Facile preparation of cellulose nanofibers prepared by TEMPO-mediated oxidation

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Abstract. Cellulose nanofibers (CNFs) with width of 20 nm and lengths of up to several µm were fully disintegrated from water hyacinth (Eichhornia crassipes) with aids of the 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation and mild-mechanical treatment. TEMPO-oxidized CNFs were characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). FTIR reveals the conversion of C-6 hydroxyl groups to sodium carboxylate groups, and lower thermal degradation was obtained from the TEMPO-oxidized CNFs in comparison to untreated cellulose fibers. The as-prepared TEMPO-oxidized CNFs might be possibly used in packaging and composite applications.

1. Introduction
Due to outstanding features such as low density, low thermal expansion, superior mechanical properties, biodegradability, biocompatibility and a large surface-to-volume ratio, cellulose nanofibers (CNFs) have gained much attention in applications such as nanocomposites, biomaterials, paper packaging, electronic devices and filtration membranes [1-4]. Many attempts have been made to extract CNFs from low-value agricultural wastes, for instance, banana [5], bamboo [6, 7], oil palm [8], pineapple leaf [9], wheat straw [7] and residues from industries such as tobacco [10], carrot [11] and barley [11] in order to use these materials in a greater beneficial way than landfills or animal feedstocks. In a tropical country like Thailand, water hyacinth (Eichhornia crassipes) grows rapidly on water surface in open areas, causing environmental problems for fish populations, irrigation and water transportation [12, 13]. It has been reported that water hyacinth contains high cellulose and low lignin contents [12-14].

Although CNFs can be disintegrated using mechanical treatment such as high-pressure homogenization [15], sonication [16, 17], high-speed blending [18, 19] and grinding [2], these processes require high demand of energy [20]. It has been reported that the high energy consumption of 700 – 1400 MJ is required to prepare 1 kg of CNFs [21], in comparison to that of ~40 MJ kg⁻¹ for flex fiber production [22]. Therefore, chemical or enzymatic treatments have been used to reduce the time and energy consumption [23]. For example, the reduction in energy consumption to less than 7 MJ kg⁻¹ has been reported with an aid of 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation to prepare nanofibers [21]. The TEMPO mediated oxidation has been investigated to chemically modify primary hydroxyl groups at the C-6 position of D-glucose units in cellulose chains into carboxylic
groups [24, 25]. With assistance of the mild mechanical disintegration, TEMPO-oxidized CNFs could be finally prepared.

Here, water hyacinth (Eichhornia crassipes) was used as a raw material to prepare CNFs with the TEMPO-mediated oxidation process with a high content of sodium hypochlorite (NaOCl) to skip chemical pre-treatment steps. Then, the mild mechanical treatment was introduced to disintegrate CNFs. Morphology, chemical groups and thermal properties of the CNFs were investigated.

2. Materials and methods

2.1. Materials

Water hyacinth fibers (Eichhornia crassipes) were purchased from a small-medium enterprise called Ban Pak Top Chawa, Thailand. 2,2,6,6-tetramethylpiperidine (TEMPO) was supplied from Sigma Aldrich while sodium bromide (NaBr), sodium hypochlorite (NaClO), sodium hydroxide (NaOH) and ethanol were provided by Polysci Service Co., Ltd. All chemicals and solvents were used as received without purification.

2.2. Preparation of TEMPO-oxidized cellulose nanofibers

Briefly, 5 g of the dried water hyacinth fibers were dispersed in 500 ml of distilled water, and TEMPO (0.08 g), NaBr (0.50 g) and NaOCl (30 mmol g⁻¹) were wisely dropped in the fiber suspension. The suspension was continuously stirred at 25 ± 3 °C for 180 min. Then, 20 ml of ethanol was added to stop the reaction, and the TEMPO-oxidized fibers were washed for several times until neutral. Subsequently, the TEMPO-oxidized fibers were disintegrated using a mixer grinder (MX-AC400, PANASONIC, Thailand) for 15 min. The as-prepared suspension of the TEMPO-oxidized cellulose nanofibers (CNFs) was stored in a refrigerator at 5 °C before use.

2.3. Characterizations of TEMPO-oxidized cellulose nanofibers

Morphology of the TEMPO-oxidized CNFs was investigated using a scanning electron microscope (JSM-6610 LV, JEOL Ltd., Japan) with an acceleration voltage of 20 kV. Before each observation, a sample was coated with thin layers of gold using a sputter coater (108 auto, Cressington Scientific Instruments Ltd., UK) for 100 s.

Chemical functional groups of the original water hyacinth fibers and TEMPO-oxidized CNFs were investigated using a Fourier-transform infrared (FTIR) spectrometer (Nicolet iS5, Thermo Fisher Scientific Inc., USA) equipped with an attenuated total reflectance (ATR) mode. The measurements were recorded between 600 – 4000 cm⁻¹ with a resolution of 4 cm⁻¹ and an overall scan of 32.

Thermogravimetric analysis (TGA) was performed using a thermal analyzer (TG-209 F3, NETZSCH-Gerätebau GmbH., Germany). ~10 mg of the untreated fibers and TEMPO-oxidized CNFs were measured with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere, and the measurements were recorded until 800 °C.

3. Results and discussion

Figure 1(a) and (b) present the fiber suspension before and after the TEMPO-mediated oxidation process. Obviously, the color of fibers was changed from brownish to white after the oxidation treatment. This change resulted from the high concentration of NaOCl (30 mmol g⁻¹) as an oxidant used in this work to eliminate lignin, pectin and hemicellulose. Therefore, the use of the TEMPO-mediated oxidation process with a high amount of NaOCl could skip the pre-treatment steps to purify fibers such as alkaline or bleaching treatment [26, 27]. The scanning electron microscopy (SEM) image reveals the full disintegration of CNFs after the TEMPO-mediated oxidation process and high speed blending for 15 min. The TEMPO-oxidized CNFs with widths of 20 nm and lengths of more than 1 µm were observed. The similar morphology of the TEMPO-oxidized CNFs has been previously prepared from bamboo [20] and biomass residues such as soybean hull, wheat straw and softwood flour [28].
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FTIR spectra of the raw and TEMPO-mediated oxidized fibers are shown in Figure 2(a). The peaks located at ~3400 and 2800, corresponding to O-H stretching of the hydroxyl group and C-H stretching of CH2 in the cellulose chains, were observed from both untreated and treated fibers [20]. After the treatment of the TEMPO-mediated oxidation process, the higher intensity of these peaks was observed. This might be due to the removal of lignin and hemicellulose from the fibers. This has been well-agreed with a previous investigation where with increasing NaClO concentrations, higher contents of the hemicellulose and lignin were removed [20]. Also, the higher intensity of the peak located at 1600 cm⁻¹ corresponding to COONa stretching vibration, was observed from the spectrum of the chemical-treated fibers, confirming the successful conversion of C6 hydroxyl groups to sodium carboxylate groups induced by the TEMPO-mediated oxidation process [20, 28]. Also, the disappearance of the peak located at 1730 cm⁻¹, attributing to C-O stretching of the aryl group in lignin, was observed [28].

Figure 1. Appearance of the suspension of the water hyacinth fibers (a) before and (b) after the TEMPO-mediated oxidation process, and (c) scanning electron microscopy (SEM) image of the TEMPO-oxidized Cellulose nanofibers (CNFs) extracted from water hyacinth fibers.

Thermogravimetric (TG) curves of the untreated water hyacinth fibers and TEMPO-oxidized CNFs are presented in Figure 2(b). The onset degradation temperature of the TEMPO-oxidized CNFs with sodium carboxylate groups was 237.1 °C while that of the untreated fibers was 285 °C. The significant decrease in the onset degradation temperature of the TEMPO-oxidized CNFs was caused by the degradation of the sodium carboxylate groups generated during the TEMPO-oxidation process [24]. The higher residue content at 800 °C was obtained from the TEMPO-oxidized CNFs (25.4%) in comparison with that of the untreated fibers (22.4 %). This higher ash content was due to sodium carboxylate groups. It has also been reported that the addition of sodium on the cellulose surface may increase the ash content [29].

Figure 2. (a) Fourier-transform infrared (FTIR) spectra and (b) thermogravimetric (TG) curves of raw water hyacinth fibers and TEMPO-oxidized Cellulose nanofibers (CNFs).
4. Conclusions
TEMPO-oxidized CNFs with widths of 20 nm and lengths of up to several µm were successfully prepared from water hyacinth fibers with the assistance of the mild mechanical disintegration. The TEMPO-mediated oxidation process used in this work was adequate to purify fibers without any introduction of the pre-treatment steps. With the conversion of C6 hydroxyl groups to sodium carboxylate groups, the significant decrease in the thermal degradation temperature of the TEMPO-oxidized CNFs was observed.

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6. References
[1] Tanpichai S, Quero F, Nogi M, Yano H, Young R J, Lindstrom T, Sampson W W and Eichhorn S J 2012 Biomacromolecules 13 1340
[2] Abe K, Iwamoto S and Yano H 2007 Biomacromolecules 8 3276
[3] Varanasi S, Henzel L, Sharman S, Batchelor W and Garnier G 2018 Carbohydr. Polym. 184 307
[4] Tanpichai S, Witayakran S and Boonmahitthisud A 2019 J. Environ. Chem. Eng. 7 102836
[5] Khawas P and Deka S C 2016 Carbohydr. Polym. 137 608
[6] Chang F, Lee S-H, Toba K, Nagatani A and Endo T 2012 Wood. Sci. Technol. 46 393
[7] Chen W S, Yu H P, Liu Y X, Hai Y F, Zhang M X and Chen P 2011 Cellulose 18 433
[8] Fahma F, Iwamoto S, Hori N, Iwata T and Takemura A 2010 Cellulose 17 977
[9] Cherian B M, Leao A L, de Souza W M, Costa L M M, de Oliveira G M, Kottaisamy M, Nagarajan E R and Thomas S 2011 Carbohydr. Polym. 86 1790
[10] Tuzzin G, Godinho M, Dettmer A and Zattera A J 2016 Carbohydr. Polym. 148 69
[11] Berglund L, Noël M, Aitomäki Y, Öman T and Oksman K 2016 Ind. Crops. Prod. 92 84
[12] Abral H, Kadriadi D, Rodianus A, Mastariyanto P, Ilhamdi, Arief S, Sapuan S M and Ishak M R 2014 Mater. Design. 58 125
[13] Sundari M and Ramesh A 2012 Carbohydr. Polym. 87 1701
[14] Tanpichai S, Biswas S K, Witayakran S and Yano H 2019 ACS. Sustain. Chem. Eng. 7 18884
[15] Wang Y H, Wei X Y, Li J H, Wang F, Wang Q H, Chen J C and Kong L X 2015 Fiber. Polym. 16 572
[16] Tanpichai S, Sampson W W and Eichhorn S J 2012 Compos. Pt. A-Appl. Sci. Manuf. 43 1145
[17] Tanpichai S, Sampson W W and Eichhorn S J 2014 Compos. Pt. A-Appl. Sci. Manuf. 65 186
[18] Uetani K and Yano H 2011 Biomacromolecules 12 348
[19] Tanpichai S and Wootthikanokkhan J 2018 Sci. Engr. Compos. Mater. 25 395
[20] Chitbanyong K, Pitiphatiharaworachot S, Pisutpiched S, Khantayanuwong S and Puangsin B 2018 Bioresources 13 4440
[21] Isogai A, Saito T and Fukuzumi H 2011 Nanoscale 71 71
[22] Dissanayake N P J, Summerscales J, Grove S M and Singh M M 2009 J. Nat. Fibers. 6 331
[23] Fujisawa S, Okita Y, Fukuzumi H, Saito T and Isogai A 2011 Carbohydr. Polym. 84 579
[24] Fukuzumi H, Saito T, Okita Y and Isogai A 2010 Polym. Degrad. Stab. 95 1502
[25] Tang Z, Li W, Lin X, Xiao H, Miao Q, Huang L, Chen L and Wu H 2017 Polymers 9 421
[26] Yuwawech K, Woothikanokkhan J and Tanpichai S 2018 Mat. Renew. Sustain. Energy. 7 21
[27] Tanpichai S, Witayakran S, Srimarut Y, Woraprayote W and Malila Y 2019 J. Mater. Res. Technol. 8 3612
[28] Sinclair A, Jiang L, Bajwa D, Bajwa S, Tangpong S and Wang X 2018 J. Appl. Polym. Sci. 135 46304
[29] Faradilla R H F, Lee G, Arns J-Y, Roberts J, Martens P, Stenzel M H and Arcot J 2017 Carbohydr. Polym. 174 1156