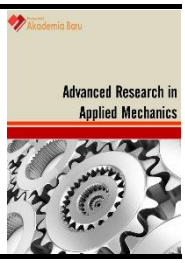
Penerbit Akademia Baru

Journal of Advanced Research in Applied Mechanics

Journal homepage:
http://www.akademiabaru.com/submit/index.php/aram/index
ISSN: 2289-7895



The Effect of Chemical and High Pressure Homogenization Treatment Conditions on the Morphology of Nanocellulose

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ABSTRACT

Nanocellulose was fabricated from empty fruit bunch (EFB)-derived microcrystalline cellulose (MCC) through combined acid hydrolysis with sulfuric and hydrochloric acids and high-pressure homogenization. The effects of acid-to-MCC ratio and the number of high-pressure homogenizations passes on nanoparticle morphology were investigated. The MCC was treated with different concentrations of sulphuric acid (5% to 25%) through the hydrolysis process. The diameter of the acid treated MCC fibres was reduced to roughly 8 m in Scanning Electron Microscopy (SEM) micrographs, while the length of the fibres was reduced by several microns when compared to untreated fibres. The suspensions of MCC were passed through a high pressure homogenizer at a constant pressure of 800 bar with passing times of 10, 20 and 30 cycles. After 30 cycles, the final suspension of nanocellulose (NC) became cloudy. This was a visual indication that the particles were converted to smaller sizes and were less entangled. Field Emission Scanning Electron Microscopy (FESEM) results showed that the particle size of nanocellulose ranged between 18 to 20 nm. As a result, the combination of sulphuric acid hydrolysis and high-pressure homogenization operations could be used as an efficient chemo29 mechanical technique for producing nanocellulose from various cellulosic sources.

Keywords:
acid hydrolysis; empty fruit bunch fibre;
high pressure homogenizer;
microcrystalline cellulose; nanocellulose

Received: 27 March 2022	Revised: 28 April 2022	Accepted: 2 May 2022	Published: 20 May 2022

1. Introduction

Cellulose is the most abundant organic biopolymer on the planet, and it can be found in a wide variety of living species, including plants, animals, and certain microorganisms [1]. It is a key structural component of plants which is regaining significance as a renewable chemical resource to replace petroleum-based products [2,3]. The development of the palm oil industry has led to the generation of massive amounts of agricultural biomass by-products in Malaysia [4]. In 2017, the total oil palm biomass residues (dry weight basis) available for replanting, pruning, and milling activities in Malaysia were estimated to be 51.19 metric tonnes (MT) out of 101.02 MT of processed oil palm empty fruit bunch fibre (OPEFB) [5]. OPEFB is a lignocellulosic residue with 50% cellulose, 25% hemicellulose, and 20% lignin, as well as extractives in the cell wall [6].

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The cellulose has a crystalline structure and is insoluble in water, whereas the remaining components are porous amorphous materials [7]. Cellulose nanocrystals are isolated crystalline domains of pulp fibers [8]. By acid hydrolysis, cellulose can be converted into micro cellulose (MCC) and nano-cellulose (NCC), which are known as crystalline cellulosic fibres, and thus improve its performance as a reinforcing component in composites [9]. Due of its inherent unique qualities, such as high strength, high surface area, and flexible surface chemistry, nanostructured cellulose has gained a great deal of interest, in addition to being abundant and renewable. Nanocellulose is a biodegradable white, ultrafine, odorless crystalline powder that can be extracted from pure cellulose using acid hydrolysis. It can also be obtained through homogenization, microfluidization or grinding routes [10].

High pressure homogenizers (HPH) have been used widely in recent years to separate nanocellulose from different lignocellulosic sources. HPH has been regarded as an important method of high pressure efficiency grinding the fibre. Dilute slurries of cellulose fibres are pumped at high pressure and fed through a high-pressure spring loaded valve assembly in the homogenization process. The fibres are exposed to a significant pressure drop with shearing and impact forces as this valve opens and closes in rapid succession. This combination of forces facilitates a high degree of cellulose fiber microfibrillation, leading to micro/nanofibrillated cellulose [11]. The only downside of the homogenization process is that the device is often obstructed by long fibers, particularly at the in-line valves, which must then be disassembled and cleaned. Therefore, HPH alone is not adequate for nano-size fibrillation of cellulose and requires pre-treatment and a combination of additional chemical and mechanical treatments prior to the HPH process to minimize the size of the fibre and prevent the small HPH orifice from stacking [12].

This research aimed to provide a comparative study for producing nanocellulose in a more cost-effective and environmentally friendly manner. This method used acid hydrolysis in conjunction with high-pressure homogenization. The specific goals were to investigate the impact of acid-to-MCC ratio and the number of high-pressure homogenization treatments on the resulting nanocellulose. Field Emission Scanning Electron Microscopy (FESEM) was used to examine the morphology of cellulose nanostructure. The pioneering work on the isolation of MCC and NCC from OPEFB, which could be used as bio-based fillers for environmentally friendly composites, is mentioned in this article.

2. Methodology

2.1 Materials

OPEFB fiber samples were gathered from the Palm Oil Milling Technology Centre (POMTEC) in Labu, Negeri Sembilan. The EFB fibers were then delivered to the Malaysian Pam Oil Board (MPOB) headquarters in Selangor for subsequent processing. Merck Sdn. Bhd. Provided analytical grade sodium hydroxide, monochloroacetic acid (MCAA), and glacial acetic acid (Malaysia). The local market provided isopropanol (IPA), ethanol, and methanol (Systerm). The sodium chlorite ($NaClO_2$) used in this study was 80 percent pure and acquired from Acros (Belgium), while the sulphuric acid (95-98%) AR/ACS was purchased from R&M. OPEFB cellulose was made at the lab scale using an ASTM standard procedure (ASTM D 1104-56 and ASTM D 1103-60).

2.2 Preparation of Microcrystalline Cellulose

Acid hydrolysis of waste OPEFB cellulose was conducted with different concentrations of sulphuric acid (5%, 15%, 25%). The mixture was hydrolysed in an autoclave for about 1 hour and then treated by the ultrasonicator at 50 °C for 3 hr. After the ultrasonication process, the suspension was

then washed repeatedly with distilled water until it became acid-free (the filtrate showed a near to neutral pH) and filtered to separate the MCC. The MCC was then dried in an oven to constant weight for 24 h and ground into fine powder afterwards. Therefore, MCC was produced at three concentrations of sulphuric acid namely MCC A (5% of sulphuric acid), MCC B (15% of sulphuric acid) and MCC C (25% of sulphuric acid).

2.3 Preparation of Nanocellulose from MCC by Mechanical Treatment

The isolation of nanocellulose was carried out in two steps of the mechanical treatments, which were mechanical disintegration and high-pressure homogenization processes. Mechanical disintegration was done to liberate and soften the treated fibres, as well as to decrease the MCC diameter to micron size through high shear. MCC with optimised conditions was dispersed in distilled water and mechanically treated using an Ultra Turrax system (IKA T10 basic) for 30 minutes. High Pressure Homogenization (HPH) is the last stage of the nanocellulose (NC) isolation process. The MCC suspension was passed through a high-pressure homogenizer (Model: APV Model 1000 Homogenizer) at a constant pressure of 800 bar with varying passing times of 10, 20 and 30 cycles. The NC which was successfully isolated from the MCC suspension at an optimised HPH passing time was freeze-dried in a freeze dryer. The white cotton-like NC sample from the freeze dryer was then characterized using FESEM to detect the finest possible dimension of NC.

2.4 Characterization of Microcrystalline Cellulose (MCC) and Nanocellulose

The detailed characteristic and morphology of MCC were characterized using SEM analysis while the morphology of nanocellulose was characterized using FESEM analysis.

2.4.1 Scanning Electron Microscopy (SEM).

A Hitachi S2700 SEM was used to evaluate the microscopic features of the samples. A dry sample piece was placed on the SEM sample lens, and the lenses were then placed in a vacuum chamber to prevent particulates from obstructing and polluting the image. The lenses were helpful in directing electrons towards the sample. A three-dimensional picture was transformed into the electron imprint. A magnification power of 1000x was used for the samples.

2.4.2 Field Emission Scanning Electron Microscope (FESEM).

The surface morphology of NC was investigated using FESEM brand JEOL (Tokyo, Japan) model JSM7600F. All images were taken at a few magnifications using 5 kV of accelerating voltage.

3. Results

3.1 SEM Analysis of MCC

Figure 1 depicts the morphological structures of MCC after hydrolysis process. The morphology of MCC alters following therapy, as seen by the images. The morphology of MCC demonstrated that as the quantity of sulphuric acid increased, the diameter size of MCC reduced along with the length of the fibres. Additionally, it can be clearly seen that a rough and irregular structure for MCC was observed. While the raw fibres of OPEFBs before treatment are made up of bundles held together by lignin and hemicellulose, the morphology of the fibres bundle has an uneven and rough surface [13].

MCC's structure differed from that of cellulose due to the depolymerisation of cellulose polymers, resulting in a shorter chained MCC [14]. The findings show that the acid treatment substantially reduced the width of the fibres and their morphology was comparable to commercialised MCC (**Figure 1**). When compared to untreated fibres, the overall diameter of the acid treated MCC fibres had highly decreased to around 8 µm while the length of the fibres was shortened to several microns. This finding is similar with the findings of Fahma [15], who discovered that the shape and diameter of the MCC produced are highly dependent on the concentration of acid and the acid-fibre ratio. In comparison, the external surface of the MCC was clearly demonstrated to be smooth and irregular in shape, most likely due to the removal of silica, hemicellulose, and lignin.

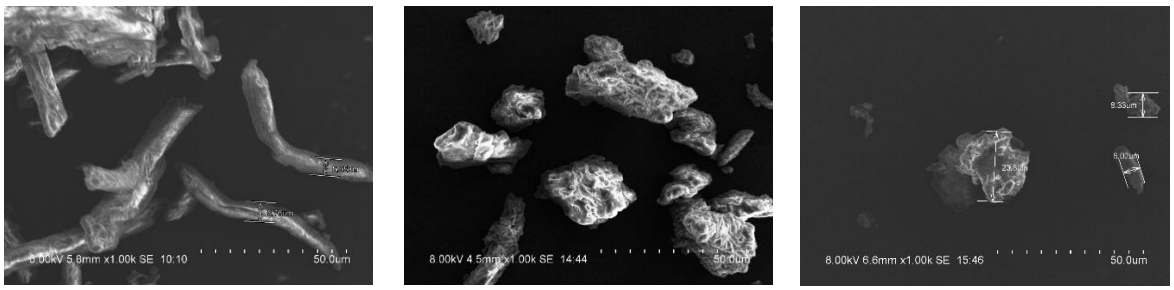


Fig. 1. The SEM micrograph of MCC (after acid hydrolysis)

3.2 Physical appearance of nanocellulose solution after HPH Process

There were three samples of MCC with different acid concentrations at 5 %, 15 % and 25 % which had undergone the acid hydrolysis process for 1 hr. Three MCC suspensions were passed through a high-pressure homogenizer at a constant pressure of 800 bar with passing times of 10, 20 and 30 cycles, respectively. From **Figure 2**, the suspension of MCC at 0 cycle became cloudier from 10 to 30 cycles. This indicates that the particles were converted to smaller sizes and were less entangled [16]. Thus, the NC produced with three concentrations of sulphuric acid (5 %, 15 % and 25 %) at three different passing time (10, 20, 30) were namely as NC A10, NC A20, NC A30 (A = 5% of sulphuric acid), NC B10, NC B20, NC C30 (B = 15% of sulphuric acid) and NC C10, NC C20, NC C30 (C = 25% of sulphuric acid).

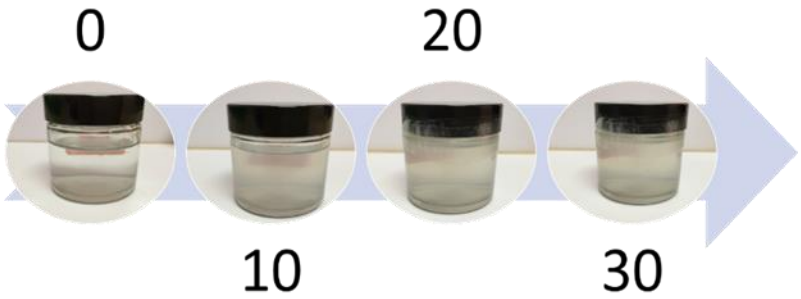


Fig. 2. Observation on color changes of OPEFB particles from zero to 30 cycles during the HPH process

3.3 FESEM Micrographs of Nanocellulose

Successful extraction of nanocellulose (NC) was confirmed through FESEM. FESEM micrographs of NC for 5%, 15% and 30% of sulphuric acid concentration with three different passing time (10, 20, 30) are shown in **Figure 3**. The size of nanocellulose particles were measured about 20 nm and this indicates that the diameter of NC after being treated by HPH has reached on the scale of a nanometre. The FESEM micrographs demonstrated the efficiency of the combination of chemical and mechanical treatments and illustrates the structure of nanocellulose which was mainly agglomerates. The same phenomenon was reported by Micheal [17], where distinct agglomeration mechanisms occurred among the crystal nanocellulose particles during each drying method. Generally, all of the NC experienced similar changes upon homogenization, which involves a reduction in diameter size and extensive deconstruction of the cell walls. There were only small differences among the treated NC at different passing times where fibres no longer existed, and only small rod-like/whisker-shaped structures in nanometre dimension were observed (**Figure 3**).

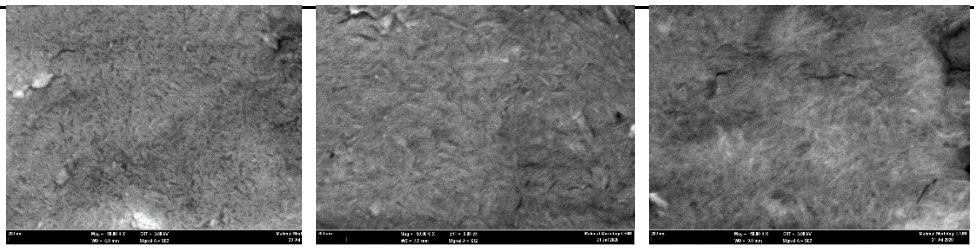
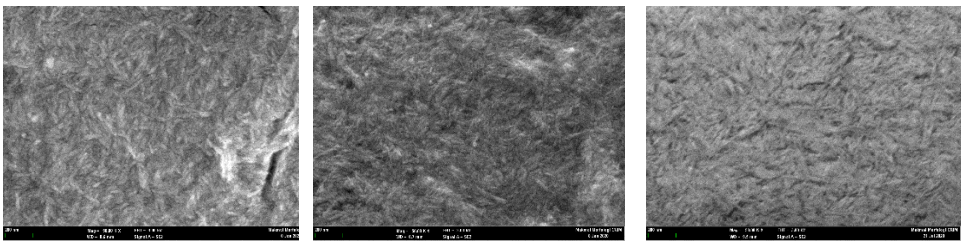
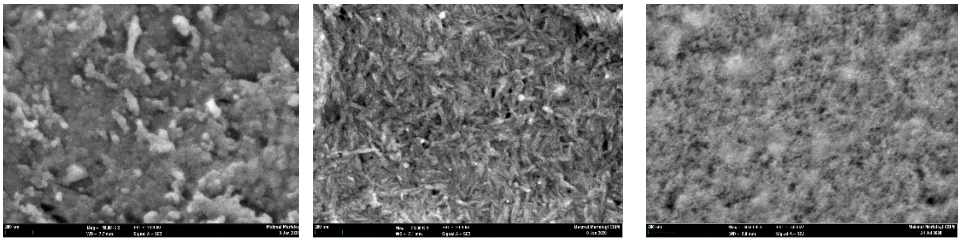
Sulfuric Acid Concentration	**Number of Cycles**		
	10	20	30
5%			
15%			
25%			

Fig. 3(a). Nanocellulose at 5% H_2SO_4

Fig. 3(b). Nanocellulose at 15% H_2SO_4

Fig. 3(c). Nanocellulose at 25% H_2SO_4

Fig. 3. FESEM micrograph of nanocellulose (5%, 15%, 25% H_2SO_4) at 500K magnification.

4. Conclusions

In this study, nanocellulose were successfully extracted and isolated from oil palm empty fruit bunches using a chemo-mechanical technique, involving a combination of sulphuric acid hydrolysis, mechanical disintegration and high-pressure homogenization. Analysis of the FESEM micrographs revealed that the diameter size of the NC was difficult to determine due to the above mentioned agglomerated network structure, thus consequently the NC diameter was estimated to be below 20 nm. Based on the results, it was evident that the isolation of NC using combinations of sulphuric acid hydrolysis and high-pressure homogenisation processes has the potential to become quality reinforcing agents for composite materials due to its prospective minimal particle size formation.

Acknowledgement

The authors would like to thank the support from the Malaysian Palm oil Board (MPOB) for financial support in completing this project.

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