Tailoring nanofibrillated cellulose through sonication and its potential use in molded pulp packaging

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ABSTRACT
Nanofibrillated cellulose (NFC) was systematically tailored by ultrasonic-assisted esterification with lactic acid at different amplitudes and times, which led to modified NFC (mNFC) with different degrees of substitution (DS), between 0.21 and 0.55, as confirmed by titration, FTIR, and C-13 NMR. A partial fragmentation and decrease in crystallinity of mNFC were revealed by TEM and XRD. To form molded pulp sheets, 5 wt% mNFC was added into a bagasse (BG) pulp slurry, then partially dewatered before hot-pressed. mNFC worked effectively as self-retention aid, partly solving the issue of drainage during sheet forming as commonly observed from unmodified NFC. The BG/mNFC (DS 0.55) sheet exhibited an enhancement in tensile properties. Water resistance and barrier performance of the current sheets were also evidently increased. The results suggested that the higher DS on mNFC can improve water resistance and mechanical properties, simultaneously overcoming drainage challenges in processing of molded pulp products.

GRAPHICAL ABSTRACT

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KEYWORDS
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1. Introduction

With the increasing awareness and concern towards sustainability, paper and pulp packaging from wood and non-wood resources has gained significant amount of attention lately to replace current petrochemical-based packaging materials [1]. To improve the performance of pulp packaging, the use of nanofibrillated cellulose (NFC) as strength additive has been widely investigated owning to its several unique properties, including the extremely large specific surface area, high aspect ratio, high strength, high stiffness, renewability, and biodegradability. Moreover, NFC could lead to a superior structure of paper packaging or self-binding all-cellulose construction materials with low porosity and low gas permeability [2–4]. However, during the pulp forming process, a lengthy dewatering step of the cellulose pulp/NFC slurry along with loss of NFC are hindering the scaling up of the process towards the industrial manufacturing [5]. Because of the same anionic character of charges on pulp and NFC, the
electrostatic repulsion prevents NFC integration in the network of pulp microfibers during drying. In addition, NFCs can block some pores of the network and eventually the draining flow channels, resulting in a reduced dewatering rate of the pulp/NFC slurry combined with a loss of NFCs. To overcome this problem, a selection of suitable additives has been proven an efficient strategy over last few years [6], with a range of retention aid additives such as cationic polyacrylamides (CPAM) [7–9] have been explored to promote the electrostatic attraction between NFC and pulp, hence to help retain NFC within the pulp network and reduce blockage of the water drain flow channels [10]. However, additional preparation steps are required when these additives are used, which increases manufacturing complexity, cost, and environmental impact [11].

With three hydroxy groups per repeating unit of cellulose on its surface, NFCs present anionic charges and preferably interact with water molecules by hydrogen bonding, which causes a low water resistance. Once the surface of NFC is chemically modified by substitution with other functional groups, the nature of NFC can be substantially altered [12]. Esterification is one of the important chemical modification techniques that have been extensively used to modify the structure of cellulose. This reaction introduces an ester functional group onto the surface of cellulose by condensation of esterifying reagents with cellulosic hydroxy or alcohol groups [13]. An attractive way to prepare “greener” esterified NFC is the modification reaction using fatty acids [14] owing to their renewability and biodegradability. In previous work, Sethi et al. [15] reported nanopapers with significantly decreased draining time and increased elastic modulus when cellulose nanofibers (CNFs) were modified with lactic acid [15,16]. However, the study on effect of degree of substitution (DS) or average number of sites reacted per anhydroglucose unit in cellulose [17], which in principle could greatly influence actions of modified CNFs, was not carried out.

In order to increase barrier properties of a paper or pulp packaging towards gas and moisture, it is typically laminated with synthetic polymer films such as polyethylene (PE). Although laminated pulp packaging shows good barrier properties, the synthetic polymer film is difficult to separate or degrade in the environment, making the whole packaging not truly sustainable [8]. Chemical modification of cellulose nanofibers has also been demonstrated to improve barrier properties of food packaging [18]. Hence, from this point of view, the use of modified NFCs is of great interest to tailor and advance properties of the pulp packaging, while keeping them fully sustainable [9].

The aims of this study are therefore; (i) to chemically modify NFCs using fatty acid (mNFCs) with a systematic variation of DS, (ii) to integrate mNFCs to a bagasse (BG) pulp and iii) to prepare and characterize modified nanopapers. The effect of mNFCs on draining time during sheet forming as well as surface morphology, physical and mechanical properties, and water resistance of the prepared BG/mNFC sheets were investigated and compared with the pure BG, BG/NFC, and BG/NFC + CPAM sheets.

2. Experimental

2.1. Materials

The bleached bagasse (BG) paper was kindly supplied by Biodegradable Packaging for Environment Public Co., Ltd., Thailand. Cationic polyacrylamide (CPAM) was supported by Welkin Enterprise, Thailand. Nanofibrillated cellulose (NFC) prepared from bleached softwood was purchased from Cellulose Lab Co., Canada. L-[(+)-lactic acid (LA) (80% w/v) was purchased from Union Science, Thailand.

2.2. Preparation of modified NFC (mNFC) with different degree of substitution (DS)

The NFC stock solution was prepared to 0.4 wt% suspension and then 4.4 wt% LA loading content (according to the unmodified NFC dry content) was added. The suspension (~50 mL) was stirred at 400 rpm for 5 min using a homogenizer and sonicated with a 750 W and 20 kHz ultrasonic probe (VCX750, Sonics Materials Inc., USA) with a probe diameter of 13 mm to different amplitude percentages (30%, 50%, 70% and 90%) and time (10 to 60 min) for the anticipating different DS from varied ultrasonication energy input [19]. Then, all suspensions were kept in the oven at 100 °C for 36 h, detailed steps can be found in Sethi et al. [15,16]. The obtained mNFCs at different amplitudes (mNFC30, mNFC50, mNFC70, and mNFC90) were characterized and analyzed in terms of the DS, structure, and morphology.

2.3. Preparation of molded sheets and NFCs and mNFCs modified molded sheets

BG pulp was used as a base material to prepare molded sheet samples. The small pieces of BG paper were soaked in tap water overnight, and then defibrillated into a pulp slurry by using a kitchen blender (House Worth, HW-BDC2PC) at the speed of 15,000 rpm for 5 min. After that, the unmodified NFC or mNFC solution with 5 wt% loading content (according to the dry BG pulp weight) was added to the BG slurry (2% pulp consistency). Then, the BG/NFC and BG/mNFC mixtures were blended at the speed of 450 rpm for another
minute before pouring each mixture into a circular mold (diameter of 16 cm) with metal meshes (no. 400) to partially dewater and preform the sheet. Next, the mold set was hot-pressed at 130 °C under the pressure of 159 kPa for 5 min. The system of BG/NFC sheet with addition of a typical retention aid additive CPAM was also prepared for comparison. The 0.05 wt% CPAM solution was added into the BG/NFC slurry at the loading content of 0.15 wt% based on the dry BG pulp weight, then preformed and hot-pressed to obtain the BG/NFC + CPAM sheet. This CPAM loading content was chosen based on previous works [17,18] that showed high dewatering efficiency of more than 50% during sheet forming. A blank (or pure) BG sheet without addition of neither NFC nor CPAM was also made for comparison, following the same procedure. All molded sheets prepared were aimed to be about 350 g/m² and their sample codes and compositions were summarized in Table 1.

2.4. Characterization

2.4.1. Fourier-transform infrared spectroscopy (FTIR)

About 2 mg of each NFC and mNFC solid sample was manually ground with KBr powder (a ratio of 1:100) and then pressed into a circular pellet (10 mm diameter). FTIR spectroscopic analysis of the samples was performed by Perkin Elmer (Model spectrum GX, USA) with a resolution of 4 cm⁻¹ and a scanning range from 500–4000 cm⁻¹ [21].

2.4.2. Degree of substitution (DS) determined by titration

A solid sample of 0.5 g was added to 40 mL of aqueous ethanol (70%) and stirred with a magnetic bar at 400 rpm for 30 min. Stirring was continued for 48 h at 50 °C, after addition of 20 mL of a 0.5 M NaOH solution. Afterward, the unreacted NaOH was back-titrated with a 0.5 M HCl solution and the ester content (EC) was calculated using the following equation:

\[
EC(\%) = \frac{\left[ (V_d - V_b)\times N_b - (V_d - V_c)\times N_a \right] \times M_w}{10 \times G}
\]

where \(V_d\) and \(V_b\) represent the volumes (mL) of a strong base (NaOH) solution added to sample and blank, respectively, \(V_d\) and \(V_c\) are the volumes (mL) of strong acid (HCl) added to sample and blank, respectively, \(N_b\) and \(N_a\) are the respective the concentration (molarity) of NaOH and HCl solutions, \(M_w\) is the molecular weight of acid reagent and \(G\) is the weight (g) of the sample. DS was then calculated by the following equation [20]:

\[
DS = \frac{162 \times EC}{M_w \times 100 - EC \times M_w - 1}
\]

where 162 is the molecular weight of anhydroglucose monomer unit.

2.4.3. Solid-State \(^{13}\text{C}\) nuclear magnetic resonance (NMR)

Solid-state \(^{13}\text{C}\) cross polarization-magic angle spinning (CP-MAS) NMR spectra of both NFC and mNFC were recorded at room temperature on a Bruker Avance III HD/Ascend 400 WB, USA using a MAS rate of 5 kHz, a contact time of 500 μs, at a frequency of 100.61 MHz. Samples were packed in MAS 4 mm diameter zirconia rotors and all spectra were run for 3 h [21].

2.4.4. X-ray diffraction (XRD)

XRD was used to determine the crystallinity of both NFC and mNFC (X’Pert Pro MPD, UK). The X-ray diffraction patterns were recorded in a 2θ angle range of 10° to 40° at a step width of 0.02° with a scan speed of 2°/min. The crystallinity index (CI) of the samples was calculated using Segal’s equation below [22]:

\[
CI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100
\]

where \(I_{002}\) is the maximum intensity of the 002 lattice diffraction at \(2\theta = 22^\circ\) and \(I_{am}\) is the intensity of amorphous cellulose at \(2\theta = 18^\circ\).

2.4.5. Transmission electron microscope (TEM)

A 0.001% suspension of both NFC and mNFC (X’Pert Pro MPD, UK) was prepared and sonicated in a bath with power of 73 W (Crest Ultrasonics, 690HTAE, NY, USA) for 2 min, then a 2% uranyl acetate (UA) solution was added for contrast enhancement in TEM micrographs. A drop of the suspension was deposited on a copper grid with Formvar film (200 mesh—Ted Pella) and allowed to dry in a desiccator for 24 h before examination at the acceleration voltage of 80 kV (Hitachi, HT7700, Japan).

Table 1. The sample code and composition of all molded sheets prepared in this study.

| Sample code | Conc. BG suspension (%w/w) | NFC loading contents (%) | mNFC loading contents (%) | CPAM loading contents (%) |
|-------------|----------------------------|--------------------------|--------------------------|--------------------------|
| BG          | 2                          | –                        | –                        | –                        |
| BG/NFC      | 2                          | 5                        | –                        | –                        |
| BG/mNFC30   | 2                          | –                        | 5                        | –                        |
| BG/mNFC90   | 2                          | –                        | 5                        | –                        |
| BG/NFC + CPAM | 2                      | 5                        | –                        | 0.15                      |
2.4.6. Drainage test
To evaluate the draining ability of the slurries or suspensions of BG, BG/NFC, BG/mNFC and BG/NFC + CPAM, each sample was diluted to 0.2 wt% solid content and mixed by a homogenizer for 5 min (according to TAPPI T221). Then, water was drained off the suspension under a vacuum through a 0.45 μm Durapore PVDF membrane filter. A standard stop-watch was used to record the draining time (sec) which was assumed to be completed when the time difference between the consecutive drops falling from the glass funnel connected with a vacuum was more than 30 sec.

2.4.7. Scanning electron microscopy (SEM)
The surface morphology of molded sheet samples were observed at an accelerating voltage of 10 kV by using SEM (LEO/1450 VP, USA). All samples were cut into 5 mm × 5 mm and coated with gold before observed.

2.4.8. Grammage and density measurement
The grammage of prepared sheets were measured in unit of gram per square meter (g/m²). Each molded sheet was prepared into a size of 150 mm × 150 mm before pre-conditioned at room temperature (RT), 50% relative humidity (RH), for overnight before weighing (TAPPI T410). Five random positions of samples were measured for thickness using a digital Vernier caliper. Then, the average density values of the sample sheets were calculated by its weight and dimension (mass/volume).

2.4.9. Tensile testing
Testing was performed according to TAPPI T494 by using a universal testing machine (Instron Model 5566, USA, 1 kN load cell equipped). The sheet samples with a size of 1.5 cm × 8 cm and gauge length of 5 cm were pre-conditioned at 50% RH and 25°C overnight before the test. The testing speed of 7 mm/min was applied and at least 7 specimens were tested for each sample. The average tensile strength (UTS), modulus of elasticity (MOE), and elongation at break (EAB) of the sheet samples were evaluated subsequently from the test results.

2.4.10. Water vapor transmittance rate (WVTR)
The WVTR of all sheet samples were evaluated according to ASTM E96/E96M procedure. Each sample sheet was cut into circles of approximately 8 cm diameter and mounted onto a circular aluminum cup. Beforehand, 10 g of desiccant silica gel was added to the cup. Bees wax was used to fixate the sheet sample tightly against the cup. After that, each sample cup was weighed for the first time with an analytical balance and then placed in a vacuum desiccator chamber under testing conditions of 25°C and 70% RH with a continuous air circulation. Weighting was repeated until constant weight to determine the amount of vapor transferred into the desiccant. WVTR was later calculated from the following equation:

\[
WVTR = \frac{W_v}{t \times A}
\]

where \(W_v\) is the amount of water vapor (g), \(t\) is the time (days), and \(A\) is the sheet area (m²).

2.4.11. Water contact angle
The surface wettability of each sheet sample was estimated by contact angle measurement (KINO, SL200KS, USA). The sheets were cut into small pieces of about 10 mm × 10 mm. A droplet of water (5 μL) was then deposited on the specimen surfaces and the contact angle was measured at 0.1 sec after drop deposition. To reduce a possible influence of the surface heterogeneity, a minimum of ten readings were taken on each sample.

2.4.12. Statistical analysis
The analysis of variance (ANOVA) was used to analyzed the data and values of \(p < 0.01\) were considered statistically significant.

3. Results and discussion
3.1. Tailoring NFC at different sonication amplitude and time: degree of substitution, chemical structure, crystallinity, and morphology
In this work, NFC was modified via esterification reaction using lactic acid. The change in chemical structure after modification was confirmed by FTIR spectra in Figure 1. The unmodified NFC showed the characteristic bands corresponding to the stretching mode of C-H of hydrocarbon at 2086 cm⁻¹ [23]. For both NFC and mNFC samples, a broad characteristic absorption peak of O-H at 3336 cm⁻¹ can be found, attributing to the stretching induced by hydrogen bonds, while a small peak at 2901 cm⁻¹ was observed, corresponding to the stretching vibration of methyl and methylene C-H bonds in cellulose. The characteristic bands at 1642 and 899 cm⁻¹ denoted the vibration of H-O-H absorbed water molecules and β-glycosidic linkages between glucose units, respectively. Upon NFC esterification, a strong stretching vibration peak at 1745 cm⁻¹ (assigned to ester C=O moieties) appeared in all mNFC samples, confirming the successful modification of NFC after esterification process. With the increase of sonication amplitude during reaction (percentage from mNFC30 to mNFC90), the relative intensity of the ester peak
gradually increased. Also, the intensity of the band corresponding to asymmetric bending of CH$_3$ appeared at 1370 cm$^{-1}$ and the bands appeared at 1229, 1118 and 1031 cm$^{-1}$ representing symmetric and asymmetric of C-O-C stretching modes were found to increase [24]. Furthermore, a reduction of the intensity of the band associated with the vibration of OH groups (at 3336 cm$^{-1}$) implied the substitution or replacement of a fraction of hydroxy groups that took place in the mNFC samples.

The degree of substitution (DS) of all mNFCs are presented in Figure 2, with sonication energy calculated based on various sonication amplitudes and times employed during the reactions. With 10 min sonication time, the DS of mNFCs increased linearly with increasing sonication amplitude percentage from 0.21, 0.34, 0.41 to 0.55 for mNFC30, mNFC50, mNFC70, and mNFC90, respectively. This implies that the increase in reaction amplitude or energy has led to an increase in cavitation during reaction, leading to activated reagents and enhanced chemical reactivity [25–28]. In addition, with increased sonication energy, NFC might become finer hence having a higher specific surface area with increased amount of OH groups accessible for esterification reaction. When the amplitude is fixed at 90% and the sonication time was increased to 30 and 60 min, the calculated energy for the reaction increased tremendously, however, the DS was found to be slightly decreased. This is believed due to the lengthen reaction or excessive sonication which might cause a reverse in the esterification reaction of NFC [25] while the NFC might get damaged during the course of the reaction.

The proposed mechanism of the NFC modification reaction is shown in Figure 3. With the applied energy from sonication, initially, hydroxy radicals are generated from water molecules which can then further react non-selectively. The hydroxy radicals can capture hydrogen atoms on both lactic acid and NFC, leading to generation of radicals on lactic acid and NFC structures. When both radicals react, the esterification occurs and then propagates which possibly creates oligomer of lactic acids on the surface of NFC as later suggested by C$^{13}$ NMR (Figure 4) [29,30]. Three hydroxy groups in the cellulose structure including the primary hydroxy group at C6 and secondary hydroxy groups at C2 and C3 can all possibly participate in the esterification reaction [31]. However, the hydroxy group at C6 in the repeating unit of cellulose is expected to be the most reactive site for the reaction, since only C6 hydroxy are oriented outwards from the surface of the nanofibers [32]. Between secondary hydroxy groups of C2 and C3, the secondary hydroxy group of C2 might also have a higher possibility to participate in the reaction than that of C3 as a result of the intramolecular hydrogen bonds formed at the position of C3 hydroxy groups [33].

The solid-state $^{13}$C-NMR spectra of unmodified NFC and mNFCs prepared at different sonication amplitudes and times determined by a back-titration method.
amplitudes (mNFC30, mNFC50, mNFC70, and mNFC90) are shown in Figure 4(A–C). All samples showed the signals at δC 106.5, 70.1, 72.5, 88.5 and 66.5 ppm which were assigned to the carbon peaks on the glucose rings at C1, C2, C3, C4, C5 and C6, respectively [27]. In the mNFC30 (DS 0.21) and mNFC50 (DS 0.34) spectra (Figure 4(B)), the new peaks of three carbonyl carbons (C=O) at δC 169.4, 173.6 and 175.5 ppm can be found, while the overlapping chiral methine carbons (CH) of lactide with those of NFC were shown at δC 69.7 ppm and the methyl groups (CH3) appeared highfield at δC 16.7 and 20.0 ppm [28]. These results further confirmed the successful esterification process of the mNFC. Since the methyl group of lactic acid should only appear as a singlet at around δC 16.7 ppm, these two methyl signals at δC 16.7 and 20.0 ppm suggested the presence of oligomer of lactic acids in these mNFC samples. On the other hand, for the mNFC70 (DS 0.41) and mNFC90 (DS 0.55) samples (Figure 4(C)), the carbonyl carbons were observed with four positions at δC 169.4, 173.6, 175.5 and 178.2 ppm. The stronger overlapping peaks of chiral methane carbons and methyl groups, however, appeared at the same positions as did in the spectra of mNFC30 and mNFC50. This result indicated that not only DS of mNFCs was increased with increasing sonication amplitude during the reaction but also the length of lactic acid oligomers substituted on the current mNFCs [34,35].

Figure 3. Proposed mechanism for the esterification of NFC with lactic acid in water medium, accelerated by sonication energy.

Figure 5. The XRD patterns obtained from NFC and mNFCs are shown in Figure 5. All samples exhibited the typical diffraction of native cellulose I at the main angle (2θ) at around 22° (002)). When the sonication amplitude percentage used in reaction to prepare mNFCs increased, a clear decreasing and broadening trend of all peak intensities were observed. From the titration results, it was found that when the higher sonication amplitude was used, the mNFCs with higher DS were obtained ranging from DS of 0.21 (mNFC30) to DS of 0.55 (mNFC90). This clearly indicated that the more substituted units on mNFC chains, the more cellulose crystalline structure was disrupted and then converted to amorphous phase. In addition, it was possible that the hydrodynamic forces associated with ultrasound during sonication could do damage to the crystalline domains of mNFC samples [36,37]. The crystallinity index (CI) calculated from their diffractograms was also shown to be decreased gradually with increasing sonication energy. A similar decline in CI of cellulose nanocrystals (CNCs) dispersed in aqueous PVA matrix as ultrasonication treatment time and amplitude increased was reported by Shojaeiarani et al. [19].

From TEM images in Figure 6, the unmodified NFC (Figure 6(A)) showed a typical characteristic of long fibrillated cellulose nanofibers. After the sonication-assisted modification reaction, the morphology of the mNFC nanofibers appeared to change progressively. For the mNFC30 sample, the fibrillated portions around the main nanofibers were largely removed and became more like individual nanofibers with clean surfaces (Figure 6(B)). At higher sonication energy condition (mNFC90), rod-like small fragments were observed together with the main cellulose nanofibers (Figure 6(C)). This suggested that the sonication power not only disrupted crystalline region in mNFCs but also induced the shearing stress which led to a partially hydrolysis of cellulose...
and size-reduced the nanofibers into smaller fragments [38]. As a result, the initial crystal structure of NFC was therefore diminished to certain extent, in agreement with the XRD results as presented earlier.

3.2. Integration of NFC, mNFCs, and CPAM + NFC in molded pulp sheets: draining time, morphology, physical, mechanical, and water resistance

To form a molded pulp, the draining of water from the pulp slurry using vacuum assisted system is required before hot-pressing the dewatered pulp into a desired shape. In this study, when NFC (5 wt%) was added into the BG pulp slurry, a substantial delay in drainage was recorded (Figure 7(A)). This is due to an extremely high specific surface area of NFC containing numerous hydroxy groups, resulting in extremely high level hydrophilicity with extensive interactions with water molecules [39,40]. Moreover, anionic charges on both NFC and BG cellulose pulp creates an electrostatic repulsion that pushes away NFC from the network of BG pulp fibers [41,42]. As a result, a major portion of NFC mitigated with the draining flow and

Figure 4. Solid-state $^{13}$C-NMR spectra of (A) NFC; mNFCs prepared at (B) 30% and 50% sonication amplitude and (C) 70% and 90% amplitude. The structural formula shows the characteristic carbons of the anhydroglucose unit in cellulose (NFC) and the appearance of characteristic carbon of $\equiv O$, CH and CH$_3$ indicating the lactic acid substitution in mNFC samples.
started to block porous structures of the water flow channels, delaying the drainage process (Figure 7(B)). In the real production or manufacturing molded pulp packaging which normally is in a many million pieces per day scale, if the forming and dewatering time (one of the main step processing times) increases to double, the production rate could be seriously declined [43]. Furthermore, during the vacuum drainage process, certain amounts of NFCs could be forced to penetrate through the filtering layer, hence leading to a partial loss of NFC contents in the final BG/NFC molded sheets.

With mNFCs addition, the draining time was evidently reduced as compared to the NFC system. This is believed due to the lactic acid oligomers on mNFC surfaces which can provide a bulky effect to expand the flow channels for drainage (as illustrated in Figure 7(B)). These substituted oligomers are more hydrophobic than hydroxy groups, leading to a reduced water bonding capability [44]. As expected, the mNFC90 with more substituted ester groups (DS 0.55) and longer oligomer chains showed a greater effect on drainage than the mNFC30 (DS 0.21), with a much shortened drainage time of 10 s only. On the other hand, the addition of CPAM also showed a positive outcome on drainability of the BG/NFC system. This was attributed to the positive charge of CPAM that can bind NFC to the BG pulp fibers and thus enable the retention of NFC in their microfiber network, providing the flow pathways for water to drain off [45].

After forming molded pulps, the surfaces of the prepared sheet samples were observed. As shown in Figure 8, the pure BG sheet surface (Figure 8(A)) showed typical micro-sized cellulose fiber morphologies with certain overlapping as well as some gaps between microfibers and bundles. With the addition of NFC (5 wt%), traces of finer networks of possible fibrillated nanofibers were obtained on the surface of the BG/NFC sheet (Figure 8(B)). On the other hand, the surfaces of the BG sheets integrated with either mNFC90 or NFC + CPAM were found to be much smoother and denser with less porous features when compared to the previous sheets. It seemed that, for these two sheets (Figure 8(C,D)), mNFC and NFC could be retained more on their surfaces so the nanofiber networks bridged the microfibers, therefore, filling and closing those gaps [46,47].

From Table 2, both the areal weight and density of the BG-based sheets shown a slight increase with addition of 5 wt% of NFC. At the same content of mNFC, the grammage and density slightly increased with higher amplitude of sonication process, further indicating an increase in the final solid content and confirming the retention of added nanofibers in these sheets [48]. With these increased sheet densities, an expected improvement in tensile strength (UTS) of around 10 MPa based on a typical strength of cellulose nanopaper (~200 MPa) and composite rule of mixture (ROM) was obtained only in BG/mNFC sheets [49,50]. This is attributed to the retained nanofibers which can promote the contact areas between BG microfibers and increase the number of hydrogen bonding (inter-fiber bond density) and inter-fiber bond strength within the structures, facilitating stress transfer in cellulose networks and providing reinforcement to the sheet.
properties [51–53]. Although the mNFCs were modified or partially substituted with ester groups which can lead to a slightly reduced hydroxy groups, the tensile properties of the BG/mNFC sheets were significantly higher than those of the BG/NFC sheet, confirming the remaining content of nanocellulose in the sheets should be predominant. The obtained improvement levels of mechanical properties are in good agreement with literature reporting paperboards with the addition of CNFs and modified CNFs (10 wt%) [15]). Nonetheless, the modulus of elasticity (MOE) of current mNFC integrated BG sheets were not reached an expectation (~1 GPa increment) considering the 5 wt% mNFC addition and possible contribution from a typical cellulose nanopaper’s modulus (~20 GPa). The plausible explanation should involve the larger degree of deformation (strain) allowed from segment motion of molecules in amorphous region of nanocellulose fibers in these mNFC integrated samples. However, the deformation degree of cellulose nanopapers is still restricted since slippage and large scale reorientation of cellulose nanofibers in the network were not likely to occur in a dry state [50].

When CPAM is added into the system with NFC, the density of the BG/NFC + CPAM sheet was increased slightly (Table 2). Its tensile strength and modulus were also found to increase in comparison

Figure 6. TEM images of (A) NFC, (B) mNFC30, and (C) mNFC90, the fragmented parts from the main nanofibers indicated by black arrows. Partial enlargements of (A), (B), and (C) are in the right column.
Figure 7. (A) Comparison of drainage time in the different systems; BG pulp slurries with NFC, mNFCs, and NFC + CPAM. The values represent means ± SD of four replicates. Means with different letters indicate the statistically different data groups based on ANOVA test ($p < 0.01$). (B) Schematic illustrations demonstrating the effect of NFC, mNFC, and CPAM additions on dewatering process of the slurries during vacuum filtering.

Figure 8. SEM photographs of the surfaces of (A) pure BG sheet, (B) BG/NFC, (C) BG/mNFC90, and (D) BG/NFC + CPAM. The circles indicate the retaining NFC and mNFC that bridges between the BG microfibers and fills up gaps on the sheet surfaces.
to the BG/NFC sheet. Among all samples in this study, the highest elongation at break of the sheet with CPAM addition was observed. This enhancement is believed to originate mainly from a characteristic of the CPAM polymer structure which increases free volume and, hence, degree of flexibility of the sheet [54]. In addition, the bridging between NFC-CPAM-BG microfibers might not be as strong as the secondary bonding between NFC-BG or mNFC-BG networks, therefore, allowing more deformation before breaking and a good measure of the sheet toughness [55].

Water resistance of pulp products or surfaces is usually low due to the high affinity of cellulose structure towards water molecules. So, when adding NFC into the BG pulp sheet, the water resistance of the BG/NFC sheet surface or water contact angle was reduced (Figure 9(A)). This is due to the hydrophilic nature of NFC together with its exceedingly high surface area [56]. The addition of CPAM into the BG/NFC sheet increased the contact angle from 26° to 39°. One reason is because CPAM or cationic polyacrylamide is more hydrophobic than NFC [57]. Moreover, this polymer additive resulted in a denser sheet surface as seen in the SEM images (Figure 8).

For the BG specimens with integration of mNFCs, the existence of hydrophobic substituted groups of ester oligomer chains on the nanocelluloses led to a clear effect on the surface water resistance of the BG/mNFC sheets. A contact angle of 52° was obtained, showing an over 70% increase compared with pure BG specimens. As expected, higher contact angles were obtained from mNFC90 with higher DS than the mNFC30. The water vapor transmittance rate (WVTR) results are presented in Figure 9(B), showing a good agreement with the water contact angle data. After statistical analysis, it was found that only the BG/mNFC90 sheet had a significant improvement in water vapor barrier properties ($p < 0.01$) when compared to the other sheets. Thus, it should be noted that the degree of modification or ester group substitution on NFC is rather important when water barrier properties of the sheets are relevant to applications.

### Table 2. Grammage (GSM), density ($\rho$), ultimate tensile strength (UTS), modulus of elasticity (MOE), and elongation at break (EAB) of the sample sheets.

| Sample code | GSM (g/m²) | $\rho$ (g/cm³) | UTS (MPa) | MOE (GPa) | EAB (%) |
|-------------|------------|----------------|-----------|-----------|---------|
| BG          | 352        | 0.74 ± 0.02    | 28.36 ± 2.82 | 3.07 ± 2.75 | 1.67 ± 0.15 |
| BG/NFC      | 354        | 0.78 ± 0.03    | 31.70 ± 2.65 | 3.15 ± 1.44 | 1.86 ± 0.19 |
| BG/mNFC30   | 357        | 0.81 ± 0.04    | 37.32 ± 1.98 | 3.28 ± 1.79 | 2.23 ± 0.27 |
| BG/mNFC90   | 359        | 0.84 ± 0.03    | 39.12 ± 1.13 | 3.31 ± 2.98 | 2.60 ± 0.35 |
| BG/NFC+CPAM | 358        | 0.80 ± 0.02    | 35.59 ± 2.60 | 3.26 ± 2.61 | 3.43 ± 0.18 |

Superscript letters indicate significant differences between data groups with a 99% significant confidence limit ($p < 0.01$).

4. Conclusions

In this work, nanofibrillated cellulose (NFC) was modified by esterification using a sonication-assist method, with systematic characterization performed including FTIR and C$^{13}$ NMR to confirm the degree of substitution. It was shown that the sonication amplitude (30%-90%) and time (10–60 min) used for the reaction influenced the degree of ester group substitution on NFC and also the length of oligomeric substituents. High sonication energy led to a partial fragmentation and a decrease in crystallinity...
of modified NFC or mNFC as revealed by TEM and XRD results. From back-titration, it was found that a lengthy reaction time could also result in a reversed reaction, with damaged NFC and lower the DS of mNFCs.

When mNFCs were integrated into the BG pulp slurries, the drainage problem during sheet forming as commonly occurs in systems based on NFC was successfully overcome, achieving a similar high efficiency of adding extra retention aid additives (CPAM). After forming the molded sheets, the sheets integrated with mNFCs and NFC+CPAM retained more nanocellulose fibers on both surfaces and internal structures, leading to a denser structure with enhanced mechanical properties. Increased water contact angles were also observed in mNFC specimens, showing improved surface resistance to water thanks to the substituted ester groups on mNFC. It is worth noting that only the sheet integrated with mNFC90 (DS 0.55) demonstrated a significantly lower water vapor transmission rate than the other samples, indicating that a sufficient level of the degree of NFC modification by esterification is essential for water vapor barrier properties of the molded pulp products.

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Disclosure statement

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Authors contribution

Supattra Klayya: Formal analysis, Investigation, Methodology, Validation, Visualization, Writing—Original Draft. Nattaya Tawichai: Resources, Validation. Uraiwan Intatha: Formal analysis, Funding acquisition. Nattakan Soykeabkaew: Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing—Original draft & Revision. Emiliano Bilotti: Funding acquisition, Writing—Original draft & Revision. Han Zhang: Funding acquisition, Writing—Original draft & Revision.

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