

Production of Esterified Nanofibrillated Cellulose from a Lesser-known Wood Species (*Macaranga hypoleuca*)

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Macaranga hypoleuca, a lesser-known and rarely used wood species, is a pioneer species in the secondary succession that is classified as a fast-growing plant with long fibers. *M. hypoleuca* was composed of holocellulose, lignin, and extractives, at contents of $68.1 \pm 0.5\%$, $25.5 \pm 0.6\%$, and $4.7 \pm 0.1\%$, respectively. In this study, refined *M. hypoleuca* pulp was treated by alkali treatment, delignification, and maleic acid hydrolysis. The pre-treated pulp was further disintegrated by mechanical treatment, which produced nanofibrillated cellulose (NFC) with a yield of $53.5 \pm 2.7\%$. The average diameter of the NFC was 43.0 ± 4.9 nm. The use of maleic acid ($C_4H_4O_4$) hydrolysis also reduced the hydrophilicity of the NFC, as confirmed by the Fourier-transform infrared (FTIR) spectra. It was determined that the *Macaranga* tree is a suitable lignocellulose source to produce NFC, which can be used in transparent flexible substrates, coating, and composite applications.

DOI: 10.15376/biores.17.1. 922-938

Keywords: Nanofibrillated cellulose; *Macaranga hypoleuca*; Fabrication; Chemical compounds; Pulp

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INTRODUCTION

Macaranga hypoleuca is a natural resource that is easily found in secondary successions. *M. hypoleuca* is a fast-growing species that is widely distributed in Southeast Asia, especially in Indonesia, Malaysia, Singapore, and Thailand (Slik and Van Welzen 2001). Compared to other fast-growing tree species such as *Cratogeomys arborescens*, *Terminalia microcarpa*, *Artocarpus hispidus*, and *Ochroma pyramidata*, the *Macaranga* species has the fastest growth rate (Román-Dañobeytia *et al.* 2015; Yamada *et al.* 2016; Lampela *et al.* 2017; Junaedi 2018). The *Macaranga* species grow in height and diameter at an average annual rate of 2.3 m and 2.6 cm, respectively (Junaedi 2018). Furthermore, *Macaranga* pulp is capable of producing fibers with a yield, fiber length, and diameter of 45.4%, 1.4 to 1.7 mm, and 24.5 to 29.8 μ m, respectively (Frianto and Rinanda 2015; Takeuchi *et al.* 2016). These properties present *M. hypoleuca* as a potential source to prepare nanofibrillated cellulose (NFC).

NFC has attracted great interest because of its superior characteristics such as strength, thermal expansion, and degradability (Kargarzadeh *et al.* 2018; Tanpichai *et al.* 2019; Tanpichai *et al.* 2019; Meng *et al.* 2020; Tanpichai *et al.* 2020). It has been widely reported that NFC is suitable in the manufacturing of nanocomposites, coatings, food packaging materials, conductive inks, and printed electronic devices (Koga *et al.* 2013; Wang *et al.* 2013; Nogi *et al.* 2015; Guo *et al.* 2016; Biswas *et al.* 2019). In general, chemical and mechanical treatments are used to purify and extract NFC (Tanpichai and Witayakran 2016; Petroudy *et al.* 2017; Tanpichai and Witayakran 2017; Trache *et al.* 2017; Wang *et al.* 2018; Yue and Qian 2018). Pelissari *et al.* (2014) reported that chemical treatment alone was not able to disintegrate NFC from microfibrils. Therefore, the defibrillation process is required to fibrillate NFC from the bounded microfibrils after the typical chemical treatment (Chen *et al.* 2011a; Tonoli *et al.* 2012; Zhao *et al.* 2013). During the chemical treatment, acid penetrates the plant cell walls and attacks the amorphous parts. The solvent concentration and the reaction time used during the acid hydrolysis depends on the type of materials used (Pelissari *et al.* 2014; Khawas and Deka 2016). Sulfuric acid (H₂SO₄), classified as a non-environmentally friendly and corrosive chemical, can contaminate the cellulose nanomaterials and cause difficulties in functionalization due to the presence of the sulfate groups (Chen *et al.* 2016). In addition, the presence of active sulfate groups on the fiber surface leads to low thermal stability of the cellulose (Chen *et al.* 2017). Thus, an alternative acid for hydrolysis process may be more suitable for the production of NFC.

Maleic acid (C₄H₄O₄), a type of dicarboxylic acid, is a capable acid that is used in the acid hydrolysis process. At ambient temperature, C₄H₄O₄ has low water solubility, so it can be crystallized. This results in a low recovery cost *via* crystallization (Chen *et al.* 2016). The optimum concentration of C₄H₄O₄ can degrade hemicellulose and depolymerize cellulose (Bian *et al.* 2017a). Moreover, due to the hydrophilicity of NFC, it is difficult for NFC to fully disperse in hydrophobic polymers. Most commodity plastics are made up of hydrophobic polymers such as polyethylene, polypropylene, or natural rubber. In order to improve the dispersion of NFC in hydrophobic polymers, a coupling agent or cellulose functionalization is required. Kargarzadeh *et al.* (2017) reported that the grafting of long molecular chains on the NFC surface enhanced the dispersibility of NFC in a hydrophobic matrix due to the steric barrier and interparticle distances. In addition, C₄H₄O₄ is environmentally friendly and can be used several times. Herein, C₄H₄O₄ was used for acid hydrolysis to functionalize NFC extracted from a fast-growing wood species, *M. hypoleuca*. The steps of the popular NFC fabrication were improved. In the pre-treatment phase, base-acid agents were employed to eliminate hemicellulose and lignin. By such means, it was possible to remove the lignin with just one treatment while other researchers have used repeated bleaching treatments (4 to 5 times). Furthermore, this work provides an alternative potential hydrolysis process using the weak acid for NFC fabrication.

EXPERIMENTAL

Materials

The *M. hypoleuca* pulp (Reichb.f. & Zoll., Müll. Arg.), the raw material for the NFC production, was obtained from the Research and Development of Forest Fiber Technology Institute of the Ministry of Environment and Forestry of the Republic of Indonesia (2 g with 10.37% of water content). The potassium hydroxide (KOH) and the sodium hydroxide (NaOH) were obtained from Carlo Erba Reagents (Barcelona, Spain).

The sodium chlorite (NaClO_2) and the hydrochloric acid were obtained from Ajax Finechem Pty, Ltd. (New South Wales, Australia). Maleic acid ($\text{C}_4\text{H}_4\text{O}_4$) was obtained from Merck KGaA (Darmstadt, Germany), and acetic acid (CH_3COOH) was obtained from RCI Labscan (Bangkok, Thailand). All of the chemicals were analytical grade.

Pre-treatment of the Pulp

The dried *M. hypoleuca* pulp (1 g) was immersed in 50 mL of 10% w/v KOH solution under continuous stirring at room temperature for 14 h. The treated pulp was washed several times with distilled water until the pH became neutral. The pulp was then bleached once with a 10% w/v acidified NaClO_2 solution at 70 °C for 2 h. After that, the pulp was treated with 30% w/v NaOH solution at 170 °C for 1.5 h. Finally, the pulp was washed with distilled water until the pH reached a neutral level. The pre-treated pulp was kept in the wet condition until further use.

Preparation of the NFC

The chemical and mechanical treatments were used to produce the NFC from the *M. hypoleuca* pulp. The pre-treated pulp was first hydrolyzed using an 80% w/v $\text{C}_4\text{H}_4\text{O}_4$ solution at 120 °C for 4 h. The pulp was separated from the solution using centrifugation at 10,000 rpm for 20 min, and neutralized in a dialysis bag with distilled water. Subsequently, the treated pulp in the pre-treatment phase (with a yield of $67.8 \pm 0.1\%$) was added into 120 mL deionized water before mechanical treatment, and the temperature was kept at less than 10 °C. It was disintegrated with an ultrasonication processor (Cole Parmer, Vernon Hills, IL, United States) for 30 min at an output power of 2,000 W. Finally, the NFC suspension was stored in a refrigerator at a temperature of 5 °C. Figure 1 shows the pre-treatment steps and the NFC preparation process which were adopted from Pelissari *et al.* (2014) with modifications. The formulation of the modified schemes was based on the preliminary data of this study.

Characterizations of the NFC

Chemical composition of the pulp

The contents of the cellulose, hemicellulose, and lignin were analyzed according to the standards of the Technical Association of the Pulp and Paper Industry (TAPPI). Briefly, an extractive-free pulp sample of 0.5 to 1 g was hydrolyzed with 3 mL of 72% H_2SO_4 at 30 °C for 1 h. The suspension was diluted to 4% and autoclaved for 1 h at 120 °C. The remained material was filtered as insoluble lignin, according to the TAPPI standard T222 om-11 (2015). The holocellulose content was determined according to the TAPPI standard T9 wd-75 (2015). The extraction process was done in accordance with the TAPPI standard T280 wd-06 (2015). The extractive-free pulp sample (1 to 2 g) was dispersed in 5 mL of deionized water. Then, 2 mL of CH_3COOH and 5 mL of 80% NaClO_2 were added to the suspension. The suspension was soaked in a 90 °C water bath for 1 h. After that, 4 mL of CH_3COOH and 10 mL of 80% NaClO_2 were added to the solution and the reaction continued for 1 h at 90 °C. The insoluble material was washed with deionized water, filtered and dried at 105 °C. The remaining material was the holocellulose. Furthermore, the holocellulose (0.5 to 1 g) was treated with 8 mL of 17.5% NaOH for 30 min at room temperature. Subsequently, 8 mL of deionized water was added to the suspension and the reaction continued for another 30 min. The solid material from this process was washed and soaked in 20 mL of 1.0 M CH_3COOH for 5 min. The solid material residue was alpha-cellulose.

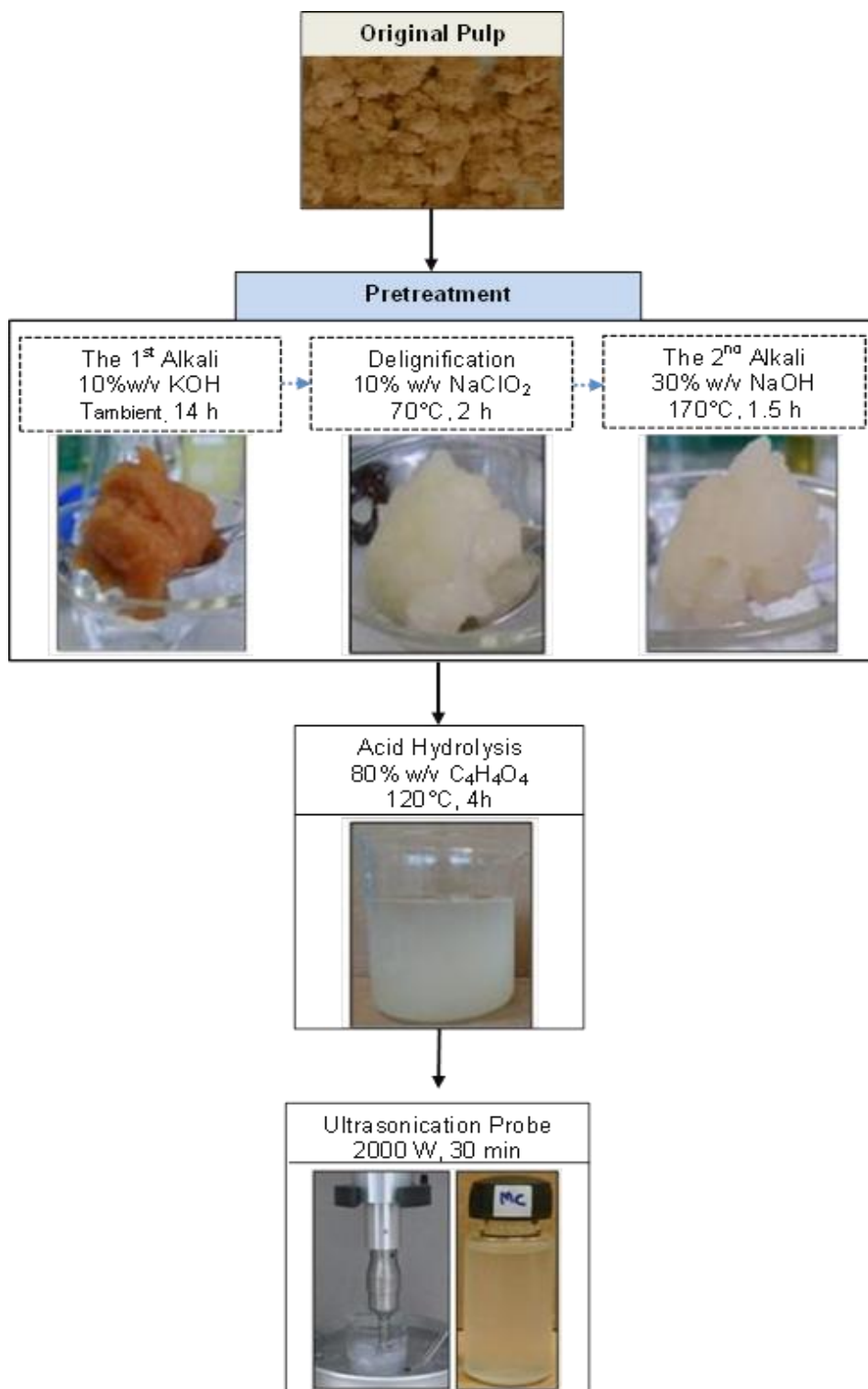


Fig. 1. Schematic illustration of the pre-treatment and the NFC preparation

NFC yield

The NFC yield was calculated by the difference in the weight of the dried original pulp and the weight of the dried NFC, as seen in Eq. 1,

$$\text{Yield (\%)} = \frac{\text{NFC weight (g)}}{\text{Samples weight (g)}} \times 100 \quad (1)$$

Scanning electron microscopy

The morphology of the original pulp and NFC were investigated using a JSM-6610-LV scanning electron microscope (SEM) (JEOL Ltd., Tokyo, Japan). A diluted cellulose suspension was dropped on a stub and dried in an oven at 50 °C for 3 h. Before the measurement, the sample was coated with a thin layer of gold to enhance the conductivity. These SEM images were used to measure the average diameters of NFC using Image-J software. Each zone of NFC was measured with 10 replications. Data of diameters from the five zones were calculated to get the average and distribution of NFC diameters.

X-ray diffraction

The freeze-dried samples were subjected to a reflection mode of the X-ray diffraction (XRD) measurement. The XRD patterns were obtained by a D8 DISCOVER diffractometer (Bruker, Billerica, MA) with CuK α radiation (40 kV and 40 mA). The diffraction data of the cellulose samples were collected with an angular 2θ range from 2 to 50°, with a scanning speed of 1.2°/min. The crystallinity index (CI) of the samples was estimated from the diffraction intensity (Segal *et al.* 1959) using Eq. 2,

$$CI = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (2)$$

where I_{200} is the maximum intensity of the (200) lattice diffraction and I_{am} is the intensity diffraction of the amorphous region.

Fourier-transform infrared spectroscopy analysis

Fourier-transform infrared (FTIR) spectra of the cellulose samples were recorded by a Nicolet 6700 Spectrometer (Thermo Fisher Scientific, Waltham, MA). The analysis was performed in the infrared region within a range of 600 to 4000 cm⁻¹.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) of the intact pulp and the NFC were investigated using a TGA/DSC 1 Stare system (Mettler Toledo, Columbus, OH). The dried samples were heated from 25 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere at a flow rate of 100 mL/min.

RESULTS AND DISCUSSION

Chemical Composition of the Pulp and NFC

The chemical compositions of the *M. hypoleuca* pulp and other pulps from the *Macaranga* genus are presented in Table 1. The *M. hypoleuca* pulp suitable for the NFC fabrication, compared to the other pulps from the *Macaranga* family because the *M. hypoleuca* pulp has a lower content of lignin. Therefore, fewer amounts of chemicals and energy are required for the preparation of NFC, since lignin acts as a glue to adhere the nanofibrils together.

Table 1. Chemical Compositions of the Pulps from the *Macaranga* genus

Lignocellulose Source	Chemical Composition (%)					Reference
	Holocellulose	Alpha-cellulose	Hemicellulose*	Lignin	Extractive	
<i>Macaranga gigantea</i>	55.14	n/a	n/a	35.97	n/a	Frianto and Rinada (2015)
<i>Macaranga bancana</i>	n/a	n/a	n/a	27.20	n/a	Takeuchi <i>et al.</i> (2016)
<i>Macaranga pearsonii</i>	n/a	n/a	n/a	28.00	n/a	
<i>Macaranga hypoleuca</i>	68.1 ± 0.5	65.6 ± 0.1	2.5 ± 0.6	25.5 ± 0.6	4.7 ± 0.1	This work

*The hemicellulose content was calculated by subtracting the alphacellulose content from the holocellulose content (Cruz *et al.* 2018)

Pre-treatment is generally used to eliminate the non-cellulosic components (hemicellulose, lignin, and extractive substances), and increase the purity of the cellulose content. For the selection of pre-treatment chemicals, it is important to consider the ability of the chemical to penetrate the vessels of the wood tissue (Wang *et al.* 2018). In this work, KOH, NaClO₂, and NaOH were the chemicals used in the pre-treatment steps. After pre-treatment, the fiber yield was 67.8 ± 0.1%.

The acid hydrolysis of the pre-treated pulp was further carried out using C₄H₄O₄ solution. After the chemical and mechanical treatments, the yield of the NFC extracted from *M. hypoleuca* was reduced to 53.5 ± 2.7% which was higher than that of NFC derived from poplar wood (32%) (Yue and Qian 2018).

Morphology of Pulp and NFC

The structure of the *M. hypoleuca* pulp as a lignocellulosic resource was altered after each chemical treatment. The effect of each treatment on the chemical phase is shown by the red arrows in Figs. 2(b) through 2(d). The size of the raw materials decreased after the pre-treatment to purify the matter from lignin and hemicellulose. Higher amounts of disintegrated microfibrils were observed due to the elimination of the non-cellulosic components.

Lastly, the NFC obtained from the mechanical treatment is shown in Figs. 2(e) and 2(f). The diameter contribution of the NFC produced from the *M. hypoleuca* pulp hydrolyzed by C₄H₄O₄ was in the range of 8 to 62 nm with the median of 43.0 ± 8.5 nm, as shown in Fig. 3.

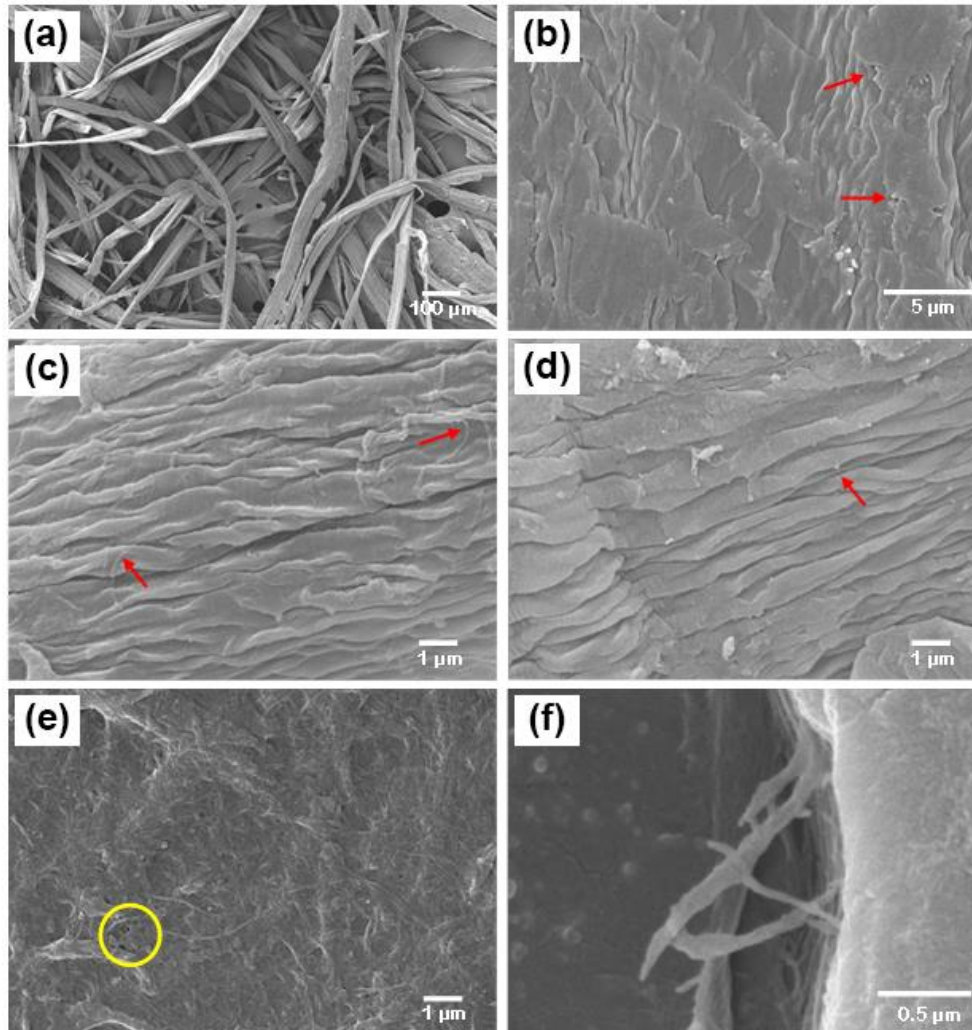


Fig. 2. Scanning electron microscopy (SEM) images of the *M. hypoleuca* pulp that was subjected to (a) no treatment, (b) pre-treatment, (c) alkali treatment, (d) acid hydrolysis, and (e,f) ultrasonication

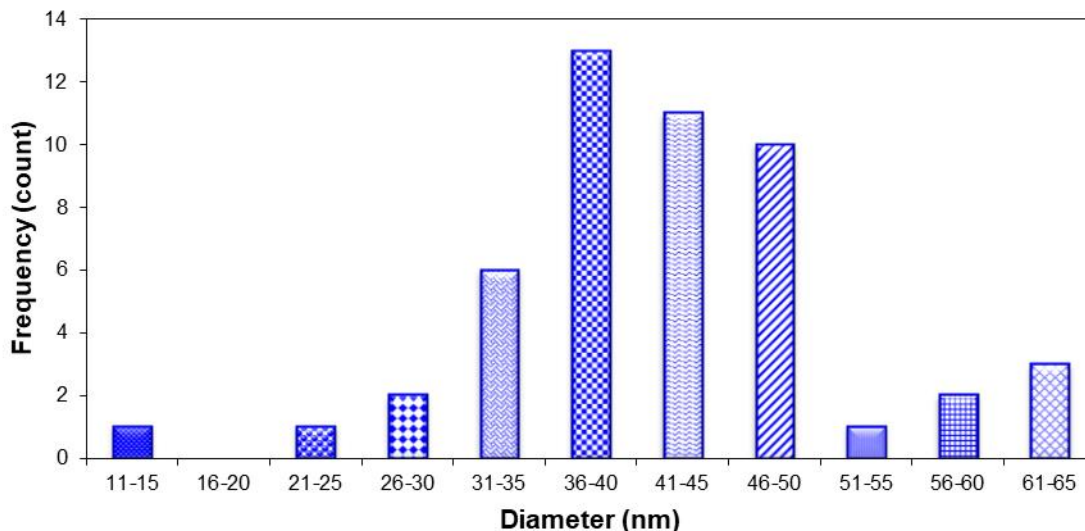


Fig. 3. Distribution of the diameters of NFC made from the *Macaranga* pulp

XRD Analysis

Figure 4 shows the XRD patterns of the untreated pulp, the treated pulp, and NFC. The NFC and untreated pulp had different patterns. The crystallinity of the NFC was observed at 2θ of 11.88° (1-10), 19.88° (110), and 21.74° (200). The shift of these cellulose peaks indicated the changes of the crystal type from type I to type II (French 2014). This transformation was caused by the alkali treatment (Li *et al.* 2014). The CI of NFC was 78.4% which was higher than that of the *M. hypoleuca* pulp (64.1%). The increased CI was attributed to the reduction in the amorphous region. The fluctuation of crystallinity index is related to intramolecular and intermolecular hydrogen bonds, whereas the alkaline treatment process affected the extent of hydrogen bonds within the cellulose, as well as changing the morphological structure (Ciolacu *et al.* 2011). Moreover, the reduction of CI in the NFC has been reported to depend on the power setting of the ultrasonication probe used for mechanical treatment, and/or high concentration of chemical solvents which destroyed the amorphous zone (Chen *et al.* 2011b). It was noted that the CI of the NFC extracted from *M. hypoleuca* was higher than that of the *Pinus* (43.4%) and *Eucalyptus* (49.3%) (Poletto *et al.* 2014). The variation of the cellulosic material types and fabrication conditions (*e.g.* the concentration of the chemical liquid, the reaction time, and the temperature) could play a vital role in this case. The increased CI has been correlated to a higher Young's modulus value through the schemes of transfer crystal energy (Ratanaphan *et al.* 2015). Therefore, the NFC prepared in this work could be suitable as a reinforcing material in composites (Phiriyawirut and Maniaw 2012; Yue and Qian 2018).

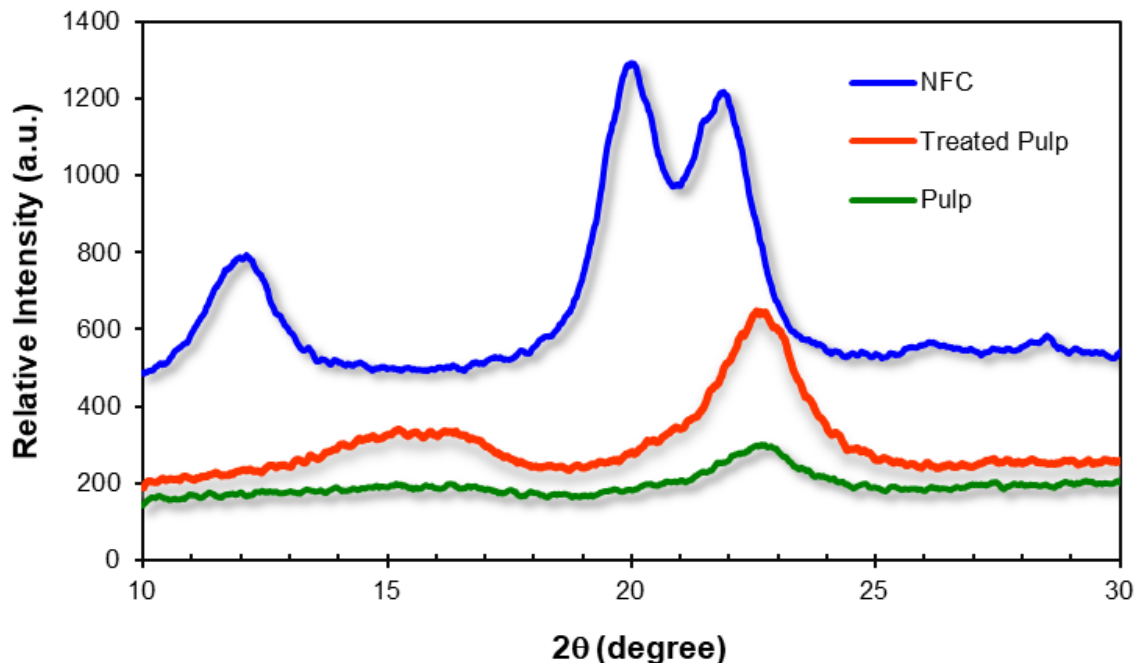


Fig. 4. X-ray diffraction (XRD) patterns of the *M. hypoleuca* pulp, treated pulp, and NFC

FTIR Analysis

FTIR was used to investigate changes in chemical structures obtained after the esterification process. The FTIR spectra of the original *M. hypoleuca* pulp and NFC are shown in Fig. 5(a). The peak shift, corresponding to the O-H stretching vibration in cellulose (Oh *et al.* 2005; Poletto *et al.* 2014), was seen from the 3340 cm^{-1} peak of the pulp to the 3443 cm^{-1} peak of the NFC. This shift was due to cellulose transformation from type I to type II and the loss of the non-cellulosic components (Wang *et al.* 2018).

The peak at 2898 cm^{-1} is assigned to the C-H stretching vibrations from the cellulose molecules, hemicellulose, and lignin (Pacheco *et al.* 2018; Tanpichai, Witayakran, and Boonmahitthisud 2019). The peak at 1591 cm^{-1} observed from the pulp represents the aromatic ring vibration and the C-H deformation vibration of the lignin from the wood fibers (Chen *et al.* 2011b), while this peak disappeared from the NFC spectrum due to the removal of the lignin (Tibolla *et al.* 2018). The difference in the sharpness of the existing peak indicates the quantity of the wood chemical compounds which were affected by the fabrication process. From all the peaks, it can be implied that the NFC produced from the softwood pulp still contained lignin and hemicellulose. The peaks located at 1162 and 1022 cm^{-1} corresponding to C-O-C symmetric stretching in cellulose were observed for both cellulose pulp and NFC (Tibolla *et al.* 2018).

The presence of the carboxylate groups within NFC introduced by the esterification with the $\text{C}_4\text{H}_4\text{O}_4$ could be confirmed by the peak located at 1722 cm^{-1} , corresponding to the C=O vibration in the carbonyl groups (Bian *et al.* 2017b). The presence of ester bonding was attributed to the transformation of the hydroxyl (-OH) groups to carboxylic groups (-COOH) (Chen *et al.* 2016), as shown in Fig. 5(b). The carboxyl content could affect the surface charges of NFC as well as its dispersion in a solvent. The carboxyl content of NFC determined using titration was found to be 0.33 mmol/g . Also, according to visual observation, the result of NFC was comparable to eucalyptus pulp hydrolyzed by maleic

acid with the carboxyl content of 0.05 to 0.15 mmol/g (Bian *et al.* 2017) and eucalyptus pulp hydrolyzed with oxalate acid with the carboxyl content of 0.39 mmol/g (Chen *et al.* 2016). Additionally, the carboxylation transformation could result in less hydrophilic properties for cellulose (Sethi *et al.* 2018).

Thermal Properties

The degradation of the hemicellulose and cellulose has been found at approximately 300 and 350 °C while lignin degraded between 250 and 600 °C, respectively (Poletto *et al.* 2014). The TGA and derivative thermogravimetric (DTG) curves of the untreated *M. hypoleuca* pulp and NFC are shown in Fig. 6.

As can be seen in Fig. 6(a), the initial weight loss of both cellulose samples began at around lower 100 °C owing to the evaporation of the water molecules in the cellulose (Pacheco *et al.* 2018). The weight losses of the untreated pulp and NFC at this transition were approximately 10 and 5%, respectively. The lower weight loss obtained from the NFC might be because some of the hydroxyl groups (-OH) on the NFC surfaces were converted to carbonyl groups (C=O) through esterification and the ester groups minimized the hydrophilic properties of the cellulose. The second thermal decomposition began at 220 °C for the NFC and 250 °C for the untreated pulp. The final decomposition occurred at 280 and 365 °C for the NFC and the untreated pulp, respectively (Fig. 6(b)). The differentiation of the thermal stability of the cellulosic materials has been reported to be influenced by the presence of the hemicellulose and lignin as the non-cellulosic components (Zhao *et al.* 2013). At 800 °C, the weight loss of the NFC was 81%, while the weight loss of the pulp was 87%. The presence of the non-cellulosic component could protect the cellulosic material from heat effects. The decomposition (pyrolysis) process is influenced by the release of hydrogen and oxygen molecules from water through the process of dehydration, the decarbonylation process into monoxide, and the decarboxylation into carbon dioxide.

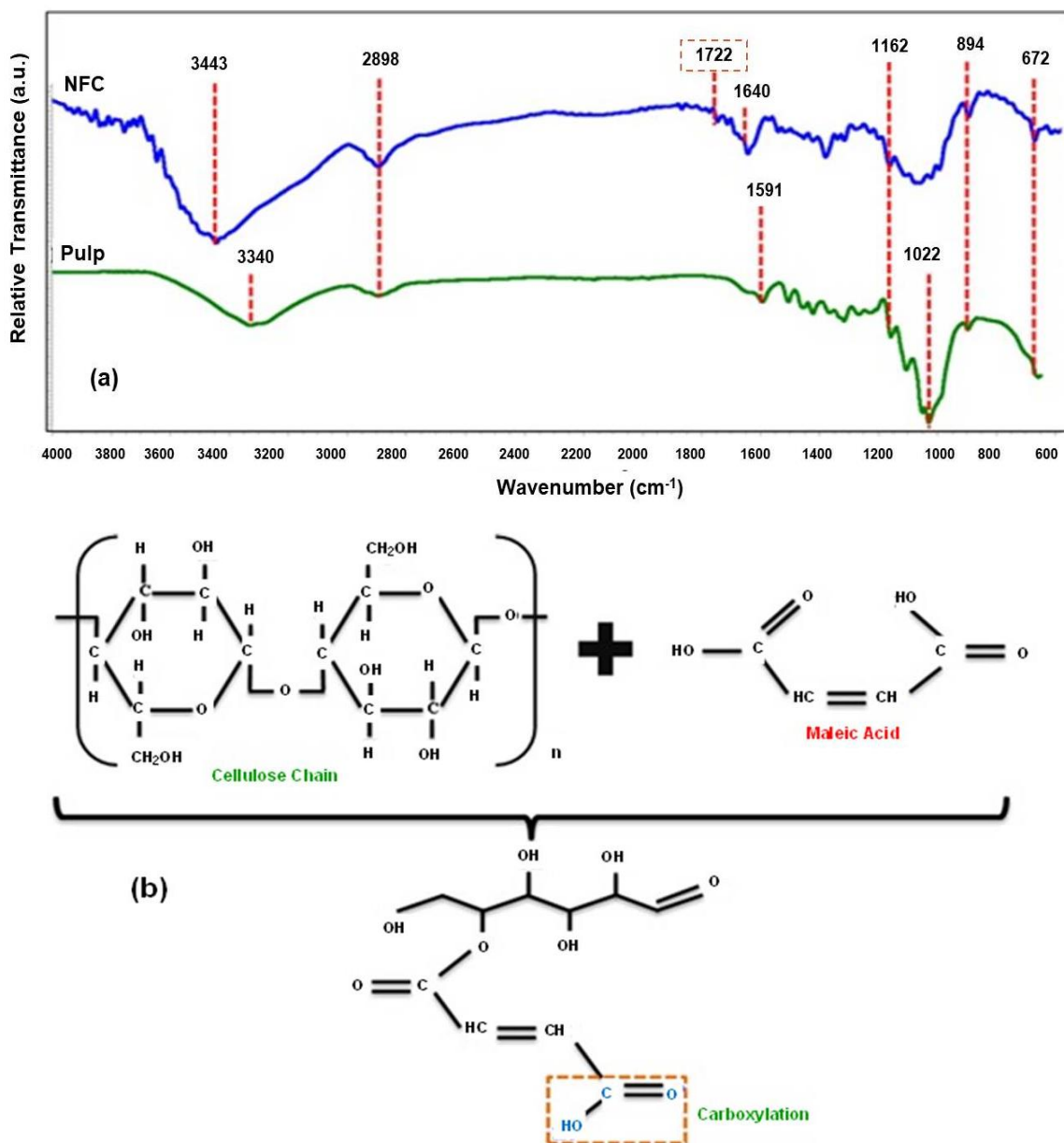


Fig. 5. (a) Fourier-transform infrared (FTIR) spectra of the untreated *M. hypoleuca* pulp and NFC and (b) esterification process induced by the C₄H₄O₄

The NFC made from the *M. hypoleuca* pulp with C₄H₄O₄ treatment decomposed at a lower temperature in comparison with pulp. This indicated the NFC produced by the esterification treatment had lower thermal stability. This may be because of the disruption of hydrogen bonding by the carboxyl groups (-COOH) at the C6 of the cellulose (Sharma and Varma 2014a) associated with the reduction in the molecular weight by defibrillation (Sharma and Varma 2014b). Moreover, the presence of the carboxyl groups would act as the catalyst for the decomposition (Chen *et al.* 2016), and the breadth of the higher surface area of the NFC would easily transfer the heat to each other (Bian *et al.* 2017a). Even though the NFC was produced by this treatment had lower thermal stability, the esterified NFC could be applied for nanocomposite applications (Ahuja *et al.* 2020).

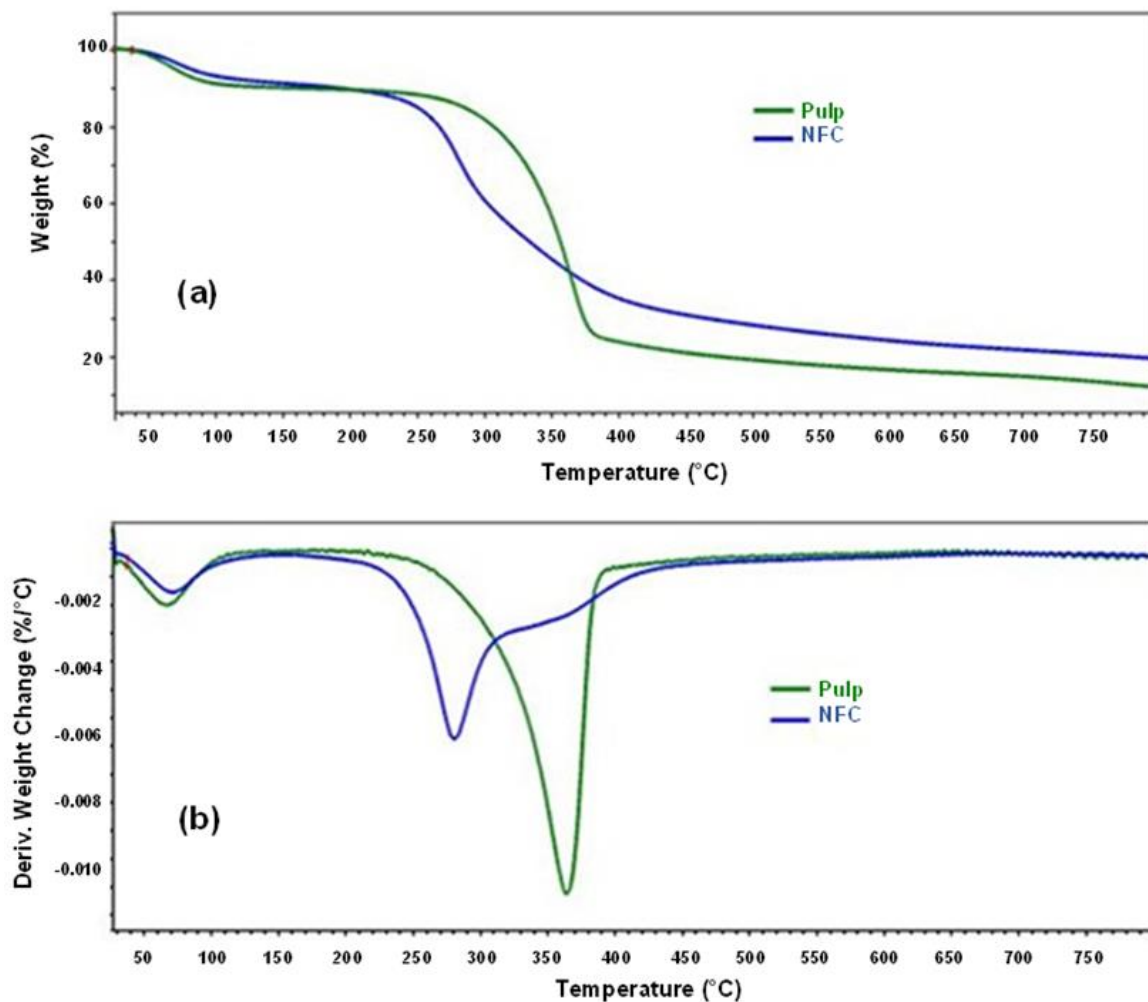


Fig. 6. (a) Thermogravimetric analysis (TGA) and (b) derivative thermogravimetric (DTG) curves of the untreated *M. hypoleuca* pulp and NFC

CONCLUSIONS

1. The isolation of nanofibrillated cellulose (NFC) from the *M. hypoleuca* wood species was successfully carried through a combination of chemical treatment (based on dicarboxylic acid) and mechanical treatment.
2. The NFC obtained had an average diameter of 43.0 ± 8.6 nm, a higher degree of crystallinity, and lower thermal stability compared to the NFC prepared from other wood species.
3. The Fourier transform infrared (FTIR) results showed that the NFC contained hemicellulose and lignin, and the cellulose structure was changed from type I to type II.
4. Based on the properties of the NFC prepared in this study, the *Macaranga* tree could be a suitable alternative source of lignocellulosic materials to produce NFC.
5. NFC prepared in this work would be useful for transparent flexible substrates, coatings, and composite materials.

ACKNOWLEDGMENTS

This research was funded by Thailand Science Research and Innovation Mid-Career Research Grant 2020 from the National Research Council of Thailand (Grant No. RSA6180085). The Research and Development of Forest Fiber Technology Institute, the Ministry of Environment and Forestry of the Republic of Indonesia also supported this work by supplying the raw material (*M. hypoleuca* pulp). The authors wish to thank the Department of Chemistry (Faculty of Science), Department of Tool and Materials Engineering (Faculty of Engineering), the Department of Production Engineering (Faculty of Engineering), and the Laboratory of Integrative Biorefinery (the Joint Graduate School of Energy and Environment), King Mongkut's University of Technology Thonburi, for providing the characterization instruments. An author (ES) would like to acknowledge the Petchra Pra Jom Klao Master Scholarship of King Mongkut's University of Technology Thonburi for the academic and financial support and Asst. Prof. Manisara Phiriyawirut and Asst. Prof. Sutatch Ratanaphan for the experimental suggestions.

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Article submitted: November 3, 2020; Peer review completed: December 20, 2020;
Revised version received and accepted: November 23, 2021; Published: December 13, 2021.

DOI: 10.15376/biores.17.1.922-938