

Nanofibrillation of a Bleached Acacia Pulp by Grinding with Carboxymethylation Pretreatment

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Abstract: In this study, carboxymethylation, which introduces carboxyl groups to hydroxyl sites in pulp fibers, was used as a pretreatment before mechanical nanofibrillation. The carboxyl group content of the pulp fibers was greatly affected by the dosage of chloroacetic acid and the reaction temperature. During the following fibrillation process, it was found that pulp fibers with higher carboxyl group content exhibited higher water holding capacities and smaller dimensions. A more homogenous structure with a higher amount of individual fibrils was also observed in FE-SEM images of pulp fibers with high carboxyl group content. This can be explained by a high ionic group content in the fiber wall resulting in lower delamination resistance, making the fibrils easier to separate. Carboxymethylation pretreatment as a facilitator of fibrillation in cellulosic pulps is an efficient way to obtain cellulose nanofibrils and consequently decrease the energy consumption of the process.

Keywords: nanofibrillation; grinder; carboxymethylation; pretreatment; bleached acacia pulp

1 Introduction

Cellulose is the most abundant renewable natural biopolymer on earth, and can be derived from a variety of sources including plants, animals, and some bacteria^[1]. With increasing demand for environmentally friendly products as well as an increasing interest in nanotechnology, the development of novel cellulosic materials with at least one dimension at the nanoscale has received considerable attention^[2]. Due to the hierarchical structure of cellulose, it is possible to obtain nanocellulose by breaking down the cell wall into nanoscale cellulose with different morphologies according

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to the extraction method. The two main types of nanocellulose are cellulose nanocrystal (CNC) and cellulose nanofibril (CNF). CNC is obtained from fibers after a complete hydrolysis of the amorphous regions, while CNF is produced mainly through an intensive mechanical shearing action to break the cell walls of fibers and release cellulose fibrils in the form of bundles of elementary fibrils^[3].

CNF is currently manufactured from a variety of cellulosic sources. Wood is obviously the most important industrial source of cellulosic fibers, and thus the main raw material used to produce CNF. Bleached kraft pulp is most often used as a material for CNF production^[4-5]. Generally, CNF or cellulose microfibrils (CMF) can be produced by mechanical disintegration, such as refining or high-pressure homogenization^[6], microfluidization^[7], grinding^[8-9], or high-intensity ultrasonication^[10].

Although the chemical composition and high aspect ratio of cellulose fibrils can be preserved, these methods require high energy input. In order to fibrillate fibers effectively, many researchers use oxidative or hydrolytic methods (carboxylation, sulfonation, TEMPO oxidation, etc.) to swell fiber and break down the cell wall, followed by mechanical treatment. By these methods, the properties of the fibrils such as their size and surface charge can be modified^[11].

The introduction of negatively charged (e.g., carboxyl or carboxymethyl) groups on cellulosic fibers is known to improve delamination of the nanofibrils. This is due to electrostatic repulsion between the negatively charged cellulose nanofibrils. Carboxymethylation is one of the chemical pretreatments which can introduce ionic groups to fibers. It was reported that carboxymethylation pretreatment induces electrostatic repulsion between fibers, enabling disintegration of fibers into fibrils^[12]. Wågberg et al reported using high-pressure homogenization of carboxymethylated cellulose fibers followed by ultrasonication and centrifugation to remove the residual non-fibrillated fibers^[13]. The nanofibrillated cellulose particles were cylindrical in

shape with a diameter of 5~15 nm and a length of up to 1 μm ^[13]. It was also reported that the resulting CNF had slightly lower and more uniform dimensions compared to those of enzymatically pretreated CNF^[14]. Siro et al indicated that the films produced by homogenized carboxymethylated cellulose had high transparency^[15].

The aim of this work is to investigate the influence of carboxyl group content introduced by carboxymethylation pretreatment on CNF production efficiency, evaluated by degree of fibrillation and consumption of energy. To accomplish these goals, the degree of CNF fibrillation was quantified by the apparent viscosity, water retention value (WRV), and particle size distribution of CNF suspensions. Furthermore, changes in morphology during the fibrillation process were analyzed by scanning electron microscopy (SEM).

2 Experimental

2.1 Materials

A commercial bleached acacia pulp (April, Indonesia) with a cellulose content of 81.7% (determined according to TAPPI standard 203 cm-09) and a hemicellulose content of 16.5% (measured as solubility in 17.5% NaOH) was used as the raw material for this study. Chloroacetic acid (ClCH_2COOH , 99.0%, Sigma-Aldrich), acetic acid (CH_3COOH , 99.5%, Sigma-Aldrich), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.9%, Duksan Reagents), isopropanol ($\text{CH}_3\text{CHOHCH}_3$, 99.5%, Duksan Reagents), methanol (CH_3OH , 99.8%, Duksan Reagents), and sodium hydroxide (NaOH, 98.0%, Duksan Reagents) were used for carboxymethylation treatment.

2.2 Carboxymethylation treatment

The acacia pulp fibers were disintegrated with a laboratory disintegrator at 1% consistency for 5 min and beaten to 450 mL CSF by using a Valley beater before pretreatment. Then the pulp fibers were dispersed in deionized water and solvent-exchanged to ethanol 3 times. The fibers were impregnated with a solution of monochloroacetic acid in isopropanol for

30 min. The fibers were added to a NaOH solution in methanol and isopropanol with agitation for 30 min. In order to investigate the effects of chloroacetic acid dosage and reaction temperature on the carboxyl group content of the fibers in the carboxymethylation pretreatment, the conditions chosen were 1 and 3 mmol/g chloroacetic acid, and temperatures of 55°C and 65°C. After the carboxymethylation step, the fibers were washed repeatedly with distilled water until the pH value was (7.0 ± 0.5) and the electrical conductivity was 30 $\mu\text{S}/\text{cm}$ or less. A conductometric titration method (SCAN-CM 65:02) was used for quantitative analysis of the carboxyl groups ($-\text{COOH}$)^[16].

2.3 CNF production

A grinder (Supermasscolloider MKCA6-2, Masuko Sangyo, Japan) was used for fibrillation. This grinder is equipped with a power meter to record electrical energy input. Pulp feeding was achieved by gravity. The rotational speed was set to 1800 r/min, and the gap of the two disks was adjusted to $-150 \mu\text{m}$ from motion zero position after the pulp was loaded. The fibrillated pulp suspension was discharged by centrifugal force and sampled after 5, 10, and 15 passes.

2.4 Characterization of CNF

2.4.1 Apparent viscosity

The apparent viscosity of the manufactured CNF was measured with a Brookfield RVDV-II viscometer (Brookfield AMETEK, USA) as described by He et al^[17]. The standard method is based on vane geometry, which is widely recommended for paste-like materials, gels, and fluids. All CNF samples were diluted to a concentration of 1% beforehand, then were measured at 20 r/min by a Vane-spindle (V73). The sample temperature was maintained at 25°C by a laboratory water bath.

2.4.2 Water retention value

A modified water retention value (WRV) measurement was used in estimating the water holding capacity of CNF. The method was developed from the SCAN-C 62:00 standard. The WRVs of pulp samples were determined as WRV_0 in advance, then a mixture of 90%

raw pulp with 10% CNF produced from it was held in a glass filter (1G4). The mixture was centrifuged at 3000g for 15 min. The WRV (g/g) of the CNF is calculated from the measured WRV of the mixture as shown below:

$$\text{WRV}_{\text{CNF}} = \frac{\text{WRV}_{\text{mix}} - 0.9\text{WRV}_0}{0.1}$$

An average of five measurements was reported.

2.4.3 Field emission SEM analysis

The collected CNF samples were vacuum filtered at a pulp consistency of about 0.1% using a polytetrafluoroethylene membrane filter (0.2 μm mesh) and the water in the wet mat was replaced by t-butanol, then the samples were freeze-dried using a freeze-dryer (ALPHA 1-2 LD, Christ Co., Ltd., Germany). The morphologies of CNF samples were observed by a Field emission scanning electron microscope (FE-SEM, S-4300/HITACHI, Japan) operated at a voltage of 5.0 kV. Before SEM observation, the samples were coated with a 1 nm layer of osmium by using an osmium plasma coater (NEOC-AN, Meiwa Fosis, Tokyo, Japan).

2.4.4 Particle size distribution

The particle size distribution of CNF samples was determined by using a laser diffraction analyzer (Mastersizer-ZS90, Malvern Instruments Ltd., England). This technique allows the analysis of particles in the size range between 0.3 nm and 10 μm . The intensity of size distributions was obtained from analysis of the correlation function using the CONTIN algorithm in the instrument software. A very dilute suspension, approximately 0.01% pulp consistency, was prepared by dispersing the sample with an ultrasonic homogenizer (HD 2200, BANDELIN Electronic Co., Germany) for 10 s. Three measurements of 100 s each were taken and averaged and the results were an average of five replicated measurements.

3 Results and discussion

3.1 Carboxyl group content of pulp fibers

The pulp fibers were modified by carboxymethylation

pretreatment, using various chloroacetic acid dosages and reaction temperatures, before nanofibrillation. In order to evaluate quantitatively the degree of substitution of carboxyl groups, a conductometric titration was carried out as shown in Table 1. For easy understanding, four experiments with different reaction conditions were labeled as samples A, B, C, and D. The carboxyl group content of pulp fibers increased with an increase in either the chloroacetic acid dosage or the reaction temperature. The untreated pulp in this work was measured to have an carboxyl group content of about 50 $\mu\text{mol/g}$, due to the presence of hemicellulose in the pulp^[18].

Among the four types of carboxymethylated pulp fibers, sample A had the lowest degree of substitution, with a carboxyl group content of 245 $\mu\text{mol/g}$, while sample D had the highest degree of substitution with a carboxyl group content of 485 $\mu\text{mol/g}$. To evaluate the effect of carboxyl group content on CNF production efficiency, sample A was chosen to represent low carboxyl group content fibers, and designated L-CM, while sample D was chosen to represent the high carboxyl group content fibers, designated as H-CM in the subsequent fibrillation process.

Table 1 Carboxyl group content of pulp fibers under different reaction conditions

Samples	ClCH_2COOH dosage/%	Temperature / $^{\circ}\text{C}$	Carboxyl group content /($\mu\text{mol} \cdot \text{g}^{-1}$)
A	1	55	245
B	1	65	310
C	3	55	365
D	3	65	485

3.2 Particle size distribution

The particle size distribution of CNF from different pulp fibers after 5 passes of grinding is shown in Fig.1. It should be noted that the Malvern Mastersizer 2000 assumes spherical particles when calculating particle size. This means that the reported particle sizes should be considered to be relative, since CNFs have high aspect ratios (4~20 nm in wide, 500~2000 nm in length) and deviate considerably from spherical geometry^[19]. The mean sizes of CNF from untreated fibers, L-CM,

and H-CM were 396, 255, and 164 nm, respectively. As clearly shown in Fig.1, the intensity distribution of the CNF from untreated pulp fibers has the highest size value, with a broad range of size from about 220 nm to 500 nm. The CNFs from H-CM showed a unimodal peak with the lowest mean size. From these results, it is evident that CNFs from H-CM have greater uniformity in size distribution than those from the untreated pulp fibers, and are mostly comprised of nanofibrils. This might be due to higher electrostatic repulsion between fibrils, from which thin and uniform CNFs were obtained.

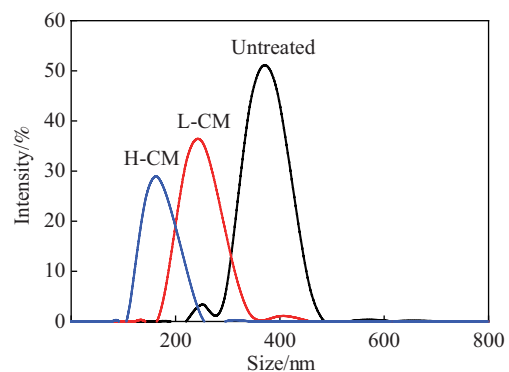


Fig.1 Particle size distribution of CNFs after 5 passes of grinding

3.3 Morphological properties

To gain an accurate understanding of the morphology of the prepared fibrillated samples, FE-SEM analysis was carried out on pulp mats. In Fig.2, FE-SEM images of cellulose nanofibrils with different carboxyl group contents are shown, after 5 passes of grinding. It is known that the mechanical fibrillation process causes external and internal fibrillation. External fibrillation is the raising of fibrils on the fiber surface through abrasive action, whereas internal fibrillation is related to the breakage of crosslinking between cellulose fibers and causes fiber delamination^[20]. In Fig.2(a), Fig.2(b), and Fig.2(c), some fiber fragments or fibril bundles are observed for all CNF samples, but they are more frequently observed with CNFs from untreated pulp fibers than with CNFs from carboxymethylated fibers. Compared with the CNFs from untreated pulp fibers in Fig.2(a) and CNFs from L-CM in Fig.2(b), a more homogenous structure is seen for CNFs from H-CM in

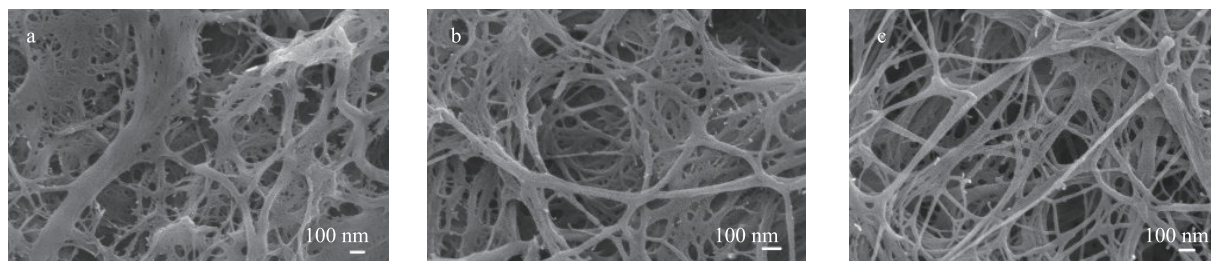


Fig.2 FE-SEM images of CNFs with different carboxyl group contents after 5 passes of grinding:
(a) Untreated; (b) L-CM; (c) H-CM

Fig.2(c), with a higher amount of individual fibrils. This observation corroborates the particle size findings, and can be explained by a high level of ionic groups in the fiber wall resulting in lower delamination resistance, making the fibrils easier to separate^[19].

3.4 Apparent viscosity and WRV

It is well known that one of the characteristics of CNF is its high viscosity. Its associated rheological properties at low concentrations are interesting for many applications, for example, as a rheology modifier in food, cosmetics, and coatings^[21]. The influence of grinding passes on apparent viscosity during the mechanical fibrillation is shown in Fig.3. An increasing trend of apparent viscosity is observed for all types of pulp in the fibrillation process. This is not surprising since in the initial stage, cellulose fibrils and microfibrils extracted by external fibrillation are known to hydrogen bond strongly with each other and this creates physical cross-linking, leading to high viscosity^[22]. At the same number of grinding passes, the highest apparent viscosity is observed in the sample

from H-CM, because of the presence of large fibril bundles, which are disrupted enough to hydrogen bond strongly with each other^[17]. It seems that a higher degree of substitution with carboxyl groups facilitates the nanofibrillation process.

A technique that is often used to measure swelling is the water retention value (WRV), which gives a value of the fiber saturation point or the total amount of water held by the fibers. Similar to what occurs in refining, fiber fracture occurs, and fibers start to unravel by grinding, causing both inter-fiber bonding and water retention capacity to increase. The effect of mechanical fibrillation on WRV as a function of the number of grinding passes is shown in Fig.4. At the same number of grinding passes, the highest WRV is observed in the sample from H-CM. The sample from untreated pulp fibers with the lowest carboxyl group content showed the lowest apparent viscosity and WRV in all samples. It seems that the mechanical fibrillation of untreated pulp fiber was the most inefficient, which resulted in heterogeneous material consisting of fiber fragments and less fibrillated fibrils as shown in

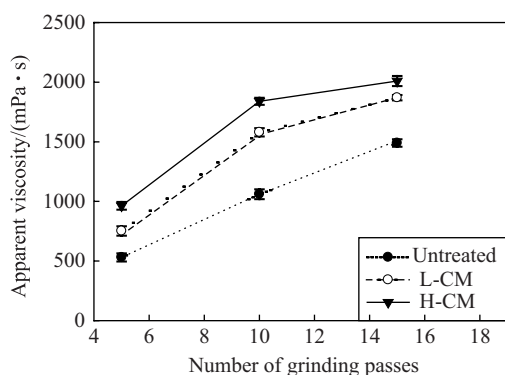


Fig.3 Apparent viscosity as a function of number of grinding passes

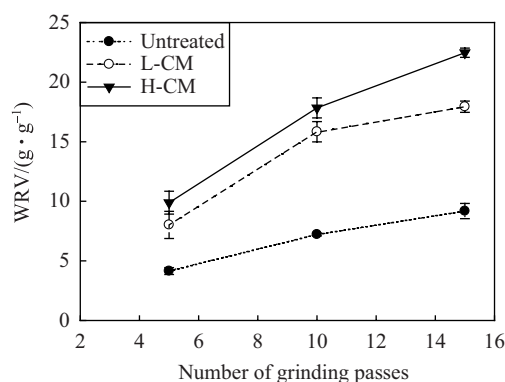


Fig.4 WRV as a function of number of grinding passes

Fig.2(a). On the other hand, the sample from H-CM showed the highest water holding capacity. The reason may be the good dispersibility and the smaller width dimension of the sample from H-CM. Moreover, this suggests that carboxymethylated nanofibrils are mechanically entangled well and are dispersed in water by electrostatic repulsion^[23].

4 Conclusions

A bleached acacia pulp with carboxymethylation pretreatment was prepared for nanofibrillation by grinding. The carboxyl group content of pulp fibers was greatly affected by chloroacetic acid dosage and reaction temperature. The fibrillated fibers were characterized at various points during the fibrillation process. As the carboxyl group content of fibers increased, the fibrillation efficiency increased. At the same number of grinding passes for the production of CNF, pulp fibers with high carboxyl group content produce smaller and more uniform CNFs. This can be explained by a high level of ionic groups in the cell wall, resulting in lower delamination resistance, making the fibrils easier to separate. The production of cellulose nanofibrils from pulps with carboxymethylation pretreatment can result in new applications (reinforcement, viscosity control) for CNF as well as a cost reduction in processing by reducing the energy and chemical requirements.

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