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Effect of Acid Concentration on the Properties of Microcrystalline Cellulose from Pineapple Crown Leaf

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Abstract

Microcrystalline cellulose was first extracted from pineapple crown leaf waste which is used very rarely as an alternative material from agricultural residue and then characterized. Microcrystalline cellulose was extracted from this waste through acid hydrolysis with various concentrations. The effect of acid concentrations with sulfuric acid (H_2SO_4) on microcrystalline cellulose properties was investigated to determine its potential application as a material. Pineapple crown leaf was hydrolyzed for 2 hours at 45℃ along with various sulfuric acid concentrations (1, 2, and 3 M). The properties of the cellulose were evaluated by Scanning electron microscopy (SEM), Fourier transforms infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Among all the hydrolysis conditions carried out, the best hydrolysis condition was 3 M sulfuric acid. At this hydrolysis condition, the microcrystalline cellulose presented a rod-like shape, high crystallinity at 83.16%, and have average crystal size of 17.99 nm. The functional group and morphology analysis showed that the resulted product is maintained cellulose I structure and removal of non-cellulosic constituents and the chemical compositions. As for the thermal analysis, the temperature decreased from 177℃ (2 M sulfuric acid) to 149℃ (3 M sulfuric acid) because of the incorporation of sulfate groups after the hydrolysis process. Therefore, microcrystalline cellulose obtained from pineapple crown leaf waste has great potential as reinforcement in the manufacture of composites.

Keywords: Acid hydrolysis, microcrystalline cellulose, physicochemical properties, thermal analysis

1. Introduction

Cellulose is the main part of component in plant cell walls and considers the most abundant natural and renewable bioresources in the world (Zhang et al., 2014). This component has been one of the materials with remarkable functional and potential applications in the development of new performance materials with low impact on the environmental (Zhang et al., 2014). One of the materials that can be produced from cellulose is microcrystalline cellulose, with large surface areas, relatively high strength, and stiffness (Sri Aprilia et al., 2016). Microcrystalline cellulose also has highly relevant properties to the development of renewable biomaterials in many fields of chemistry, food, pharmacy, and has recently been widely used as polymer reinforcement, adsorbent, additives for biodegradable products, membrane reinforcement, and composite materials (Santos et al., 2013; Sri Aprilia et al., 2016).

Extraction of these materials from lignocellulosic bioresources to yield pure cellulose fibers and microcrystalline cellulose is the first important stage for another development processing to make advanced in functional materials. In recent studies, several methods for extraction microcrystalline cellulose from various plant fibers such as acid hydrolysis, enzymatic hydrolysis, oxidation, and steam explosion processes have been done (Voronova et., 2013). Acid hydrolysis is one of the most conventional processes for the preparation of microcrystalline cellulose (Sri Aprilia et al., 2016). Especially sulfuric acid hydrolysis is often used in this process. During the acid hydrolysis process, the amorphous part of the cellulose component dissolves into the acidic solution, resulting in crystalline particles and different degrees of crystallinity

index (Sri Aprilia et al., 2016; Fitriani et al., 2020). However, because the structure and distribution of crystalline and amorphous regions of cellulose change dramatically between species, types, environments, and even with different parts of the same plants, there are no practical conditions for the extraction of microcrystalline cellulose (Yu et al., 2013).

Several studies also reported that hydrolysis conditions such as acid concentration and type of acid and duration of hydrolysis give major effects on the properties of produced microcrystalline cellulose (Santos et al., 2013; Sukaimi et al., 2019; Fitriani et al., 2020). Until now, a variety of microcrystalline cellulose has been obtained from agricultural by-products such as wood fiber, cotton fiber, bamboo, kenaf bast, corn stalk, and rice husk (Habibi et al., 2010; Kumar et al., 2013; Zhang et al., 2014; Sri Aprilia et al., 2016; Azeredo et al., 2017). Nevertheless, the effect of various acid concentrations in the hydrolysis process on the morphology and structure of the resulting microcrystalline cellulose has not been fully explored yet.

Theoretically, microcrystalline cellulose can be prepared from any lignocellulosic source fibers material. However, the renewability, availability, and sustainability of lignocellulosic sources must be carefully examined for practical and future usage. One type of plant that is widely used as a source of food in the world and industry is the pineapple plant. Generally, one part of the plant, namely pineapple crown leaf is made up of 79-83% cellulose, 19% hemicellulose, and 5-15% lignin (Brinchi et al., 2013). The processing of pineapple plants produced 3 billion tons of by-products each year (Prado and Spinacé, 2019).

Furthermore, in large quantities, pineapple crown leaves are dry and burned in an open environment, which causes environmental pollution issues (Santos et al., 2013). Then it is necessary to reduce environmental pollution by utilizing pineapple crown leaf waste as a source of microcrystalline cellulose. The use of pineapple crown leaf fibers as one of the cellulose bioresources is still little published. This may be attributed to the fact that pineapple crown leaves are usually shorter than pineapple plant leaf (Prado and Spinacé, 2019). However, pineapple crown leaf fibers have similar properties and chemical compositions with pineapple leaf (Prado and Spinacé, 2019; Santos et al., 2013).

In this case, it is significant to have a better understanding of the study of how the properties of the extracted microcrystalline cellulose are affected by various acid concentrations. The acid concentration is one of the important parameters in the acid hydrolysis process. The acid hydrolysis process reduces the degree of polymerization as a function of acid concentration. Increasing the acid concentration has a great effect on the cellulose because of the β-1,4 glycosidic bond to acid and eliminate the amorphous region during the process (Fitriani et al., 2020). In another study of microcrystalline cellulose with different acid concentrations (1.5, 2.5, and 3.5 M) gives higher crystallinity with increasing acid concentration (Sukaimi et al., 2019). However, the literature review shows that extraction of microcrystalline cellulose from pineapple crown leaf are still needed for further research and have great potential as a renewable material. Therefore, this study aims to describe the influence of various sulfuric acids on the properties of microcrystalline cellulose from pineapple crown leaf waste. The characterization of the microcrystalline cellulose properties such as morphology, functional group, crystallinity index, and thermal stability was analyzed.

2. Methodology

2.1. Materials

Pineapple crown leaf (PCL) waste was supplied by local markets in Banda Aceh, Indonesia. Sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) were used as alkali and bleaching agents, while sulfuric acid (H_2SO_4) was used for acid hydrolysis. All the chemicals were purchased from CV. Karya Graha Agung, Medan, Indonesia.

2.2. Preparation of Microcrystalline Cellulose

The pineapple crown leaf fibers were washed in running water to remove soluble components and impurities. Dried PCL fibers were first washed with water to remove the impurities component and then dried in an oven dryer at 60℃ for 24 h. The PCL fibers were cut into small pieces before the next process of treatment. The alkali and bleaching treatments of fibers were performed with NaOH 1 M and H_2O_2 1 M at 80°C for 1 h. After the treatment process was completed, the samples were rinsed repeatedly with distilled water. The samples were hydrolyzed using various acid concentrations (1, 2, and 3 M) at 45°C for 2 h. The reaction in acid hydrolysis was stopped by adding 500 ml of distilled

water and then cooled in a water bath for 24 h. The microcrystalline cellulose suspension was washed, centrifugated (2000 rpm for 30 min), and ultrasonicated (30 min) to remove the excess of acid until pH of 5 was reached. Finally, the resulting product was grounded into powder using a blender after the drying process and was stored until further analysis.

2.3. Functional Group Analysis

Functional group analysis was carried out and recorded using IRAffinity-1S FTIR spectrometer in the scanning ranges of 400-4000 cm^{-1} at room temperature. The pineapple crown leaf fiber and microcrystalline cellulose were ground and mixed with potassium bromide, followed by pressing the mixture into ultra-thin pellets.

2.4. Morphology Analysis

The morphology of microcrystalline cellulose was examined on a Scanning Electron Microscope (JSM-636OLA). In each analysis, a small quantity of sample was put on a plate and was observed and imaged with 1000x magnification.

2.5. Crystallinity Analysis

X-ray diffraction (XRD) was used to determine the crystallinity index and crystal size of microcrystalline cellulose. Each sample in the form of powder was placed on the sample holder to obtain full and uniform X-ray exposure. The sample was analyzed using X-ray diffraction Shimadzu XDR 7000 at an operating voltage of 40 kV and the applied current was 30 mA. This measurement was performed using Cu Kα radiation at an angular incidence of 10-40° (2θ angle range). The crystallinity of the samples was calculated from diffraction intensity data using the empirical method with the Segal formula as shown in Equation 1.

$$\text{Crl}\ (\%) = \left(\frac{I_{200} - I_{AM}}{I_{200}}\right) \times 100 \quad (1)$$

where Crl is the crystallinity index, I_{200} is the maximum intensity of the diffraction at 2θ=22.5° (amorphous and crystalline fractions) and I_{AM} is the intensity of the background scatter at 2θ=15° (amorphous region) (Segal et al., 1959). The crystal size of the sample was determined based on the Scherrer formula as shown in Equation 2.

$$D\ (\%) = \left(\frac{K\lambda}{\beta cos\theta}\right) \times 100 \quad (2)$$

where D is the crystal size (nm), K is the Scherrer constant with 0.94, λ is the wavelength of X-rays (nm), β is the full width of the peak at half maximum intensity (FWHM) and θ is the half of Bragg angle or diffraction angle range. The crystallite size measurement of the sample can be usually carried out by X-ray diffraction reflection broadening by the Scherrer equation (Mongkolsuttirat and Buajarern, 2021).

2.6. Thermal Analysis

The thermal stability of about 5 mg of microcrystalline cellulose samples was determined by a thermogravimetric instrument. The sample was heated from 25 to 500℃ with a heating rate of 10℃ min^{-1} under an inert atmosphere.

3. Results and Discussion

3.1. Functional Group of Microcrystalline Cellulose

Figure 1 shows the FTIR spectra recorded for PCL fibers and microcrystalline cellulose treated with various sulfuric acid concentrations (1, 2, and 3 M) for 2 h. The dotted line highlights the changes of the sample before and after alkali, bleaching, and hydrolysis treatments. All samples display absorbance in the regions of the broadband located in the range of 3000-3500 cm^{-1} which is attributed to the stretching vibration of the hydroxyl group (O-H). The peak at 2885 cm^{-1} and the small narrow peak at 800 cm^{-1} in all samples can be attributed to the strain of C-H and stretching vibration of C-O (Zhang et al., 2014). The peak at 1734 cm^{-1} is attributed to the C=O group of uronic acids from the hemicellulose component (Prado and Spinacé, 2019). This peak is also related to the acetyl ester groups of hemicellulose or ester linkage of carboxylic acids in lignin (Prado and Spinacé, 2019). In addition, the absorbance peak at 1640, 1514, and 1254 cm^{-1}, which are caused by the C=C stretching of aromatic rings in lignin, also disappeared after the alkali and bleaching process (Zhang et al., 2014). Figure 1 shows that the peak is disappeared after chemical treatments in microcrystalline cellulose with various acid concentrations and also indicated the successful removal of hemicellulose and lignin.

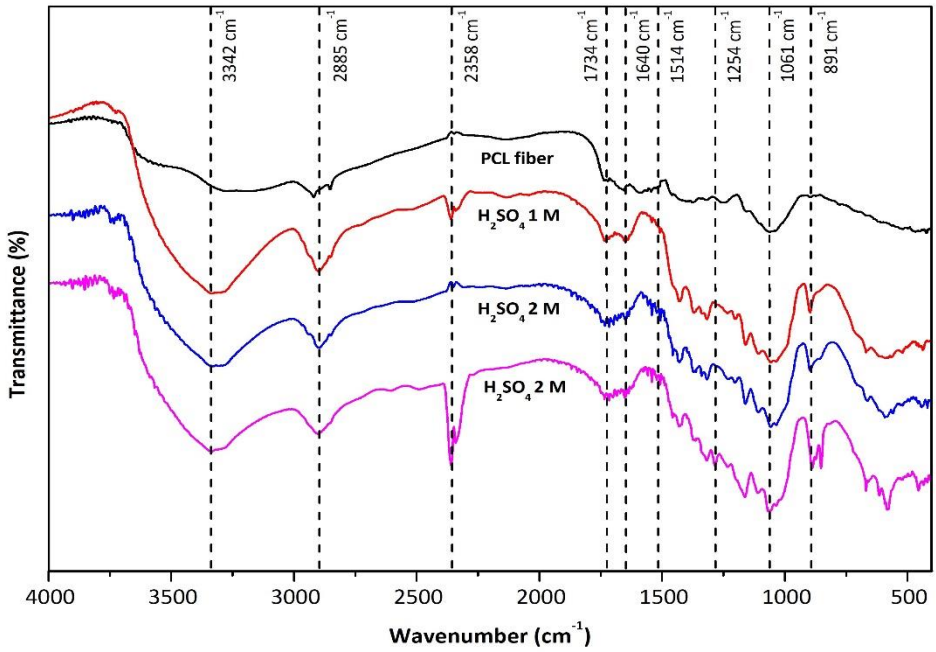

Figure 1. FTIR spectra of microcrystalline cellulose from pineapple crown leaf waste hydrolyzed with 1, 2, and 3 M concentrations of sulfuric acid.

The peak at 1061 cm^{-1} is associated with the C-O stretching and the C-H vibrations of the cellulose (Santos et al., 2013). The small increase in this peak for the sample with various acid concentrations compared to pineapple crown leaf fibers indicates that the samples have higher cellulose content. The difference in the peak also shows that the hydrolyzed sample with 3 M acid concentrations has a higher content of cellulose compare to other acid concentrations.

3.2. The Morphology of Microcrystalline Cellulose

Morphological structure analysis of cellulose microcrystal from pineapple crowns was analyzed using Scanning Electron Microscope (SEM). Figure 2 shows a micrograph of microcrystalline cellulose hydrolyzed with various acid concentrations which shows that almost all samples are rod-shaped structures. In previous literature, the resulted study compared the structure of these rods to those of porous glass fiber (Sri Aprilia et al., 2016). The acid concentration and the nature of the raw material largely determine the particle size distribution of the cellulose (Yu et al., 2013). In Figure 2, the morphology of all samples was rod-like and aggregate, but in samples, it is seen that the size of the microcrystalline cellulose shrinks, and smaller particles form as the acid concentration decreased. The reduction in particle size is caused by the removal of the amorph cellulose portion produced during the hydrolysis process (Fitriani et al., 2020; Sri Aprilia et al., 2016).

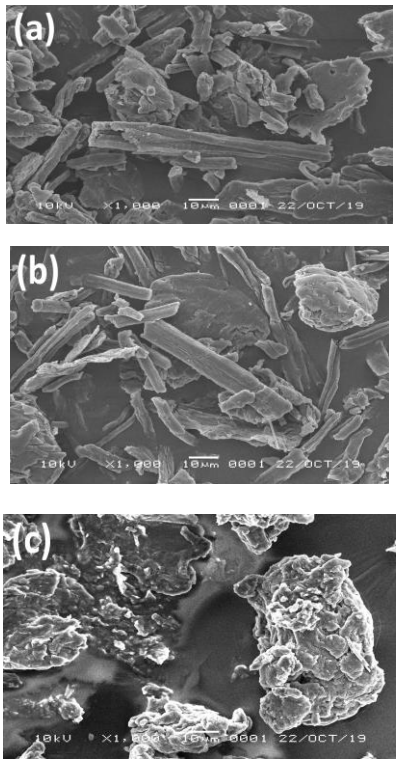

Figure 2. Micrographs of microcrystalline cellulose from pineapple crown leaf waste with (a) 1 M, (b) 2 M, and (c) 3 M acid concentrations.

In another study revealed that the formation of crystals with small sizes is related to the decrease of the acid concentration (Azeredo et al., 2017). This is also evidenced in the results of crystallinity which decreases with lower acid concentration. The aggregate and non-uniform particle size distribution are caused by strong agglomeration between individual particles with one another, which makes it difficult to see the morphology of a single particle. A previous study suggested that this agglomeration can be caused by crystals clings together when the final drying process after hydrolysis (Santos et al., 2013).

3.3. The Crystallinity of Microcrystalline Cellulose

The XRD patterns of microcrystalline cellulose with various concentrations were obtained at room temperature within the 2θ range from 10 to 40°. Figure 3 shows the regular patterns of the semi-crystalline components with an amorphous broad bend and crystalline peak. The presence of peak on all samples at 2θ = 15, 22.5, and 34° is corresponding to cellulose type I (Aprilia et al., 2018; Santos et al., 2013). The crystallinity percentage and crystal size are calculated using equations (1) and (2). The crystallinity percentage and crystal size are summarized in Table 1.

Table 1. Crystallinity percentage and crystal size of microcrystalline cellulose.

Sample	Crystallinity (%)	Crystal size (nm)
1 M	62.33	17.99
2 M	67.87	19.31
3 M	83.16	17.99

The crystallinity index was found to be about 62.33, 67.87, and 83.16% for the microcrystalline cellulose with various acid concentrations at 1, 2, and 3 M, respectively. The higher crystallinity index value of microcrystalline cellulose with 3 M acid concentration is because of partial removal of the amorphous regions of cellulose and crystalline region during the acid hydrolysis (Santos et al., 2013). During the acid hydrolysis process, the amorphous part in fibers is dissolved and finally released more individual crystals and improves the cellulose crystallinity (Aprilia et al., 2018). These results were in agreement with the report from a previous study that acid concentrations in hydrolysis treatment could significantly affect the crystallinity index of cellulose from natural fibers (Aprilia et al., 2018; Santos et al., 2013; Zhang et al., 2014). A higher value in crystallinity is also related to increases in the rigidity of the cellulose structure, which can lead to higher tensile strength in all samples (Aprilia et al., 2018). The size of crystalline in cellulose increase with increasing of acid concentrations in the hydrolysis process. The removal of non-cellulosic components in the hydrolysis process caused some dense cellulose and was responsible for an increase in the crystalline size value (Aprilia et al., 2018; Fitriani et al., 2020).

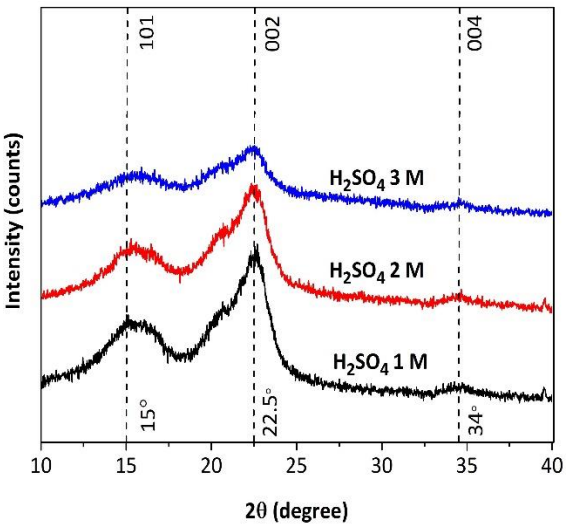

Figure 3. X-ray diffraction patterns of micro-crystalline cellulose from pineapple crown leaf waste hydrolyzed with 1,2 and 3 M concentrations of sulfuric acid.

3.4. Thermal Stability of microcrystalline cellulose

The application of microcrystalline cellulose as fillers in composite materials makes the thermal stability of cellulose crystals need to be analyzed to see their effectiveness as fillers in the material (Santos et al., 2013). The thermogram in Figure 4 shows a slight decrease in all TG curves at around 100°C, which corresponding to the removal of absorbed water on the surfaces of these materials (Zhang et al., 2014).

In Table 2 T_{onset} obtained in microcrystalline hydrolysis with 1,2 and 3 M acid concentrations were 156, 177, and 149 ° C, respectively. These results show that the increase in acid concentration from 1 M to 2 M also increases the thermal stability of the sample. However, when the hydrolysis is increased to 3 M concentration, cellulose begins to degrade at low temperatures, which makes its thermal stability decrease. The same results were also obtained in previous studies, treatment with sulfuric acid leads to a remarkable decrease in thermal stability of

microcrystalline cellulose. This result occurs probably because of the incorporation of sulfate groups on the surface of the cellulose after hydrolysis (Santos et al., 2013; Sri Aprilia et al., 2016).

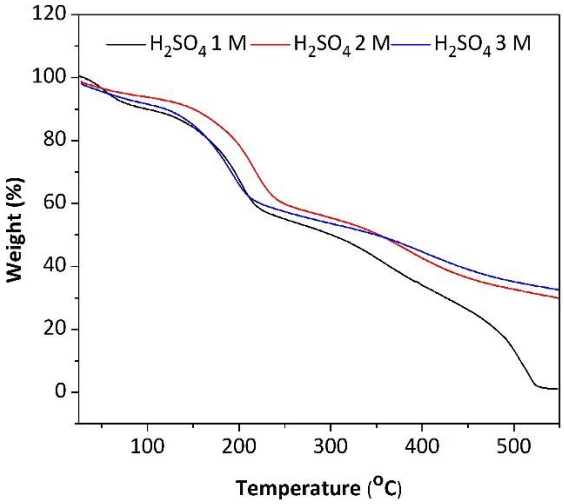

Figure 4. Thermogram of microcrystalline cellulose from pineapple crown leaf waste hydrolyzed with 1,2 and 3 M concentrations of sulfuric acid.

Table 2. Thermal analysis of microcrystalline cellulose.

Sample	T_{onset} (℃)
1 M	156
2 M	177
3 M	149

4. Conclusion

Microcrystalline cellulose has been successfully extracted from pineapple crown leaf fiber using consecutive chemical treatments involving mercerization, bleaching, and acid hydrolysis. The various acid concentrations used in the hydrolysis process had a significant influence on the crystallinity, structure, morphology, and thermal stability of microcrystalline cellulose. The results obtained from functional group analysis confirmed the removal of the non-cellulosic compounds of pineapple crown leaf fibers and maintained the structure of cellulose type I. The crystallinity analysis shows that the resulted sample for acid concentrations for 1, 2, and 3 M sulfuric acid were 62.33, 67.87, and 83.16% respectively. The result in crystallinity analysis proves that the increase in acid concentration for hydrolysis also increases the crystallinity of cellulose. Through the morphology analysis, it was observed that rod-like structures in cellulose and the size of the microcrystalline cellulose shrinks, and smaller particles form as the acid concentration decreased. The thermal stability of microcrystalline cellulose also increased significantly from 1 M to 2 M acid concentration. However, the decrease in 3 M sulfuric acid is probably because of the incorporation of sulfate groups in the surface of cellulose after hydrolysis. It can be concluded from these results that microcrystalline cellulose obtained from pineapple crown leaf with high acid concentrations on hydrolysis process has interesting properties and potential that can be used in several applications as a reinforcement agent in composite materials.

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