Optimizing crystal transitions in low-temperature, low-concentration NaOH solutions to prepare cellulose I and II composite materials

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Running head: Quenching on cellulose with NaOH solution

Abstract

Cellulose II exhibits exceptional attributes, including flexibility, high stainability, and gloss. However, its strength is lower than that of cellulose I due to reduced crystallinity during the crystal transition. In this study, we devised a novel method to regulate the proportion and distribution of cellulose I and II crystals. This was achieved by employing a low-concentration alkaline solution and liquid nitrogen, resulting in a high-strength composite material that retained the excellent properties of cellulose II. When cellulose powder was immersed in an 8 wt% NaOH solution and quenched with liquid nitrogen, the crystal transition from cellulose I to II occurred outward from the sample periphery to its center. The percentage of cellulose II increased proportionally with treatment time. This technique was extended to cellulose I-rich cotton fibers, facilitating the creation of a composite fiber with cellulose I at the core and cellulose II on the surface. The tensile strength and Young's modulus of the composite fiber were greater than those of the mercerized cellulose II fiber. Additionally, the elongation at break and toughness of these fibers surpassed those of conventional cotton fibers. This innovative method allows for the preparation of cellulose I and II composite materials with diverse properties.

Keywords: Cellulose/Crystal transition/Liquid nitrogen/Low-temperature alkali treatment/Mercerization

Cellulose is the most abundant biopolymer in nature, and cellulose materials, such as pulp, cotton, rayon, and lyocells, have many applications [1]. The natural cellulose in plants, algae, and bacteria contains cellulose I crystals. Cellulose I transforms to cellulose II through regeneration from the dissolved state or through mercerization using a strong sodium hydroxide (NaOH) solution [2,3]. Mercerization can improve the mechanical and chemical properties of cellulose fibers, such as their dimensional stability, dyeability, reactivity, luster, and smoothness [4]. Moreover, dissolution methods employing low-concentration NaOH aqueous solutions have attracted attention due to their cost-effectiveness and low toxicity. The crystal transition from cellulose I to II does not occur during alkali treatment using an 8 wt% NaOH solution at room temperature [5]. However, cellulose can be dissolved in NaOH solutions at low temperatures (–20 °C) [6,7], and in even the undissolved crystals, the crystal transition from cellulose I to II have also been observed [7]. Cellulose I crystals exhibit high crystallinity and Young's modulus; however, the crystallinity decreases during the crystal transition from cellulose I to II, leading to the reduced mechanical strength of cellulose II compared with that of cellulose I. Therefore, the fabrication of high-strength cellulose II materials holds promise for the development of innovative cellulose applications.

Fabricating high-strength cellulose II materials could potentially involve

56 combining cellulose I and II, as in an all-cellulose composite [8]. Several studies [9–11] have
57 reported that the main methods utilized for fabricating these composites include
58 impregnation and surface dissolution. In the surface dissolution approach, the cellulose
59 material is soaked in a solvent, and the outer layer is partially dissolved, with the
60 undissolved core acting as a reinforcement. However, the dissolution capacity of cellulose
61 in a low-concentration NaOH solution is limited by the degree of cellulose polymerization
62 [7]. Establishing a novel approach to selectively induce the solid-state crystal transition of
63 cellulose I to II on the surface of cellulose resources, rather than partially dissolving the
64 surface, holds significant potential for developing high-strength cellulose materials.

65 We aimed to establish a novel approach for controlling the proportion and
66 distribution of cellulose I and II in solid-state cellulose resources using low-temperature
67 treatment in a low-concentration NaOH solution. We previously reported that the crystal
68 transition from cellulose I to II was completed quickly when the cellulose powder, which
69 was soaked in an 8 wt% NaOH aqueous solution, was quenched with liquid nitrogen [12].
70 We hypothesized that controlling the proportion of cellulose I and II is possible through
71 quenching treatments. In this study, we traced the progression of the crystal transition
72 from cellulose I to II on cellulose powder and cotton fibers during quenching treatments
73 with liquid nitrogen. The crystal transition progressed from the outer area of the fiber to

74 the central area of the fiber. The quenching treatment of fiber samples suggested the
75 preparation of fiber samples with cellulose I as the core and cellulose II as the surface.
76 This quenching treatment has potential as a new approach for fabricating high-strength
77 cellulose materials.

78 In this study, the crystal form of the obtained samples was evaluated using solid-
79 state ^{13}C cross-polarization magic angle spinning (CP/MAS) nuclear magnetic
80 resonance (NMR) measurements and Fourier transform infrared (FT-IR) spectroscopy.
81 The surfaces of the cotton fiber samples were observed using scanning electron
82 microscopy (SEM). The mechanical properties of the cotton fiber samples were
83 evaluated using tensile tests. The experimental procedure is detailed in the
84 Supplementary Materials.

85 Fig. S2 shows the solid-state ^{13}C CP/MAS NMR spectra of the cellulose powder
86 samples obtained by the quenching treatments. As the treatment time increased, the C6 *tg*
87 resonance line decreased, and the C6 *gt* resonance line increased. Fig. 1 exhibits the
88 proportions of cellulose I, cellulose II, and surface/amorphous regions determined by C6
89 resonance line-fitting analysis of the solid-state ^{13}C CP/MAS NMR spectrum shown in
90 Fig. S2. As the proportion of cellulose I decreased, the proportion of cellulose II increased,
91 and that of surface/amorphous regions remained nearly constant with some minor

92 fluctuations. As mentioned above, in our previous report, the crystal transition from
93 cellulose I to II occurred rapidly in a low-concentration (8 wt%) NaOH aqueous solution,
94 followed by quenching with liquid nitrogen [12]. The transition in Fig. 1 is believed to be
95 basically caused by the same mechanism. The temperature is very important in this
96 transition, and the transition is completed at temperatures below –17 °C. The transition
97 time becomes shorter with decreasing temperature [12]. The results of the ^{23}Na NMR
98 relaxation time measurements and other data confirm that low temperature allows NaOH
99 to enter the cellulose crystal, breaking the intrachain hydrogen bonds of cellulose, and
100 that the crystal transition from alkali cellulose to cellulose II is completed by
101 neutralization, washing, and drying treatments. The difference between the quenching
102 treatment experiment in our previous report [12] and the experiment in Fig. 1 is the size of
103 the container used for the treatment. In our previous study [12], a 2 ml Eppendorf tube was
104 used, and the crystal transition was completed 30 s after the quenching treatment.
105 Alternatively, in this study, a larger container (50 ml centrifuge tube) was used, which
106 may have increased the time required for the crystal transition. This suggests that the
107 thermal conductivity and heat capacity of the system may be among the factors
108 determining the progress of the crystal transition in quenching treatments. The amount of
109 cellulose II increased proportionally over 30 and 90 s, suggesting that the quenching

110 treatment time can control the amount of cellulose II.

111 During the quenching treatments, the cellulose powder froze from the outside to
112 the inside of the sample, and the amount of frozen material gradually increased with
113 increasing treatment time. It is essential to consider the relationship between the freezing
114 behavior of these samples and the increase in the proportion of cellulose II. Celluloses I
115 and II were present in the sample that was cooled for 30 s. The frozen and unfrozen
116 portions were present when the sample transitioned from liquid nitrogen temperature to
117 room temperature. The outer portions were frozen, and the central portions remained
118 unfrozen. Individual samples were separated and subjected to neutralization, water
119 washing, and drying. Fig. 2 shows the solid-state ^{13}C CP/MAS NMR spectra of these
120 dried samples. The frozen portion contained cellulose I and II, whereas the unfrozen
121 portion contained only cellulose I, indicating that the crystal transition proceeded from
122 outside the sample. Hence, by this quenching treatment, the distribution of cellulose I and
123 II is expected to be controlled such that the outer portion is cellulose II and the central
124 portion is cellulose I. The rate of crystal transition, of course, largely depends on the
125 chosen system's heat capacity and thermal conductivity. Nevertheless, the results
126 obtained with our system have been sufficiently reproducible. Quenching treatments were
127 performed on the cotton fibers to fabricate cellulose materials featuring a cellulose I core

and a cellulose II surface.

Fig. S3 shows the prepared cotton fiber, the sample obtained after quenching for 90 s, and the sample obtained through mercerization treatment with a 25 wt% NaOH solution at room temperature for 2 h. Although the mercerized sample shrank from 40 to 28 cm, the length of the quenched sample decreased from 40 to 38 cm, indicating that the quenching treatment resulted in less sample deformation.

Fig. S4 shows the solid-state ^{13}C CP/MAS NMR spectra of the as-prepared cotton fiber samples obtained by the treatments using 8 and 25 wt% NaOH solutions at room temperature. The sample soaked in an 8 wt% NaOH solution contained cellulose I, confirming that the crystal transition did not progress. In contrast, in the mercerized sample containing cellulose II, the crystal transition continued.

Fig. S5 shows the solid-state ^{13}C CP/MAS NMR spectra of the cotton fiber samples obtained by the quenching treatments. Similar to the quenching treatments of cellulose powder, with increasing treatment time, the C6 *tg* resonance lines decreased, and the C6 *gt* resonance lines increased. Fig. 3 reveals the proportions of each region in the cotton fiber samples determined by the C6 resonance line fitting of the solid-state ^{13}C CP/MAS NMR spectra shown in Fig. S5. Similar to the quenching treatment of cellulose powder, the proportion of cellulose II increased as that of cellulose I decreased, while that

of the surface/amorphous region remained nearly constant with minor fluctuations. This suggests that the crystal transition also progressed from the surface of the cotton fiber. In Fig. S6, via the attenuated total reflection (ATR) method, the FT-IR spectra are displayed for the surfaces of the as-prepared cotton fiber, the mercerized cotton fiber, and the cotton fiber samples after 15 s and 30 s quenching treatments. Fig. 4 presents the spectra ranging from 3,800 cm^{-1} to 3,000 cm^{-1}. The crystal forms of cellulose were determined by the band at 3,345 cm^{-1}, which is attributed to O3-H-O5 in cellulose I, and the bands at 3,488 and 3,445 cm^{-1}, which represent the OH stretching region of cellulose II [13]. The sample subjected to a 15 s quenching treatment exhibited a band corresponding to cellulose I and slight bands corresponding to cellulose II. Furthermore, in the sample quenched for 30 s, the intensity of the cellulose I band decreased, and the intensity of the cellulose II band increased. This result indicates that cellulose I decreased and cellulose II increased in the depth range of approximately 1.6 μm below the sample surface. Fig. S7 shows the SEM images of the as-prepared cotton fiber, the mercerized cotton fiber, and the cotton fiber samples obtained through quenching treatments for 15 and 30 s at 25 ×, 2,500 ×, and 10,000 × magnifications. The as-prepared cotton fibers exhibits a flat morphology, with some visible fibrils on the surface, while the mercerized sample has a smooth morphology and displays fibril adhesions and gaps where no fibrils exist. These adhesions arise from

164 the formation of stronger bonds between fibrils during mercerization [14,15]. During the
165 quenching treatments, some fibril adhesions were observed after 15 s, and more adhesions
166 were observed after 30 s of quenching. This result supports the NMR and FT-IR analyses,
167 indicating that the crystal transition proceeded on the fiber surface.

168 In summary, we report that quenching increases the proportion of cellulose II on
169 the surface and controls the crystal distribution in the cellulose I core and on the cellulose
170 II surface. These cotton fiber samples are expected to exhibit superior mechanical strength
171 compared to that of cellulose II because the cellulose I core acts as a reinforcement.
172 Therefore, the mechanical properties were evaluated by tensile tests.

173 Fig. 5 shows the S–S curves of the as-prepared cotton fiber, the cotton fiber
174 samples obtained by quenching for 15 and 30 s, and the mercerized cotton fiber sample.
175 Table S1 summarizes the maximum stress, breaking strain, elastic moduli, and toughness
176 of the samples. The maximum stress and elastic moduli (E_H) of the fiber samples obtained
177 by the quenching treatments were greater than those of the mercerized fiber sample. This
178 indicates that the cellulose I core serves as a reinforcement, resolving the low mechanical
179 strength of cellulose II. The breaking strain and toughness of the composite fiber samples
180 were greater than those of the cotton fibers and less than those of the mercerized fibers.
181 Furthermore, all the mechanical properties listed in Table S1 changed as the treatment

time increased for the samples obtained by the quenching treatments. This is expected to be due to an increase in the proportion of cellulose II as the quenching treatment time increased. This result indicates that by adjusting the treatment time, the proportion and distribution of cellulose I and II can be controlled, and the mechanical properties can also be altered.

This study demonstrates the potential to regulate the proportions and distribution of cellulose I and II through quenching. During the quenching treatment of cellulose powder, the crystal transition progressed from the edge of the tube toward the center of the tube, with both an increasing proportion of cellulose II and treatment duration. A similar crystal transition was observed in the cotton fibers, suggesting the presence of cellulose I in the interior and cellulose II on the surface. However, the detailed crystal distribution, such as the thickness of the cellulose I core and its uninterrupted extension throughout the fiber, remains uncertain and warrants further analysis. Additionally, these composite materials exhibited superior maximum stress and elastic moduli compared to those of the mercerized cotton fiber sample, indicating the potential to control the mechanical properties through treatment duration. The advantages of this method are twofold, namely, the proportion and distribution of cellulose crystals can be determined, and a crystal transition in the solid-state can be induced without significantly deforming

200 the material shape of cellulose samples. This suggests the possibility of adapting it to
201 already-fabricated films, sponges, and so on. Optimizing this quenching treatment can
202 lead to the development of high-strength cellulose materials.

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Author contributions

Yuki Kugo: Conceptualization, methodology, investigation, and writing – original draft preparation. Takuya Isono: Supervision. Masashi Fujiwara: Supervision. Toshifumi Satoh: Supervision. Hirofumi Tani: Supervision. Tomoki Erata: Supervision, writing, reviewing, and editing. Kenji Tajima: Supervision, writing, reviewing, and editing.

Declaration of competing interest

The authors declare that they have no financial or personal relationships that may be considered potential competing interests.

Data availability

The data will be made available upon request.

Supplementary information is available at the *Polymer Journal* website.

References

1. Klemm D, Heublein B, Fink HP, Bohn A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie - International Edition* **44,** 3358–3393 (2005).
2. Okano T, Sarko A. Merceization of cellulose. II. Alkali-cellulose intermediates and a possible mercerization mechanism. *J Appl Polym Sci* **30,** 325–332 (1985).
3. O'sullvian AC. Cellulose: the structure slowly unravels. *Cellulose* **4,** 173–207 (1997).
4. Goswami P, Blackburn RS, Taylor J, White P. Sorption of dyes on cellulose II: effect of alkali treatment of fibre and dye structure. *Cellulose* **18,** 1063–1072 (2011).
5. Dinand E, Vignon M, Chanzy H, Heux L. Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose II. *Cellulose* **9,** 7–18 (2002).
6. Kamide K, Okajima K, Matsui T, Kowsaka K. Study on the solubility of cellulose in aqueous alkali solution by deuteration IR and 13C NMR. *Polym J* **16,** 857–866 (1984).
7. Isogai A, Atalla RH. Dissolution of cellulose in aqueous NaOH solutions. *Cellulose* **5,** 309–

319 (1998).

8. Nishino T, Matsuda I, Hirao K. All-Cellulose Composite. *Macromolecules* **37,** 7683–7687 (2004).

9. Huber T, Müssig J, Curnow O, Pang S, Bickerton S, Staiger MP. A critical review of all-cellulose composites. *J Mater Sci* **47,** 1171–1186 (2012).

10. Li J, Nawaz H, Wu J, Zhang J, Wan J, Mi Q, et al. All-cellulose composites based on the self-reinforced effect. *Composites Communications* **9,** 42–53 (2018).

11. Tanpichai S, Boonmahitthisud A, Soykeabkaew N, Ongthip L. Review of the recent developments in all-cellulose nanocomposites: Properties and applications. *Carbohydr Polym* **286,** 119192 (2022).

12. Kugo Y, Nomura S, Isono T, Sato S, Fujiwara M, Satoh T, et al. Elucidating the structural changes of cellulose molecules and dynamics of Na ions during the crystal transition from cellulose I to II in low temperature and low concentration NaOH solution. *Carbohydr Polym* **332,** 121907 (2024).

13. Horikawa Y, Konakahara N, Imai T, Kentaro A, Kobayashi Y, Sugiyama J. The structural changes in crystalline cellulose and effects on enzymatic digestibility. *Polym Degrad Stab* **98,** 2351–2356 (2013).

14. Wang H, Li D, Yano H, Abe K. Preparation of tough cellulose II nanofibers with high thermal

stability from wood. *Cellulose*, **21**, 1505–1515 (2014).

15. Sharma S, Nair SS, Zhang Z, Ragauskas AJ, Deng Y. Characterization of micro fibrillation process of cellulose and mercerized cellulose pulp. *RSC Adv* **5,** 63111–63122 (2015).

Titles and figure legends

Fig. 1. Time-course changes in the proportions of cellulose I, cellulose II, and surface/amorphous regions for the cellulose powder samples obtained by the quenching treatments, determined by the line fitting of the C6 resonance lines of the solid-state ^{13}C CP/MAS NMR spectra shown in Fig. S2. *Color code:* red line, cellulose I; blue line, cellulose II; and green line, surface/amorphous region.

Fig. 2. Solid-state ^{13}C CP/MAS NMR spectra of the frozen and unfrozen portions of the samples obtained by quenching for 30 s.

Fig. 3. The time-course changes in the proportions of cellulose I, cellulose II, and surface/amorphous regions for the cotton fiber samples obtained by the quenching treatments determined by the line fitting of the C6 resonance lines of the solid-state ^{13}C CP/MAS NMR spectra shown in Fig. S5. *Color code:* red line, cellulose I; blue line, cellulose II; green line, surface/amorphous region.

Fig. 4. Fourier transform infrared spectroscopy (FT-IR) spectra from the attenuated total reflection (ATR) method for the surface of the as-prepared cotton fiber, the cotton fiber

293 samples obtained by quenching for 15 and 30 s, and the mercerized sample ranging from
294 3,800 cm^{-1} to 3,000 cm^{-1}.
295
296 Fig. 5. Stress–strain curves of the cotton fiber samples. *Color code:* black line, the as-
297 prepared cotton fiber; red line, the sample obtained by quenching treatment for 15 s; green
298 line, the sample obtained by quenching for 30 s; blue line, the mercerized cotton fiber
299 sample.