Characterisation of microfibrils cellulose isolated from oil palm frond using high-intensity ultrasonication

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Abstract. This study highlighted the utilization of agricultural byproducts as an alternative fiber resource to be used as one of the materials for reinforcement biocomposite. Cellulose was extracted from oil palm frond using the alkaline treatment and successfully isolated into microfibril via the combination of carboxymethylation pre-treatment ultrasonication to get highly crystalline and good thermal stable microfibers. 4% NaOH was used during alkaline treatment and followed by oxidative bleaching with 30% H\(_2\)O\(_2\). Once the extracted cellulose is chemically pre-treated with monochloroacetic acid, it was subjected to 30 minutes ultrasonication treatment to reduce its size. The detailed comparative analysis using SEM, FTIR and TGA was conducted in this work revealed some breakages of intramolecular hydrogen bonds and glycosidic bonds that occurred during the alkaline and bleaching treatment of oil palm biomass. The SEM images showed significant morphology of rigid, organized and highly ordered cellulose fibrils changed into aggregated fibril bundles of microfibrils after ultrasonication. The results from the infrared spectrums revealed that the mild alkaline treatments and oxidative bleaching were able to remove a large fraction of lignin and hemicelluloses to leave a clean cellulose sample. The isolated microfibrils cellulose exhibit good thermal stability as almost 50% of its initial mass remains at a temperature of 300 °C. These findings demonstrate that oil palm fronds can be utilized for biocomposite reinforcement applications.

1. Introduction

Malaysia is located in the tropical region, where it receives a fair amount of sunshine and an abundance of rainfall throughout the year. This climate puts the country in an excellent position to promote agricultural activities as its major commodity. Around 4.06 million hectares of land have been used for agriculture to contribute up to 56.4 % of Malaysia’s national gross domestic products (GDP) [1]. However, activities from the agricultural sector create high amounts of biomass, particularly from palm oil plantations. It was reported that Malaysia produces approximately 168 million tons of biomass each year [2] at which 30 million tons of biomass produced are contributed from Malaysia oil palm industry, in the form of empty fruit branches (EFB), oil palm trunks (OPT) and oil palm fronds (OPF) [3]. The concern of environmental issues has encouraged efforts toward increasing the efficient utilization of raw
resources and reduce waste productions. One of the approaches in minimizing the waste from this industry is by converting it into useful products such as fibers with thermal stability characteristics to be utilized as reinforced filler for biocomposite.

The detrimental environmental and ecological impacts of synthetic filler materials in polymer composite have forced researchers to pursue renewable biomass materials like cellulose for the replacement. Cellulose is a high molecular weight linear polymer consisting of a repeating D-glucose unit bound together between C1 and C4 through glycosidic bonds [4]. It is widely employed as starting materials to produce micro sizing cellulose, microcrystalline and microfibrillated cellulose. Despite various approaches to convert oil palm waste into wealth, OPF has not yet obtained an adequate industrial application for the past years. Studies have shown that OPF contains 84% holocellulose, out of which 44–58% is cellulose [5–7]. Cellulose constituent in the agricultural biomass together with the complex structure is responsible for the high thermal strength of the processed fiber produced. Recent studies have shown that cellulose becomes a desirable filler for biocomposite due to its thermally stable characteristic [8,9] and relatively strong (high crystallinity index).

The characteristic of extracted cellulose muchly depends on the cellulosic source and the treatment process during which the isolation is carried out, as reported by Chen et al. [10]. Multi-sized aggregate bundles of elementary microfibrillated cellulose (MFC) require intensive mechanical refinement of purified cellulose pulp to break the cell walls of fibers and release cellulose fibrils. Mechanical refinements such as refining or high-pressure homogenization [11], microfluidization [12], grinding [13] and twin screw extrusion [14] are often associated with high energy consumption. Therefore, the application of the hydrodynamic forces due to the high pressure associated with the collapse of cavitation bubbles during the ultrasonication treatment is now of great interest. A study has shown successful isolation of nanofibrils cellulose from wood using high-intensity ultrasonication with alteration in fiber properties [15]. To assist the degradation of the cellulosic fiber, oxidative or hydrolytic methods were suggested to swell the fiber and break down the cell wall at significantly lower mechanical forces. In the past few years, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)-mediated oxidation was used to assist the ultrasonication isolation method as the presence of carboxylate group effectively break the inter-fibril hydrogen bonding [16]. Until recently, the combination of carboxymethylation and ultrasonication is still not widely reported.

The isolation methods cellulose fiber creates a distinct distribution of amorphous and crystallinity value of the fiber and hence influences the character of the cellulose fibers differently. So, this work aims to extract the cellulose from the oil palm frond using simple alkalization treatment and to isolate the oil palm frond cellulose microfibrils by using the combination of carboxymethylation treatment and ultrasonication method (chemo-mechanical method). The physicochemical characteristics of the cellulose fiber extracted after ultrasonication treatment were studied. The reuse of this agricultural biomass for a potential value-added product will become one of the additional revenues as well as develop the diversification of the agricultural industry.

2. Methodology

2.1. Raw Materials

Samples of the oil palm fronds used for the cellulose extraction were obtained from an oil palm plantation in Terengganu, Malaysia. The raw samples were washed for disinfection, cut into small pieces, and dried at a temperature of 60–85 °C for 48 h. The dried samples were ground into a powder and sieved until specific sizes were reached. Commercially available microcrystalline cellulose, NaOH, H₂O₂, sulphuric acid, monochloroacetic acid, isopropanol, acetic acid, methanol, and ethanol were from Sigma-Aldrich and used as received. All chemicals were of analytical reagent grade (suitable for laboratory use).
2.2. Extraction of cellulose
The oil palm fronds (OPF) powder was directly treated with 4 wt.% NaOH at 90–100 ºC for 2 hours. The obtained black slurry from alkaline treatment was filtered and washed solid residue with distilled water several times until the pH of the filtrate is neutral. The residue was then dried in the oven at 55 ºC to constant weight for 24 hours. At this stage, oil palm frond cellulose was obtained. The OPF cellulose was bleached with 30% H₂O₂ at 90 ºC for an hour. The bleaching step was repeated three times until the cellulose turns white. The bleached OPF cellulose was rewashed using distilled water and filtered using the Buchner filter system. After filtration, the bleached OPF cellulose was dried in the oven at 55 ºC.

2.3. Carboxymethylation treatment
Five grams of bleached cellulose powder was alkalized in 30 % (w/v) NaOH at 30°C for 60 min with the presence of isopropanol as a solvent. The carboxymethylation process is followed by the addition of 6 g of monochloroacetic acid at 55°C for under constant stirring conditions for 180 mins. The slurry was filtrated, and the solid residue was soaked in methanol overnight to remove impurities. The suspension is neutralized with 90% acetic acid. The solid residue was washed with ethanol, and the obtained carboxymethylcellulose was dried using a freeze dryer for 48 hours at -82 ºC temperature.

2.4. Ultrasonication
Carboxymethylated cellulose powder was soaked in distilled water (0.1 % w/v) before the suspension was subjected to ultrasonic treatment for 30 min using an ultrasonic processor at 20 kHz and output power of 130 W. The final suspension of fibrillated cellulose was collected and freeze-dried for characterisation.

2.5. Characterization

2.5.1. Fourier Transform Infrared (FTIR). Infrared spectroscopy of extracted cellulose from oil palm fronds was carried out using Bruker Tensor 27. Bands were recorded in the region from 4000 cm⁻¹ to 600 cm⁻¹. The spectrum was compared with commercial crystalline cellulose for analysis.

2.5.2. Scanning Electron Microscopy (SEM). The morphological studies of extracted cellulose from OPF and ultrasonicated CMC were carried out using a scanning electron microscope. The samples were first coated with gold/palladium by using a sputter coater device from Bal-Tec (Multi Coating System MED20), which is a good sample preparation technique. Then, SEM (JEOL-JSM-6010LA) was applied at an acceleration voltage of 15 kV for the characterisation of the samples.

2.5.3. Thermogravimetric analysis/Differential thermal analysis (TGA/DT). Thermal behaviour of raw OPF, cellulose extracted and carboxymethylated cellulose (CMC) was investigated using simultaneous thermal analyser NETZSCH STA 449F3. The samples were heated from ambient temperature up to 900 ºC with a heating rate of 10 ºC/min¹ under a nitrogen gas atmospheric condition.

2.5.4. X-ray Diffraction. The crystallinity phase of the extracted cellulose samples was evaluated through an X-ray diffractometer, (Bruker AXS-D8 Advance). The diffraction patterns were recorded using Cu radiation at 40 kV and 40 mA with a wavelength (λ) of 0.15406 nm.

3. Results and Discussion

3.1. Infrared spectroscopy
The FTIR spectra of the raw oil palm frond and the extracted cellulose were measured to investigate changes in the chemical structures occurring during the alkalinization and oxidative bleaching treatment. From the FTIR spectra shown in figure 1, the spectrum of the extracted cellulose is closely similar to commercial crystalline cellulose indicates the effectiveness of the extraction method. The peaks in the regions 3200 and 3300 cm⁻¹ correspond to the stretching vibration of the hydroxy groups (O-H), the
main functional groups for cellulose. The intensity of the peak reduced in the extracted cellulose sample compared to raw OPF indicates the reduction in the O-H concentration as the alkaline treatment reduced the hydrogen bonding in cellulosic hydroxyl groups [17]. The absorption band at 2897 cm$^{-1}$, associated with the stretching vibration of the C-H bond of cellulose, appears in all the extracted samples but intensified in the extracted cellulose sample.

The peaks between 1650 and 1630 cm$^{-1}$ were attributed to C-H and O-H stretching in the lignin and hemicellulose, which has shown a significantly low intensity in extracted cellulose samples when comparing to raw OPF. The mercerization (alkaline treatment) has removed hemicelluloses and partially removed the lignin during this process [18]. Glycosidic bonds in the hemicelluloses are hydrolyzed during mercerization treatment and promote the ester bonds’ cleavage between the hydroxyl groups of lignin and the carboxyl groups of the hemicelluloses. The low intensity of the peak within this region, attributed to the lignin aromatic ring, was also recorded due to the oxidative bleaching process. The bleaching process was responsible for oxidizing the ether bonds between the hydroxyl groups of lignin and the carbohydrates [7]. The peaks, which are also typical for cellulose compounds present in the bands at 1160 and 896 cm$^{-1}$, were also recorded in the extracted cellulose from the oil palm frond. The peaks were associated with the C–O and C–H stretching of glycosidic linkages.

![Figure 1. Comparison of FTIR spectra of; a) raw oil palm frond (OPF), b) extracted cellulose from the oil palm frond, and c) commercial microcrystalline cellulose.](image)

3.2. Morphology Observations
It is observed that the colour of the raw oil palm frond fibers changed from brown to white after treatment, as shown in figure 2. Significant colour changes were due to the removal of lignin and other extractives during mercerization and bleaching treatments, resulting in a lighter colour and smoother surface of the fibers, respectively. The same physical observation was recorded during cellulose extraction from OPT using potassium hydroxide and hydrogen peroxide bleaching process [19]. The presence of phenolic substances such as lignin and extractive are responsible for the wood’s dark colour. The removal of these substances has caused a notable colour change in the extracted cellulose sample [20].
Figure 2. Comparison of the appearance of a) raw OPF, and b) extracted cellulose.

The individual micro-sized fiber bundles were captured in SEM images of the surface structure of the extracted cellulose sample, as shown in figure 3(a), which is caused by the solubilization of hemicellulose and the disruption of lignin. The irregular and rougher fiber cells with many fibril bundles attached were observed in the SEM images of cellulose from the alkali-treated bamboo [20]. The combination of carboxymethylation and ultrasonication treatment has caused the surface morphology changes from a fibrous cellulose structure to a finely laminated structure, as can be seen in figure 3(b). The lateral size of cellulose fibrils isolated using ultrasonication was recorded within 2.5–5 µm in width. Therefore, the interconnected network microfibers obtained in this study could provide a great reinforcing capability for biocomposite applications.

Figure 3. Comparison of the SEM image of; a) extracted cellulose from OPF and b) ultrasonicated carboxymethyl cellulose (CMC) under 100× magnification.

3.3. Thermogravimetry analysis (TGA) and differential thermal analysis (DTA)

Figure 4 shows the thermogram of TGA of all three different types of samples; raw oil palm frond, extracted cellulose and ultrasonicated carboxymethyl cellulose (CMC) as compared to microcrystalline cellulose (commercial). The thermograms of all the samples exhibited two distinctive mass loss stages: 1) temperature range below 150 °C and 2) temperature between 160 and 600 °C. The small drop of mass loss that occurs at a temperature lower than 100 °C was attributed to the water evaporations in all cellulosic samples. The second stage of weight loss occurs in the raw OPF sample at a lower temperature (165°C) than the extracted cellulose sample (275 °C) signify the mass loss due to decomposition of lignin and hemicellulose [21]. The occurrence can be deduced from the DTG image of all the samples, as shown in figure 5. The mass loss at a temperature ranges from 180 to 300 °C represents the degradation of lignin and hemicellulose in the raw OPF sample. Two small stages of mass loss occurring in raw OPF samples do not appear in the DTG image of the extracted cellulose image. The observation could indicate a successful removal of hemicelluloses and lignin during alkalinization and bleaching procedures. The major mass loss at a temperature range of 300 to 350 °C represents cellulose degradation in the OPF-cellulose sample.
The effects of ultrasonication treatment on the thermal stability of carboxymethylated cellulose were also conducted using thermogravimetry analysis. The thermogram of the CMC sample in figure 4(d) has shown two distinct weight losses are observed from the results. The first decomposition occurs in the temperature range of 30 and 130 °C, where the weight loss is about 14.5 %. The initial weight was attributed to the loss of moisture in the sample. A similar observation has been reported by Moussa et al. [22] for the carboxymethyl cellulose extracted from almond shells, almond stems, and fig stems. The second decomposition temperature started at 245 °C showing a rapid weight loss up to 300 °C due to the loss of COO⁻ from the polysaccharide [23]. This second stage weight loss in ultrasonicated CMC shifted to a comparatively lower temperature than that of cellulose confirms a relatively lower thermal stability of ultrasonicated CMC within the temperature range. Though, its thermal stability is still good. The thermogram shifted a little bit to the left due to the presence of carboxymethyl functional group catalyse the degradation of carboxymethyl cellulose [24]. The conversion of extracted cellulose from OPF changes both the molecular structure and bonding energy which subsequently affects the thermal behavior of CMC differently. Alkaline treatment during the production of CMC increases the amorphous structure of CMC [25], which degrades at a lower temperature than that of crystalline structure. At 300°C, the residue mass of CMC was about 50 %, and decomposition slowly continues as temperature increases. Complete decomposition of the carboxymethylated cellulose (CMC) did not take place within the temperature range, as the residue mass remained about 24 % even when the temperature reached 900 °C. The same observations were reported by Han et al., as the residue mass of CMC remains about 60 % when the temperature reached 600 °C [26].

Figure 4. Thermogram image of the (a) raw oil palm frond, (b) extracted cellulose, (c) commercial microcrystalline cellulose and (d) ultrasonicated carboxymethyl cellulose (CMC).
3.4. X-ray Diffraction
Crystallinity is another essential property of cellulosic materials as it may affect their mechanical properties as biocomposite reinforcement materials [27]. Figure 6 shows the x-ray diffraction spectra of extracted cellulose, CMC and ultrasonicated carboxymethylated cellulose to study the change of crystallinity upon chemical and physical treatments. The diffractogram of extracted cellulose from the oil palm frond has shown a major peak at $2\theta = 22.5^\circ$, which is believed to represent the typical cellulose (I) [28] and indices the 002 crystal phase of cellulose. This type of cellulose is naturally found in the plant. The cellulose extracted from OPF was highly amorphous, as indicated by a relatively low peak intensity in the diffractogram, which implies a more disordered structure. As the extracted cellulose is converted into carboxymethyl cellulose, the major peak of the diffractogram shifted to $2\theta = 20^\circ$ due to the broadening or cleavage of hydrogen bonds by carboxymethyl substitution at the hydroxyl groups of cellulose [22].

During the production of carboxymethyl cellulose, alkalinization and etherification destroy the crystalline form of cellulose, and some hydrogen bonds are opened for the formation of cellulose ether [29]. The swelling of the cellulose in an alkaline solution causes a stretching to the neighboring crystalline cellulose molecules and tends to distort them. As the CMC is subjected to high-intensity...
ultrasonication, the crystallinity reduces due to the breakdown of the hydrogen bonds of the cellulose microfibrils. This reveals that the ultrasonication treatment caused damage to the crystalline domain of the microfibrils. The same observation was reported by Lu et al. [30] in their study related to the production of cellulose nanocrystal from bamboo pulp via ultrasonication-assisted FeCl₃-catalyzed hydrolysis process.

4. Conclusions
High-quality cellulose was successfully extracted from oil palm frond using simple alkalinization pretreatment followed by oxidative bleaching technique using hydrogen peroxide. FTIR measurements of the fibers revealed that alkaline and oxidative treatment effectively remove the hemicellulose and lignin. Cellulose microfibrils were isolated from oil palm frond using the combination of carboxymethylation and high-intensity ultrasonication, with smaller apparent width than that isolated untreated pulp. This concludes the presence of the charged ether group reduces the effect of hydrogen bonding, thereby easing fibrillation. Carboxymethylated cellulose fiber also exhibited enhanced thermal properties, with residual mass remains 50% with thermal degradation temperatures higher than 300°C. The crystallinity of the ultrasonicated cellulose fibers also higher than their original extracted cellulose. Micro-sized cellulose extracted from oil palm frond using relatively cheap chemo-mechanical process has the potential to be used as reinforcement materials for biocomposite to increase its mechanical properties.

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