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Porosity, density and mechanical properties of the paper of steam exploded bamboo microfibers controlled by nanofibrillated cellulose



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ABSTRACT

This study focused on preparation of microfibers from bamboo culms using steam explosion with and without chemical treatments, and utilization of the isolated fibers in formation of bamboo paper fabricated with nanofibrillated cellulose (NFC). Compared with those obtained from the steam explosion alone (S), the bamboo microfibers isolated using the steam explosion followed by bleaching process (S/A) exhibited a significantly reduced fiber width of 7.5 μm and a markedly increased cellulose content of 97.85%. The S/A fiber showed an increased decomposition temperature, corresponding with lower contents of hemicellulose and lignin than those of the S fiber. The S/A microfibers were subsequently proceeded to paper formation. Physical and mechanical properties of the paper with an introduction of different NFC concentrations (0–50 wt%) were investigated. The linear relationship between the density, porosity and mechanical properties of the paper and NFC contents was observed. The more the NFC content, the greater the density and the lower the porosity the paper exhibited. At 50 wt% NFC, the paper density increased to 0.64 g cm^{-3} , and the paper porosity decreased to 57.0% whereas the paper without NFC showed a density of 0.39 g cm^{-3} and porosity of 73.6%. Tensile strength and strain of the paper composed with 50 wt% NFC were 10-fold and 3-fold, respectively, greater than those of the paper without NFC. The addition of NFC could manifest paper mechanical properties and porosity within the paper structure, which would be useful for scaffold and membrane applications.

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1. Introduction

The use of renewable biomass resources has been of worldwide interest as it encourages sustainability and environmental conservation [1–4]. Bamboo, a perennial woody grass widely distributed in Asian countries, has become one of the most potential renewable non-woody cellulosic materials because of its high productivity, rapid growth and easy propagation [5,6]. The annual production of bamboo is approximately 20 million tons globally [7]. Today, bamboo is used in many applications such as handicrafts, musical instruments, furniture, building, textiles and paper manufactures [5,6].

Steam explosion treatment is one of the pre-treatment techniques to breakdown structure of the hemicellulose and lignin, assisting the extraction of plant fibers from cellulosic materials. The technique utilizes saturated steam conditioned at high temperature and pressure to penetrate into the fibers without chemical usage [3,8]. When the pressure is rapidly released, the depressurization damages fiber cell walls, and weakens hydrogen bonding between fibers, resulting in the fiber isolation [9]. The advantages of the steam explosion procedure are energy efficiency, large production capacity and less adverse effects on environment [10]. Additionally, it is feasible to apply this method to extract fibers with large quantities of the biomass within a short period of time [10]. Steam explosion method has been used to extract fibers from agricultural wastes such as pineapple leaves [11–13], rice straw [14,15] and sugarcane bagasse [3,16].

Generally, conventional paper exhibits low mechanical properties due to weak interaction between fibers [17]. The paper strength is enhanced by the defibrillation of the cellulose fibers by increasing the surface area of the fibers through chemical or mechanical treatments, facilitating hydrogen bonding among fibers to the greater extent [18]. However, the attempt to isolate cellulose particles from cellulose pulp has been limited by requirement of the laborious separation steps such as screening and configuration [19]. Recently, nanofibrillated cellulose (NFC), a web-like structure of nanofibers with widths of 10–100 nm and lengths of up to several μm , has been commercially available. Productions of NFC are achieved by the force generated by a machine such as microfluidization, sonication, high pressure homogenization, high speed blending and grinding [19–21]. Due to its light weight, abundance, biodegradability, renewability, availability and superior mechanical properties [18,20,22], the interest of NFC as a paper additive has been increasing. The improved mechanical properties of the paper with the addition of NFC could reduce grammage (fiber quantities to manufacture paper) and energy consumption of the fiber refining [23]. The chemical or enzymatic pre-treatment has been introduced prior to mechanical treatment to decrease energy consumption [19–21].

Although NFC films have been widely studied, the information regarding combination of NFC and microfibers to form paper is still limited. The objectives of this work were to investigate the effects of isolation method, i.e. steam explosion either with or without the combination of chemical treatment, on characteristics of microfibers from bamboo culms, and to evaluate the relationship between porosity, density

and mechanical properties of the paper prepared from bamboo microfibers fabricated with different NFC concentrations. Microfibers with a high content of cellulose were extracted from bamboo culms using the combination of the steam explosion, alkaline treatment and bleaching process. Changes of the chemical compositions, chemical structure, thermal stability and morphology of the bamboo extracted fibers after the steam explosion and chemical processes were studied. The paper sheets of the extracted bamboo fibers and NFC were subsequently formed using a conventional drying method. This method would prepare numbers of samples within the short period of time and accurately follow target parameters during the preparation step. The prepared porous paper of bamboo fibers and NFC would be a promising alternative material for networks of electrospinning fibers with weak mechanical properties in membrane and scaffold applications.

2. Experimental

2.1. Materials

Bamboo culms of *Bambusa beecheyama* were supplied from Chiang Mai province (Thailand), and cut into the size with widths in the range of 0.5–1 cm, lengths of 10–15 cm, and thicknesses of 0.1–0.3 cm. Nanofibrillated cellulose (NFC), catalogue number KY100S, was supplied by Daicel Corporation.

2.2. Preparation of bamboo microfibers

Two hundred grams of the bamboo strips were conditioned under pressure of 18 kgf cm^{-2} (210°C) in a 2-litre steam explosion chamber. After soaking for 5 min, the valve was opened to disintegrate bundles of the bamboo fibers into microfibers due to the explosive depressurization. The disintegrated fibers were then washed with water and dried. To eliminate hemicellulose and lignin, the steam exploded fibers were treated with 17 wt% sodium hydroxide (NaOH) at 165°C for 1 h, and the ratio of the fibers to the solution was 1 g to 7 ml. The yield of the fibers after the chemical pre-treatment was 36.02%. Subsequently, the steam exploded bamboo fibers were purified by the elemental chlorine free (ECF) bleaching process [24,25]. Briefly, the three-bleaching stages (D_0ED_1) were used to further remove lignin to obtain high purified bamboo fibers. Firstly, the chlorine dioxide (ClO_2) bleaching stage (D_0) was carried out at 60°C for 60 min with 10% fiber consistency and pH of 2.5 where the ClO_2 charge was 18%. Next, the fibers were subjected through the alkaline extraction stage (E). The 10% of the fiber consistency was treated with the NaOH charge of 2% on the oven dried fibers at pH of 11.5 at 70°C for 60 min. Finally, in the D_1 stage, the D_0E -bleached fibers were treated with 2% of active chlorine of ClO_2 and 0.4% of NaOH charge on oven-dried fibers at 60°C and pH of 3.5 for 180 min. Later, the bleached bamboo fibers were filtered, and washed with water until neutralization. The fibers treated with the steam explosion were coded as “S” while the “S/A” fibers were the bleached steam exploded bamboo fibers.

Table 1 – Component compositions of the cellulose paper.

Materials	Bamboo microfibers (S/A) (wt%)	NFC (wt%)
B100	100	0
B90	90	10
B80	80	20
B70	70	30
B60	60	40
B50	50	50

2.3. Preparation of paper of the nanofibrillated cellulose and bamboo microfibers

Six hundred milligrams of the overall weight of NFC and extracted bamboo microfibers (S/A) were soaked in distilled water, and mixed using a Panasonic MX-AC400 mixer grinder for 2.5 min with 1 min interval. This step was repeated for 4 times. Later, the cellulose suspension was poured into a Teflon Petri dish, and dried in an oven at 55 °C. The component composition of each paper sample is presented in Table 1.

2.4. Scanning electron microscopy (SEM)

To evaluate the fiber morphology after the introduction of the pre-treatments, the treated fiber sample was placed on an aluminum stub with a double-sided tape and coated with a gold layer using a 108 auto sputter coating afterwards (Cressington Scientific Instruments Ltd., UK). The microscopic images of the fibers were viewed under a scanning electron microscope (JSM-6610 LV, JEOL Ltd., Japan) with an acceleration voltage of 10 kV. The surface morphology of the paper formed by the mixed components of the extracted bamboo microfibers and NFC was also observed using the same procedure.

2.5. Chemical component measurements

The contents of the cellulose, hemicellulose and lignin in the bamboo fibers before and after the treatments were determined in comparison with the untreated bamboo culms according to the Technical Association of the Pulp and Paper Industry (TAPPI) test method [26].

2.6. Fourier-transform infrared spectroscopy (FTIR)

Effect of the steam explosion and chemical treatments on chemical functional groups of the bamboo fibers was analyzed in the range of 600–4000 cm^{-1} using a Nicolet iS5 spectrometer (Thermo Fisher Scientific, USA) equipped with an attenuated total reflectance mode. The experiments were performed with a resolution of 4 cm^{-1} and an overall of 32 scans for each material.

2.7. Thermogravimetric analysis (TGA)

Thermogravimetric measurements were conducted using a thermal analyzer (TG-209 F3, NETZSCH-Gerätebau GmbH, Germany) under the nitrogen atmosphere with a constant heating rate of 10 °C min^{-1} . A ~10 mg fiber sample was stabilized at



Fig. 1 – Appearance of the bamboo fibers after the steam explosion (left) and the combined steam explosion and chemical treatments (right).

110 °C for 10 min to eliminate moisture effect, and further heated to 800 °C.

2.8. Density and porosity

Before weighing on an analytical scale, a paper sample was oven-dried at 60 °C for 24 h. The width and length of the paper were measured using a Vernier (Mitutoyo, Japan) while thickness of the cellulose paper was determined using a thickness gauge (Mitutoyo, Japan). The density of the paper (ρ_m) was obtained from the ratio of the weight of the paper to the volume of the paper. Then, the porosity (ε) of the paper was calculated using the following equation [22].

$$\varepsilon (\%) = \left[1 - \left(\frac{\rho_m}{\rho_{\text{cellulose}}} \right) \right] \times 100 \quad (1)$$

where $\rho_{\text{cellulose}}$ is the density of the cellulose (1.5 g cm^{-3}).

2.9. Mechanical properties

Mechanical properties of the cellulose paper of the disintegrated bamboo S/A microfibers and NFC were determined using a universal testing machine (5583, Instron Corp., USA) with a load cell of 5 kN. A sample with the width of 10 mm and length of 50 mm placed between two grips with a gauge length of 20 mm was tested with a crosshead speed of 10 mm min^{-1} . The width and thickness of the sample materials were measured using a Vernier and micrometer, respectively. The average and standard deviation values of the tensile strength, Young's modulus and tensile strain were calculated from five samples for each material.

3. Results and discussion

3.1. Fiber characterizations

Appearance of the bamboo fibers treated with either steam explosion alone (S fibers) or with the combination of the steam explosion, alkaline treatment and bleaching (S/A fibers) is presented in Fig. 1. The markedly difference in color between the S and S/A fibers was readily observed. The S fibers (Fig. 1, left) yielded a dark brown material whereas the S/A samples appeared white (Fig. 1, right). The impact of steam explosion on discoloration cellulose fibers was also reported in previous

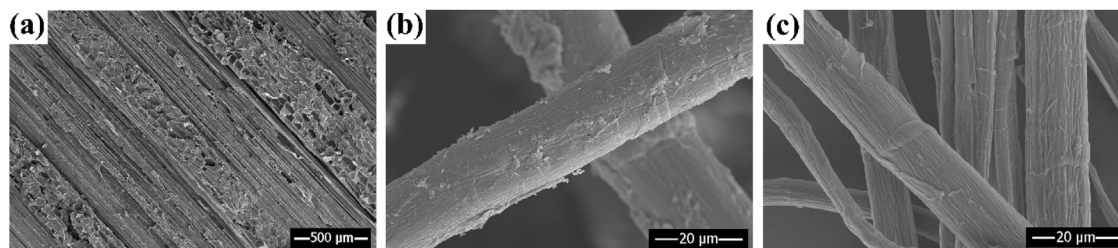


Fig. 2 – Scanning electron microscope images of the (a) longitudinal bamboo surface and bamboo fibers disintegrated after (b) the steam explosion process and (c) the combined steam explosion and chemical treatments.

Table 2 – Chemical compositions of bamboo fibers before and after treatments.

Components	Raw fibers (%)	S fibers (%)	S/A fibers (%)
Alpha cellulose	35.65 ± 0.23	59.29 ± 0.19	97.85 ± 0.04
Hemicellulose	24.69 ± 0.31	9.15 ± 0.17	1.95 ± 0.04
Lignin	16.14 ± 0.24	15.27 ± 0.50	0.20 ± 0.03

studies in which the lower the hemicellulose remained in the resulting fiber samples, the darker the samples appeared [27–29]. It has been also suggested that the discoloration of the exploded fiber materials is the consequence of chemical degradation of cell wall components, particularly lignin and wood extractives, under an extreme thermal condition [27]. Hydrolyzed hemicellulose and depolymerized lignocellulosic materials, including tannins, flavonoids or solubilized sugars, could undergo condensation reactions and react with furfural and hydroxymethyl furfural into large molecules responsible for brownish color [3,23,27,30].

The effects of the steam explosion and chemical treatment on fiber disintegration are shown in Fig. 2. When the bamboo culms consisting of fibrous (2–3 mm long and 8–20 μm wide) and parenchyma cells (60–120 μm long and 30–50 μm wide) [31] were subjected to the steam explosion, the microfibril isolation was observed during the rapid depressurization. The average width of the S fibers was found to be $16.7 \pm 4.8 \mu\text{m}$ with residuals of hemicellulose and lignin acting as a binder on the surface (Fig. 2(b)). The width of the S/A fibers was significantly reduced to $7.5 \pm 3.2 \mu\text{m}$ after the introduction of the alkaline treatment and bleaching process to the S fibers. This reduction in the fiber width could be attributed by the removal of hemicellulose and lignin, causing the separation of the individual microfibrils with the smooth surface [8,32,33]. Consistent with the current findings, the decrease in the fiber width after the alkaline method was also found in isora fibers [33].

Chemical composition of the fibers was modified after the fibers were subjected with the treatments (Table 2). The raw bamboo fibers contained a high content of hemicellulose (24.69%) and lignin (16.14%) but a low cellulose proportion (35.65%) which were consistent with the main compositions found in plant fibers [33,34]. When the fibers were subjected to the steam explosion treatment, the cellulose proportion remarkably increased from 35.65 to 59.29% whereas the hemicellulose content dramatically reduced from 24.69 to 9.15% in comparison with those in the original bamboo fibers. The partial decrease in the lignin component was also found in the S samples. The findings were in accordance

with a previous report addressing that steam explosion majorly promotes hemicellulose hydrolysis with minor effect on lignin removal [35]. Such chemical changes could be the consequence of the depolymerization of hemicellulose and the cleavage of β-O-4' linkages in the lignin structure [3,5,23,30] upon the contact with steam. This breakdown of lignocellulosic structures during the steam explosion process could lead to defibrillation. When the alkaline and bleaching treatments were introduced to the S fibers, the dramatic increase in the cellulose proportion was observed. The S/A samples possessed 97.85% of cellulose, 1.95% of hemicellulose and only 0.20% of lignin. The tremendous reduction in hemicellulose and lignin contents was attributed to the cleavage of ether bonds of lignin and hemicellulose through the chemical treatments [33,36]. The cellulose content of the S/A fibers was higher than those of the other cellulose fibers prepared by a series of the pre-treatments, as reviewed in Table 3. For example, a cellulose content of 80.5% was reported from *Hibiscus sabdariffa* var. *altissima* fibers [34] treated with alkaline, steam explosion and bleaching methods. 54.6% of the cellulose content was prepared from the oak shell treated with sulfuric acid, alkaline and steam explosion treatments [36]. More than 80% of the cellulose portion was obtained when the fibers such as wood, bamboo, straw and flax were subjected to sodium chlorite at 75 °C for 1 h for 5 times, potassium hydroxide at 90 °C for 2 h, sodium chlorite at 75 °C for 1 h and potassium hydroxide at 90 °C for 2 h [37].

FT-IR spectra of the untreated, S, and S/A samples are shown in Fig. 3. All bamboo fiber samples showed similar FT-IR spectra, indicating the similar main components in the fibers which were cellulose, hemicellulose and lignin. There are two outstanding bands at the regions from 2800 cm⁻¹ to 3500 cm⁻¹ (high wavenumbers) and from 600 cm⁻¹ to 1800 cm⁻¹ (low wavenumbers). The broad adsorption peak within the range of 3000–3600 cm⁻¹ relates to the OH stretching [38]. The increased intensity of this peak was found due to a higher content of cellulose in the treated fibers (S and S/A) [3]. A small peak located at ~2910 cm⁻¹ is attributed to aliphatic C–H stretching vibration in cellulose and hemicellulose [3]. The band located at 1730 cm⁻¹, attributed either to acetyl and uronic ester groups of hemicellulose or to the ester linkage of carboxylic groups of ferulic and *p*-coumaric acid in lignin or hemicellulose, and the bands at 1510, 1375 and 1228 cm⁻¹, associated with the aromatic skeletal vibration of lignin, were clearly observed in the spectra of the raw bamboo sample and S fibers. This was because a high amount of hemicellulose and lignin was observed in these fiber samples. However, the

Table 3 – Comparison of contents of cellulose, hemicellulose and lignin of the cellulose fibers before and after a series of the pre-treatments.

Cellulose resources	Treatment procedure	Before pre-treatments			After pre-treatments			Ref.
		C*(%)	H*(%)	L*(%)	C*(%)	H*(%)	L*(%)	
Bamboo fibers	Steam explosion at 18 kgf cm ⁻² (210 °C) for 5 min.	35.7	24.7	16.1	59.3	9.2	15.3	This work
Bamboo fibers	(1) Steam explosion at 18 kgf cm ⁻² (210 °C) for 5 min. (2) Sodium hydroxide (17 wt%) at 165 °C for 1 h. (3) Three-bleaching stages (D ₀ ED ₁)	35.7	24.7	16.1	97.9	2.00	0.2	This work
Rice straw	Steam explosion at 160 °C and 2 bar for 54 h.	44.3	33.5	20.4	69.2	14.1	8.2	[14]
Cactus rocket	Steam explosion at 220 °C, 2 bars and pH of 2 for 1 h.	26.7	15.3	2.5	80.0	3.6	0.03	[40]
Hibiscus <i>sabdariffa</i> var. <i>altissima</i> fiber	(1) 2% of sodium hydroxide in an autoclave with a pressure 20 lb at 120 °C for 1 h. (2) Sodium chlorite. (3) Oxalic acid in an autoclave with a pressure 20 lb at 120 °C for 1 h.	62.5	16.5	12.8	80.5	4.6	1.5	[32]
Oak shell	(1) 2% (w/v) sulfuric acid for 48 h at a solid loading of 8% (w/v). (2) 2% (w/v) sodium hydroxide for 48 h at a solid loading of 8% (w/v). (3) Steam explosion at 118 °C with 1.0 MPa for 480 s.	34.4	20.4	36.6	54.6	–	11.5	[36]
Bagasse	(1) Steam explosion at 195 °C for 5 min and 205 °C for 5 min. (2) 20% (w/w) sodium hydroxide using a liquid to solid ratio of 20:1 at 80–90 °C for 2 h. (3) 4% (w/w) sodium chlorite using a liquid to solid ratio of 20:1 at 80–90 °C for 2 h. (4) 2% (w/w) sodium hydroxide using a liquid to solid ratio of 20:1 at 80–90 °C for 30 min.	41.4	28.4	19.0	90.9	8.0	0.7	[3]
Pineapple leaf fibers	(1) Steam explosion under 20 lb pressures for 1 h. (2) A mixture of the solution (sodium hydroxide and acetic acid) and sodium chlorite in a ratio of 1:3 for 6 times. (3) 11% oxalic acid under a pressure of 20 psi in an autoclave for 15 min. This process was repeated for 8 times	81.3	12.3	3.5	98.6	0.5	0.8	[30]
Pineapple leaf fibers	(1) Steam explosion at 210 °C and 18 kgf cm ⁻² for 5 min. (2) 8% (w/v) sodium hydroxide for 24 h.	64.5	20.9	4.2	77.7	14.1	0.6	[34]
Barks of <i>Helicteres isora</i>	(1) 2 wt% sodium hydroxide in an autoclave and kept under 25 psi at 110 °C for 1 h. (2) A mixed solution of a mixture of sodium hydroxide and acetic acid and sodium chlorite in a ratio of 1:3 for 6 times. (3) 10% oxalic acid under a pressure of 25 psi in an autoclave for 15 min.	71.0	3.1	21.0	93.0	0.5	1.1	[33]

– Table 3 (Continued)

Cellulose resources	Treatment procedure	Before pre-treatments			After pre-treatments			Ref.
		C*(%)	H*(%)	L*(%)	C*(%)	H*(%)	L*(%)	
Wood fibers	(1) Sodium chlorite at 75 °C for 1 h for 5 times. (2) 2 wt% potassium at 90 °C for 2 h. (3) Sodium chlorite at 75 °C for 1 h. (4) 5 wt% potassium at 90 °C for 2 h.	46.4	27.1	25.0	80.2	17.7	1.1	[37]
Bamboo fibers	(1) Sodium chlorite at 75 °C for 1 h for 5 times. (2) 2 wt% potassium at 90 °C for 2 h. (3) Sodium chlorite at 75 °C for 1 h. (4) 5 wt% potassium at 90 °C for 2 h.	41.8	27.2	23.2	84.4	14.6	0.9	[37]
Wheat straw fibers	(1) Sodium chlorite at 75 °C for 1 h for 5 times. (2) 2 wt% potassium at 90 °C for 2 h. (3) Sodium chlorite at 75 °C for 1 h. (4) 5 wt% potassium at 90 °C for 2 h.	39.8	34.2	19.8	84.1	13.9	1.9	[37]
Flax fibers	(1) Sodium chlorite at 75 °C for 1 h for 5 times. (2) 2 wt% potassium at 90 °C for 2 h. (3) Sodium chlorite at 75 °C for 1 h. (4) 5 wt% potassium at 90 °C for 2 h.	75.4	13.4	3.4	88.8	9.1	0.4	[37]

*C is a content of cellulose.
H is a content of hemicellulose.
L is a content of lignin.

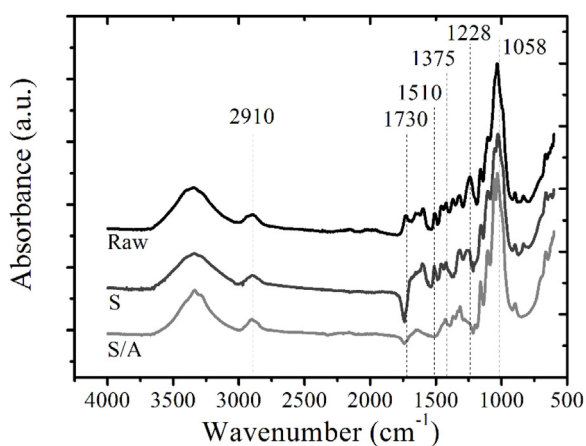


Fig. 3 – FT-IR spectra of the untreated, steam exploded (S), and combined steam explosion and chemical-treated (S/A) fibers isolated from bamboo culms.

disappearance of these three peaks was observed when the bamboo fibers were subjected to the steam explosion followed by the chemical treatments (S/A) which well agreed with the capacity of the such treatment in removal of hemicellulose and lignin from the fibers [3,23,33,36]. The absorption band at 1058 cm⁻¹ assigned to C–O–C pyranose ring skeletal vibration of cellulose was found from all materials [3,39,40]. The intensity of these peaks was higher after fibers were treated with the alkaline and bleaching solution, owing to the increased proportion of cellulose content in the S/A fibers.

The presence of the hemicellulose and lignin in the fibers affects the decomposition stages of the fibers. Fig. 4

shows thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the bamboo fibers after the treatments, and Table 4 lists temperatures of the thermal decomposition, DTG, and char yields at 800 °C of untreated and treated bamboo fibers. Once any lignocellulosic fibers are subjected to TGA, an initial weight loss is observed between 25 and 150 °C due to moisture evaporation [32,38,41], but this general first mass loss step was not observed from all fiber samples in this work because the fiber samples were stabilized at 110 °C for 10 min. The second weight loss of fiber usually occurs between 220 and 300 °C due to the thermal depolymerization of hemicellulose and breakdown of the glycosidic linkages of cellulose [1,32]. Then, cellulose starts to decompose between 275 and 400 °C while lignin, a component with a complex structure, degrades in the temperature range of 250–700 °C [9]. Herein, the TGA data were consistent with those obtained from the chemical component and FT-IR testings. The intact bamboo samples began to decompose at 260.7 °C which was significantly lower than that of the S (334.3 °C) and S/A fibers (338.7 °C), corresponding with a low decomposition temperature of hemicellulose and pectin and a large temperature degradation range of lignin [9]. In this regard, when hemicellulose and lignin were removed, the thermal decomposition of the S and S/A fibers was shifted to a higher temperature. The S/A fibers showed the highest decomposition temperature as it comprised the lowest hemicellulose and lignin content. Meanwhile, the raw fibers showed the low DTG peak temperature at 328.1 °C, suggesting an inferior thermal stability compared with the treated fibers. The DTG peak temperature of the S fibers was found to be slightly higher than that of the S/A fibers due to a higher lignin content in the S fibers than S/A fibers [9]. Although thermal stability of the S fibers

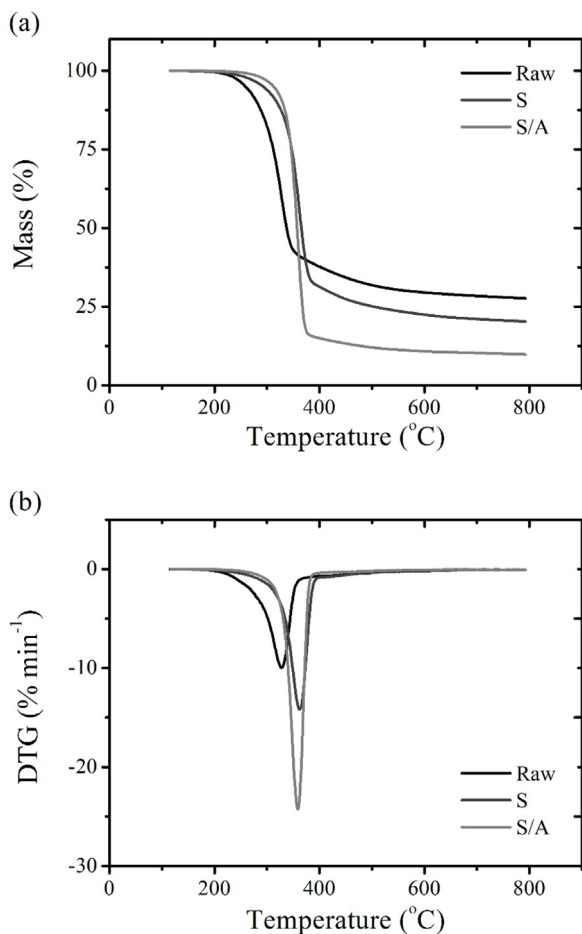


Fig. 4 – (a) Thermogravimetric and (b) derivative thermogravimetric curves of the raw and treated bamboo fibers.

Table 4 – Thermal stability data of the untreated and treated fibers extracted from bamboo.

Materials	Onset decomposition temperature (°C)	DTG peak temperature (°C)	Char residue (%)
Raw fibers	260.7	328.1	27.6
S fibers	334.3	362.6	20.3
S/A fibers	338.7	358.1	9.8

was comparable to that of the S/A fibers, the darker color of the S sample might limit its use in further applications. Additionally, there were fiber residues remained at 800 °C, corresponding to the carbonaceous materials. Significant difference in the residue contents between the untreated and treated fibers was observed. The S/A fibers presented the lowest char yield of 9.8% which was in accordance with the further removal of the hemicellulose and lignin in the fibers. The S fibers showed a lower amount of the char residues (20.3%) than the raw fibers (27.6%) because of the partial removal of the noncellulosic materials during the steam explosion treatment [33]. A higher residue content at high temperature has been observed from lignin than cellulose and hemicellulose [42]. The fibers with high thermal properties obtained from

this work using the steam explosion and chemical treatments would broaden the applications of the cellulose fibers at high temperatures.

3.2. Paper properties

The effects of NFC addition on microscopic characteristics of the bamboo paper were investigated using a SEM. Surface morphology of the paper fabricated with different concentrations of NFC are shown in Fig. 5. The widths of the NFC fibrils were in the range of lower than 100 nm, and the lengths of the NFC fibrils were up to several μm , as presented in Fig. 6. In the B100 sample, the S/A fibers were randomly deposited without any preferred orientation with large pores between the fibers. With increasing a content of NFC, cavities were filled with NFC fibrils, resulting in less cavities within paper and the disappearance of the large holes. At 40 and 50 wt% of NFC, only small cavities without any large holes in the paper were observed.

The addition of NFC transformed porous paper with low density to paper with less porosity and higher density, as shown in Fig. 7. The B100 paper had a density of $0.39 \pm 0.01 \text{ g cm}^{-3}$, and with increasing a NFC content the paper density increased proportionally. The density of the B50 sample was $0.64 \pm 0.08 \text{ g cm}^{-3}$. The increase in the paper density was attributed to the filling of NFC in the cavities among the bamboo microfibrils within the paper. With increasing the NFC content, the porosity of the paper decreased from $73.6 \pm 0.9\%$ of the B100 material to $57.1 \pm 5.3\%$ measured from the B50 paper. This reduction was due to less and smaller gaps resulted from the introduction of the NFC fibrils within the paper. The density and porosity of the paper prepared from the bamboo fibers fabricated with NFC were linearly proportionally influenced by the NFC concentrations with a coefficient of determination (R^2) of 0.98. This indicated that the addition of NFC could control pore sizes within the paper and porosity of the paper. In this case, the pore size in the paper became smaller when more NFC fibrils were added. It has been previously reported that pore sizes between fibrils could be controlled by the fiber width. The formation of paper using fibers with smaller widths resulted in the paper with small pore sizes [22]. The findings in this study may offer an opportunity to tailor materials with desirable pore sizes that can be used as a substrate for bone tissue engineering [43].

The reduction in porosity of the paper has been reported to improve mechanical properties of the paper owing to the increased hydrogen bonding introduced by NFC with high surface area [18]. Fig. 8 presents stress-strain curves of the bamboo paper with NFC, and mechanical properties of these materials are summarized in Table 5. Tensile strength of the bamboo paper (B100) was as low as 1.60 MPa. An introduction of NFC to the bamboo paper appeared to significantly increase tensile strength of the paper. A linear increase of tensile stress was evaluated with increasing NFC contents in paper. By introducing 10 wt% of the NFC, tensile strength of the paper was improved by 86% as observed in the B90 sample and such parameter could be increased to as high as 17.6 MPa (approximately 10 fold) from the control (B100) with the introduction of 50 wt% of NFC to the paper (B50). The increase in tensile strength could be speculated to be a consequence from the

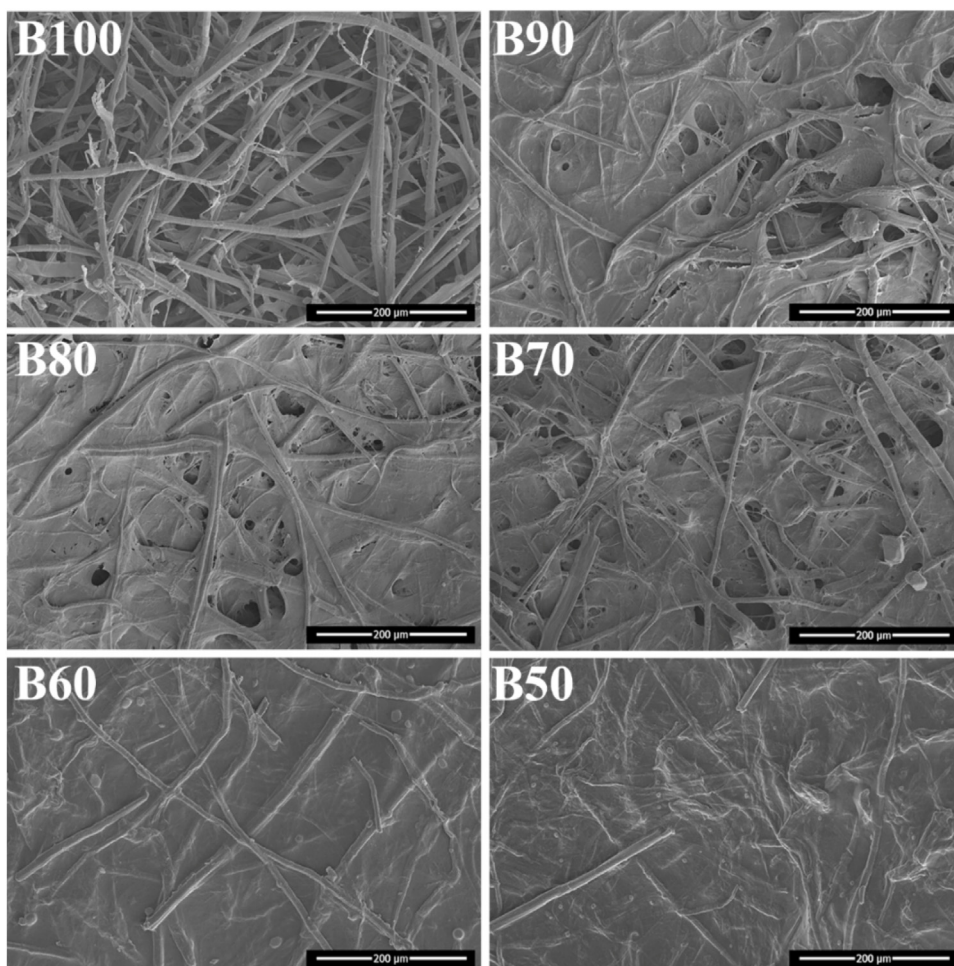


Fig. 5 – Surface morphologies of the paper of the NFC and extracted bamboo microfibrils (S/A).

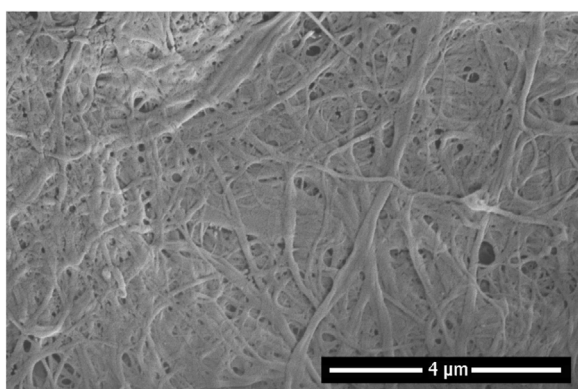


Fig. 6 – Scanning electron microscope image of NFC fibrils.

greater hydrogen bonding between bamboo fibers and NFC fibrils. The degree of bonding has been reported to dominate stress distribution in paper. Load can be more efficiently transferred between fibers with the high degree of bonding [44,45]. In addition, the stress of NFC has been reported to be higher than micron-sized fibers [18].

In addition to the improved tensile strength, the increased hydrogen bonding between the fiber and NFC could manifest the material behavior of the paper. The paper became stiff-like

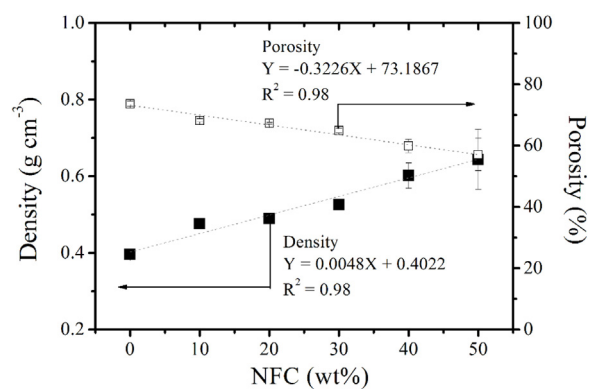


Fig. 7 – Density (■) and porosity (□) of the paper of the bamboo isolated fibers (S/A) as a function of the NFC content.

material with increasing NFC content. Upon the deformation of the B100 paper, the fiber debonding from the paper and fiber slippage within the structure occurred, leading to fiber pull-out failure mechanism [34,46]. By increasing the NFC content, the greater hydrogen bonding combined with low porosity of the prepared paper exhibited the different failure mechanism of the paper, resulting in the immediate

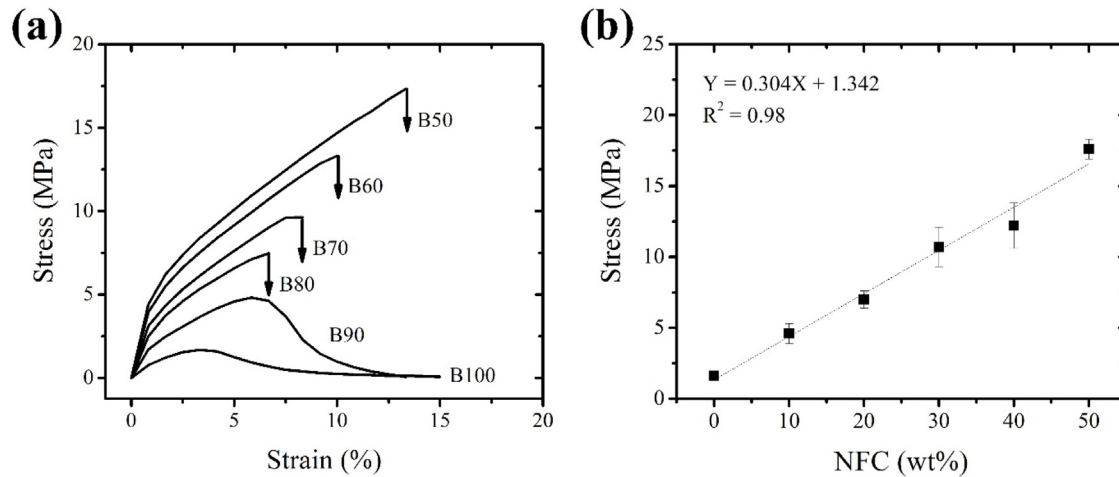


Fig. 8 – (a) Stress–strain curves of the paper of the extracted bamboo microfibers (S/A) and NFC and (b) relationship between stress of the paper and NFC concentrations.

Table 5 – Summary of the mechanical properties of the bamboo paper with NFC. The significant difference of the data with a P value of less than 0.05 was presented by a different alphabet (a–e), according to a t-test analysis.

Materials	Tensile strength (MPa)	Strain at the maximum force (%)
B100	1.6 ± 0.2^a	3.5 ± 0.4^a
B90	4.6 ± 0.7^b	5.3 ± 1.1^b
B80	7.0 ± 0.6^c	6.7 ± 0.7^b
B70	10.7 ± 1.4^d	8.9 ± 1.0^c
B60	12.2 ± 1.6^d	10.0 ± 0.1^c
B50	17.6 ± 0.7^e	14.0 ± 0.4^d

breaking of the sample. The compatible failure mechanism was observed in the literature [17,34]. Moreover, with the greater content of the NFC, tensile strain at the maximum force increased due to the high degree of hydrogen bonding formed between NFC itself and between NFC and bamboo microfibers.

3.3. Fabrication discussion

Electrospinning has been widely studied in the area of preparing porous structured materials with nanofibers from various types of polymeric materials derived from natural or petroleum sources [47–49]. Although this technique fabricates nanofibers with widths of 50–500 nm, it is time-consuming with a limited production rate, and high efficient equipment and maintenance costs are required [49]. Electrospinning fiber morphology and properties are affected by many parameters such as flow rate, voltage, polymer concentration, conductivity and so on [49]. These limitations are critical for product applications, and carefully handling is required during preparation. Therefore, using a conventional drying procedure to prepare porous paper may be able to fill this gap in terms of production scalability and facile preparation as the oven-drying is economically available.

Regarding the cost of NFC, this material may currently be considered expensive and may not be feasible for industrial-scaled production. However, similar to other technologies, the cost is usually reduced in the future as the technology is further developed. Above all, the cost of the used technique financially depends on the final application of the products. As shown in this study, the use of NFC in this case not only improved mechanical properties of the paper, but also controlled the paper porosity. The results herein could lay a foundation for preparing tailor-made paper with designed porosity and mechanical properties to replace networks of electrospinning fibers. This material can potentially be applied in several applications such as a membrane or scaffold for tissue engineering and separator in lithium-ion batteries.

4. Conclusions

Bamboo microfibers with the widths of $7.5 \pm 3.2 \mu\text{m}$ and cellulose content of 97.85% were successfully extracted from bamboo culms using the combined steam explosion, alkaline treatment and bleaching process. Thermal stability of the bamboo fibers was found to be dependent on contents of cellulose, hemicellulose and lignin. The S/A fibers with a higher content of cellulose and lower portions of hemicellulose and lignin exhibited the onset thermal degradation of 338.7°C while the untreated bamboo started to degrade at 260.7°C . Regarding its superior characteristics, the S/A microfibers were used in the subsequent studies in which the fibers were mixed with nanofibrillated cellulose (NFC) to form paper. The increased in paper density and reduction in porosity were proportionally affected by the NFC contents. With 50 wt% NFC, the paper density increased by 62.8% from 0.39 g cm^{-3} while the paper porosity decreased from 73.6% to 57.1%. These changes were due to the small diameters and high surface area of NFC. The significant improvement in mechanical properties of the paper was observed with increasing NFC concentrations. Tensile strength and strain of the paper was significantly improved to 17.7 MPa and 14.0%, respectively, in comparison

with 1.6 MPa and 3.5% for the tensile stress and strain at break of the paper without the addition of NFC. The designed porosity and mechanical properties would be useful for scaffold and membrane applications.

Conflicts of interest

The authors declare no conflicts of interest.

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