Characterisation of structural and physical properties of cellulose nanofibers from *Pennisetum purpureum*

R Revati, *M S Abdul Majid*, M J M Ridzuan and N F Mohd Nasir

Universiti Malaysia Perlis (UniMAP), Kampus Tetap Pauh Putra, 02600, Pauh, Perlis

Abstract

Recently, cellulose nanofiber (CNF) and its applications gain immense attraction in both research and industrial areas due to its attractive properties such as excellent mechanical properties, high surface area, rich hydroxyl groups for modification, and natural properties with 100% environmental friendliness. *Pennisetum purpureum*, also known as Napier grass fibre is a newly-identify plant which is highly sustainable throughout Malaysia. In this study, the typical extraction of cellulose nanofiber from *Pennisetum purpureum* method is summarised, in which the cellulose nanofiber extraction concerning alkali treatment and planetary ball milling is mainly introduced. Cellulose nanofiber from *Pennisetum purpureum* also has been extracted using different concentration acid hydrolysis, such as 20% and 30% to observe the effect towards the fibre bonding. The morphology, chemical structure and crystallinity of the fibre were obtained using scanning electron microscopy SEM, Fourier transform infrared spectroscopy FTIR, and X-ray diffraction XRD. SEM clarifies that the increment of acid hydrolysis lowers the fibre-fibre bonding upon freeze-drying of the cellulose nanofiber suspensions. The result of XRD and SEM shows that 30% of acid hydrolysis gives higher crystallinity and chemical effect towards the structure of cellulose nanofibers.

Keywords: *Pennisetum purpureum*, cellulose nanofiber, acid hydrolysis, ball milling

1. Introduction

Biomedical application using nanocellulose and nanocomposite is only recently discovered [1,2]. In order to enhance the physical and mechanical properties of the cellulose, most researchers aim to improve the extraction process. Many techniques were used to extract nanocellulose, including ball milling, ultrasonic technique and acid hydrolysis [1–3]. Ball milling is considered to be an attractive process that can be used to prepare nano-scale materials due to its simple operation and cost-effectiveness [4–6]. Thus, new bast fibres can be extracted into nanocellulose. The application potentials of *Pennisetum purpureum* (Napier grass) has yet to be explicitly explored on their applications in the bio-nanocomposites [7–10]. Cellulose obtained from this bast fibre can be potentially used as one of the nanomaterials to form a bio-nanocomposite since it possesses biocompatibility and biodegradability, in addition to an excellent physical property [11,12].

This study represents the extraction of nanocellulose from *Pennisetum purpureum* using acid hydrolysis together with the ball milling process. The production of nanocellulose from ball milling
was supposed to increase the surface area and crystallinity of the cellulose. Based on several background research, acid hydrolysis has increased the crystallinity of the material, whereas ball milling is increased the surface area of cellulose. Characterisation including Scanning electron microscopy (SEM), Fourier transforms spectroscopy (FTIR), and X-ray diffraction (XRD) were conducted to investigate the structural and physical properties of the prepared cellulose nanofiber from *Pennisetum purpureum*.

2. Materials and Methods

2.1. Materials

*Pennisetum purpureum* fibres were purchased from Bukit Kayu Hitam, Kedah, Malaysia. Sodium hydroxide (NaOH), and sulphuric acid (H$_2$SO$_4$) were obtained from Fisher Chemical Co. Throughout the experiment, distilled water (DI) was used as a medium for multiuse.

2.2. Preparation of cellulose nanofiber (CNF) from *Pennisetum purpureum*

The *Pennisetum purpureum* (PP) fibres were extracted from the bast fibres using the water retting process. The powder of *Pennisetum purpureum* was treated using 12% sodium hydroxide (w/v) water solution for 2 h to eliminate lignin and hemicellulose completely. The residual was further processed using acid hydrolysis technique with varying concentration; in this study, the fibres undergo hydrolysis process with 20% and 30% concentration, CNF-PP$_{20}$ and CNF-PP$_{30}$ respectively. At the end of hydrolysis, the residue was dialysed with distilled water for 3 days until the neutral pH was reached. Nanocellulose was prepared using planetary ball milling with distilled water. Initially, cellulose was placed in a 160 mL zirconia container with distilled water and zirconia balls (15 mm in diameter). The ball milling was performed for 3 h at 14 Hz. The milled product was further sonicated for 10 minutes before the cellulose nanofiber was freeze-dried.

2.3. Characterisation

The morphologies of the extracted cellulose nanofibers were studied using SEM (JEOL, JSM 6460-LA). Samples were coated with a layer of platinum, Pt using a sputter coater and further analysed at 3 kV.

The crystalline structure and crystallinity index of the cellulose nanofiber was investigated by XRD (D2 Phase company Bruker).

The FTIR spectra of cellulose were recorded in the spectral region between 400 to 4000 cm$^{-1}$ using an FTIR spectrometer (Perkin-Elmer RX1, UK) to study the chemical changes occurred during the extraction process from *Pennisetum purpureum*.

3. Results and Discussions

3.1 SEM

The morphologies of freeze-dried samples from CNF suspensions are shown in Figure 3.1. The dried sample of cellulose nanofiber CNF from *Pennisetum purpureum* with 20% and 30% of acid hydrolysis and ball milling, formed fibrous and agglomerate particles. Researchers have reported that the agglomeration of cellulose nanofiber CNF may occur during the freezing stage of the drying process[13]. In the freezing stage, the non-freezing bound fluid is eliminated by heating the samples under vacuum. The water vapour hence diffuses and induces structural development and rearrangement of cellulose nanofiber CNF particles. Thus, the enormous length (up to a hundred micrometers) and width (tens to hundreds of micrometers) are the consequence of the lateral agglomeration of the cellulose nanofiber CNF. Based on Figure 3.1(a), scanning electron microscopy (SEM) of CNF-PP$_{30}$ shows the formation of a finely blended and interconnected fibrous structure. Irregularly shaped particles were obtained from samples CNF-PP$_{20}$ and CNF-PP$_{30}$. CNF-PP$_{30}$ shows
that the size of particles is smaller compared to CNF-PP20. The interconnection structure bonding of CNF-PP30 are not strong, and the structure is easy to break. As a conclusion, smaller fibres appear in the SEM images as the concentration of the acid hydrolysis increases. This apparently clarifies that the increment of acid hydrolysis lowers the fibre-fibre bonding upon freeze-drying of the cellulose nanofibers suspensions. Thus, different concentration of acid hydrolysis influences the cellulose nanofiber suspensions with different particle sizes and structural morphologies.

3.2 XRD
The influence of acid hydrolysis and ball milling on the microstructure and morphology of isolated cellulose nanofiber from Pennisetum purpureum was analysed using X-Ray diffraction (XRD). Figure 3.2 (a) and (b) shows the XRD profile of developed cellulose nanofibers. Similar patterns are observed for both samples, which are CNF-PP20 and CNF-PP30, respectively. Different concentration of acid used will give different effect towards the crystallinity of the cellulose nanofibers Pennisetum purpureum fibres.

Figure 3.2: X-Ray Diffraction pattern of (a) CNF-PP_20 and (b) CNF-PP_30.
result of XRD for CNF-PP30, the main peak pattern $2\Theta \approx 21.66^\circ$ are higher than Figure 3.2 (b), and the remaining peak of the graph are 33.37$^\circ$, 47.62$^\circ$, and 52.79$^\circ$. Thus, the higher the acid concentration, the higher the crystallinity peak of cellulose nanofibers. This phenomenon proves that the role of chemical treatment successfully increased the cellulose fibre crystalline due to the removal of hemicellulose and lignin contents during the chemical treatment.

3.3 FTIR

The FTIR spectra of cellulose nanofiber from Pennisetum purpureum shows two distinctive peaks absorption region in the spectrums of 2800-3600cm$^{-1}$ and 750-1750cm$^{-1}$ were recognised in the spectra, as shown in Figure 3.3. Interestingly, the FTIR spectrum explains that significant changes between the cellulose nanofibers obtain under different acid hydrolysis were not detected. A broad band in the region 3335cm$^{-1}$ observed from both samples; this indicates the O-H free stretching vibration of the CH2-OH structure on cellulose nanofiber and OH groups, which complement to inter and intramolecular hydrogen bond appear in absorbed water and cellulose. The bands noticed at 1316cm$^{-1}$ are relevant to the C=C stretching or /and CH2 symmetric bending in an aromatic group of cellulose due to crystallinity band. The spectra of cellulose nanofibers achieved from CNF-PP30 shows a significant increment in the intensity of crystallinity functional group compared to the CNF-PP20. This result proves that the concentration of acid hydrolysis might have increased the level of crystallinity of the cellulose nanofibers, as observed from the XRD result.
4. Conclusion
The main objective of this study was to extract and develop a cellulose nanofiber from Pennisetum purpureum fibre. A combination of few techniques was used for the extraction process of cellulose nanofiber from cellulosic materials, where acid hydrolysis with different concentration was used to weaken the fibrous structure, the extraction process was then continued with ball milling to crushed the weakened fibres. Those techniques were applied in this study to facilitate the conversion of cellulose into nano-sized fibres within the short term. SEM studies on the morphologies of dried samples of CNF-PP20 and CNF-PP30 shows that the higher concentration of acid hydrolysis used in this study is easier to weaken the interconnection or bonding of the fibre structure. The XRD graph showed that the highest crystallinity peak was observed at CNF-PP30 sample. There are almost 10% different of crystallinity percentage for both concentrations, which are 59.956% for CNF-PP30 sample, and 50.856% for CNF-PP20. Thus, different chemical and mechanical method for the extraction process will affect the crystallinity structure. Meanwhile, the higher concentration used for the acid hydrolysis process, the crystallinity structure of cellulose nanofiber will increase. Next, characterization-using FTIR shows the result that the spectra of cellulose nanofibers achieved from CNF-PP30 show a significant increment in the intensity of crystallinity functional group compared to the CNF-PP20. This result proves that the concentration of acid hydrolysis might have increased the level of crystallinity of the cellulose nanofibers, as observed from the XRD result.

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5. References

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