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Supplementary Material

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

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Experimental

Materials

A 100–200 mesh filter paper pulp powder divided from cotton linter and commercial organic cotton yarn for handicrafts were purchased from Advantech Co., Ltd. (Tokyo, Japan) and MOTOHIRO Co., Ltd. (Kyoto, Japan), respectively. NaOH (>97.0%) and sulfuric acid (H_2SO_4; >95.0%) were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan).

Quenching treatments on cellulose powder

The quenching treatments were performed on cellulose powder and cotton fiber. The cellulose powder was soaked in an 8 wt% NaOH solution at room temperature (24 °C) in a 50 mL centrifuge tube with a diameter of 2.8 cm. The samples were centrifuged at 1,000 × g for 5 min. The supernatant was removed, and the precipitate was cooled in a container filled with liquid nitrogen for up to 120 s. The samples were then thawed by immediately adding a sufficient amount of a 10 vol% H_2SO_4 solution to bring the pH below 7.0 at room temperature (24 °C). The samples were washed with deionized water and air-dried at room temperature (24 °C).

Quenching treatments on cotton fiber

The cotton fibers were cut to a length of 40 cm. The fiber was soaked in an 8 wt% NaOH solution in a beaker at room temperature (24 °C) for 10 min. The samples were wrapped after being taken from a beaker, and chilled in a container filled with liquid nitrogen for up to 90 s. Similar to the quenching treatments on cellulose powder, the samples were neutralized, washed, and air-dried at room temperature (24 °C). Furthermore, to compare the effect of temperature and alkali concentrations, the room temperature treatment and the mercerization treatment using a high-concentration NaOH solution were conducted. For room temperature treatment, the cotton fibers were soaked in an 8 wt% NaOH solution for 10 min at room temperature (24 °C). Similar to the quenching treatments on cotton fiber, the samples were neutralized, washed, and air-dried at room temperature (24 °C). For mercerization, the cotton fibers were soaked in a 25 wt% NaOH solution at room temperature (24 °C) for 2 h. These fiber samples were neutralized with a 20 vol% H_2SO_4 solution. After neutralization, the samples were washed with deionized water and air-dried at room temperature (24 °C).

Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR measurements

Solid-state ^{13}C CP/MAS NMR measurements were performed using a Bruker Avance 500 spectrometer (Bruker, Germany) at Instrumental Analysis Support Office, Frontier Chemistry Center, Faculty of Engineering, Hokkaido University, Japan. The dried samples were packed in a 3.2-mm rotor. The MAS frequency was set to 10 kHz. All solid-state ^{13}C CP/MAS NMR spectra were recorded at 125 MHz, using a ^{1}H 90° pulse length of 4.0 μs, a contact time of 1.5 ms, and a repetition time of 4 s. Ramp and tppm-15 sequences were used for the contact pulse and decoupling, respectively. The chemical shifts were calibrated using the carbonyl carbon of glycine at 176.46 ppm. The proportions of cellulose I, cellulose II, and the surface of cellulose fibrils and amorphous (surface/amorphous) region were determined by fitting the C6 resonance line of the ^{13}C NMR spectra. The differences in the chemical shifts were due to the conformations of the O6 hydroxymethyl group; the conformations in cellulose I, cellulose II, and the surface/amorphous regions are *tg* (*trans-gauche*), *gt* (*gauche-trans*), and *gg* (*gauche-gauche*), respectively [1,2]. Deconvolution of the C6 resonance lines was based on the chemical shifts of the *tg* (66.0, 65.5, and 65.2 ppm), *gt* (63.3 and 62.6 ppm), and *gg* (61.9, 61.5, and 61.0 ppm) conformations, as shown in Fig. S1 [3]. The C6 resonance lines were deconvoluted using the DMfit2017 line fitting program [4]. A Lorentzian shape was used for each line. The proportions of cellulose I, cellulose II, and surface/amorphous region

were calculated using the integrated areas of each resonance line by using the following equations:

$$\text{Proportion of cellulose I (\%)} = \frac{A_{tg}}{A_{tg}+A_{gt}+A_{gg}} \times 100$$

$$\text{Proportion of cellulose II (\%)} = \frac{A_{gt}}{A_{tg}+A_{gt}+A_{gg}} \times 100$$

$$\text{Proportion of surface/amorphous region (\%)} = \frac{A_{gg}}{A_{tg}+A_{gt}+A_{gg}} \times 100$$

where A_{tg} is the integrated area of the *tg* lines, A_{gt} is the integrated area of the *gt* lines, and A_{gg} is the integrated area of the *gg* lines.

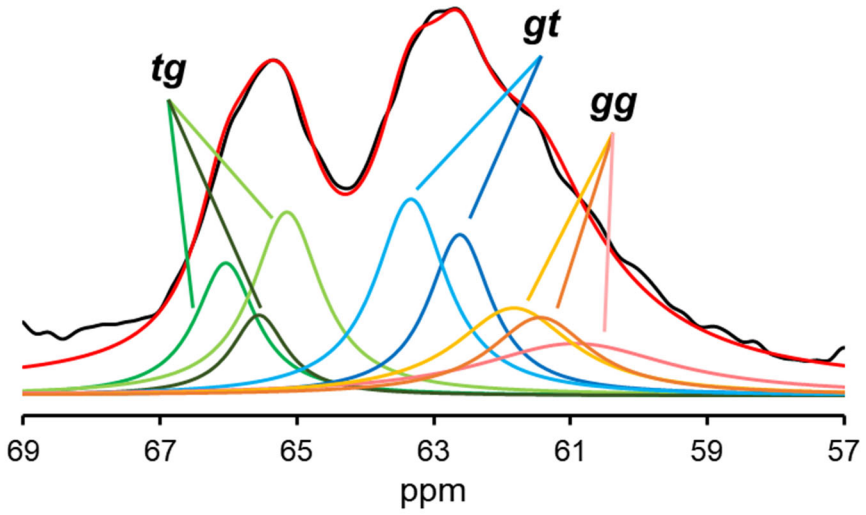

Fig. S1. C6 resonance line fitting model in the solid-state ^{13}C CP/MAS NMR spectrum [3].

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR measurements were performed on the as-prepared cotton fiber, the mercerized cotton fiber, and cotton fiber samples obtained by the quenching treatments

for 15 and 30 s using a Fourier transform infrared spectrometer (FT/IR-4200, JASCO Corp., Tokyo, Japan) ranging from 4,000 cm^{-1} to 550 cm^{-1}. The spectra were recorded with attenuated total reflection (ATR) methods using a ZnSe ATR prism and a TGS detector at a penetration depth of approximately 1.6 μm from the sample surface. The spectra were recorded with a spectral resolution of 4 cm^{-1} and an acquisition of 64 scans. The obtained spectra were normalized at 1,161.9 cm^{-1} of the glycosidic bonding of cellulose. The crystal forms of cellulose were determined by the band at 3,345 cm^{-1} attributed to O3-H-O5 in cellulose I, and the bands at 3,488 and 3,445 cm^{-1} in the OH-stretching region of cellulose II [5].

Scanning electron microscopy (SEM)

The as-prepared cotton fiber, the mercerized cotton fiber, and the cotton fiber samples obtained by the quenching treatment for 15 and 30 s were fixed on the sample stand with carbon tape and gold deposition was conducted using a vacuum deposition instrument (E-1010, Hitachi, Ltd., Tokyo, Japan). Subsequently, microscopic observations were performed using SEM (JSM-70001FA, JEOL Ltd, Tokyo, Japan) at the High-voltage Electron Microscope Laboratory, Faculty of Engineering, Hokkaido University, Sapporo, Japan using an acceleration voltage of 5.0 kV. SEM images were

acquired at 25 ×, 2,500 ×, and 10,000 × magnification.

Tensile tests

Tensile tests were performed on the as-prepared cotton fiber, the mercerized cotton fiber, and the cotton fiber samples obtained by the quenching treatments for 15 and 30 s using an AG-100kNXplus (SHIMADZU CORPORATION, Kyoto, Japan) at the Industrial Research Institute, Industrial Technology and Environment Research Department, Hokkaido Research Organization, Sapporo, Japan. The samples were fixed using a pneumatic capstan-type yarn gripper (SHIMADZU CORPORATION, Kyoto, Japan) and pulled from a distance of 10 cm at a speed of 1 mm/s. A stress-strain curve (S-S curve) was drawn for each sample, with stress on the X-axis and strain on the Y-axis. The maximum stress, the breaking strain, the elastic moduli, and the toughness of each sample were determined. The curve obtained exhibited a J-shaped S-S curve with distinct slopes in the initial region and the region under high stress [6]. In this study, the elastic moduli at the initial region are denoted as E_I (Elastic moduli of the Initial region), and the elastic moduli under high stress are denoted as E_H (Elastic moduli under High stress). The slope of the S-S curves of the initial region represented E_I. E_H was calculated as the slope of S-S curves within the range of 40% to 80% of the maximum stress, which was

relatively linear, as follows:

$$Elastic\ moduli\ (E_H)\ [cN/dtex] = (\sigma_{80} - \sigma_{40})/(\frac{\varepsilon_{80} - \varepsilon_{40}}{100})$$

where σ_{40} is 40 % of the maximum stress, σ_{80} is 80 % of the maximum stress, ε_{40} is the strain at 40 % of the maximum stress, and ε_{80} is the strain at 80 % of the maximum stress.

The toughness was calculated as the integral area under each S-S curve.

Results and Discussions

The quenching treatments on cellulose powder

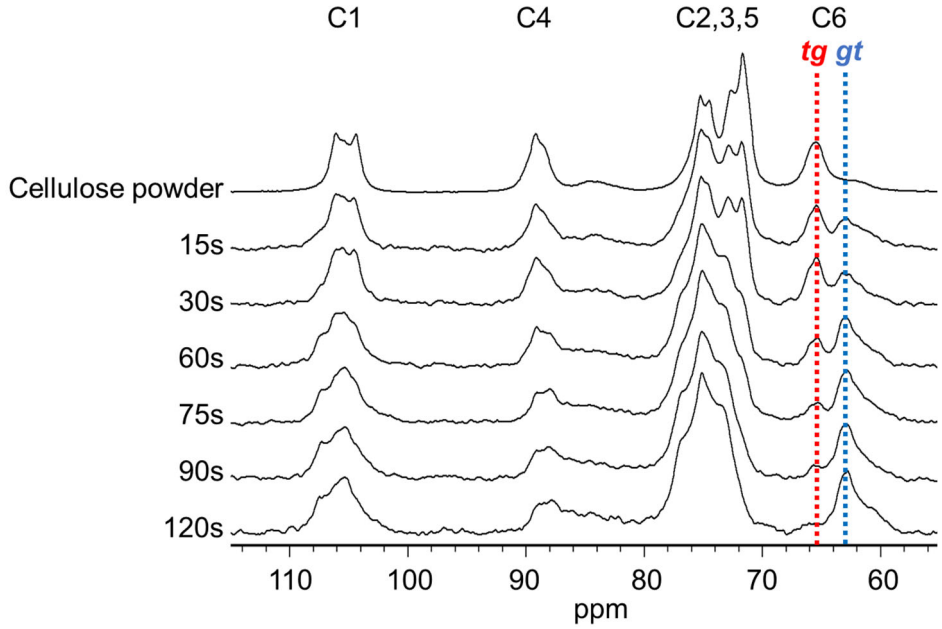

Fig. S2. Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra of the cellulose powder samples obtained by the quenching treatments.

The quenching treatment on cotton fiber

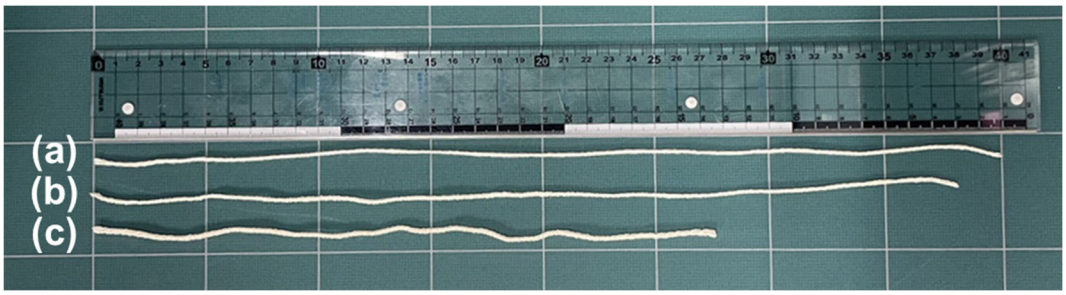

Fig. S3. The morphology of the samples of (a) the prepared cotton fiber, (b) the obtained sample after quenching treatment for 90 s, and (c) the sample after mercerization treatment with a 25 wt% NaOH solution at room temperature.

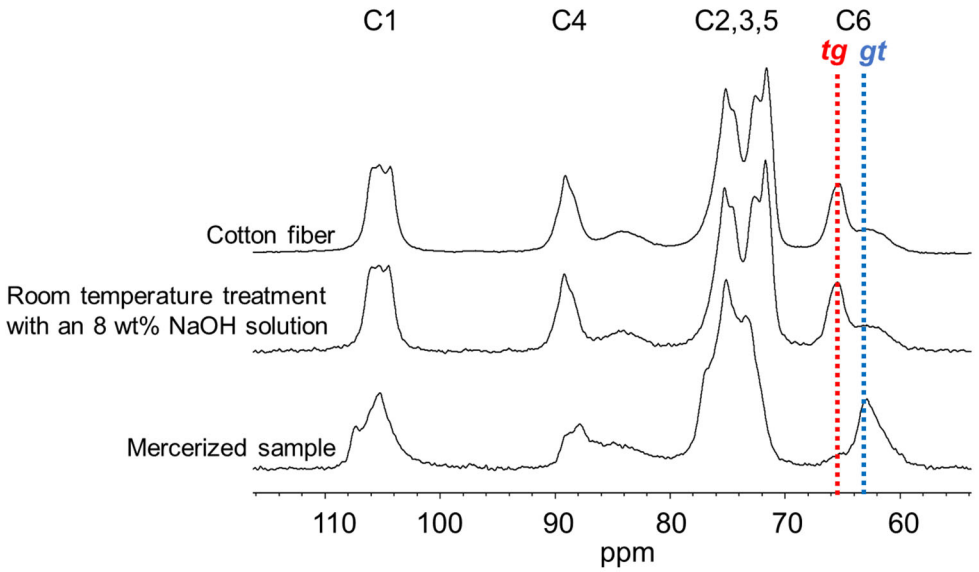

Fig. S4. Solid-state ^{13}C CP/MAS NMR spectra of the as-prepared cotton fiber and the samples obtained by the room temperature treatments using 8 and 25 wt% NaOH solutions.

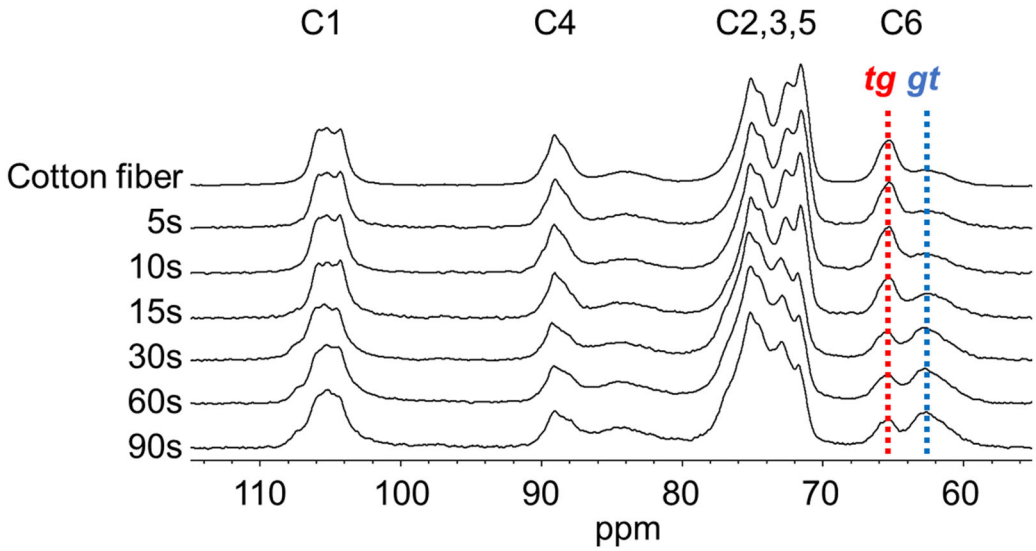

Fig. S5. Solid-state ^{13}C CP/MAS NMR spectra of the cotton fiber samples obtained by the quenching treatments.

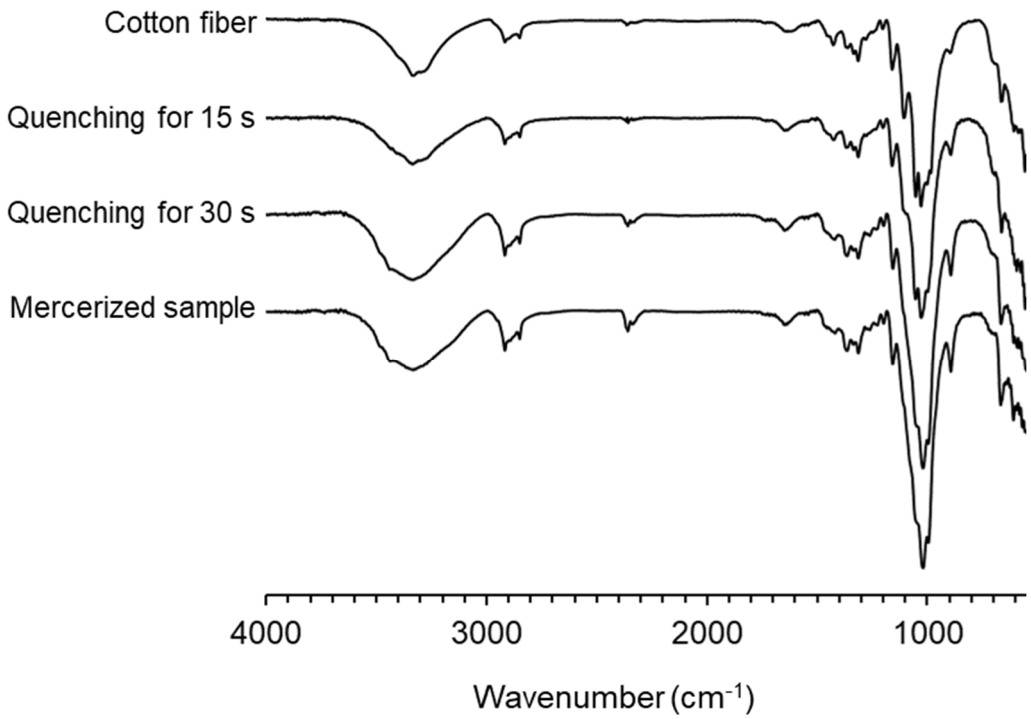

Fig. S6. The Fourier transform infrared spectroscopy (FT-IR) spectra from the attenuated total reflection (ATR) methods for the surface of the cotton fiber samples ranging from 4,000 cm^{-1} to 550 cm^{-1}.

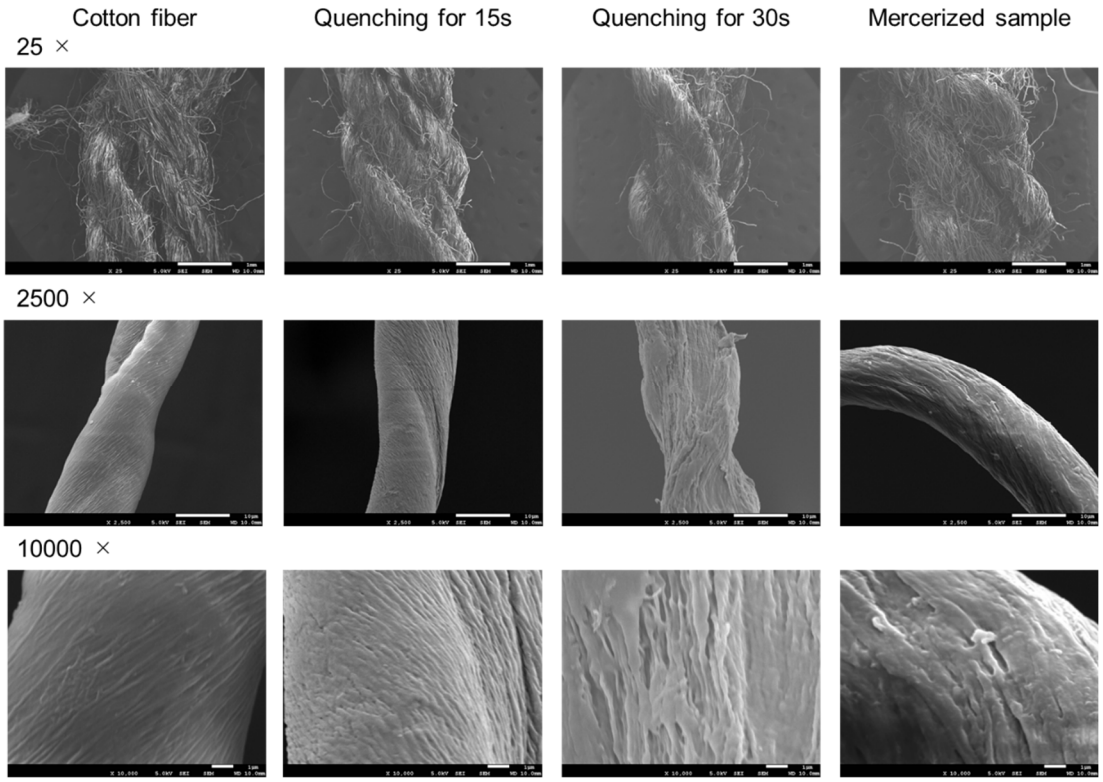

Fig. S7. Scanning electron microscopy (SEM) images of the as-prepared cotton fiber, the cotton fiber samples obtained by the quenching treatments cooled for 15 and 30 s, and the mercerized cotton fiber sample at 25 ×, 2,500 ×, and 10,000 ×.

Table S1. Maximum stress, breaking strain, elastic moduli, and toughness of the as-prepared cotton fiber, the cotton fiber samples obtained by the quenching treatments cooled for 15 and 30 s, and the mercerized cotton fiber samples.

sample	Maximum stress (cN/dtex)	Breaking strain (%)	Elastic moduli (E_I) (cN/dtex)	Elastic moduli (E_H) (cN/dtex)	Toughness (cN/dtex) × 100^{-2}
Cotton fiber	1.32 ± 0.06	15.3 ± 1.1	3.01 ± 0.34	11.28 ± 0.03	8.8 ± 1.2
Quenched sample for 15 s	1.43 ± 0.17	31.8 ± 2.9	0.68 ± 0.18	6.90 ± 0.12	16.4 ± 2.8
Quenched sample for 30 s	1.49 ± 0.15	34.3 ± 1.4	0.39 ± 0.05	7.27 ± 0.26	16.8 ± 1.8
Mercerized sample	1.34 ± 0.05	43.9 ± 1.5	0.70 ± 0.24	4.26 ± 0.21	23.1 ± 2.2

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