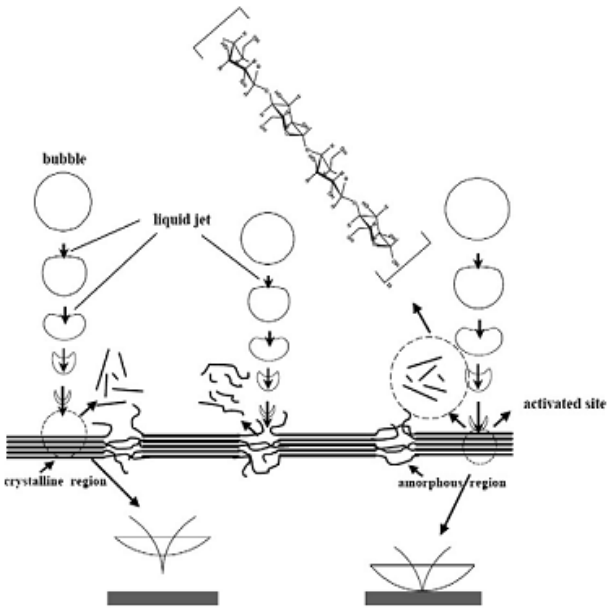

Figure 3. Ultrasonic mechanism of cellulose[18].

Based on several studies on this study try to do a combination of sonication and hydrothermal processes, the results revealed a high yield and crystallinity. The effect of temperature in this study will determine the results obtained, the longer reaction times and higher temperatures cause the hydrolysis of crystalline cellulose degradation and produce a lower yield. Therefore, temperature and reaction time becomes the main parameters that are important in this study.

EXPERIMENT

Chemicals and instrumentations

OPEFB bioamass wastes were taken from CPO processing plants, chemical that are used to OPEFB delignification is NaOH 17.5% and NaOCl 2% from Merck Inc. The acid were used to hydrolysis of cellulose is HCl 37 % from Sigma Inc.

Instrumentations applied for analysis were FTIR spectrophotometer (Nicolet 8700 FT-IR spectrophotometer) and X-ray diffractometer Philips PZ1200 using Cu Kα X-rays with a voltage of 40 kV and current of 30 mA.

Procedure

Preparation of cellulose

50 gram OPEFB was mixed with 250 mL 17.5% NaOH and then the mixture was transferred to three-neck flask. OPEFB was refluxed for 2 hour at 80^{o}C. Further the suspension was bleached with 250 mL of NaOCl 2% for 1 hour at 70^{o}C. Then the celullose obtained was filtered and washed with aquadest until neutral pH. The purpose of process to reduce lignin from OPEFB, producing cellulose.

Preparation of cellulose nanocrystal

To produce CNCs, Cellulose 1:60 HCl 2M (g/mL) was firstly sonicated in ultrasonic bath type SU-27 TH capacity 477(W) x 272(D) x 200(H) mm, frequency 28 kHz, output 300 watts and heater 500 watts for 30 minutes at 40^{o}C. After that cellulose was hydrolyzed at

hydrothermal reactor Parr USA pressure batch reactor for 0,1,2,3,4,5 hours at 110 and 120°C respectively.

The chemical structures of OPEFB and the resulting cellulose were characterized on FT-IR spectrophotometer. FTIR spectra were recorded in the spectral range of 4000–400 cm^{-1}.

The crystal structure was characterized by X-ray diffractometer. X-ray diffraction data were taken through various angle 0-50° with the initial step 0.02° at room temperature. The index of crystalinity (Xc) of the sample is determined by segal method (1959):

$$Xc = \frac{I(crystaline) - I(amorf)}{I(crystaline)} 100\ \% \quad \text{..... (1)}$$

where I (crystalline) is the maximum crystal peak intensity at 2θ between 22° and 23° and I (amorphous) is the minimum intensity at 2θ between 18° and 19°.

RESULT AND DISCUSSION

Physic Analysis

Physically the color change of OPEFB may be seen in Fig 4, OPEFB colors that has been treated with alkali (delignification) becomes clearer. It showed reduced levels of lignin and hemicellulose that contained in OPEFB. However, celullose nanocrystal has dark color, because acid treatment prolonged so that it had carbonation in cellulose nanocrystal [8].

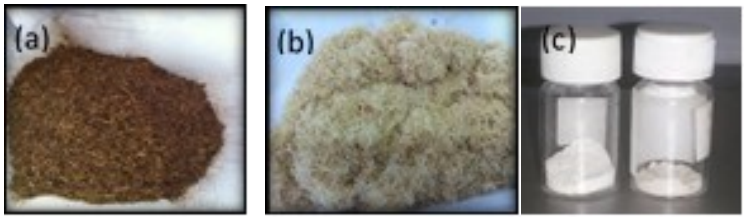

Figure 4. OPEFB (a) untreated (b) Treatment with alkali (delignification) (c) Cellulose nanocrystal

FT-IR Analysis

As shown in Fig 5, all of the samples is divide into two main absorbance region that is absorbance high wavenumber (2800-3500 cm^{-1}) and lower wavenumber (800-1700 cm^{-1}). The similarity of the chemical composition can be seen from the result of FT-IR on all samples. Strong and extensive absorption may be observed at a wavenumber of about 3300 cm^{-1}. These wavenumber are shown in the chain stretching absorbance of hydrogen (O-H) on cellulose and OPEFB. In the region of 3200-3500 cm^{-1} is representating OH vibration. Previous literature has divided this region into three types of hydrogen chain in cellulose, such as O(2)H---O(6) intramolecular, O(3)H---O(5) intramolecular, O(6)H----O(3) intramolecular [19].

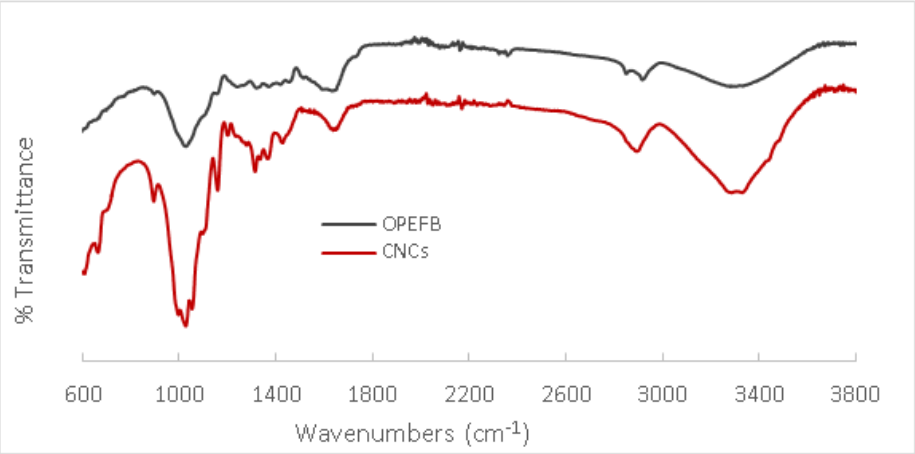

Figure 5. The result of FT-IR analysis of OPEFB and CNCs

Peak that has perceptible change in region of 1590 cm^{-1} is showing vibration chain aromatic lignin. This peak on cellulose is more disappear than after the OPEFB in delignification treatment, it indicates that the alkali treatment has eliminated the lignin content in OPEFB. According to Johar, the peak is related to the bending form water molecules due to a strong interaction between the cellulose and water, whereas the absorption peak of the sample CNCs is gone this is because the structure has become crystalline cellulose so it no longer binds with water [20]. Absorption peak at 1400-1450 cm^{-1} in spectrum OPEFB is suspected area bending vibration of O-C-H derived from lignin components, it is consistent with that obtained by Yu [8]. In addition, the absorption peaks in the region 1300-1365 cm^{-1} in all samples is vibration band of C-H and C=O were associated with an aromatic ring polysaccharide, is consistent with the absorption band analyzed by Nacos [21]. Absorption peak at 1100 cm^{-1} shown in the spectrum of CNCs was caused by the deformation of the vibration of C-H and C-O-C pyranose is more prevalent. According to Kargarzadeh changes in the spectral characteristics of this cellulose demonstrated elimination of hemicellulose and lignin [22]. CNCs show an increase in the intensity of the band 1053 cm^{-1} which shows the stretch ring pyranose C-O-C, according to Correa, this implies there has been an increase in the value of crystalline cellulose [17]. The peak shown at 895 cm^{-1} which appears on CNCs is glucose ring strain, according Li the absorption peaks at 895 cm^{-1} is C-H lowest vibration of cellulose (anomeric vibrations, specific for β-glucosides) [23].

X-RD Analysis

X-ray diffraction has purpose to determine the change of crystalinity of cellulose in the each of different conditions of acid hydrolisis. In the XRD pattern of OPEFB contained in Fig 6 has crystal regions which are common to native cellulose or cellulose I. It can be seen with peak at $2\theta = 22.8^{o}$ (based on ICDD 00-003-0289). As similarly on the cellulose shows crystalline region that normally present on the cellulose I which can be seen in the peak that appears at $2\theta=22^{o}$-23^{o} [18].

Diffraction in the Fig. 6(b) hydrolyzed at 110^{o} C temperature showed highly crystalline product which indicates the crystal structure of cellulose I without cellulose II, which is indicated by the absence of doublet at 22.6^{o} [24,25]. Where peak diffraction located in 22.6◦ becomes sharper which showed an increase in crystallinity as shown by Hafiz [26]. Increased crystallinity is related to the increased rigidity of the structure of cellulose to produce high tensile strength [24,26,27]. All the patterns of CNCs of hydrolyzed using HCl 2M at

temperature 110°C and 120°C under sonication-hydrothermal show similarities with pattern of the cellulose peak. It indicates that hydrolysis with HCl can maintain the position of crystalline cellulose.

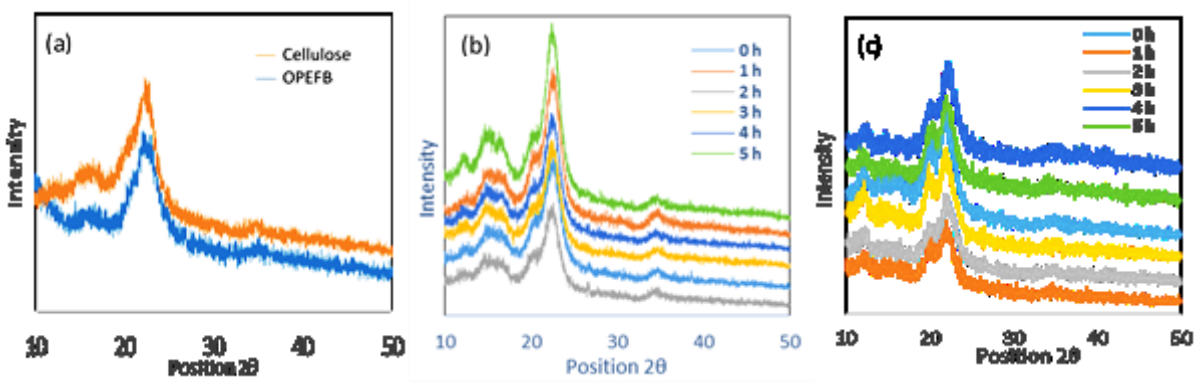

Figure 6. Result of X-RD (a) OPEFB and cellulose, (b) CNCs at temperatur 110°C with 2M acid concentration and (c) CNCs at temperature 120°C with 2M acid concentration

CNCs crystalinity resulting from hydrolysis process using 2 M HCl at temperatures of 110°C and 120°C at different reaction time are showen in Fig. 7. Temperature and reaction time is the most influential factor to produce the desired CNCs [8]. At temperatures of 110°C crystalinity of CNCs increased from 1 hour until 5 hours of reaction time, this is because the acid is able to eliminate the amorphous region in the cellulose chain so that the grade of crystalinity increases as the longer the reaction time. It causes a lot of amorphous regions are missing, leaving a crystal region. The reduction of hemicellulose and lignin and the decline of amorphous cellulose chain may also increase the crystalinity as well. But crystalinity of CNCs at the reaction temperature of 120°C has increased until 4 hour then decline at 5 hours, this is because the acid hydrolysis on the longer time may damage crystalline regions of cellulose. So that reaction time is an important parameter to consider in improving the crystalinity CNCs.

Overall the value of crystaline cellulose at temperature 110°C higher than at temperature 120°C. This proves that the temperature is the most influential factor in the hydrolysis of cellulose. The higher temperature, the content of H^+ is produced more than leading to acidic condition. So that on the higher temperatures can damage the crystal region and lead to decline in the crystal value.

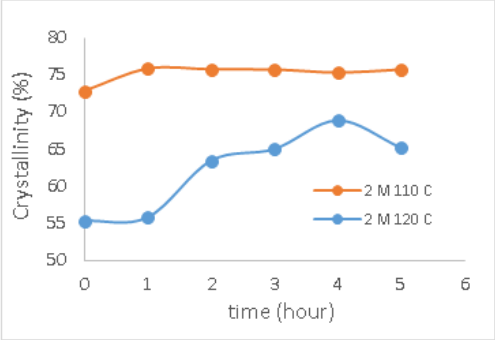

Figure 7. Crystalinity grade at reaction temperature 110°C and 120°C

CONCLUSION

The research of the production of CNC has been presented through hydrochloric acid hydrolisis from cellulose of OPEFB under sonicatin- hydrothermal. The chemical structur and CNC show a reduction in lignin an hemicellulose that shown in FT-IR. X-RD analysis show that CNC has high cristalinity index. It is proved that hyrochloric acid hydrolisis is able to perservering on 2θ between 22^o – 23^o. Crystalinity can be achieved by hydrolysis using HCl at concentration 2M which is 75.87%.

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