

Physicochemical properties and characteristics of microcrystalline cellulose derived from the cellulose of oil palm empty fruit bunch

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Abstract. Cellulose from oil palm empty fruit bunch was hydrolyzed with different concentration of hydrochloric acid (HCl) viz. 2; 2.5; 3; 3.5 N to prepare microcrystalline cellulose (MCC). The temperature of hydrolysis process was at 75 °C. The physicochemical properties such as organoleptic characteristic, water soluble substance, and loss on drying were conducted during this study. Infrared, x-ray diffraction, and scanning electron microscope (SEM) image were also performed to investigate the effect of hydrolysis on the molecular structure, crystal structure and morphology of the MCC, respectively. The results have showed, in term of the physicochemical properties, for all concentrations of HCl the MCC was obtained. The FTIR results showed the –OH functional group tended to reduced as alpha cellulose has changed to MCC. The x-ray diffraction pattern revealed that the crystal structure was traced on MCC where the highest was observed at hydrolysis process of 2.5N HCl. The image from SEM displayed an individualized and fibrous MCC on the treatment of 2.5N HCl.

1. Introduction

The main content which has a potential to be used as raw material of microcrystalline cellulose is fibrous material having cellulose content. Oil palm empty fruit bunches (EFB) containing cellulose w/w 35% which is high enough to be used as raw material for the manufacture of microcrystalline cellulose [1]. The selection of EFB rather than palm fronds, due to the age factor of oil palm. Oil palm plants have a lifespan that is long enough to remain productive of fruit. If the palm fronds used as the main raw material, the possibility of getting palm fronds of plants that are not productive is small. As for the EFB, it is still be generated during oil palm industry in operation [2].

Microcrystalline cellulose has been made from several natural sources, such as from kenaf fibers [3], saw dust [4], rice hull and bin hull [5], corn cobs [6], groundnut shell [7], cotton linters [8], rice straw [9], sisal fibers [10], cotton rags [11] and oil palm empty fruit bunch [12]. Some methods have been related to the manufacture of microcrystalline cellulose such as reactive extrusion [13], enzymatic hydrolysis [14], partial hydrolysis with oxygen and/or carbon dioxide [15], microorganism [3] and acid hydrolysis [16-19]. From all of methods for manufacturing of microcrystalline cellulose, acid hydrolysis



has been chosen because it is shorter time reaction and economic. Therefore, in this study, the effect of variations of hydrochloric acid (HCl) concentration on the physicochemical properties and characteristics of microcrystalline cellulose were investigated.

2. Method

2.1 Materials

Raw material used in this study was cellulose derived from oil palm empty fruit bunches, supplied by Oil Palm Research Center in Medan, Indonesia. Other chemicals such as HCl (37%), NaOH, NaOCl were supplied Sigma-Aldrich and used as received.

2.2 Isolation of α -cellulose

A total of 75 g cellulose derived from oil palm empty fruit bunches added with 500 mL of 17.5% NaOH and heated at 80°C for 30 min. The results are filtered using a cloth napkin, washed with water and squeezed. The solid mixture is added to 500 mL of 3.5% NaOCl and water (1:1) and heated at 100°C for 5 min, then filtered using a cloth napkin, washed with water until the filtrate is clear. The solid were then squeezed and dried at 60°C for 4-5 h in the oven and then α -cellulose was obtained. A method of Ohwoavworhua *et al.*, (2009) was adopted for this isolation [20].

2.3 Procedure of Making Microcrystalline Cellulose

A total of 1 g of α -cellulose put in glass Beaker and hydrolyzed with HCl with concentration varied viz. 2 N; 2.5 N; 3 N and 3.5 N of 20 mL by boiling with a temperature 75 °C for 15 min. After cold, the hydrolyzed α -cellulose was added with 50 mL aquadest while stirring strongly with a spatula and let stand for overnight. The solution was filtered through Whatman filter no.1 and then dried at a temperature of 57-60 °C for 3 h. After the microcrystalline cellulose crushed dried and stored at room temperature in a desiccators. A method of Yuvraj *et al.*, (2009) was adopted for this preparation [21].

2.4 Characteristics of Microcrystalline Cellulose (MCC).

The physicochemical properties such as organoleptic characteristic, pH, water soluble, and loss on drying were conducted during analysis. Other characterization such as x-ray diffraction (XRD), infrared diffraction (FTIR) and scanning electron microscope (SEM) image were also investigated. XRD was

recorded in 6100 Shimadzu. FTIR were carried out using Shimadzu IR-Prestige 21. SEM images were analyzed using EVO MA 10 ZEISS.

3. Results and Discussion

3.1 Physicochemical

The results of the effect HCl concentration on the microcrystalline cellulose product show that, for all HCl concentrations, the physicochemical properties are in accordance with the standards of British Pharmacopeia 2009 specification [22]. Table 1 shows some physicochemical properties of microcrystalline cellulose derived from oil palm EFB.

Table 1. Physicochemical properties of microcrystalline cellulose

TEST	MCC
Organoleptic	Odorless, tasteless and white fine powder
pH	6-7
Water soluble substances	$\leq 0.25\%$
Loss on drying	0 – 1.64%

From the table, the organoleptic observation shows odorless, tasteless and white fine powder, whereas the value of pH on microcrystalline cellulose is in range 6-7. The results of water soluble substances for each varied HCl concentration on microcrystalline cellulose product in have been meet the requirements of British Pharmacopeia 2009 i.e $\leq 0.25\%$ [22]. This value giving an indication of crystal phase was appeared in microcrystalline cellulose. This could be attributed to the process where during hydrolysis process the glucose content in α -cellulose was diluted. Consequently, in microcrystal cellulose the soluble substance was low. On the other hand, the value obtained for loss on drying is 0-1.64% which is in accordance with British Pharmacopeia 2009 i.e $\leq 6\%$ [22]. Here, crystalline phase was difficult to absorb store water as compared to amorphous phase; so that the value of loss on drying would be low because of store water was not too high due to its crystalline structure. Since water contains OH functional group, the evidence of the appearance of crystal in MCC can be explaining using FTIR spectra. The molecular structure of MCC as compared to two other celluloses (cellulose and α -cellulose) is show in Figure 1.

It shows the shift of maximum absorbance of functional group of OH decreased (3340 cm^{-1}) as compared with other two samples of cellulose (3363 cm^{-1} and 3446 cm^{-1} for α - cellulose and cellulose, respectively). Moreover, the functional OH group of MCC is less intense than those of two other celluloses. This shift and intensity have proved that MCC is more crystalline than other samples.



Figure 1. Infra-red spectra of a. cellulose; b. α - cellulose; c. MCC (2.5N HCl)

All observations of physicochemical properties viz. organoleptic, pH, water soluble substances and loss of drying have shown that for all variations of acid concentrations (2; 2.5; 3; and 3.5N) the results meet the requirements of British Pharmacopoeia (2009) as microcrystalline cellulose. However, due to the efficiency concern of using acid (HCl) during hydrolysis process, the use of concentrations 2 and 2.5N have been selected.

3.2 X-ray Diffraction (XRD)

The x-ray diffraction spectra of cellulose, α - cellulose, MCC (2.5N HCl) and MCC (2N HCl) is shown in Figure 2 below.

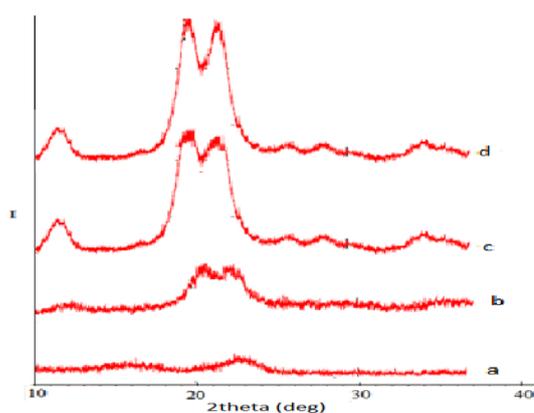


Figure 2. X-ray diffractograms of a. cellulose; b. α - cellulose; c. MCC (2N HCl); d. MCC (2.5 N HCl)

The figure above exhibits different diffraction pattern amongst samples where cellulose derived from oil palm empty fruit bunch was highly amorphous as indicated by the least peak in the diffractogram (Figure 2a). The peaks that appeared at diffraction angles (2θ) ranging from 20° to 24° . This behaviour was attributed to the presence an amorphous aromatic compounds such as lignin and hemicellulose. The crystallinity has been already traced on the α -cellulose (Figure 2b) due to removal of hemicellulose and lignin which existed in amorphous region during delignification process. In this case, the diffraction peaks of the 2θ angles at 18° to 24° . However, these two peaks are smeared and appeared as one broad peak. Figure 2c and 2d show MCC product diffractograms using 2N HCl and 2.5N HCl, respectively. These diffractions revealed similar patterns, where the appearance of two peaks are an evidence of the coexistences of cellulose I and cellulose II allomorphs. The appearance of two significant peaks indicating the highly crystalline structure of MCC. The higher crystal structure was obtained for MCC due to removal of the amorphous phase in α -cellulose by acid hydrolysis. During hydrolysis acid process, an amorphous cellulose near surface is hydrolyzed and followed by slower rate of hydrolysis of amorphous in deeply microfibrils. Here, the diffraction peaks of the 2θ angles for MCC are shown at 12° ; 20° and 22° . However, the peaks of MCC (2.5N HCl) (Figure 2d) is slightly higher intensity than MCC (2N HCl) (Figure 2c).

3.3 Scanning Electron Microscopy (SEM)

To determine the characteristics at each stage of cellulose into α -cellulose and microcrystalline cellulose product, the SEM images can be viewed in Figure 3 below. Figure 3a shows microfibril cellulose molecules bound to one another to form long polymer chains and interconnected. There is an insulation on the surface microfibrils due to the presence of amorphous phase such as lignin and hemicellulose. Here, during first alkali treatment, the removal of an amorphous structure such as cellulose and lignin was not perfect. Therefore, it is clearly shows the shape and distribution of the microfibrils in cellulose was not uniform. However, for the α -cellulose (Figure 3b), the microfibrils structure shows amount of naked microfibril bundles. The insulation contains lignin and hemicellulose which have appeared in microfibrils was removed due to the subsequent alkali treatment. On the other hand, the MCC image shows an individualized and fibrous structure (Figure 3c). In this case, after microfibrils were hydrolyzed and rinsed, the volume of amorphous cellulose was occupied by water molecule and then removed. However, the image of MCC (2N HCl) (Figure 3d) shows the structure of microfibrils is slightly different where

there is an insulation on the crystalline surface; this is due to the amorphous phase could not well dissolved during hydrolyzing process.

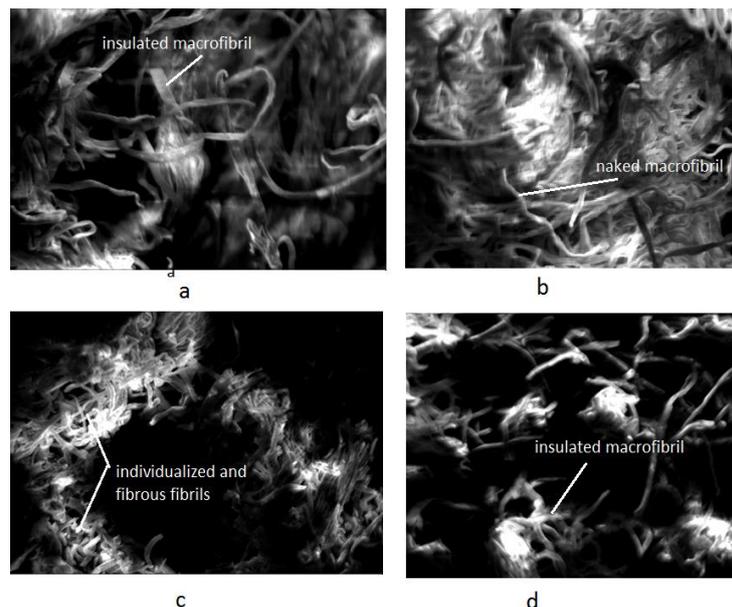


Figure 3. SEM with mag. of 500x a.cellulose; b. α - cellulose; c. MCC (2.5N HCl); d. MCC (2N HCl)

From FTIR, XRD and SEM characterizations, the results have indicated the crystal part was traced on MCC, where the $-OH$ groups tended to reduced as alpha cellulose has changed to MCC and the appearance of two peaks in diffractogram. Moreover, SEM image have shown the individualized and fibrous structure which indicated the appearance of crystal structure.

4. Conclusion

The results showed for all concentration of HCl in term of the physicochemical properties the MCC have been obtained. The organoleptic characteristics such as odorless, tasteless, white and fine powder; the pH value of 6-7; the value of water soluble substances $\leq 0.25\%$ and the value of loss on drying 0-1.64% have meet in *British pharmacopeia* 2009. From XRD spectra and SEM image, the results have indicated the crystal structures were occurred in MCC especially in 2.5N HCl of hydrolyzed process.

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