Preparation and Characterization of Cellulose Microcrystalline (MCC) from Fiber of Empty Fruit Bunch Palm Oil

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Abstract. Alpha cellulose which was isolated from cellulose of fiber empty fruit bunch palm oil was hidrolized with hydrochloric acid (2,5N) at 80°C to produce microcrystalline cellulose (MCC). Microcrystalline cellulose is an important additional ingredient in the pharmaceutical, food, cosmetics, and structural composites. In this study, MCC, alpha cellulose, and cellulose were characterized and thereafter were compared. Characterizations were made using some equipment such as x-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and thermogravimetry analyzer (TGA). X-ray diffraction and infrared spectroscopy were studied to determine crystallinity and molecular structure of MCC, where scanning electron microscopy images were conducted for information about morphology of MCC. Meanwhile, thermal resistance of MCC was determined using thermogravimetry analyzer (TGA). From XRD and FTIR, the obtained results showed that the crystalline part was traced on MCC, where the –OH and C-O groups tended to reduced as alpha cellulose has changed to MCC. From SEM the image showed the reduction of particle size of MCC, while the thermal resistance of MCC was found lower as compared with cellulose and alpha cellulose as well, which was attributed to the lower molecular weight of MCC.

1. Introduction

The Empty fruit bunch palm oil (EFBPO) is a renewable agricultural residue represent abundantly, generated from palm oil mills. Each year, the processing produce millions tonnes of residues. This material can be modified for the production of novel materials for environmentally friendly applications after some chemical modifications. Three major structural polymeric component of EFBPO are lignin, cellulose and hemicellulose. Hemicellulose and lignin are both amorphous substances, while cellulose forms a microcrystalline structure with high order region (crystalline region) and low order region (amorphous region) [1]. Cellulose, one of the major component in EFBPO is a polydisperse polymer of high molecular weight and comprised long chains of D-glucose units joined together by β-1,4 glucosidic bonds [2]. Among other uses such as pulp and paper product, cellulose is also widely employed as a
starting material for the production of microcrystalline cellulose. Microcrystalline cellulose (MCC) is a polymer has been widely used in a variety of commercial applications in the food, structural composite, and pharmaceutical industries. This polymer has a high amount of amorphous regions that occurs as a white, odourless, tasteless, crystalline powder composed of porous particles [3]. The MCC was obtained by partially hydrolyzing cellulose with mineral acid to remove amorphouse regions in forming microcrystal.

A conventional method for producing MCC from cellulose is acid hydrolysis process. The hydrolysis of cellulose can be accomplished using mineral acid [4-10], enzymes [11], and microorganism [12]. However, different properties of MCC such as crystallinity, moisture content, molecular weight, surface area and porous structure, thermal resistance were also obtained from different sources of raw material. Reports have shown that MCC can be produced from kenaf fibers [12], rice hull and bin hull [3], cotton linters [13], sawdust [4], rice straw [14], Oil Palm Empty Fruit Bunches [15], groundnut shells [16], corn cobs [17], sisal fibers [5], cotton rags [6].

This article reports the preparation and characterization of MCC by acid hydrolysis method using hydrochloric acid. Characterization was studied by FTIR, XRD, SEM and TGA.

2. Methode

2.1. Raw material
Cellulose derived from the EFBPO which was isolated earlier was kindly supplied by Oil Palm Research Centre in Medan, Indonesia. Sodium hydroxide (NaOH), sodium hypochloride (NaOCl), and hydrochloric acid (HCl) (37%) were supplied by Sigma-Aldrich and used as received.

2.2. Production of alpha cellulose
Alpha cellulose was obtained from the cellulose using 17.5% sodium hydroxide (NaOH) at 80°C for 0.5 h. Bleaching was then carried out with 3.2% sodium hypochloride (NaOCl) at 100°C for 1.5 h.

2.3. Production of MCC
The alpha cellulose powder derived from cellulose was hydrolized using 2.5N hydrochloric acid (HCl) at 80°C for 15 min. The hydrolized cellulose was thoroughly washed with cold distilled water until neutral to litmus paper and then dried.

2.4. Characterization

2.4.1. Fourier Transform Infrared (FTIR). Infrared spectroscopy of cellulose, alpha cellulose and MCC were carried out using Shimadzu IR-Prestige 21. Bands were recorded in the region from 4000 to 500 cm⁻¹.

2.4.2. X-ray diffraction (XRD). X-ray diffractometry patterns of cellulose, alpha cellulose and MCC were pressed to form pellets and recorded in 6100 Shimadzu.

The crystalline index (Ic) was determined by Eq (1) using the intensity of I₀₀₂ peak at about 2θ = 21.9° and Iₐₐₐ is the intensity corresponding to the peak at about 2θ = 12°-18°

\[ I_c = \left( \frac{I_{002} - I_{am}}{I_{002}} \right) \times 100 \]  

(1)

2.4.3. Morphological characteristic. Scanning electron microscopy (SEM) was used to examine the microscopic structure and the surface morphology of the prepared cellulose, alpha cellulose and MCC. For SEM measurement the instrument used for morphological observation was SEM EVO MA 10 ZEISS.
2.4.4. Thermal analysis. Thermogravimetry analysis was utilized using Shimadzu Simultaneous TGA/DTA Analyzer DTG-60 to investigate the thermal properties of cellulose, alpha cellulose and MCC.

3. Results and Discussion

3.1. Infrared spectroscopy

The molecular structure of the cellulose isolated directly from EFBPO, alpha cellulose and MCC. Are shown in Figure 1.

![FTIR spectra](image)

**Figure 1.** FTIR spectra of a. Cellulose; b. Alpha cellulose; c. MCC

FT-IR spectra of the different samples of cellulose were recorded in the range of 4000–500 cm$^{-1}$. A slight difference is observed in the region of the intermolecular hydrogen bonding (3200–3400 cm$^{-1}$). The shift of the maximum absorbance band of stretching vibration of OH group of MCC to lower wave number (3340 cm$^{-1}$) as compared with other two samples of cellulose (3363 cm$^{-1}$ and 3400 cm$^{-1}$ for alpha cellulose and cellulose, respectively). This shift proves that MCC is more crystalline than both samples. Moreover, the characteristic intermolecular and intramolecular OH stretching vibration band in the spectrum of MCC appeared broader than those of alpha cellulose and cellulose. This is due to the degradation of the hydrogen bond between the cellulosic chains during the hydrolysis process. Here, the first part hydrolyzed and degraded by acid were an amorphous region.

The C–H stretching vibration absorbance intensity in MCC (2892 cm$^{-1}$) is slightly decreased upon acid hydrolysis of alpha cellulose; this is due to the presence of –CH$_2$ moieties in the samples [18]. The absorption bands at 1635 cm$^{-1}$ corresponds with 1639 cm$^{-1}$ and 1631 cm$^{-1}$ were attributed to O-H bending, the vibration of adsorbed water molecules [19]. This peak could be due to the presence of small amounts from hemicellulose. The presence of this peak may be arising from the oxidation of the C–OH groups.

The peaks related to –CH or C-O bending vibrations (1369, 1374 cm$^{-1}$) in the polysacharide aromatic rings (20) are less intense in the spectrum of MCC than those of alpha cellulose and cellulose. The band
at 1064 cm⁻¹ corresponds with 1061 and 1053 cm⁻¹ appears is due to -CH₂-O-CH₂ pyranos ring stretching vibration. In addition, the band at about 898 cm⁻¹ in the spectrum of MCC is attributed to the asymmetric out of plane ring stretching in cellulose due to the β glucosidic linkage between glucose unit in cellulose. It is noted the linkage stands for the increase in crystallinity of the material [21].

3.2. X-ray diffraction
Figure 2 shows the x-ray diffraction spectra of cellulose, alpha cellulose and MCC.

![X-ray diffraction spectra](image)

**Figure 2.** X-ray diffraction of a. Cellulose; b. Alpha cellulose; c. MCC

The powder x-ray diffraction spectra of the three cellulose samples exhibit different diffraction patterns. Cellulose derived from oil palm empty fruit bunch fibre was highly amorphous, as indicated by the less peaks in the diffractogram (Fig 1a). An amorphous region implies a more disordered structure, resulting in a low crystal region.

The crystallinity is traced on the alpha cellulose diffractogram (Fig. 1b). This is due to removal of hemicellulose and lignin, which existed in amorphous region leading to realignment of cellulose molecules. However, These two peaks are smeared and appear as one broad peak. A smeared out diffractogram was observed for samples, especially the peaks that appeared at diffraction angles ranging from 20°-24° for cellulose and from 18°-24° for alpha cellulose indicating a low degree of order. This results are similar with the study have reported by Mat Soom et.al [15]. However, the higher peak of alpha cellulose in comparison to cellulose, indicating that the crystalline behaviour of alpha cellulose was higher than for cellulose. The presence of amorphous aromatic compounds such as lignin, polysacharide polymers and many others was attributed to this behaviour.

Figure 1c shows the x-ray diffraction spectra of MCC. The highest crystal structure was obtained for MCC due to the removal of the amorphous regions of alpha cellulose by acid hydrolysis, realoeasing individual crystallites. It is interesting to note that the MCC in the present case shows doublet in the intensity of the main peaks corroborating the coexistence of cellulose I and cellulose II allomorphs. The large different spectra between MCC with cellulose and alpha cellulose results in the appearance of two significant peaks indicating the highly crystalline structure of MCC. High crystallinity indicates an ordered compact molecular structure, when the crystalline cellulose content is high, these two peaks are more pronounced.
The peak intensity of MCC appeared to be higher than that of alpha cellulose indicating that the MCC is more crystalline than alpha cellulose. The peaks at MCC spectra are more defined suggesting that the hydrolysis acid process removed some of the amorphous material from the alpha cellulose. The process was initiated in the fast removal of amorphous cellulose near the surface of macrofibrils, which leads to the exposure of microfibril bundles. An amorphous cellulose near surface is hydrolyzed first and followed by crystalline cellulose near surface. The amorphous cellulose deeply buried in the bulk leach out from macrofibrils during hydrolysis at slower rates due to barriers caused by the microfibril bundles. This process repeats during the hydrolysis process until cellulose degradation occurs [22]. During processing to MCC, the alpha cellulose was hydrolyzed and depolymerized to remove a large portion of the amorphous region, leaving the crystalline cellulose. The diffractograms for MCC exhibit diffraction patterns typical of cellulose, with diffraction peaks of the 2θ angles at 12, 20, 22 and 21.9°. The index crystallinity (CI) which is calculated according to the equation (1) gives a quantitative measure of the crystallinity in powders. Here the crystallinity index of MCC from hydrolyzation process is 73%. Since cellulose from different source differs in properties, different properties of MCC obtained from source are expected and the condition of hydrolysis process also affect the properties. Some studies about the effect of sources on the percent crystallinity of MCC have been reported such as Kenaf is 70% [12], cotton linter is 76% [14], groundnut shells is 74% [16], baggas is 76% [10], rice straw is 78% [10], cotton stalks is 77% [10] and sisal is 60% [5].

3.3. Scanning Electron Microscopy (SEM)
Figure 3 shows the surface morphology of cellulose, alpha cellulose and MCC using SEM.

![Figure 3. SEM images (mag. of 5000) of a. Cellulose; b. alpha cellulose; c. MCC](image)

Figure 3a shows SEM images of cellulose derived from EPFBO under 5k magnification. It clearly shows the macrofibril shape and distribution of the macrofibrils in cellulose not uniform. On treating firstly with alkali, hemicelluloses and lignin was removed from around the fiber. However, it observed
the macrofibril interconnections were occurred as the hemicellulose could not well dissolved during treatment.

The SEM micrographs for the alpha cellulose (Figure 3b), showed a smaller diameter as compared to the cellulose (Figure 3a). On subsequent treatment with alkali, the hemicelluloses, which was still remain in cellulose, was hydrolyzed and becomes water soluble. These help in defibrillation of the fibrils and result in micrograph, whereby the diameter of the fibrils is reduced to a great extent. However, the interconnections amongst fibrils were still occured.

On the other hand, the MCC image shows a fibrous structure and individualized (Figure 3c). The MCC obtained showing fibers strands which appear like rod-shaped. The MCC appeared to be irregular fiber fragments and also show a network-structure (13). In this case, after macrofibrils were hydrolyzed and rinsed, the volume of amorphous cellulose was occupied by water molecules that were then removed; the remaining macrofibrils contain large amounts of naked microfibril bundles.

3.4. Thermal Resistance

Figure 4 below shows the thermal resistance of cellulose, alpha cellulose and MCC.

![Figure 4. SEM images (mag. of 5000 ) of a. Cellulose; b. alpha cellulose; c. MCC](image)

The thermograms curves of cellulose (a), alpha cellulose (b), and MCC (c) are shown ini Fig...The initial weight losses starting at 60°C for all samples may be attributed to the evaporation of loosely bound moisture on the surfaces of these samples.

The thermogravimetry curve for cellulose and alpha cellulose follow similar degradation pattern. The first stage degradation for cellulose and alpha cellulose occurs at a temperature range of 225-350°C and 220-355°C, respectively with a total weight loss of 80% for cellulose and 75% for alpha cellulose. The second stage started at about 350°C for cellulose and 355°C for alpha cellulose and reached a maximum at 480°C for both samples with a total weight loss of 85%.

In the alpha cellulose the removal of all non cellulosic materials helps to make the cellulose structure more dense and compact and hence a slightly rise in the temperature of degradation have occured.
The degradation of MCC appears to follow different mechanism where the temperature at a range of 285-340°C with a total weight loss of 85%, which is due to the degradation of cellulose. The rest of degradation occurred during heating at 340-480°C with a total weight loss of 90%.

A notable difference, in particular between MCC sample and two other samples (cellulose and alpha cellulose), is observed at the temperature at which 20% weight loss of the samples is degraded. This temperature is lower for cellulose and alpha cellulose (275°C) as compared to the MCC (285°C). This result might be attributed to the higher crystallinity and lower moisture contents of the MCC. The rearrangement and reorientation of the crystals in MCC offers to raise the onset temperature of degradation. Additionally, higher onset temperature are associated with high thermal stability. However, start at a temperature of 325°C the degradation of MCC shows more drastic as compared with two other samples. This temperature corresponds with 40% weight loss of MCC, while the other two samples (cellulose and alpha cellulose) show 35% of weight losses. It may attributed to the reduction in molecular weight of MCC during hydrolysis process. Hydrolysis process have made the MCC is more susceptible to degrade when temperature increases. It is also believed that hydrolysis of cellulose not only dissolves the amorphous regions, but also some crystalline regions (21). Similar results have been reported by El-Sakhawy and Hassan (10) when producing MCC from bagasse fibers.

4. Conclusion
The microcrystalline cellulose (MCC) was obtained from alpha cellulose which was isolated from cellulose derived from EFBPO. The three samples were then compared in terms of molecule structure, crystallinity, morphology and thermal stability. MCC was prepared by hydrolysis acid using hydrochloric acid (2.5N). Some structures of the molecules have been changed due to the hydrolysis process. In addition, the x-ray diffractograms proved that the MCC samples are more crystalline compared to two other samples (cellulose and alpha cellulose). On the other hand, it was noticed by the SEM that hydrolysis treatment affected the morphological structure of the resulting microfibrillated cellulose. However, the thermal stability of the MCC samples starting at temperature at 325°C were lower as compared to the corresponding other two samples which was attributed to the reduction of molecular weight of MCC.

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References
[1] Li X, Tabil L G and Panigrahi S C 2007 Chemical treatments of natural fibre for use in natural fibre-reinforced composites: a review J. Polym. Environ. 15 pp 25–33.
[2] Klemm D, Philipp B, Heinzle T, Heinzle U and Wagenknecht W 1998 Comprehensive cellulose chemistry Weinheim Wiley–VCH pp 9–25.
[3] Adel A M, El-Wahab Z H A, Ibrahim A A and Al-Shemy M T 2011 Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: Physicochemical properties Carbohydrate Polymers 83 pp 676–687.
[4] Oyeniyi Y J and Itiola O A 2012 The Physicochemical characteristic Of microcrystalline cellulose, derived from sawdust, agricultural waste products Int J Pharm Pharm Sci vol 4 pp 197-200.
[5] Bhimte N A and Tayade P T 2007 Evaluation of Microcrystalline cellulose prepared from sisal fibers as a tablet excipient: A Technical Note, AAPS PharmSciTech 8 Article 8 (http://www.aapspharmscitech.org).
[6] Chauhan, Y P R, SAPKAL S, SAPKAL V S and ZAMRE G S 2009 Microcrystalline cellulose from cotton rugs (waste from garment and hosiery industries) Int. J. Chem. Sci. 7(2) pp 681-688.
[7] Hafiz M K M, Eichhorn S J, Hassan A and Jawaid M 2013 Isolation and characterization of microcrystalline cellulose from oil palm biomass residue Carbohydrate Polymers 93 pp 628–634.

[8] Ejikeme P M 2008 Investigation of the physicochemical properties of microcrystalline cellulose from agricultural wastes I: orange mesocarp Cellulose 15 pp 141–147.

[9] Laka M and Svetlana C 2007 Obtaining microcrystalline from softwood and hardwood pulp Bio Resources 2(3) pp 583-589.

[10] El-Sakhawy M and Hassan M L 2007 Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues Carbohydrate Polymers 67 pp 1–10.

[11] Maha M I, El-Zawawy W K, Juttke Y, Koschella A and Heinze T 2013 Cellulose and microcrystalline cellulose from rice straw and banana plant waste: preparation and characterization, Cellulose DOI 10.1007/s10570-013-9992-5.

[12] Keshk S M A S and Haija M A 2011 A new method for producing microcrystalline cellulose from Gluconacetobacter xylinus and kenaf Carbohydrate Polymers 84 pp 1301–1305.

[13] Nada A M A, El Kady M Y, El-Sayed E S and Amine F M 2009 Preparation and characterization of microcrystalline Celullose Bio Resources 4(4) pp 1359-1371.

[14] Nawar G A M, Hassan F A M, Ali K E, Kassem J M and Mohamed S H S 2010 Utilization of microcrystalline cellulose prepared from rice straw in manufacture of yoghurt Journal of American Science 6 (10) pp 226-231.

[15] Mat Soom R, Aziz A A, Wan Hasan W H and Mat Top A B G. 2009 Solid state characteristics of microcrystall cellulose from oil palm empty fruit bunches Fibre Journal of Oil Palm Research vol 21 pp 613-620.

[16] Azubuike C P, Odulaja J O and Okhamafe A O 2012 Physicotechnical, spectroscopic and thermogravimetric properties of powdered cellulose and microcrystalline cellulose derived from groundnut shells J. Excipients and Food Chem. 3 (3).

[17] Azubuike C P and Okhamafe A O 2012 Physicochemical, spectroscopic and thermal properties of microcrystalline cellulose derived from corn cobs International Journal Of Recycling Of Organic Waste in Agriculture http://www.ijrowa.com/content/1/1/9.

[18] Khalil H P A, Ismail H, Rozman H D and Ahmad M N 2001 The effect of acetylation on interfacial shear strength between plant fiber and various matrices European Polymer Journal 37(5) pp 1037–1045.

[19] Nacos M, Katapodis P, Pappas C, Daferera D, Tarantilis P A ad Christakopoulos P 2006. Kenaf xylan—A source of biologically active acidic oligosaccharides Carbohydrate Polymers, 66(1) pp 126–134.

[20] Troede, M, Sedan D, Peyratou, C, Bonnet J, Smith A and Guinebretiere R 2008 Influence of various chemical treatments on the composition and structure of hemp fibers Composites Part A- Applied Science and Manufacturing 39(3) pp 514–522.

[21] Mandal .A and Chakraborty D 2011 Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its Characterization Carbohydrate Polymers 86 pp 1291–1299.

[22] Zhao H, Ja H K, Zhang Z C, Brown H M, Arey B W and J Holladay. E 2007 Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis Carbohydrate Polymers 68 pp 235–241.