

Characterization of cellulose nanofiber from oil palm mesocarp fiber produced by ultrasonication

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Abstract. Oil palm mesocarp fibre (OPMF) is one of the major biomass generated from palm oil industry and it is currently inefficiently burnt at palm oil mill for energy and as a mean of disposal. With the growing concern on environmental sustainability and finite supply of non-renewable resources, particular attention has been given to produce value-added materials from OPMF, such as biocomposite and biocompost. Since OPMF contains mainly cellulose, there is high potential for the production of cellulose nanofiber (CNF) from OPMF. In this study, cellulose was obtained from OPMF by chemical extraction. OPMF-cellulose obtained was then soaked in distilled water [0.2 - 1% (w/v)] prior to nanofibrillation using an ultrasonicator at 125 W and 36 kHz for 3 to 12 hours. Scanning electron microscopy (SEM) micrographs of fiber undergone ultrasonication confirmed the occurrence of CNF having diameter in the range of 40-200 nm. CNF produced had crystallinity value in the range of 31-43%, and was thermally stable up to 340 °C.

1. Introduction

Palm oil industry is currently ranked fourth as the major economic contributor to Malaysia, as it is contributing approximately 8% to the country's GNI per capita and 6% of GDP [1-2]. As one of the major economic backbone to the country, this industry covers nearly three quarters of the Malaysia's agricultural land which is about 5.39 million hectares and this consequently cause an environmental issue, especially in managing wastes contributed from oil palm plantations and mills. Umar et al. (2013) [3] stated that there is about 80 million tons of oil palm biomass generated by the Malaysia's oil palm industry annually, and the value is expected to rise to 100 million tons by the year 2020. Given its abundant availability, various industries had started to use oil palm biomass as an alternative raw material for various product manufacturing such as biocomposite [4], biofuel [5], biochar [6], biocompost [7] and many more. This is due to the abundant and infinite supply of oil palm biomass that can be collected anytime due to huge plantation area and rapid fruits production.

Focus is given mainly on the utilization of oil palm empty fruit bunch (OPEFB) and palm kernel shell (PKS), leaving behind the OPMF. OPMF is the solid residue obtained from oil palm fruits after oil extraction and it is usually being left in palm oil mills to be used as a boiler fuel or burnt as a mean of disposal, which is wasteful and this indirectly contributes to various environmental pollution [8,9]. As a lignocellulosic material, OPMF has potential to be used as a raw material for various high value



bioproducts manufacturing including cellulose nanofiber (CNF). CNF which is a term referring to nano-structured cellulose is a tiny fiber with light weight, yet possesses great strength, stiffness, biodegradability and renewability [10]. Owing to their good mechanical properties, CNF can be used for several applications ranging from consumer products to high-tech industrial applications. The opportunity to utilize OPMF for the production of CNF would be a new approach in utilizing OPMF for the production of value-added products.

Nevertheless, there are few major issues in the production of CNF especially in delaminating the fibers cell wall and separating the nano-sized fibrils without affecting their properties. Due to this matter, selection of nanofibrillation method need to be carried out thoroughly to ensure the chosen materials are well fibrillated. Electrospinning is the most common and conventional method used for nanofibrillation of cellulose. Previous study by Yasim-Anuar and colleagues (2017) [11] demonstrated that OPMF can be converted to CNF by electrospinning. Nevertheless, the diameter of the CNF was larger than 200 nm. It has been reported that other nanofibrillation such as ultrasonication can produce CNF with small diameter and relatively high length fiber [12]. Ultrasonication is able to produce nano-size fibers due to its acoustic frequency cavitation which involves formation, expansion and implosion of microbubbles in aqueous solution. This process will cause erosion, which then lead to the breakage of relatively weak Van der Waals forces resulting in the separation of the microfibrils into individual fibers [13].

Even though ultrasonication has been widely studied and reported before, yet there have been lack of reports on CNF production from oil palm biomass using this method. Since each natural fiber has different physical and chemical properties, this may influence the morphology, crystallinity as well as thermal properties of the CNF. This was supported by Zhao et al. (2015) [14] that stated each natural fibers which were constituted by microfibrils defibrillated the fibers in different degree, even though similar mechanical process was conducted. This was highly attributed to the physical and chemical properties of the fibers.

Therefore, the goal of this study was to investigate the characteristics of CNF produced from OPMF using ultrasonication. The cellulose extracted from OPMF were subjected to ultrasonication at different ultrasonication duration, to identify the optimum duration to produce CNF with smallest diameter. Subsequent ultrasonication was then carried out using different cellulose concentration, to identify the effect of ultrasonication on different cellulose concentration.

2. Experimental

2.1 Materials

Samples of oil palm mesocarp fiber (OPMF) obtained from Seri Hulu Langat Palm Oil Mill (Dengkil, Selangor, Malaysia) was used to prepare cellulose nanofiber (CNF). The OPMF samples were cleaned using tap water to remove any residuals and sun dried prior to further study [15]. Cellulose extraction was conducted by treating the OPMF using sodium chlorite (NaClO_2) and potassium hydroxide (KOH) according to the method by Yasim-Anuar et al. (2017) [11]. OPMF-cellulose obtained after extraction had purity of 99 %.

2.2 Methods

2.2.1 Preparation of cellulose nanofiber. In order to produce cellulose nanofiber (CNF) by ultrasonication, the cellulose extracted from OPMF was first soaked in distilled water at 0.2, 0.4 and 0.8 % (w/v) concentration. Each cellulose suspension was then placed in an ultrasonicator (Q125, Serial No: 63863T-07-11, QSonica, Connecticut, USA) at 125 W, 20 kHz in frequency and 100 amp. In order to determine the effect of ultrasonication time on the CNF formation, ultrasonication was conducted at 3, 6, 9 and 12 hours. The ultrasonication was carried out in ice and this condition was maintained throughout the ultrasonication process to prevent suspensions from overheating as cavitation during ultrasonication may rise the temperature of the cellulose suspension (method

modified from Chen et al., 2011 [16]). After completing this process, the CNF samples were subjected to freeze drying process prior to further analysis.

2.2.2 Characterization

2.2.2.1 Scanning electron microscopy analysis (SEM). The morphology of the CNF was observed using a field-emission scanning electron microscopy (FE-SEM) (Sirion 200, FEI, Eindhoven, Netherlands) with accelerating voltage of 5 kV. The freeze-dried CNF were coated with platinum using a vacuum sputter coater prior to FE-SEM observation.

2.2.2.2 X-ray diffraction analysis. The crystallinity index of CNF was analysed using X-ray diffractometer (XRD) which was performed on a Philips PW3040/00 X'Pert MPD system (Eindhoven, Netherlands). The X-ray diffractogram was recorded in the 2θ range of 5 to 50° and the crystallinity index, Crl was calculated using the following equation:

$$Crl = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (1)$$

where I_{002} is equal to $2\theta = 23^\circ$ and it refers to the peak of the crystalline portion of biomass (*i.e.*, cellulose), while I_{am} refers to the peak at about $2\theta = 18^\circ$, which corresponds to the amorphous region [15].

2.2.2.3 Thermal stability analysis. Thermal stability and decomposition temperature of the cellulose and CNF was determined by using a thermogravimetric analyzer (TG 400, Perkin Elmer, Waltham, MA, USA). The samples (approximately 10 mg) were placed in aluminum cups, and the analysis was carried out at a heating rate $10^\circ\text{C}/\text{min}$ under nitrogen flow of $20\text{ mL}/\text{min}$ from 50 to 550°C [11].

3. Results and Discussion

3.1 Morphology of the ultrasonicated CNF

The morphology of 0.2% (w/v) ultrasonicated CNF produced at 3, 6, 9 and 12 hours was examined to observe the effect of ultrasonication time towards CNF formation. The average diameter of the CNF was determined by measuring it using Image J software. The SEM micrograph shows that the OPMF-cellulose gradually reduced in its size by time after 3 hours of ultrasonication, CNF with average size of approximately 150 to 1000 nm was produced. Prolonged ultrasonication for 6, 9 and 12 hours were able to produce CNF with diameter around 80 to 600 nm, 40 to 200 nm and 100 to 500 nm, respectively. This result indicates that the hydrogen bonding between the CNF was lower after ultrasonication and smallest diameter of CNF can be obtained after 9 hours of treatment. This proved that ultrasonication can break the relatively weak interfaces among cellulose fibers, which are bonded to each other by H-bonds. Thus, it can disintegrate the micro-size cellulose fibers into nano-size cellulose fibers [16-17].

Theoretically, it was expected that the longer the processing time, the smaller the diameter of CNF can be obtained. However, when ultrasonication was prolonged to 12 hours, the diameter of CNF was observed to be larger than CNF produced at 9 hours of processing time. From the SEM micrographs, ultrasonication did helped in breaking fibers' agglomeration. However, subsequent ultrasonication can lead to re-agglomeration of the CNF and similar results were observed from other studies by Cengiz et al., (2009), Gokce et al., (2014) and Mandzy et al., (2005) [18–20]. This phenomenon occurred probably due to the attraction of van der Waals forces and it also may be due to the reformation of H-bonds between the CNF which may be due to stress on the CNF surface because of longer processing time or because of the adhesion of CNF to one another. Based on this SEM micrograph, the smallest diameter of CNF can be produced after 9 hours of ultrasonication.

Subsequent ultrasonication was carried out using 0.4 and 0.8% (w/v) concentration to test the effect of concentration on CNF formation.

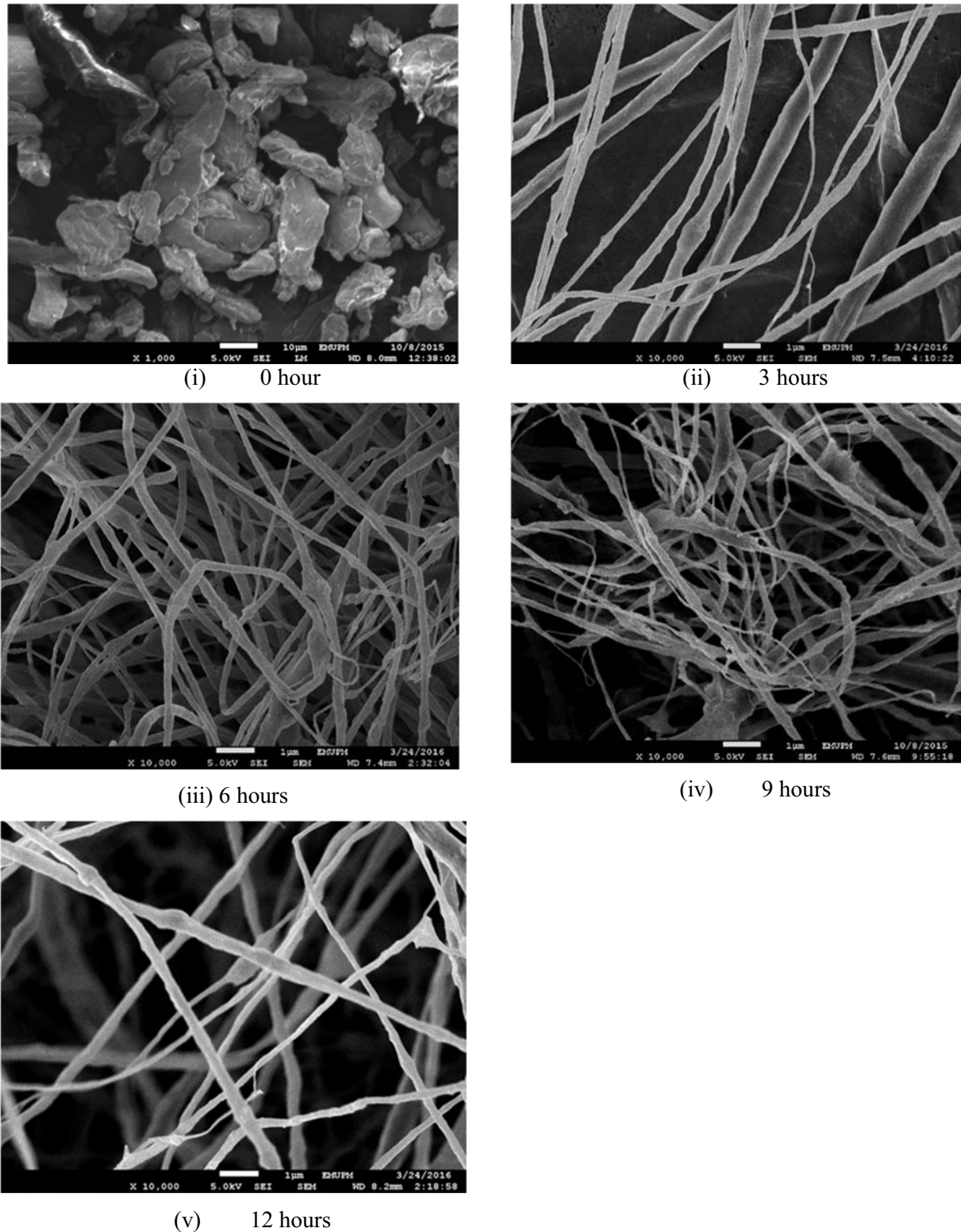


Figure 1. The SEM micrographs of (i) OPMF-cellulose, and CNF after (ii) 3 hours (iii) 6 hours, (iv) 9 hours and (v) 12 hours of ultrasonication (10,000x magnification).

In terms of the effect of concentration on the formation of CNF, the SEM micrograph shows that larger diameter of CNF was recorded when using both 0.4 and 0.8% (w/v) OPMF-cellulose concentration. The average diameter was approximately around 110 to 560 nm and 150 to 800 nm for 0.4 and 0.8% (w/v) cellulose concentration respectively. This shows that high cellulose concentration can increase the intra-molecular interaction, which consequently raised the agglomeration effect due to van der Waals forces. This was also supported by Li et al. (2014) [21] which stated that cavitation of ultrasonication requires more energy to break cellulose chains for higher cellulose concentration due to higher viscous system of the solution. Hence, it can be concluded that when the OPMF-cellulose solution was more than 0.2% (w/v), the viscosity of the solution increase hence, cellulose were not able to disperse uniformly. Therefore, it was discovered that CNF with smallest diameter can be produced using 0.2% (w/v) cellulose concentration.

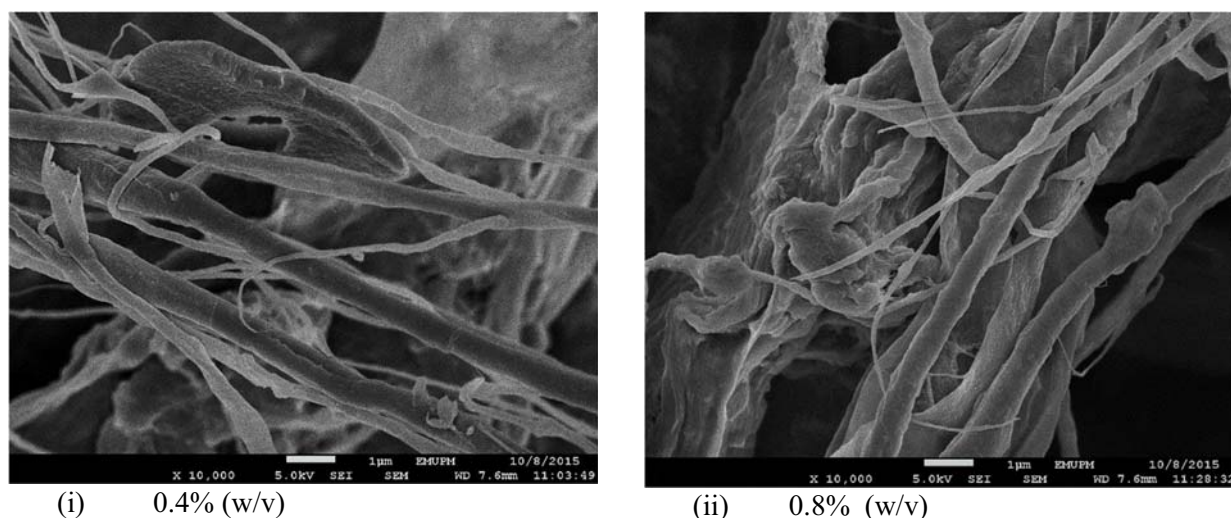


Figure 2. The SEM micrographs of CNF using (i) 0.4% and (ii) 0.8% (w/v) OPMF-cellulose for 9 hours ultrasonication (10,000x magnification).

3.2 Crystallinity by X-ray diffraction

X-ray diffraction analysis was conducted to investigate the crystallinity of the OPMF-cellulose and CNF obtained after ultrasonication. The XRD diffractograms of OPMF-cellulose and CNF produced after ultrasonication as shown in Figure 3 exhibited an intense reflection at $2\theta = 21$ to 22° , indicates the cellulose crystallographic plane (002, Bragg reflection), and another small peak at $2\theta = 18$ to 19° which corresponds to the amorphous region (101, Bragg reflection). The crystallinity index of OPMF-cellulose was 51 % and the crystallinity index of CNF after 3, 6, 9 and 12 hours of ultrasonication were 31, 37, 41 and 32 %, respectively. It is apparent that after ultrasonication, the crystallinity index of CNF decreased significantly. This result shows that the exposure to ultrasonication may disrupt the CNF structure thus, led to reduction in crystallinity. This was supported by Xie et al. (2016) [22] that stated ultrasonication may break down the hydrogen bonds of the cellulose fibers, which then consequently caused damage to the crystalline part of the CNF.

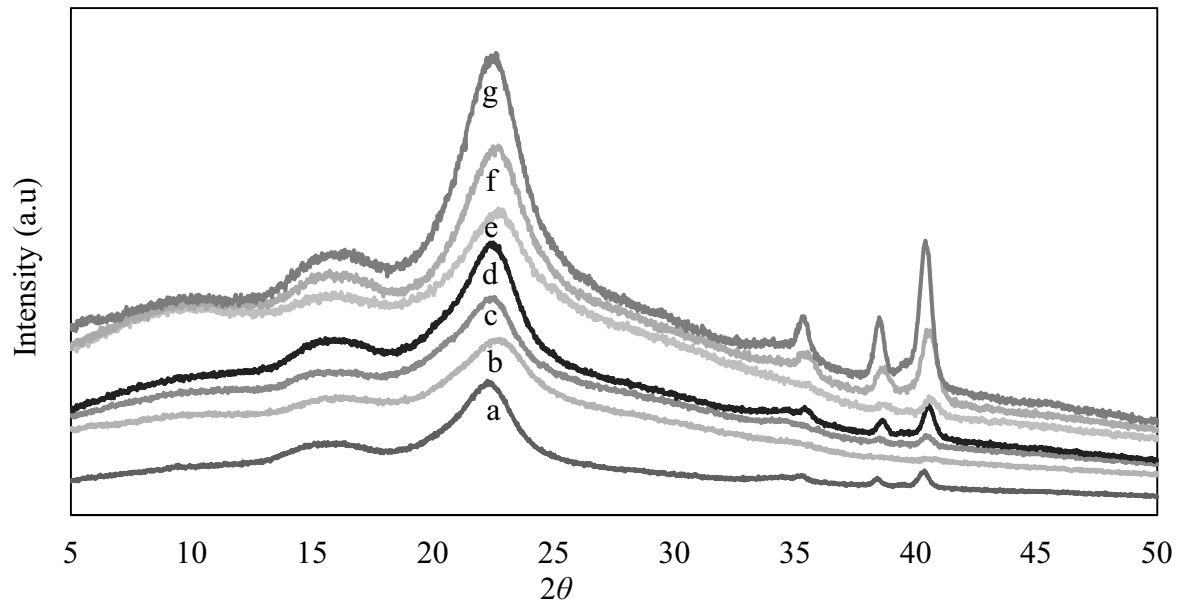


Figure 3. XRD diffractograms of (a) OPMF-cellulose, CNF from 0.2% (w/v) OPMF-cellulose ultrasonicated for (b) 3 hours, (c) 6 hours, (d) 9 hours and (e) 12 hours. While (f) CNF from 0.4% (w/v) OPMF-cellulose ultrasonicated for 9 hours and (g) CNF from 0.8% (w/v) OPMF-cellulose ultrasonicated for 9 hours.

The reduction in crystallinity after ultrasonication might be due to the impact of hot spots generated during the collapse of cavitation [23]. In this study, water which acted as a solvent and hydrolysis reagent produced bubbles throughout ultrasonication process. Those bubbles oscillated and by time, they violently collapsed, thus able to generate high pressure and temperature on the surface of the cellulose and caused damage to the crystalline parts of the CNF. Hence, it can be concluded that despite of able to broken down the microfibrils, acoustic cavitation of ultrasonication however may reduce the crystallinity index of obtained CNF.

Subsequent 9 hours ultrasonication using different OPMF-cellulose concentration; 0.4 and 0.8% were tested to determine the effect of concentration on the crystallinity of CNF. The crystallinity for CNF produced at 9 hours ultrasonication from 0.2, 0.4 and 0.8 % (w/v) OPMF-cellulose was almost similar which was in the range of 41 - 43% as shown in Table 2. This indicates that there was no significant different in terms of crystallinity between different OPMF-cellulose concentration.

Table 1. Crystallinity index of the OPMF-cellulose and CNF obtained after ultrasonication.

Samples	Crystallinity index (%)
OPMF-cellulose	51
CNF from 0.2% (w/v) OPMF-cellulose at 3 hours	31
CNF from 0.2% (w/v) OPMF-cellulose at 6 hours	37
CNF from 0.2% (w/v) OPMF-cellulose at 9 hours	41
CNF from 0.2% (w/v) OPMF-cellulose at 12 hours	32
CNF from 0.4% (w/v) OPMF-cellulose at 9 hours	42
CNF from 0.8% (w/v) OPMF-cellulose at 9 hours	43

3.3 Thermal stability of ultrasonicated CNF

The thermogram of the OPMF-cellulose and CNF samples are illustrated in Figure 4 and Figure 5 respectively. A slight weight loss at around 50 to 100 °C indicates the evaporation of moisture and initial thermal decomposition, while the broad peak between 220 to 400 °C is attributed to cellulose

degradation [13]. The TG curve of CNF shows a slight reduction at $T_{d50\%}$ which was from 343°C (OPMF-cellulose) to 342, 341, 338 and 336 °C after 3, 6, 9 and 12 hours of ultrasonication respectively. A slight decrease in thermal stability for CNF might be due to their high surface area, which was due to their nanoscale. It must be noted from FE-SEM images that the surface areas of CNF are much higher than OPMF-cellulose, hence the CNF may initiate more active sites and accelerate the decomposition [24]. This similar behavior has also been reported by Oliveira et al. (2013) [25]. This TG result is also significantly related to the reduction in crystallinity after ultrasonication and as according to Pacaphol and Aht-Ong, (2017) [26], this is due to the greater number of the chain ends in CNF, which was able to move independently when undergoing ultrasonication. In contrast to the CNF, OPMF-cellulose which appeared in microscale contained less amount of the chain ends and as a result, the degradation occurred late.

Besides that, it was also observed that by prolonged the ultrasonication duration may resulted in low thermal degradation temperature. This clearly showed that longer ultrasonication duration may disrupt the structure of the CNF, thus negatively affect the thermal stability. This was corresponds to the crystallinity index as well. On the other hand, the thermal stability of CNF from different OPMF-cellulose concentration is presented in Figure 5. The degradation temperature was almost similar for CNF produced at 9 hours ultrasonication from 0.2, 0.4 and 0.8 % (w/v) OPMF-cellulose suspension, which was in a range of 338 - 340°C. This indicated that no significant different in terms of thermal degradation temperature between different OPMF-cellulose concentration.

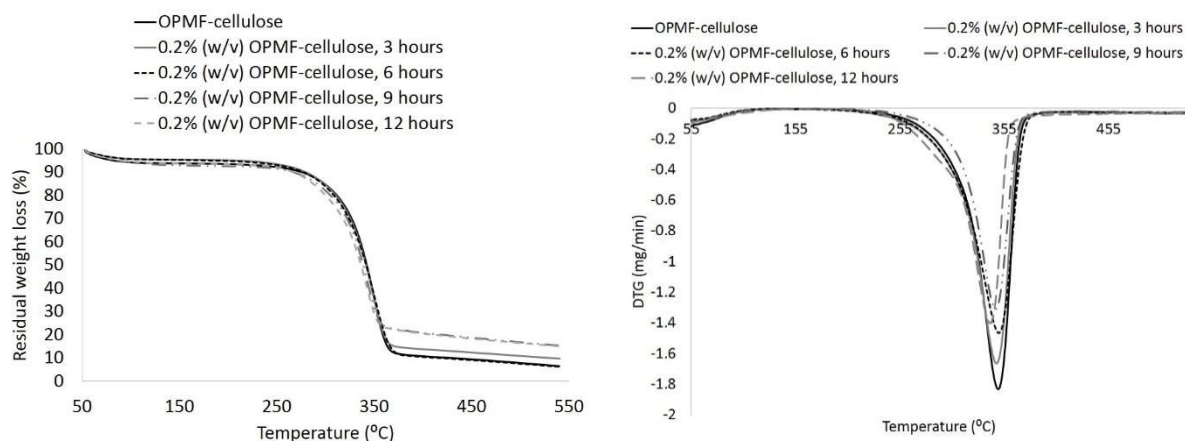


Figure 4. The TG and DTG thermograms of CNF obtained using 3, 6, 9 and 12 hours of ultrasonication from 0.2 % (w/v) OPMF-cellulose suspension.

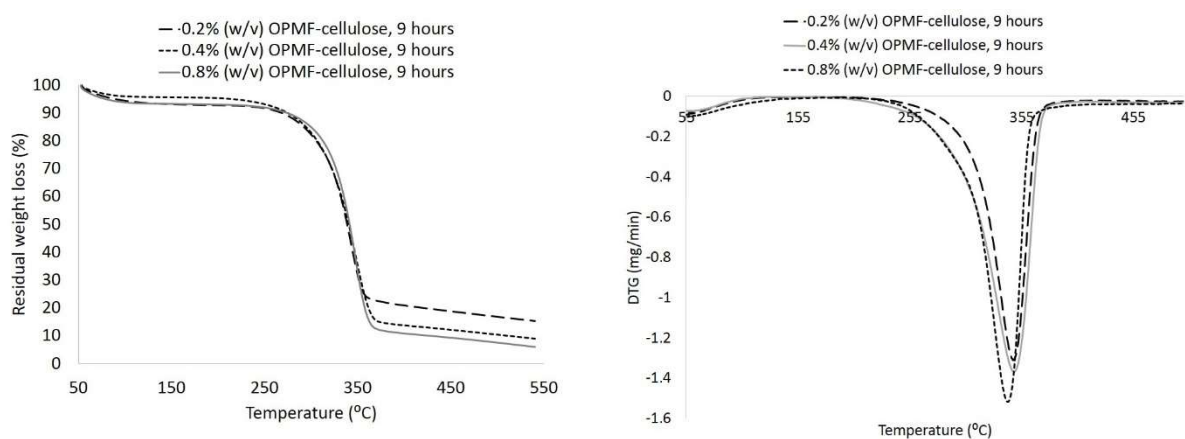


Figure 5. The TG and DTG thermograms of CNF obtained using 0.2, 0.4 and 0.8 % (w/v) OPMF-cellulose suspension at 9 hours of ultrasonication.

3.4 Comparison of CNF

Based on the morphology, average diameter, crystallinity and thermal stability of CNF produced from OPMF, it was revealed that ultrasonication exhibited excellent CNF formability using water as the main solvent throughout nanofibrillation process. The CNF produced from this method has almost similar properties to those reported in previous studies as shown in Table 2. In this study, CNF with diameter less than 200 nm, high crystallinity and thermally stable was produced without having to rely on chemicals as a solvent during ultrasonication. This is the advantage of this method as compared to other reports. For example, Wang et al. (2015) [27] suspended and ultrasonicated the cellulose fibers in several solvents such as hydrochloric acid, formic acid, and mixture of formic acid and hydrochloric acid in order to produce CNF. Li et al., (2014) [21] on the other hand used a mixture of NaOH, thiourea, urea and H₂O.

In terms of power usage and duration of ultrasonication, this study only conducted ultrasonication for 9 hours at 125 W, which was lowered than the other studies. For example, Chen et al. (2011) [16] applied ultrasonication at 1200 W for 30 minutes, despite of conducting additional chemical treatment prior to ultrasonication. Wang et al. (2015) [27] also applied high power during ultrasonication which was approximately 1080 – 1620 W for 4 – 6 hours. Li et al. (2014) [21] also conducted homogenization process after ultrasonication at 100 – 500 W to produce smaller diameter size of CNF. The comparison of the processing parameter indicates that the use of high ultrasonication power and additional nanofibrillation were not the ultimate condition to produce CNF. This study prove that ultrasonication solely can be able to produce CNF, without having to proceed with another nanofibrillation process. This is because, the cavitation energy released during ultrasonication created a mechanical shock wave, which then able to disrupt the agglomerated cellulose fibers, resulting in CNF production [21].

Table 2. Comparison of CNF properties from various sources.

Source of cellulose	Methods condition	Findings	References
Bleached softwood kraft pulp (Supplied by Suzano, SP, Brazil)	Pretreatment: NaOH: thiourea: urea: H ₂ O = 7:9:9:75 Ultrasonication: Time: 30 min Power: 100 – 500 W Solution: Mixture of NaOH, thiourea, urea and H ₂ O Additional nanofibrillation: Homogenization	Size: > 30 nm CrI: 43.7 % T _{d50%} : 370 °C	[21]
Bamboo fibers	Pretreatment: Dewaxed in benzene/ethanol solution for 6 hours followed by NaClO ₂ and 2 wt% KOH. Additional treatment: Further treatment using NaClO ₂ followed by 5 wt% KOH and 1 wt% HCl.	Size: 30 – 80 nm CrI: 61.25 % T _{d50%} : 309 °C	[16]

	Ultrasonication: Time: 30 min Power: 1200 W Solution: Distilled water		
Silk derived from <i>Bombyx mori</i> silkworm	Degummed in 0.2% (w/v) Na ₂ CO ₃ solution Ultrasonication: Time: 4 - 6 hours Power: 1080 – 1620 W Solution: hydrochloric acid, formic acid, and a mixture of formic acid and hydrochloric acid.	Size: 30 – 120 nm Crl: - T _{d50%} : -	[27]
Oil palm mesocarp fiber	Chemical pretreatment: 6% (w/v) NaClO ₂ and KOH Ultrasonication : Time: 9 hours Power: 125 W Solution: Distilled water	Size: 40 – 200 nm Crl: 41% T _{d50%} : 338 °C	This study

4. Conclusions

The present study showed that ultrasonication was successfully used to convert OPMF-cellulose into CNF. The applied acoustic cavitation reduced the crystallinity index and thermal degradation temperature after subsequent ultrasonication. The resulting CNF produced from OPMF by ultrasonication had diameter in the range of 40 to 200 nm, crystallinity index of 41% and was thermally stable with T_{d50%} of approximately 338 °C. It was also revealed that the optimum condition for CNF production by ultrasonication was at 125 W for 9 hours, with 0.2% (w/v) cellulose concentration. Overall, CNF produced from OPMF-cellulose can be considered as a promising nanomaterial as it offers high renewability, high thermal stability and high crystallinity. Due to their small diameter size and high thermal stability properties, the CNF produced in this study has potential to be used for the manufacturing of various applications such as transparent paper.

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