

# Nanofibrillation of dried pulp in NaOH solutions using bead milling

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**Abstract** The drying process in typical pulp production generates strong hydrogen bonding between cellulose microfibrils in refined cell walls and increases the difficulty in obtaining uniform cellulose nanofibers. To investigate the efficacy of alkaline treatment for cellulose nanofibrillation, this study applied a bead-milling method in NaOH solutions for the nanofibrillation of dried pulps. NaOH treatments loosened the hydrogen bonding between cellulose microfibrils in dried pulps and allowed preparation of cellulose nanofibers in 8 % NaOH with a width of approximately 12–20 nm and a cellulose I crystal form. Both the nanofiber suspensions prepared in 8 and 16 % (w/w) NaOH were formed into hydrogels by neutralization because of surface entanglement and/or interdigitation between the nanofibers. When the dried pulp was fibrillated in 16 % (w/w) NaOH, the sample after neutralization had a uniquely integrated continuous network. These results can be applied to the preparation of high-strength films and fibers with cellulose I crystal forms without prior dissolution of pulps.

**Keywords** Cellulose nanofiber · Wet bead milling · Alkaline treatment · Nanofibrillation · Hydrogel

## Introduction

Recently, cellulose microfibrils, which are a major component of plant cell walls, have received attention as an emerging bio-based nanomaterial. In nature, cellulose is insoluble in water and forms crystalline microfibrils with diameters of ~3 nm in the cell walls of higher plants (Somerville et al. 2004). The crystalline structure exhibits excellent longitudinal mechanical properties, including a high Young's modulus and a low coefficient of thermal expansion. Recent research has led to improved methods of isolation from various plant sources (Eichhorn et al. 2010; Siro and Plackett 2010). For example, our lab previously isolated cellulose nanofibers from wood, rice straw, potato tubers, and bamboo using a grinder (Abe et al. 2007; Abe and Yano 2009, 2010). The fibers prepared have a uniform width of approximately 15 nm and lengths exceeding several micrometers and correspond to cellulose microfibril aggregates in the cell walls (Awano et al. 2000; Donaldson 2007).

In our previous reports, never-dried plant sources were subjected to a mechanical fibrillation process after the removal of non-cellulosic components such as hemicelluloses and lignin (Abe et al. 2007). On the other hand, methods for nanofibrillation of dried pulps are also desired because it is one of the most available resources. However, the drying process generates strong hydrogen bonding between cellulose microfibrils in refined cell walls and increases the difficulty in

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obtaining thin and uniform cellulose nanofibers. Therefore, re-swelling of the microfibrils can facilitate the nanofibrillation of dried pulps.

Alkaline solutions are known to swell cellulose samples. Strong alkaline treatment causes even the intracrystalline swelling of cellulose, resulting in crystal conversion from cellulose I to cellulose II. For example, when commercial dried paper is immersed in 8 % (w/w) NaOH solution and lightly agitated, it is easily dispersed into individual pulp fibers due to interfibrillar swelling. This suggests that alkali-swelling disrupts hydrogen bonding between microfibrils in pulp fibers and could facilitate mechanical nanofibrillation.

Wet bead milling is an effective method for the production of fine particles using small grinding media. In this study, we tested the efficacy of nanofibrillation of dried pulp under alkaline conditions using a bead-milling method. Dried pulps were fibrillated in 8 or 16 % (w/w) NaOH solutions. Generally, 8 % (w/w) NaOH solution maintains the crystal form of cellulose, whereas 16 % (w/w) NaOH can convert the crystal form from cellulose I to cellulose II (Abe and Yano 2011, 2012). We characterized the products of mechanical fibrillation after NaOH treatment of dried pulp using field-emission scanning electron microscopy (FE-SEM) and X-ray analysis.

## Experimental

### Nanofibrillation of dried pulps

We used dried bleached kraft pulp from softwood with an  $\alpha$ -cellulose content of 90 %. We immersed 2 wt% pulps in water, 8 % (w/w) NaOH, or 16 % (w/w) NaOH aqueous solutions at room temperature. Nanofibrillation of pulps was performed using a bead mill (TSG-6U, IMEX Co. Ltd., Sooka, Japan) at 2000 rpm for 20 min with 1-mm zirconia beads at a filling rate of 50 % (v/v). The samples were separated from the beads by filtration.

### Characterization

The suspensions after bead milling were vacuum-filtered using a polytetrafluoroethylene membrane filter (0.1  $\mu$ m mesh). For the sample fibrillated in

NaOH solutions, the wet sheets were immersed in water until they were neutralized. After filtration, the wet sheets were hot-pressed at 120 °C into 60  $\mu$ m thick films and subjected to X-ray diffraction measurement in reflection mode. The diffraction patterns were obtained using an X-ray generator (UltraX 18HF; Rigaku Corp., Tokyo, Japan) with CuK $\alpha$  radiation (40 kV and 250 mA) from 5° to 40°.

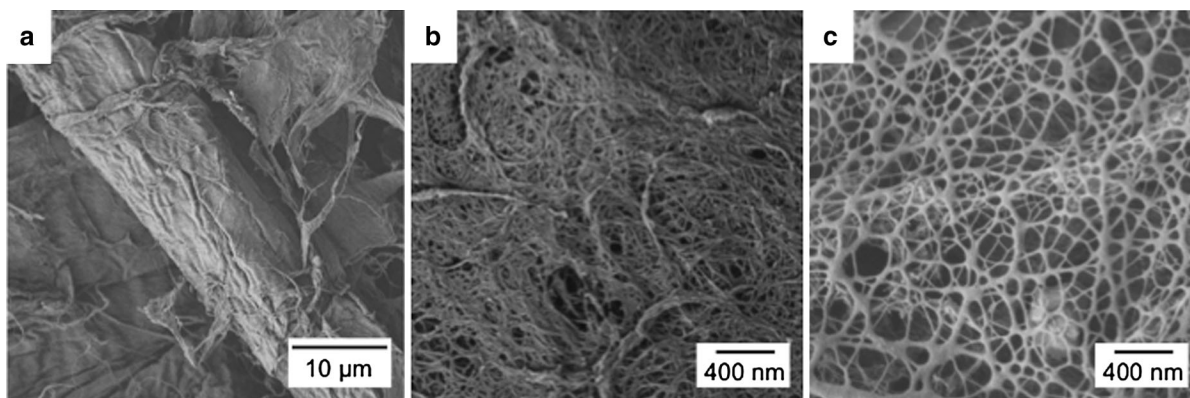
For microscopic observation, the wet neutralized sheets were dehydrated through a graded ethanol series (50 and 100 %, 3 h each) followed by acetone (3 h) and *tert*-butyl alcohol (3 h). The dehydrated samples were freeze-dried, coated with platinum by an ion sputter coater, and observed by FE-SEM (JSM-6700F; JEOL, Tokyo) at 1.5 kV.

## Results and discussion

After fibrillation by bead milling, smooth suspensions were obtained for all samples. However, when the pulp was fibrillated in water, many of the original pulp fibers remained and were easily separable with tweezers. FE-SEM analysis indicated retention of the original pulp fiber, consistent with partial fibrillation (Fig. 1a). Thus, as expected, the bead-milling method in water fibrillated only the surface of dried pulps and is insufficient for preparation of nanofibrillated dried pulps because of the strong hydrogen bonds between the microfibrils in pulp fibers.

In contrast, the suspensions prepared in 8 and 16 % (w/w) NaOH exhibited none of the original pulp structure and had higher viscosities than that prepared in water. In 8 % (w/w) NaOH, fine nanofibers with a uniform diameter of approximately 12–20 nm were formed (Fig. 1b). These nanofibers are comparable to those prepared from never-dried refined wood samples using a grinder (Abe et al. 2007). Compared with nanofibrillation from water suspensions, 8 % NaOH treatment disrupted the hydrogen bonds between microfibrils in dried pulps and improved their nanofibrillation.

In 16 % (w/w) NaOH, the neutralized sample exhibited an integrated and continuous network (Fig. 1c). Because the sample was neutralized, this result does not indicate that such a continuous network was formed in 16 % (w/w) NaOH. However, if unfibrillated thicker fibers remained after bead milling, they should be observable after neutralization.



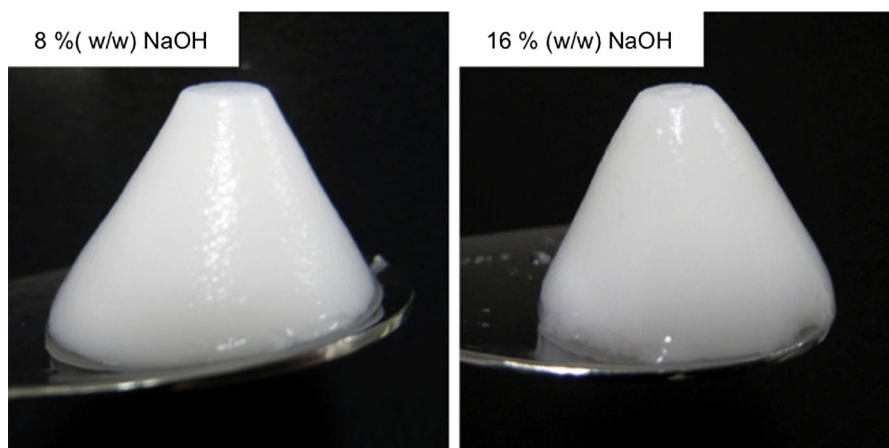
**Fig. 1** FE-SEM micrographs of freeze-dried ball-milled cellulose samples fibrillated in water (a), 8 % (w/w) NaOH (b), or 16 % (w/w) NaOH (c)

Therefore, this result suggests that bead milling in 16 % (w/w) NaOH could also finely fibrillate the dried pulps, and the alkali-swollen nanofibers formed an integrated and continuous network by aggregation and recrystallization into Cellulose II after neutralization.

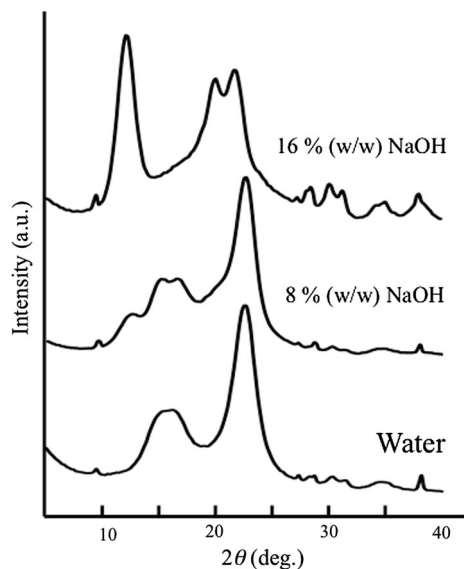
Generally, an aqueous suspension of cellulose nanofibers shows high viscosity, and the suspension is rarely precipitated by centrifugation (Abe and Yano 2012). However, the suspensions prepared in 8 and 16 % (w/w) NaOH were precipitated by centrifugation (3500 rpm), probably because of an increase in weight after alkali-swelling. Notably, the sediments from both treatments, which were concentrated to approximately 5 % (w/w), formed stable hydrogels after neutralization (Fig. 2). We previously reported the

gelation behavior (i.e., formation of a hydrogel) of cellulose nanofibers after NaOH treatment and subsequent neutralization (Abe and Yano 2011, 2012). Gelation likely occurs through interdigitation of the nanofibers during crystal conversion by alkaline treatment, thus forming continuous hydrogel networks (Okano and Sarko 1985).

Figure 3 shows the X-ray diffraction patterns of the dried hydrogels prepared from suspensions in 8 and 16 % (w/w) NaOH. The hydrogel prepared from the suspension in 8 % (w/w) NaOH exhibited an X-ray diffraction pattern indicative of typical cellulose I structures, but slight peaks derived from cellulose II were also observed. In contrast, the neutralized hydrogels prepared in 16 % (w/w) NaOH exhibited



**Fig. 2** Images of hydrogels prepared by neutralization from the concentrated suspensions in 8 % (w/w) NaOH (left) and 16 % (w/w) NaOH (right)



**Fig. 3** X-ray diffraction profiles of dried hydrogels prepared in water and 8 and 16 % (w/w) NaOH after neutralization

crystal forms that were completely converted to cellulose II with crystallinity higher than those of conventional cellulose hydrogels or aerogels prepared in alkali/urea aqueous solution (Cai et al. 2008) or LiCl/DMSO solution (Wang et al. 2012). These results are consistent with gelation through the interdigitation of cellulose nanofibers. In contrast, treatment in 8 % (w/w) NaOH caused only the surfaces of cellulose nanofibers to swell, and the entanglement and/or interdigitation of only the surface molecules contributed to connecting the nanofibers. Therefore, the interior of the cellulose nanofibers retained the cellulose I crystal form. The peaks at 9, 28 and 38° were observed probably because of the contamination by fragments of zirconia beads.

## Conclusion

In summary, this study investigated the use of NaOH solutions for facilitating the nanofibrillation of dried pulps. Bead milling in 8 % (w/w) NaOH loosened hydrogen bonding between cellulose microfibrils in dried pulps and produced cellulose nanofibers with a uniform diameter of approximately 12–20 nm. Both the suspensions prepared in 8 and 16 % (w/w) NaOH formed hydrogels after neutralization. When the suspension in 8 % (w/w) NaOH was neutralized, the

continuous network in the hydrogel seemed to be formed via the entanglement and/or interdigitation of only the surface molecules of cellulose nanofibers. Although 16 % (w/w) NaOH solution also enhanced the nanofibrillation of dried pulps, the form of original microfibrils disappeared after neutralization, and an integrated and continuous network formed by the interdigitation of cellulose nanofibers was observed instead. The gelation behavior after neutralization supports the effectiveness of nanofibrillation of dried pulps in NaOH solution because the thicker fibers produced by insufficient fibrillation cannot easily form a fine network, which would result in brittle hydrogels.

Unfortunately, our method did not allow preparation of individual cellulose nanofibers in water from dried pulps because gelation occurred after neutralization. However, we are currently applying this method to the direct preparation of high-strength cast films and spun fibers. For general preparation of cellulose-based films and spun fibers, cellulosic raw materials must be dissolved using specific chemical agents such as carbon disulfide for rayon and cellophane. In contrast, our method can introduce formability to dried pulps without any dissolution process. In particular, nanofibrillation in 8 % (w/w) NaOH solution can produce free-form cellulosic products while maintaining the original cellulose I crystal form, which has higher elastic modulus than cellulose II (cellulose I: 138 GPa, cellulose II: 88 GPa) (Nishino et al. 1995). Consequently, high-strength cellulosic products such as films and fibers can be produced with relative safety using only NaOH and coagulants. For this purpose, a bead-milling method may be not optimal for large-scale production because it is difficult to separate the beads from the viscous slurry of cellulose nanofibers. Therefore, one of challenges is preparation of a slurry with a high (8–10 %) concentration of cellulose nanofibers, for example, using twin-screw extrusion (Ho et al. 2015).

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