Isolation and characterization of cellulose nanofibers (CNFs) from *Macaranga hypoleuca*

E Sutrisno¹, ², S. Tanpichai³ and S. Chuangchote⁴*

¹ Research and Development of Forest Fiber Technology Institute, Ministry of Environment and Forestry, Kampar Regency, 28401, Indonesia
² Nanoscience and Nanotechnology Graduate Program, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand
³ Learning Institute, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand
⁴ Department of Tool and Materials Engineering, Faculty of Engineering, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand

* E-mail: surawut.chu@kmutt.ac.th

Abstract. *Macaranga hypoleuca* is one of the potential native species for natural fibers consisting of long fibers. In *M. hypoleuca* pulp the main majority is cellulose, followed by hemicellulose and lignin. Based on these characters, it is possible to prepare cellulose nanofibers (CNFs) from *M. hypoleuca* pulp. In this work, CNFs were prepared by the combination of the chemical and mechanical treatments. Those were acid hydrolysis by sulfuric acid and ultrasonication machine forwarded. The aims studies observed the potential of *M. hypoleuca* pulp as a raw material of CNFs and characteristics of CNFs from *M. hypoleuca* pulp. The results showed of the CNFs had widths of 42 ± 7.27 nm and crystallinity of 76.9%. The decomposition temperature of the CNFs was of 332 °C. This could be value added to *M. hypoleuca* trees, and the CNFs extracted from this *M. hypoleuca* pulp might be useful for composite applications.

1. Introduction

Cellulose nanofibers (CNFs) is one type of nanomaterial based on a lignocelluloses resource which is unique properties and can apply in many fields of applications. Furthermore, CNFs have become attractive because of renewability, abundance, and high mechanical properties [1]. According to the properties of CNFs, the exploration of new lignocellulose resources was needs. The exploration did to found the new species and/or value added improvement of un-economically of lesser known wood species.

*Macaranga sp* is a type of the pioneer plants in the secondary succession of tropical rainforest ecosystems and classified as fast growing species. Those are distributed in Southeast Asian. It had characteristics as long fibers with diameters of 1.69 μm and lengths of 29.90 μm [2]. In addition, *Macaranga sp* contains 69.7% cellulose, 28.2% lignin and 2.1% extractive substances [3]. Moreover, the variation of the chemical composition of macaranga sp is different from other species. For example, *Macaranga bancana* had a lignin content of 27.2% while *Macaranga pearsonii* had lignin of 28.0% [2]. *Macaranga gigantea* contained 36.0% of lignin [4]. Generally, the utilization of macaranga wood was used for material building construction. That had the other potentials refers to the chemical contained.
The fabrication of CNFs method is carried out to decomposition of polysaccharide chain which are separation and purification of cellulose from non-cellulosic component. It can be prepared using chemical, mechanical or enzymatical treatment [5]. Chemical treatments are popular and prefer to use because of easier to decipher to interact with the chemical bonds contained. On the other hand, mechanical treatment can produce of CNFs by decay the amorphous zone and decided in microfibril hydrogen bonds but needs high energy input [6]. Subsequently, it has the possibility to combine that treatment and produces of CNFs with simple and effective.

In this study, CNFs from *M. hypoleuca* pulp were prepared by the combination of chemical and mechanical treatments. The chemical treatment was conducted acid hydrolysis by sulfuric acid. Furthermore, the mechanical treatment was treated by ultrasonication machine. The details of fabrication CNFs from *M. hypoleuca* pulp will explain the next part clearly.

### 2. Materials and Methods

#### 2.1. Materials

Pulp of *Macaranga hypoleuca* (Reichb. f. & Zoll.) Müll. Arg (produced from alkali treatment and mechanical treatment by Fiber Technology of Forest Plant Research and Development Agency) was used as a raw material. The chemical reagents and solvents in AR Grade used were potassium hydroxide (Carlo Erba Reagents), sodium chlorite (Ajax Finechem Pty. Ltd), sodium hydroxide (Carlo Erba Reagents), sulfuric acid (RCI Labscan), acetic acid (RCI Labscan), and deionized water.

#### 2.2. Methods

##### 2.2.1. Cellulose nanofiber preparation

CNFs were prepared with the procedure modified [7]. Pulp was treated with 10% w/v KOH solution (with a proportion of 1 g of pulp in 50 mL of the solvent) under mechanical stirring at room temperature for 14 h. The pulp was thoroughly washed with distilled water, and then centrifuged for 20 min with a speed of 10,000 rpm. The pulp was treated for delignification by 10% w/v NaClO$_2$ at pH 5.0 (adjusted with 10% v/v CH$_3$COOH and/or 5% w/v KOH, depending on the pH condition) at 70 °C, for 2 h. Afterward, the treated pulp was washed with deionized water until pH was neutral and centrifuged for 20 min with a speed of 10,000 rpm. Subsequently, the treated pulp was further treated by 30% w/v NaOH at 170 °C for 1.5 h. The alkaline treated pulp was hydrolyzed by H$_2$SO$_4$ (30% w/v) at 80 °C for 3 h. The hydrolyzed cellulose was dialyzed with distilled water. Then, the treated cellulose was disintegrated using a ultrasonication for 30 min at an output power of 2000 W while the temperature of the cellulose suspension was controlled below 10 °C. Finally, the sample was stored in the refrigerator with a temperature of 4 °C until further use.

##### 2.2.2. Characterization

The morphology of the prepared CNFs was observed by a scanning electron microscopy (JEOL 6610-LV). X-ray diffraction patterns were investigated by a Bruker AXS diffractometer (model D8 discover) with CuKα radiation (40 kV and 40 mA) to observe of crystal structure. The thermal stability was used by TGA / DSC 1 machine, Stare system, Mettler Toledo.

### 3. Results and Discussion

#### 3.1. Morphology

CNFs produced from pulp of *M. hypoleuca* was presented in Figure 1. The solvent looks turbid and relatively viscous which was obtains CNFs. In Figure 1, there was showed cloudy that means still cellulose nanomaterial dissolved. It indicated the stabilization of dispersion and related to the dimensions of CNFs [8]. Furthermore, the examination of CNFs dimensional was observed by Scanning Electron Microscopy (Figure 1). The morphological observation obtained was only in the form of diameters due to the high concentration of CNFs suspension. The entanglement between nanocellulose
bundles was still found in the CNF form that caused the strong bonds of lignin [9] and hemicellulose [10].

Figure 1. SEM images of CNFs from *M. hypoleuca* at 30,000 magnification

Figure 2 shows the diameter distribution of CNFs with the diameter average of 42 ± 7.27 nm. This indicated that CNFs prepared in this study had larger dimensions than those produced from the other species such as 15 – 90 nm for *Pinus merkusii* [11], 4 – 24 nm for *Eucalyptus spp.* [12], and 1.2 -30.0 nm for *Hibiscus cannabinus* [13], respectively. This might be because the treatment approach used in this study did not make full defibrillation or low energy input by the ultrasonication probe. Also, the aggregation of nanocellulose bundles during drying might be the cause.

Figure 2. Diameter distribution of CNFs produced from *M. hypoleuca*

3.2. Crystal structure by XRD analysis

An XRD pattern of CNFs produced from *M. hypoleuca* by the combination of chemical and mechanical treatments is shown in Figure 3. The crystallinity index calculated using an equation introduced by Segal et al., (1959) [14] was 76.9%. This result was higher than pinus (43.4%) and eucalyptus (49.3%) [15]. The combination of the series of the chemical treatments and the mechanical treatment could mostly eliminate non-cellulosic substances. The crystallinity index has been reported to increase with the reduction of hemicellulose and lignin, and size of the materials through various treatments [16].
According to Figure 3, the XRD pattern of CNFs produced from *M. hypoleuca* was marked as cellulose type II. The transformation from the cellulose type I (raw materials) to cellulose type II could be influenced by the regeneration process caused by the alkali treatment. This mercerization process was achieved by the alkali treatment with an aim to dissolve non-cellulosic components and facilitate the separation of cellulose bundles in the microfibrils [17]. This resulted in a reduction in intramolecular hydrogen bonds, but remained stable in intermolecular bonds [11].

3.3. Thermal stability
Thermal stability of the cellulosic materials is related to chemical compositions in a cellulose sample. The degradation of hemicellulose happens at around 300 °C, followed by the degradation of cellulose at around 350 °C while lignin degrades between 250°C – 600 °C [18]. Thermal stability curve of CNFs produced from *M. hypoleuca* is shown in Figure 4. The thermal degradation peak was found to be 332 °C with the char yield at 800 °C of 20.6%.

**Figure 3.** XRD pattern of CNFs produced from *M. hypoleuca*

**Figure 4.** Thermal stability of CNFs produced from *M. hypoleuca*: weight loss (a) and derivative weight change (b).
4. Conclusions
Isolation of CNFs from *M. hypoleuca* was achieved by a combination of chemical and mechanical treatments. CNFs had diameters of 42 nm, crystallinity index of 76.9%, and decomposition temperature of 332°C. Based on these characteristics, *M. hypoleuca* can be used as a source of lignocellulose to produce CNFs which might be used as filler in composite applications.

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