Isolation and characterisation of nanowhisker cellulose from Pennisetum purpureum

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Abstract.

Pennisetum Purpureum or Napier fibre is a sustainable, renewable and biodegradable waste enriched with cellulose. The methodology to recover agriculture Pennisetum Purpureum residue is by acquiring nanowhiskers cellulose (NW\textsubscript{Cs}) from microcrystalline cellulose (MCC). In this study, acid hydrolysis with different time exposure was performed to degrade the MCC derived from Pennisetum Purpureum into NW\textsubscript{Cs}. The characterisations of the isolated NW\textsubscript{Cs} was conducted through a Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). In SEM morphology study, the NW\textsubscript{Cs} shape ribbon-like with nano scales thickness was observed, and from the SEM result shows that the thickness of the sample was in nano size. The isolated NW\textsubscript{Cs} from Pennisetum purpureum derived MCC has a high potential to be used for the manufacture of nanocomposite for the implementation of pharmaceutical and biomedical fields.

1. Introduction

In the present study, nanocrystalline cellulose (NCC) has acquired considerable attention in many potential application due to their abundance of the amount which can be inherently renewed, low cost and environmental friendly [1–3]. Variety sources of nanocrystal cellulose as known as nanowhiskers cellulose has been studied to discover the superior properties for any potential application such as Roselle, sugar palm, cotton pulp, rice, oat husks, napier and many more [4–8]. NW\textsubscript{Cs} features high mechanical properties refer to the inter/intramolecular hydrogen bond, high aspect ratios and large specific surface area that influenced by their low weight and morphological features [9]. The production of NW\textsubscript{Cs} can be obtained by chemical treatment and with or without mechanical treatment. However, the material properties like thermostability and crystallinity or even final structure and morphology were highly dependent on the drying process. The spray-dried products had higher thermal stability and crystallinity index when the nanocellulose was applied in non-polar thermoplastic compared to air-drying, freeze drying and supercritical-drying [10]. Moreover, the morphological structures of air-drying, freeze drying and spray-drying showed solid packed NCCs, ribbon-like structures and irregularly shaped particles with external voids, respectively[11]. For further utilised in some application, NW\textsubscript{Cs} have to undergo reinforcement in polymer matrices for possibilities of high-performance structural application [12].
2. Materials and methods

2.1. Materials and chemicals
The *Pennisetum purpureum* also known locally as Napier fibre, was acquired from a local plantation in Bukit Kayu Hitam, in northern Peninsular of Malaysia. Sulfuric acid (H2SO4) and Sodium hydroxide (NaOH) was purchased from Fisher Chemical Co. and dialysis tube was purchased from A.R. Alatan Sains Sdn. Bhd.

2.2. Extraction and preparation of *Pennisetum purpureum*
The leaves and the roots were eliminated from *Pennisetum purpureum* stems and underwent the water retting process. In addition, the soaked fibres were washed with running water to remove the unwanted impurities then sun-dried to expel overabundance dampness.

2.3. Alkaline treatment
The alkali treatment process was conducted to purify the Napier cellulose. The fibres were treated with 12 wt% concentration of aqueous NaOH solution. The fibres were then soaked in the solution for two hours to neutralise and remove the balance of lignin and hemicellulose.

2.4. Grinding and sieving
The dried sample that has been treated by alkali treatment was ground into a powder and sieved using 63-micron size vibrating sieve machine to obtain the fine Napier fibres powder.

2.5. Acid hydrolysis
Sulphuric acid of 64 wt% concentration was used to hydrolyse three different reaction time of 30 min, 45 min and 60 min, NCC-I, NCC-II and NCC-III respectively. It was then, followed by centrifugation to remove the excess sulphuric acid and it was dialysed for 6 days to raise the pH value to obtain a neutral pH value. Afterwards, ultra-sonication was carried out to disperse the NWC suspensions for 30 min (6 s on and 2 s off). Eventually, the supernatant NWC suspension was freeze-dried to further the process of characterisation.

2.6. Characterisation

2.6.1. Scanning electron microscopy (SEM) analysis
Scanning electron microscopy SEM was observed using, JEOL (JSM 6460-LA). Generally, material surface morphology, orientation and dispersion of nanowhiskers were determined by SEM. For this analysis, the samples were coated by platinum using auto fine coater JFC-1600.

2.6.2. Fourier transform infrared spectroscopy (FTIR) analysis
The FTIR allows the chemical structure to be characterised by identifying the functional groups from each sample. A Spectrum 65 FTIR spectrometer (Perkin Elmer) was used to record the spectra between 4000–450 cm⁻¹.

3. Results and Discussion

3.1. SEM analysis
It was noticeably that all three NWCs formed plate-like materials and have only slightly different in size even though they were treated in three different reaction times. All three NWCs undergo the same alkali treatment process; this will not affect significantly on their surface morphologies because the amorphous region or non-cellulosic compound was removed most likely at the same rate. As shown in
figure 3.1, it is observed that all three NWC-I, NWC-II and NWC-III have the thickness of less than 1 micron which can be considered as nanoscale size. Nevertheless, the length of the freeze-dried NWCs cannot be seen due to the formation of the ice crystals during the freeze-drying process. The freeze drying process is conducted in two stages. The first stage involves the freezing process and followed by the second stage; drying process. During the drying process, the froze samples in the formed of ice crystals will be sublimated. Therefore, the morphology of the freeze-dried NWCs formed has a plate-like shape as ice crystal grows in the same direction and oriented in plate-like structure in a parallel direction.

Figure 3.1. SEM micrographs of freeze-dried nanowhiskers cellulose with the treated hydrolysis reaction time (a) NCC-I, (b) NCC-II and (c) NCC-III.

3.2. FTIR analysis

The FTIR result in figure 3.2 showed similar spectra from three different acid hydrolysis time, which proved various time for acid hydrolysis process not affected the chemical structure on samples. The data for each peak at each different acid hydrolysis time was almost very similar. Figure 3.2 also showed at 3332.82 cm\(^{-1}\) that the stretching of O—H bonds was more intense with the increase of acid hydrolysis time [13]. At 2903.78 cm\(^{-1}\) (C—H symmetrical stretching) shows that prolonged reaction was affect the cellulose characteristics to be much visible [4]. The band around 1372 cm\(^{-1}\) indicated C-H asymmetric deformation. Furthermore, the hemicellulose content at 1740 cm\(^{-1}\) was also observed, but its gradually decrease as shown in figure 3.2 while the water absorption is at 1636.83 cm\(^{-1}\) (H—O—H stretching vibration) was found that the intensity is increasing[4].
4. Conclusion
The NWCs was successfully extracted and isolated by sulphuric acid through acid hydrolysis from *Pennisetum purpureum* fibres. NWCs exhibited a plate-like structure with nanoscale thickness; the morphological structure depended on final stage of the experiment which is the drying process. FTIR test which showed that the chemical structure does not affect by the time exposure of acid hydrolysis. It can be seen that the treated 64 wt% concentration acid hydrolysis of NWC-I, NWC-II and NWC-III do not have any changes in the chemical properties even though the time of acid hydrolysis treatment were different.

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