Comparative Properties Analysis between Microcrystalline Cellulose and Cellulose Nanocrystals Extracted From Rice Straw

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Abstract

Cellulose is one of the most commonly used raw material with intriguing properties and chemical structure. Over the recent years, widespread utilization of cellulose fiber in various fields had captivated remarkable recognition due to its safe and environmentally benign nature. However, current standards of technology highly focused on producing biomaterials with stronger and smaller footprint, where cellulose in its nanoscale form can be the answer to that call. Nanocellulose can be isolated from natural plant fibers either by chemical, mechanical and enzymatic methods. The objective of this study is to chemically extract and compare the properties between both microcrystalline cellulose (MCC) and cellulose nanocrystals (CNC) from an underutilized agricultural waste product, rice straw fiber. Their properties were ascertained by scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), X–ray diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy and thermogravimetric analysis (TGA). Microscopic images of CNC depicted that CNC occur in nanoscale form and possess high aspect ratio. CNC was also found to occur in a higher crystallinity than MCC, which favors its application as reinforcement filler in hydrophilic polymer composites as compared to MCC. On the other hand, MCC which was found to be more thermally stable than CNC, advocates high-temperature polymer composite applications.

Keywords: nanocellulose, microcystalline cellulose (MCC), cellulose nanocrystals (CNC), rice straw

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Introduction

Microcrystalline cellulose (MCC) which consist of linear chains of β-D-glucose units linked together by β-1,4-glycosidic linkages is an abundantly available polymeric biomaterial in nature [1–4]. The supply chain of MCC is practically inexhaustible and it can be chemically extracted from plant fibers through alkaline and bleaching treatments [4,5]. Nanocellulose, on the other hand, can be chemically extracted with acid hydrolysis treatment on MCC which yields cellulose nanocrystals (CNC) [6–9]. Recently, nanocellulose has gained insurmountable interest of researchers around the world due to its interesting and unique properties. For example, MCC can be an excellent building block for material functionalization or as reinforcement filler due to its biodegradability, biocompatibility, high mechanical strength and large surface area. This opens up a plethora of possibilities for its application in various fields such as food packaging, automotive, nanoremediation, and other industries [10–14]. Although nanocellulose can be derived from a variety of plant sources, most studies conducted of nanocellulose are from commercial microcrystalline cellulose (MCC) extracted from cotton and wood pulp [15–17]. Additional information on the fundamental aspects of nanocellulose such as on its structure and properties when it is extracted from different sources are indisputably important. Rice straw, which is a low value and underutilized agricultural waste source, is the material of interest of this study. The studies conducted in this paper was aimed towards evaluating the differences in properties of MCC and CNC extracted from one particular source and their potential applications as the studies on this type of comparison are limited. The properties of both MCC and CNC extracted from rice straw were characterized by using Scanning electron microscope (SEM), Field emission scanning electron microscope (FESEM), Fourier transform infrared (FTIR) spectroscopy, Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis.

Materials and Methods

Sample preparation

Dry rice straw was freshly collected from paddy field in Arau, Perlis (6°25'58.0"N+100°13'56.8"E). Reagents and solvents used for extraction are sodium hydroxide (NaOH), sodium chlorite ($NaClO_2$) and acetic acid glacial (CH_3COOH) which was purchased from Merck, Acros and HmbG respectively. Sulfuric acid (H_2SO_4) of 95%-97% purity was purchased from Merck.

MCC was extracted by using the same method as described elsewhere [5]. Briefly, dry rice straw was washed thoroughly to remove impurities and dried for 48 hours. The cleaned dry rice straw was milled with a grinder to pass through a 150- mesh screen. 40g of rice straw powder was then treated with 4% (w/w) aqueous solution of sodium hydroxide for 2hours at 80^{o}C under mechanical stirring. The rice straw fiber was washed several times with distilled water until pH reached 7. Subsequently, the rice straw fiber was bleached with a solution made up of equal parts (v:v) of acetate buffer (40 g NaOH and 75 mL glacial acetic acid, diluted to 1 L of distilled water) and aqueous chlorite (1.7 wt.% $NaClO_2$ in water). This bleaching treatment was also performed at 80^{o}C for 2 hours under mechanical stirring. The fiber was washed again with distilled water until pH reached 7. The rice straw fiber undergoes cyclic alkaline and bleaching treatments for a total of 4 cycles with a 1:20 fiber to liquid ratio until a milky, white colored MCC pulp was obtained.

In order to obtain CNC, acid hydrolysis was performed on MCC by using 64 wt % H_2SO_4 at 45ºC for a duration of 45 minutes. This process was done to eliminate the amorphous regions of MCC, thereby releasing highly crystalline CNC from the cellulose substrate. After 45 minutes, 10 fold of cold distilled water was added to stop the hydrolysis reaction. Then, CNC suspension was centrifuged at 10,000 rpm and washed with distilled water until pH of 6-7 was obtained.

Characterization

Infrared spectra of MCC and CNC extracted from rice straw were obtained in the range of 4000–450 cm^{-1} wavenumber (32 scans) at a resolution of 4 cm^{-1} by using PerkinElmer Spectrum 10 spectrophotometer using KBr pellet. Their crystallinity was analyzed by using Bruker D2 Phaser X-ray diffractometer with a monochromatic CuKα radiation source. Measurements were done at a step size of 0.02º in a 2θ angle range of 10º to 40º. Crystallinity index (CrI) was calculated by using Segal method [18]. The formula of calculation is as follows:

$$Crystallinity\ Index, CrI = \frac{(I_{002} - I_{AM})}{I_{002}}\ x\ 100$$

where CrI represents the degree of crystallinity (%), I_{002} represents the maximum intensity of 0 0 2 lattice diffraction and I_{AM} represents the diffraction intensity at 2θ = 18º

MCC and CNC were coated with platinum through JEOL JFC-1600 Auto Fine Coater before morphological characterization. SEM image of MCC was taken by using scanning electron microscopy (SEM) of model JEOL JSM-6460 LA. FESEM image of CNC was taken by using Carl Zeiss Leo Supra 50 VP field emission scanning microscope. Thermogravimetric analysis of MCC and CNC was carried out by using the Perkin Elmer analyzer at a temperature range from 30ºC to 650ºC under the influence of nitrogen air flow with incremental heating rate of 10ºC/min.

Results and Discussions

FTIR spectroscopy was used to gain an insight on the changes in the chemical structures and the properties of a material. As depicted in Figure 1, The –OH region (3700 cm^{-1} to 3100 cm^{-1}) of CNC was more intense and narrower when compared to MCC. This phenomenon portrays the improvement in terms of strength of hydrogen bonds of the CNC resulted from the elimination of the amorphous constituents which consequently resulted in an increase in crystallinity where this finding will be supported in the later section [19]. Success in lignin and hemicellulose removal was evident as there is no occurrence of a peak at 1736 cm^{-1} and 1514 cm^{-1} which directly corresponded towards the C=O stretching of carbonyl groups present in hemicellulose and lignin [20]. Peaks occurring at 1430 cm^{-1}, 1321 cm^{-1}, 1062 cm^{-1} and 897 cm^{-1} are typical peaks of cellulose [21]. In comparison to MCC, CNC occurs in a higher cellulosic content than MCC due to the increase in peak intensity at 1062 cm^{-1} (C–O stretching) and 897 cm^{-1} (C–H rock vibration) [21]. Peak at 1205 cm^{-1} which is commonly present in CNC as a result of the formation of S=O linkage from the esterification process during sulfuric acid hydrolysis was present [22].

XRD diffraction patterns was used to ascertain the crystallinity of MCC and CNC extracted from rice straw. Crystallinity index (CrI) which represents the ratio of the crystalline and amorphous regions of a material provides an important representation on the physical properties

of a particular material. Increase in crystallinity index will subsequently led towards an increase in rigidity and stiffness of the polymer if MCC or CNC was added as a filler, which then translate towards improved mechanical properties of the polymer composite [23].

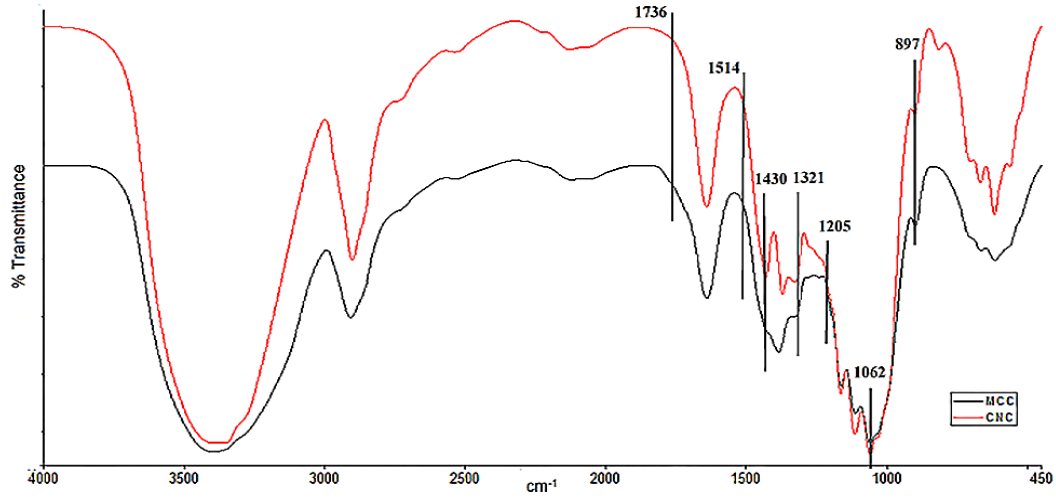

Figure 1: FTIR spectra of MCC and CNC from rice straw

Figure 2 illustrates the diffraction profiles of MCC and CNC and both the diffraction patterns revealed that the samples represented cellulose '**CSD REFCODE JINROO01'** [24]. Characteristic peaks of cellulose type I crystal lattice structure occurring at 16.1º and 22.4º can be observed on both profiles [5]. For cellulose I structure, the main diffraction peak which is at 22.4 represents the crystalline structure of cellulose. In this case, the peak for CNC is narrower and more intense than MCC, indicating that CNC occurs in a much higher crystalline nature than MCC [25]. The crystallinity index of CNC and MCC was calculated and it was found to be 74.3% and 60.8% respectively, expressing an appreciable increase of 13.5% in crystallinity. According to previous study, higher crystallinity filler such as CNC is more favourable as reinforcement filler in polymer composite [26] .

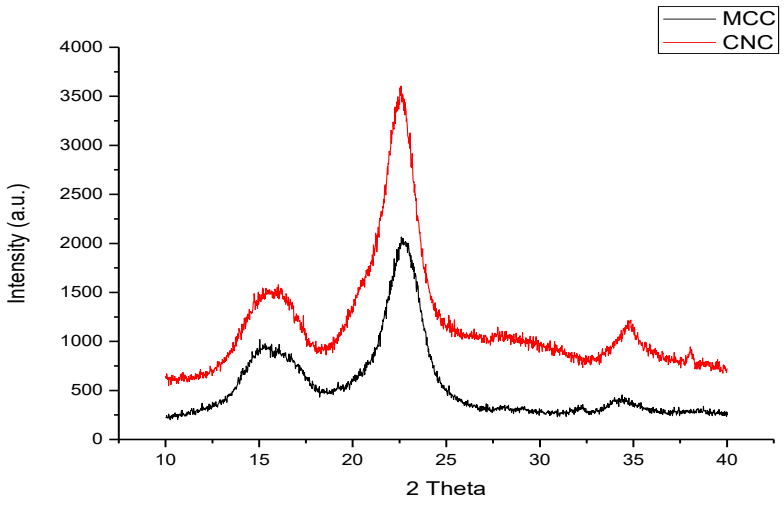

Figure 2: XRD diffraction profiles of MCC and CNC from rice straw

Figure 3(a) depicts the SEM image of MCC from rice straw. From the figure, it can be clearly noted that the fiber surface appeared smooth due to the successful removal of non-cellulosic components such as lignin, hemicellulose and silica that is attached onto the surface of the fiber during alkaline and bleaching treatments of rice straw. Size of individual MCC fibers averaged around 5µm. Figure 3(b), on the other hand, portrays the FESEM image of CNC extracted from MCC at magnification of x40000. Acid hydrolysis of MCC to yield cellulose in nanoscale was successful as the diameter of CNCs extracted average around 4-6 nm with grain-like appearance. The CNCs was found to occur in high aspect ratio.

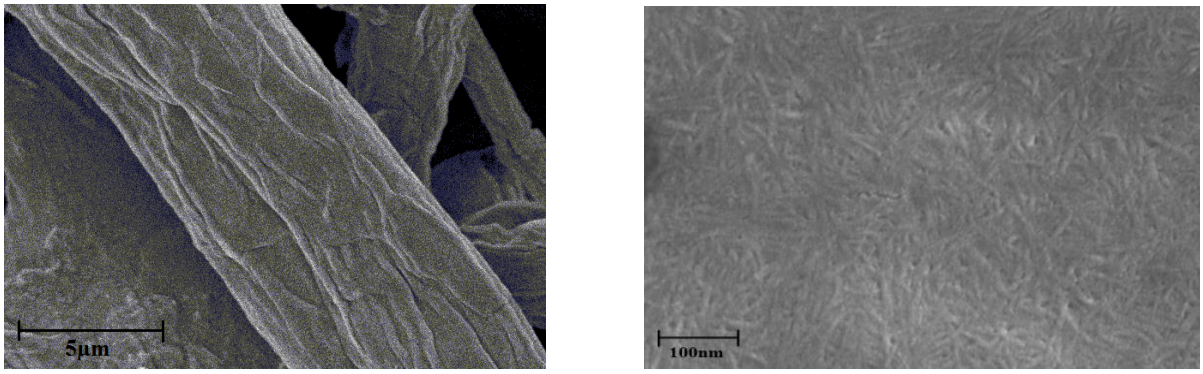

Figure 3. (a): SEM image of MCC from rice straw (Magnification: x2000), (b): FESEM image of CNC from rice straw (Magnification: x40000)

Considering that typical thermoplastic processing temperatures occur above 200°C, thermal stability is a key factor if MCC or CNC is to be used as reinforcement filler in polymer composites [27]. Figure 4 (a) and Figure 4(b) show the TGA and DTG curves of MCC and CNC respectively. Initial weight loss of the both MCC and CNC occurs in the range of 30°C to 120°C,

which can be attributed towards water evaporation in the sample due to their inherent hydrophilic nature [28]. Second stage of weight loss (289ºC - 380ºC) can be ascribed to the cellulose depolymerization, generating volatile hydrocarbons and CO_2 gases [28]. The onset degradation temperature of MCC which is at 315ºC is higher when compared to 289ºC of CNC. Additionally, the maximum decomposition temperature of MCC at 355ºC was found to be significantly higher than CNC at 300ºC. From literature, CNC normally exhibit lower thermal stability when compared to MCC due to the presence of sulfate groups which will act as flame retardant [6,29]. Additionally, the increase in surface area of CNC might be the contributing factor in its diminished thermal stability as more surface is exposed to heat which accelerated the degradation process. Two distinct decomposition stages can be observed from the DTG curve of CNC, where the earlier stage is the decomposition of sulfated crystalline domains which is highly susceptible to thermal degradation while the later stage of decomposition correspond towards the fragmentation and breakdown of unsulfated crystalline domains [30]. Therefore, MCC is more suited as a reinforcement filler for polymer composites that require filler which will contribute towards the improvement in terms of thermal stability.

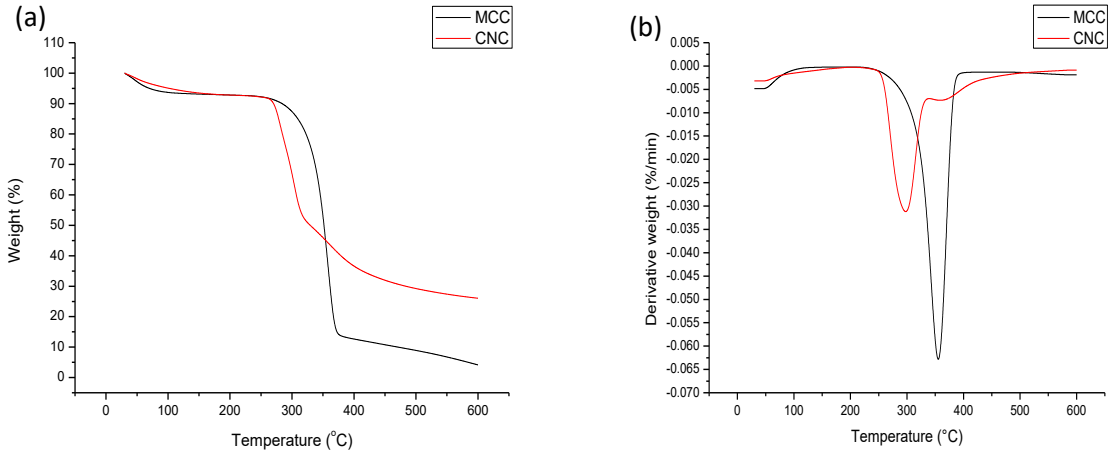

Figure 4. (a) Thermogravimetric thermogram of MCC and CNC from rice straw, (b): Derivative thermogravimetric thermogram of MCC and CNC from rice straw

Conclusion

MCC has been successfully extracted from rice straw through cyclic alkaline and bleaching treatments. CNC has also been successfully isolated from the resultant MCC by acid hydrolysis. Rice straw CNC showed increase in crystallinity due to the removal of amorphous regions present in MCC via acid hydrolysis. SEM images depict prominent changes such as the smoothness of the surface of MCC which indicated the success of cyclic alkaline and bleaching treatments in removing non-cellulosic contents of hemicellulose, lignin and silica. FESEM image portrayed grain-like shape of CNC occurring in high aspect ratio. MCC was found to be more thermally stable than CNC due to the absence of flame retardant sulfate groups present on the surface of CNC. Overall, results obtained suggest that rice straw, which is an underutilized agricultural waste,

can be valorized as a source of MCC and CNC production especially as reinforcement filler in polymer composites.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Conflict of interest

The authors have no disclosures to declare.

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