Bagasse Sheets Reinforced with Nanofibrillated Celluloses

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Abstract. The nanofibrillated celluloses (NFC) from different sources (i.e. bacterial cellulose (BC), pineapple leaf (PA) and banana pseudostem (BA)) were prepared using microfluidization. TEM and XRD results revealed diverse characteristics of the NFCs from different sources. Then, 0.1wt% of the prepared NFCs were integrated into the bagasse (BG) paper sheets. SEM images showed the densest surface of BG/NFC-BA sheet which also exhibited the highest sheet rigidity. Furthermore, the tensile tests indicated that the BG sheet reinforced with NFC-BC, possessing the highest fiber aspect ratio (L/D of 336) and crystallinity (80%), offered the highest strength and toughness. All tensile properties of the BG sheets were impressively enhanced with very low content (0.1wt%) of NFC addition. This confirmed that NFC is a highly effective reinforcement and suitable for use in paper making industry. However, suitable sources of NFCs for a particular paper product or application should be considered in advance.

1. Introduction
Nowadays, bagasse (BG) is one of important raw materials in paper and pulp industries. Papers and other related products made from BG pulp however are weaker than those made from wood pulp because BG has shorter fibers, hence, lower inter-fibers bonding [1]. Nanofibrillated cellulose (NFC) recently gains a great attention to use as a reinforcing additive to improve the physical and mechanicals properties of paper because of its unique properties such as biodegradability, high aspect ratio, high strength and high stiffness [2]. NFC can be prepared from many sources including biomass as well as bacterial cellulose (BC). It normally has a fiber diameter around 5-50 nm with a few micrometers length. NFCs extracted from different sources show specific fibers characteristic that can contribute to an effective improvement of paper quality [3-5]. The aim of this study is to assess the effect of NFCs from different sources (i.e. BC, pineapple leaf (PA) and banana pseudostem (BA)) reinforced in the BG paper sheets. The characteristic, morphology, structure, and properties of the NFCs and sheets were investigated using TEM, XRD, SEM, and tensile testing.

2. Materials and Methods

2.1. Materials
Bacterial cellulose (BC) was cultivated by Komagataeibacter nataicola in Hestrin-Schramm (HS) medium for 10 days before harvesting. Nanglae pineapple leaves used in this study were obtained from the field in Chiang Rai, Thailand. Cultivated banana pseudostem was taken from Mae Fah Luang
University Botanical Garden, Thailand. Sodium hydroxide (NaOH) was an AR grade from QRëC, New Zealand. Bleached bagasse sheet was supplied by Biodegradable Packaging for Environment Public Co., Ltd., Thailand.

2.2. Preparation of BG pulp and sheet
BG paper was torn into small pieces and soaked in tap water overnight. The soaked BG papers were defibrillated by using kitchen blender (House Worth, HW-BDC2PC) at speed of 15,000 rpm for 5 min to prepare the BG slurry. Then, it was screened on the two metal meshes no.18 and 200 with opening sieve sizes of 1 mm and 74 µm, respectively. The portion remained on mesh no.18 was rejected and the pulp on mesh no.200 was collected, then adjusted to 2% pulp consistency. Next, the BG sheet was prepared by using hot-pressing technique under pressure of 159 kPa at 105°C for 5 min.

2.3. Preparation of NFCs from BC, PA, and BA
The harvested BC was cut into small pieces and disintegrated into the suspension with 0.5% concentration. To prepare NFC-BC, the BC suspension was passed through a microfluidizer (M-110P, Microfluidics) equipped with Y-type chamber (size of 87 µm) at 25,000 psi for 10 cycles. PA and BA were cut into 10 cm and dried until constant weight. Then, they were ground into small pieces and treated with 18% NaOH at 98±2 °C for 30 min using the liquid: solid ratio of 10:1. The obtained pulps were washed with tap water to remove black liquor until cleaned and pH adjusted to 7. The pulps were then disintegrated by using a kitchen blender (House Worth model HW-BDC2PC) at 15,000 rpm for 1 min before screening by the metal meshes no. 18 and 200. To produce NFC-PA and NFC-BAs, the pulp suspension was diluted to 0.5% consistency and refined using a microfluidizer (M-110P, Microfluidics), passing through Y-type chamber (87 µm channel) under pressure of 25,000 psi for 20 cycles.

2.4. Preparation of BG/NFCs sheets
Each NFC slurry was added to BG slurry at loading content of 0.1wt% (based on dried weight of BG) and then mixed for 1 min by stirring. Next, the mixture was preformed between two metal meshes (no.400) and then partially dewatered. The preformed sheet was then hot-pressed for 5 min at 105°C under pressure of 159 kPa.

2.5. Characterization
2.5.1. Scanning Electron Microscopy (SEM). The morphology of BG fibers and sheet surfaces were examined using scanning electron microscopy (SEM, LEO/1450 VP) at an accelerating voltage of 10 kV. All samples were coated with carbon by sputtering before observed. The dimension of BG fibers was measured and averaged from 50 fibers.

2.5.2. Transmission Electron Microscopy (TEM). Each NFC suspension was diluted to 0.001% consistency and then drop on a copper grid with formvar film support. The samples were then dyed with 2% uranyl acetate (UA) for 5 min and kept overnight before examined by transmission electron microscope (TEM, Hitachi Model HT7700) with acceleration voltage of 80 kV. The NFCs dimension was measured and reported from the average of 10 fibers.

2.5.3. X-ray Diffraction (XRD). NFCs in sheet forms were irradiated by CuKα at 40 kV and 30 mA with a symmetric reflection geometry in the angular range of 5°-35° (2θ) using a scan speed of 2°/min. The crystallinity index (CrI) of specimens was calculated using this following equation:

\[ \%CrI = \left( \frac{I_{am} - I_{am}}{I_{am}} \right) \times 100 \]  

(1)
where \( I_{002} \) is the intensity reflection (\( 2\theta = 22^\circ \)) and \( I_{am} \) is the intensity of amorphous cellulose (\( 2\theta = 18^\circ \)) [1].

2.5.4. Physical properties. Each sheet sample was cut into 10 mm × 50 mm and measured for its thickness, width and length by using a digital Vernier caliper. Then, the volume (cm³) was calculated and the weight (g) the sample was recorded according to a 4-digit balance. The density of each sheet sample was calculated by dividing its weight over volume. The grammage of paper sheet was calculated from the ratio of mass (g) to area of specimen (m²). Porosity of each sample was calculated using the following equation:

\[
\text{% Porosity} = \left( 1 - \frac{\text{density of sheet}}{\text{density of cellulose}} \right) \times 100
\]

where the density of cellulose is 1.53 g/cm³ [4].

2.5.5. Mechanical properties. Tensile testing was performed by using Instron model 5566 equipped with 1 kN load cell. The gauge length of specimen was 30 mm with width of 10 mm. All specimens were pre-conditioned at 50% relative humidity and 25°C overnight before testing. The machine was set to preload at 1 N before starting the test and cross-head speed was set at 15 mm/min. The testing was evaluated in term of tensile index, breaking length, elongation and Young’s modulus. The results were obtained from the average of 5 tested specimens.

3. Results and Discussion

3.1. Characteristics of BG fibers and NFCs

SEM image of the BG pulp fibers is shown in figure 1A. The BG fibers have average length (L), diameter (D), and aspect ratio (L/D) of 274.8±105.9 µm, 11.7±4.9 µm, and 29, respectively.

![Figure 1. SEM photograph of BG fibers (A) and TEM photographs of the prepared NFCs (B-D).](image)

![Figure 2. XRD patterns of NFCs from different sources.](image)

| Type of nanofibers | Length (µm) | Diameter (nm) | Aspect ratio | CrI (%) |
|-------------------|-------------|---------------|--------------|---------|
| NFC-BC            | 3.5±2.0     | 10.5±2.7      | 336          | 80      |
| NFC-PA            | 1.7±0.5     | 15.5±3.6      | 108          | 69      |
| NFC-BA            | 1.7±0.1     | 20.0±7.6      | 86           | 61      |

For NFCs, after 10 passes through the microfluidizer, BC was observed to be defibrillated into long single nanofibers (NFC-BC) (Figure 1B). On the other hand, after 20 passes, PA and BA microfibers were size-reduced to nanofibers of NFC-PA and NFC-BA, respectively (Figure 1C and 1D). The
dimension and aspect ratio of the three NFCs are summarized in Table 1. It can be seen that NFC-BC showed the considerable higher aspect ratio than NFC-PA and NFC-BA. In addition, it seemed that NFC-BA nanofibers were partially damaged and some portions were turned into web-like networks (indicated with black arrows in Figure 1D).

XRD patterns of NFCs from BC, PA and BA were plotted together in figure 2. The sharp diffraction peaks at around 22.5° in all NFC samples designated the characteristic of cellulose I_α crystal structures at the (200) plane [6]. It was obvious that NFC-BC displayed the highest peak intensity and from the calculation using equation 1, this NFC had the highest crystallinity (CrI) about 80% (see Table 1). Perhaps, it was due to a difference in nature of cellulose sources. The lower CrI of NFC-PA and particularly NFC-BA might also indicate that after 20 passes through the microfluidizer, some portions of the crystalline nanofibers were partially damaged into amorphous phase which in line with the previous TEM results.

3.2. Morphology, Structure, and Properties of BG and BG/NFCs Sheets
With addition of only 0.1 wt% NFCs from different sources, the grammage of the obtained sheets was differently influenced and in the range of 240-340 g/m^2. Still, the density and porosity of the BG/NFC-BC and BG/NFC-PA sheets were quite similar to the pure BG sheet (see information in figure 3). Unlike the others, the BG/NFC-BA sheet showed a significant increase in density and decrease in porosity.

**Figure 3.** SEM photographs of surfaces of pure BG sheet (A); BG/NFCs sheets (B-D). Black circles indicate gaps between BG fibers. ρ = density (g/cm³); P = porosity (%).

From the series of SEM images (Figure 3), the smoother surface of BG/NFC-BA when compared to other sheets can be observed. Possibly, the NFC-BA nanofibers with also web-like network parts (Figure 1D) can fill in more gaps between the BG microfibers, leading to less porous on surface and inside structure of this sheet.

The results from tensile tests are summarized in Table 2. Only 0.1wt% NFCs addition was able to improve all tensile properties of the BG sheets. The highest tensile index and breaking length was obtained with addition NFC-BC, then NFC-PA, and NFC-BA, respectively. Tensile index generally provides a measure of inter-fiber bonding within the paper [3]. It was likely that NFC-BC with the highest aspect ratio can bridge more fibers together and increase bonding ability of BG fibers in the sheet. The BG/NFC-BC also showed the highest elongation (ability of the fiber network to stretch under load until breaking). Elongation is also a good measure of the toughness of paper [7].
enhancement was believed to mainly come from more areas of inter-fiber bonding and bridging within the sheet structure by NFC-BC [8].

**Table 2.** Tensile properties of pure BG sheet and BG/NFCs sheets.

| Samples       | Tensile index (Nm/g) | Breaking length (m) | Elongation (%) | Young’s modulus (MPa) |
|---------------|----------------------|---------------------|----------------|-----------------------|
| BG            | 28.6 ± 5.3           | 2914.0 ± 535.1      | 1.6 ± 0.3      | 3060.2 ± 592.1        |
| BG/NFC-BC     | 33.3 ± 3.9           | 3397.3 ± 400.8      | 2.8 ± 0.5      | 2764.4 ± 302.7        |
| BG/NFC-PA     | 31.8 ± 6.5           | 3246.4 ± 663.2      | 2.1 ± 0.7      | 3102.0 ± 220.4        |
| BG/NFC-BA     | 29.2 ± 2.8           | 2974.7 ± 282.0      | 1.9 ± 0.2      | 3421.0 ± 253.8        |

In case of Young’s modulus which defines rigidity or stiffness of the sheets, the BG/NFC-BA sheet exhibited the highest value (Table 2). The densest structure of this sheet possibly created the strong initial bonding of fibers. Thus, at the beginning of the test, the sheet would be hardly elongated, leading to the high modulus value. However, the low aspect ratio of NFC-BA (Table 1) resulted in an early failure of this sheet.

### 4. Conclusion

NFCs from different sources (i.e. BC, PA, and BA) were successfully prepared by using a microfluidizer. Different sources of cellulose resulted in NFCs with diverse morphology, dimension, and structure (revealed by TEM and XRD results). The prepared NFCs were used to reinforce in BG paper sheets and it was found that only 0.1wt% NFC addition can improve all tensile properties of the resulting sheets. This improvement confirmed that NFC is a highly efficient reinforcing element for use in papermaking industry. The BG/NFC-BA sheet with the highest density and smoothest surface (observed by SEM) exhibited to be the stiffest (Young’s modulus) sheet. On the other hand, the sheet integrated with NFC-BC, having the highest aspect ratio and crystallinity, was shown to have the highest strength (tensile index and breaking length) and toughness (elongation) followed by the BG/NFC-PA and BG/NFC-BA sheets, respectively. This can bring a conclusion that different NFCs characteristic clearly affected their reinforcing efficiency in the BG sheets. Therefore, a selection of suitable NFC sources for desired performance of papers and other related products has to be considered beforehand.

### 5. References

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### Acknowledgments

The joint funding support (grant code 256101A3070019) from the National Research Council of Thailand (NRCT) and National Science Technology and Innovation Policy Office (STI) is gratefully acknowledged. All supports and facilities from our industrial partner, the Biodegradable Packaging for Environment Public Co., Ltd. (Gracz) as well as Mae Fah Luang University (MFU) and the PLC Holding Co., Ltd., Thailand are also much appreciated.