
 Technical Report

Extraction of Microcrystalline Cellulose from Oil Palm Trunk

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Microcrystalline cellulose (MCC) was extracted from two types of oil palm trunks (OPT) fibers. The first sample was the leftover of OPT fibers after the sap was being squeezed out while the second sample was the leftover OPT fibers after the starch was being extracted. The chemical compositions of the two types of OPT fibers were analyzed using TAPPI standards for their extractives, holocellulose, α -cellulose, and lignin contents. Several analyses were carried out including scanning electron microscope (SEM), zeta potential, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) to determine the morphological, dispersion stability, crystallinity and thermal stability of the OPT fibers, respectively. Some changes were observed on the surface of oil palm trunk fibers and intensities in the sample spectra after acid hydrolysis. The XRD results showed an increase in crystallinity value and reached 65% after acid hydrolysis for both MCC compared to their raw OPT fibers. The TGA results of both samples MCC exhibited lower thermal stability after acid hydrolysis compared to the raw OPT fibers. The obtained MCC has a potential to be used in high composite material processing.

Key Words

Microcrystalline cellulose, Oil palm trunk, Crystallinity, Thermal stability, Acid hydrolysis

1. Introduction

The microcrystalline cellulose (MCC) is defined as the purified, partially depolymerized cellulose prepared by treating α -cellulose, which was obtained as a pulp from any fibrous plant material with mineral acids¹⁾. The MCC has the degree of polymerization typically less than 400 and the material that has a particle size of less than 5 μm which is not more than 10 %²⁾. The MCC is produced at a huge scale through acid hydrolysis of wood and cotton cellulose. The MCC from different sources has different properties since it has a different crystallinity index, moisture content, surface area, porous component and molecular weight³⁾. Different types of natural celluloses have been investigated by other researchers such as bleached kraft bagasse pulp, bleached soda pulp rice straw pulp³⁾, banana waste⁴⁾, oil palm frond⁵⁾, bagasse and rice straw⁶⁾, cotton linters⁷⁾, and Alfa fibers⁸⁾.

The MCC plays an important role as an ingredient in

the pharmaceutical, food, cosmetic and other industries. It is used widely as the anti-caking agent, a fat substitute, an emulsifier, an extender and a bulking agent. Besides, MCC is also being used in oil drilling paints, shields from heat and even flame-resistant board⁹⁾.

Compared to other lignocellulosic materials, oil palm tree contains very high levels of carbohydrates. The carbohydrates that can be found in the oil palm trunks (OPT) are usually in the form of sugar form that contains cellulose, starch, hemicelluloses, and lignin¹⁰⁾. Presence of high levels of sugar (10% free sugar) and starch (25%) inside the oil palm trunk, makes them suitable to be used in industries such as paper making and manufacturing binderless panels¹¹⁾. Generally, the holocellulose is made up of hemicellulose and cellulose. The OPT contain high cellulose content, thus, can be suitable materials for the production of microcrystalline cellulose. The objective of this study therefore is to extract MCC from oil palm trunk using a combination of chemical and mechanical treatment followed by sulfuric acid hydrolysis.

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2. Experimental

2.1 Material

The OPT were obtained from the oil palm plantation in Kuala Selangor. The OPT, then were sawn into discs, chopped, dried and later were ground into particles and passed the screening process of 1000 μm by using the Willey Mill. There were two types of samples prepared from the oil palm trunks. The first sample was the leftover of OPT fibers after their sap was squeezed out (denoted as OPT P1) while the second was the leftover OPT fibers after their starch was extracted (denoted as OPT P2). Both samples were placed in an oven at 50 °C for one night before being ground into 0.3 mm size of powder form. Both samples were placed inside the sealed plastic bag at room temperature.

2.2 Preparation of microcrystalline cellulose

The isolation of microcrystalline cellulose from the oil palm trunks was done by undergoing several processes following the procedure from previous researchers with some modification as described in our previous work^{12) 13)}. About 40 g of sugar free oil palm trunk fibers were weighed to undergo soxhlet extraction process. The soxhlet extraction was done for 4 h by using toluene to ethanol with a ratio by volume of 1:2 to remove the extractive from the fibers. Then, the extracted fibers were left air dried under the room temperature condition. The extractive free fibers were soaked four times in sodium chlorite (NaClO_2) solution with an acetic acid at 70 °C water bath for 3 h then washed with distilled water. Potassium hydroxide (KOH) solution was prepared with 6 weight % to remove the hemicelluloses from the extracted fibers by soaking it in KOH solution and then kept in the refrigerator for 24 h. The cellulose was rinsed with distilled water again. After that, the purified cellulose was hydrolyzed in 210 mL of 64% sulfuric acid (H_2SO_4) solution under strong agitation at 45 °C for 1 h. The acid hydrolysis process was terminated by adding 400 mL of cold water into the precipitate solution. The precipitate solution is diluted with distilled water until pH 5. The precipitate, then, underwent dialysis process for 3 days until the pH became constant. It was homogenized for 30 min, sonicated and freeze dried until it really dried up. The step was repeated for starch free oil palm trunk fiber sample.

2.3 Chemical composition

The chemical components of the OPT fibers were investigated. Preparations of extractive free samples were conducted according to TAPPI 264 cm-97¹⁴⁾ with a modification of the solvent ethanol-toluene ratio of 2:1. The

holocellulose content was based on the method of Wise *et al.* (1946)¹⁵⁾. The cellulose content was extracted from the percentage of holocellulose with 17.5% sodium hydroxide. Lignin content of the samples was analyzed according to TAPPI 222 om-02¹⁶⁾.

2.4 Sulfur content and zeta potential

The zeta potential of the MCC was measured at a concentration of 0.01% using a zetasizer analyzer model Malvern Nano Z Zen 2600. Deionized water was used as a dispersant. The microcrystalline cellulose suspensions were sonified for 5 min before testing. The sulfur content of the MCC was determined by using the ultimate analysis technique with an elemental analyzer. Elemental analysis was performed mainly to investigate the total sulfur content of the MCC after sulfuric acid hydrolysis. It was carried out using Perkin Elmer 2400 CHNS/O elemental analyzer.

2.5 Scanning electron microscopy

Scanning electron microscope (SEM) was employed to scan the image of the oil palm trunks (OPT) fibers and microcrystalline cellulose to obtain the morphological information. The samples were viewed under LEO Supra 50 VP field emission scanning microscope (FESEM) with ultra-high resolution. Prior to viewing all the samples were coated with gold using a sputter gold coater.

2.6 Thermogravimetric analysis

Thermogravimetric analysis was performed to determine the thermal stability of the oil palm trunk fibers after the acid hydrolysis of both OPT raw fibers and microcrystalline cellulose samples. Perkin Elmer TGA 7 was used to collect the thermal stability data. The samples of 10 to 15 mg were heated under the temperature in the range from 25 °C to 800 °C at the heating rate of 10 °C/min under a nitrogen atmosphere.

2.7 XRD analysis

The X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation with the wavelength of 1.5406 nm was used to measure the structural and phase analyses of the both samples. Then, the operating voltage and current were generated of 40 kV and 30 mA, respectively. After that, the samples were scanned at the 2° / min with a 2 θ angle which ranges from 5° to 50°. The crystallinity index value was calculated to quantify the crystallinity of the samples. The crystallinity index (C_i) is calculated with the formula by Segal¹⁷⁾.

3. Results and Discussion

3.1 Chemical composition analysis

The chemical composition of the OPT samples was depicted in Table 1. There are differences in the chemical composition for OPT P1 and OPT P2 fibers where OPT P1 sample had higher extractives and lignin contents as compared to OPT P2 samples. The difference might be due to the loss of sugar and starch during the compression process which withdraws the sugar from the oil palm trunk as well as the squeezing process where the starch had been withdrawn.

The holocellulose content for the OPT P1 fibers is 69.04%, which is lower than the OPT P2 sample that is 75.18%. For the cellulose contents, OPT P1 fibers have 40.95% and OPT P2 fibers has 41.72%. It is not much different between those two samples. The OPT P1 samples contain 20.21% lignin contents while for the OPT P2 sample, the lignin content is 18.64%. High cellulose content means the plant cell wall and the fibers have high strength and stability. The chemical composition of the oil palm trunk for both samples was within the acceptable limits comparable with those of previous research that had been done before^{18) 19)}.

3.2 Morphological studies

The changes in the morphological structure of the cellulose fibers after the acid hydrolysis process were observed under scanning electron microscope. Fig. 1 (a and b) and (c and d) shows the micrograph of both raw OPT P1 and P2 fibers while Fig. 1 (e) and (f) showed the micrographs of the microcrystalline cellulose from OPT P1 and OPT P2, respectively.

There are some impurities and starch (Fig 1. b and d) that can be observed on the surface of the raw of both fibers, but after the acid hydrolysis, all these impurities and irregularities are being removed as being shown in Fig. 1 (e) and (f). The acid hydrolysis process will not only decrease the size of the fiber from bundle size into single individual fibers, but also increase the surface smoothness of the fibers. Thus, it showed that both MCC from OPT P1 and P2 fibers are well-defined fibrils.

Table 1 Chemical composition of OPT fibers

Chemical Composition (%)	Materials	
	OPT P1	OPT P2
Extractives	11.93	6.41
Holocellulose	69.04	75.18
α -cellulose	40.95	41.72
Lignin	20.21	18.64

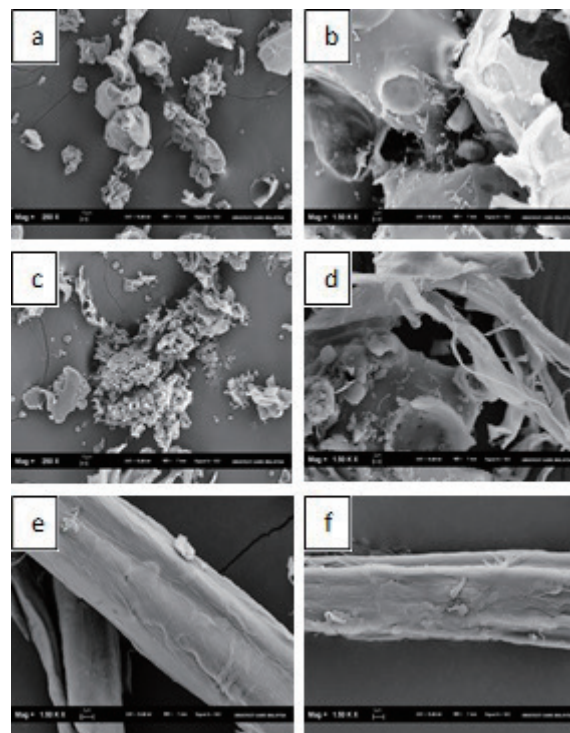


Fig. 1 SEM micrographs of (a and b) raw OPT P1 (c and d) raw OPT P2 e) OPT P1 MCC f) OPT P2 MCC

Table 2 Sulfur content, zeta potential, and crystallinity of OPT MCC fibers

	Materials	
	OPT P1 MCC	OPT P2 MCC
Sulfur content (%)	0.47	0.54
Zeta Potential (mV)	-27.1	-36.1
Crystallinity (%)	64.66	64.63

3.3 Sulfur content and zeta potential

Table 2 listed the sulfur content, zeta potential value, and crystallinity of the OPT samples. The sulfur content of OPT P1 MCC was lower (0.47%) as compared to the OPT P2 MCC (0.54%). In this study, sulfuric acid with a concentration of 64% was used, which is the common acid concentration in the acid hydrolysis process. It is interesting to point out that at this concentration, the degradation of sulfated microcrystalline cellulose to sugars might occur, resulting in reduced sulfur content²⁰⁾. The MCC with sulfate groups obtained at an acid concentration of 64% having yields below 40% and agreeable to the yields reported in this study²¹⁾.

The stability of the MCC suspensions can be derived from the zeta potential of the suspensions as reported in Table 2. The incorporation of the sulfate groups on the surface of the cellulose induces a negative electrostatic repulsion layer resulting in a more stable suspension^{20) 22)}. As shown in Table 2, the average zeta potential value of

the MCC from OPT P1 is -27.1 mV, lower than -36.1 mV for MCC from OPT P2. For the negative charge, the larger the absolute value of zeta potential is the better suspension stability that can be achieved due to the electrostatic repulsion between the nanoscale particles²³. This shows that the OPT P2 MCC has higher dispersion stability as compared to the OPT P1 MCC. The dispersion difference between both MCC could be related to the possibility of entanglement of the particle.

3.4 XRD analysis

The X-ray diffraction analysis is used to determine the percentage of crystallinity of the microcrystalline cellulose that was isolated from OPT P1 fibers and OPT P2 fibers. Basically, cellulose compounds are composed of lignin, hemicellulose, and α -cellulose. Cellulose is known as crystalline in nature while for lignin is amorphous in nature. Fig. 2 exhibits the XRD thermograms of all samples tested. The crystallinity index for raw OPT P1 and OPT P2 are 45.52% and 44.59%, respectively. After the acid hydrolysis process, the crystallinity index for the microcrystalline cellulose of both OPT P1 and OPT P2 has increased which are 64.66% and 64.63%, respectively. The results for crystallinity index is not much different from the previous work with the same materials from raw OPT, which have 47.18% and 69.61% for the nanocellulose OPT after the acid hydrolysis¹³.

The crystalline structure of cellulose is very important to determine the elasticity, rigidity, thermal stability and absorption²⁴. From the results, it can be said that the sulfuric acid attacked the amorphous region of the cellulose and then increased the crystallinity index. The acid hydrolysis also removed the non-celluloses polysaccharides

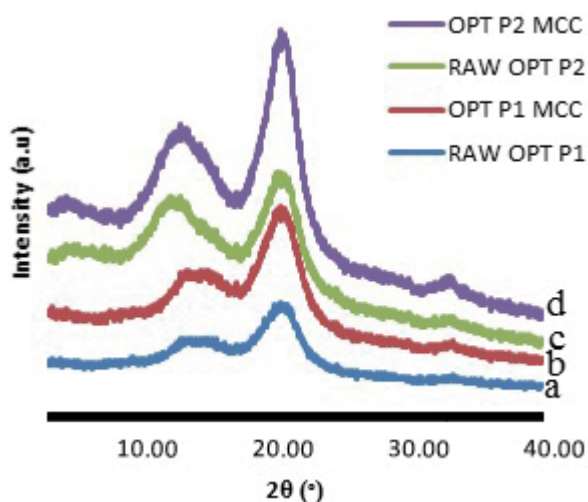


Fig. 2 XRD curves of a) raw OPT P1 b) OPT P1 MCC c) raw OPT P2) d) OPT P2 MCC

such as hemicelluloses and lignin matrix which was surrounded the cellulose fibers.

3.5 Thermal analysis

The thermal stability of the raw OPT fibers and microcrystalline cellulose after the acid hydrolysis process was shown in Fig. 3. Fig. 3 (a) and (b) shows the TGA and DTG curves for all the materials tested. Generally, the oil palm trunks which being a lignocellulosic materials start to loss weight at 50 °C due to the evaporation of water. The first degradation of the cellulose onset is due to the evolution of the non-combustible gasses such as carbon dioxide, carbon monoxide, formic acid and acetic acid. Then, the second degradation of the cellulose is because of the pyrolysis and evolution of the combustible gasses²⁵. For the raw samples of OPT, the samples are having 3-steps of degradation. The first degradation started when the temperature is less than 150 °C where the evaporation of water occurred in this step. Then, at the temperatures of 190 °C - 380 °C, the hemicellulose started to degrade. The cellulose started to degrade at 280 °C - 400 °C. When the

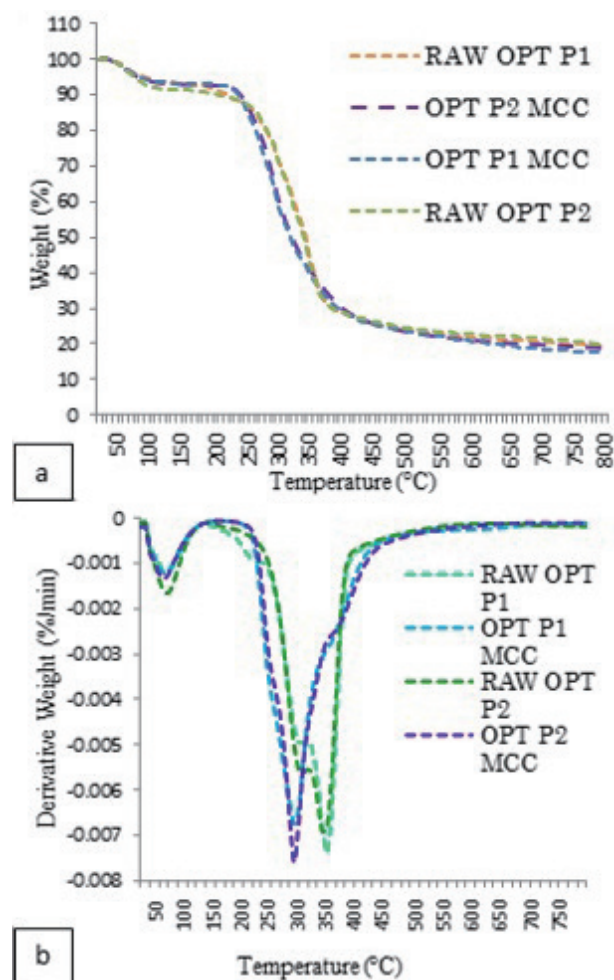


Fig. 3 TGA and DTG curves of all samples

temperatures reached 170 °C to 600 °C the lignin and others inorganic materials degraded. The raw OPT P1 started to degrade at 275.24 °C while the raw OPT P2 degraded at 274.00 °C and the MCC of P1 sample start to degrade at 254.95 °C and MCC for P2 start to degrade at 260.94 °C. The thermal degradation temperature for the MCC of the OPT P1 and OPT P2 samples are lower than the raw OPT might be due to the sulfate group that formed onto the cellulose chains during the acid hydrolysis process by using the sulfuric acid^{12) 26)}.

The weight losses for the MCC of P1 and P2 samples are higher than the raw samples of OPT for P1 and P2. This may be due to the removal of the lignin content during acid hydrolysis. The degree of crystallinity will also influence the thermal stability of the natural fibers. When the crystallinity index of the materials increased, the thermal degradation temperature also increased²⁷⁾. The reduction in the molecular weight of the materials also will increase the thermal decomposition temperature. This is due to the dissolving of the amorphous region during acid hydrolysis process which makes the materials resistant to degrade although the temperature is kept on increasing^{5) 28)}.

The acid hydrolysis will attack the crystalline region of the cellulose, which can be explained when the temperature is increased to 500 °C, the curves show the straight line due to the presence of the carbonaceous materials as the remaining residue²⁹⁾. Due to the high crystalline region in the cellulose, the cellulose has the intrinsic flame resistant properties, thus contribute to the high residue. Besides, the decrease in the degree of polymerization also can cause the thermal degradation. It can be concluded that both OPT P1 and OPT P2 microcrystalline cellulose have a good thermal stability, which can be applied in the composites industry.

4. Conclusion

Based on the findings in this study, microcrystalline cellulose was successfully extracted from the oil palm trunk (OPT) by acid hydrolysis. Results showed that the surface of the MCC was smooth and free of irregularities after acid hydrolysis. The XRD analysis showed that crystallinity increased after acid hydrolysis, showing that the crystalline nature of the isolated MCC from both OPT P1 and OPT P2 were 65%. The thermal stability of both MCC increased after acid hydrolysis compared to the raw. After removal of the lignin and hemicelluloses the crystallinity of the materials also has increased. The OPT P2 MCC (the leftover OPT fibers after their starch were being extracted) showed better crystallinity and thermal properties compared to OPT P1 MCC (the leftover of OPT

fibers after their sap were being squeezed out).

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