Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose

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Never-dried and once-dried hardwood celluloses were oxidized by a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system, and highly crystalline and individualized cellulose nanofibers, dispersed in water, were prepared by mechanical treatment of the oxidized cellulose/water slurries. When carboxylate contents formed from the primary hydroxyl groups of the celluloses reached approximately 1.5 mmol/g, the oxidized cellulose/water slurries were mostly converted to transparent and highly viscous dispersions by mechanical treatment. Transmission electron microscopic observation showed that the dispersions consisted of individualized cellulose nanofibers 3−4 nm in width and a few microns in length. No intrinsic differences between never-dried and once-dried celluloses were found for preparing the dispersion, as long as carboxylate contents in the TEMPO-oxidized celluloses reached approximately 1.5 mmol/g. Changes in viscosity of the dispersions during the mechanical treatment corresponded with those in the dispersed states of the cellulose nanofibers in water.

Introduction

Nanomaterial technologies have attracted wide attention because of their super functionalities due to their extremely large and active surface areas. Nanofibers are included in an analogous category, and are also expected to have unique properties.[1,2] Processing technologies to prepare nanofibers of synthetic and natural polymers include electrospinning, drawing, template synthesis, phase separation, sea-island composite spinning, and modified melt-blowing.[1−8] However, it is generally difficult to prepare highly crystalline nanofibers by such molecular-assembly processes.[1,2,7,9] On the other hand, there are naturally occurring nanofibers with high crystallinities that are abundantly present in nature. They are native celluloses, which consist of fibrils 2−20 nm in width and have crystallinities of 65−95%, depending on their origins.[10−15] Cellulose fibrils play a significant role in the contribution to the high strength of plant bodies through hierarchal structures consisting of plant cell walls. Hence, another approach to prepare highly crystalline nanofibers from reproducible natural materials is to extract individual cellulose fibrils from native cellulose. Bleached wood pulps and various non-wood fibers such as cotton linters have a great potentiality to be used as resources for producing cellulose nanofibers.

Cellulose fibrils in plant cell walls are, however, tightly hooked to one another by multiple hydrogen bonds, thus it is difficult to individualize cellulose fibrils only by some mechanical treatments.[16] Microfibrillated cellulose (MFC) is manufactured by repeated treatments of cellulose fiber/water slurries using a high-pressure homogenizer, and is strongly swollen in water.[17,18] However, most of the fibrils obtained consist of bundles of (not individual) cellulose fibrils. Much energy is generally required to produce MFC. Cellulose whiskers or microcrystals dispersed in water are prepared by treating native celluloses with sulfuric acid, where small amounts of sulfate ester groups are introduced to the surfaces.[19−26] This treatment is, however, hydrolytic and thus results in dramatic decreases in both the yield and fibril length down to 100−150 nm. Bacterial cellulose gels produced by *Acetobacter xylinum* consist of long and individual cellulose fibrils. Because numerous contact points exist between the bacterial cellulose fibrils in the gels, however, cellulose fibrils well dispersed in water at the individual fibril level could not be obtained from the bacterial cellulose.[27,28] Thus, so far no methods have been developed to prepare long and individualized cellulose fibrils dispersed in water, especially using only mechanical treatment of plant celluloses.

Before disintegration treatment of native celluloses, some surface modifications of cellulose fibrils are needed to prepare individualized fibrils without significant aggregation. Such modifications will make it possible to loosen the adhesion between cellulose fibrils by preventing the formation of strong interfibril hydrogen bonds. We have extensively studied the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation of celluloses for regioselective conversion of the primary hydroxyl groups to carboxylate ones in aqueous media to prepare water-soluble β-1,4-linked polyglucuronic acid (cellouronic acid).[29−34] We found in the series of TEMPO-mediated oxidation studies that significant amounts of carboxylate and aldehyde groups were introduced into native celluloses, maintaining their fibrous morphologies and crystallinities, by the TEMPO-mediated oxidation under mild conditions.[35−40] Solid-state ^{13}C NMR and other distribution analyses revealed that the carboxylate groups formed were predominantly present on the cellulose fibril surfaces, and no oxidation occurred inside cellulose crystallites.[37,38]

In our preliminary study, we successfully prepared individualized cellulose fibril/water dispersions using TEMPO-mediated

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oxidation of native celluloses followed by disintegration of the oxidized cellulose fibers in water using a Warning blender.[41] The cellulose fibril dispersions obtained were almost transparent and highly viscous. Transmission electron microscopic (TEM) observation of the dispersions showed that mostly individualized cellulose fibrils 3−5 nm in width were obtained from wood cellulose and cotton lint. However, many kinks due to mechanical damage were observed on the cellulose fibrils.

In the present report, as a full paper following our previous communication,[41] we oxidized never-dried and once-dried hardwood celluloses by the TEMPO-mediated system under various conditions. The oxidized celluloses were agitated in water using magnetic stirrers. Swelling and dispersion behavior of the oxidized celluloses in water were studied in detail in terms of the carboxylate content by spectroscopic, microscopic, and viscosity analyses.

Experimental Section

Materials. A commercial hardwood bleached kraft pulp was used as native cellulose fibers, whose carboxyl content was 0.05 mmol/g. The α-cellulose content of the pulp was 90%, and the rest was mostly xylan. Two types of this cellulose were provided by a Japanese pulp company: never-dried wet fibers with 80% water content and thermally dried fibers with 7% water content. TEMPO, sodium bromide, a 12% sodium hypochlorite solution, and other chemicals were of laboratory grade (Wako Pure Chemicals, Japan) and used without further purification.

TEMPO-Mediated Oxidation. The cellulose fibers (1 g) were suspended in water (100 mL) containing TEMPO (0.016 g, 0.1 mmol) and sodium bromide (0.1 g, 1 mmol). The 12% NaClO solution was adjusted to pH 10 by the addition of 0.1 M HCl. The TEMPO-mediated oxidation was started by adding the desired amount of the NaClO solution (1.3−5.0 mmol NaClO per gram of cellulose), and was continued at room temperature by stirring at 500 rpm. The pH was maintained at 10 by adding 0.5 M NaOH using a pH stat until no NaOH consumption was observed. The TEMPO-oxidized cellulose was thoroughly washed with water by filtration and stored at 4 °C before further treatment or analysis.[35−40] Recovery ratios of the TEMPO-oxidized celluloses after washing were over 90%. The carboxylate content of the TEMPO-oxidized cellulose was determined using an electric conductivity titration method.[35] In some experiments, sodium carboxylate groups in the TEMPO-oxidized celluloses were converted to free carboxyl ones by ion-exchange treatment; 0.1% cellulose/water slurries were adjusted to pH 2−3 with 0.1 M HCl and left at rest for 1 h followed by washing thoroughly with water.

Water-Retention Value. The wet TEMPO-oxidized cellulose was centrifuged at 4500 gravity and 20 °C for 20 min. The water-retention value (WRV) was calculated using the following equation: WRV (%) $= 100 \times (W_w - W_d)/W_d$, where W_w is the mass of the wet sample after centrifugation, and W_d is that after drying of the wet sample at 105 °C for 3 h.

Stirring of TEMPO-Oxidized Cellulose/Water Slurries. A slurry of cellulose fibers in water (25 mL) at 0.1% (w/v) consistency was agitated using a magnetic stirrer bar at 1500 rpm in an airtight bottle. After stirring from 6 h to 10 days at room temperature, the slurry was stored at 4 °C before further analyses.

Optical Transmittance. A cellulose slurry or dispersion was introduced into a poly(methyl methacrylate) disposable cuvette, and the transmittance was measured from 285 to 750 nm using a Shimadzu UV−vis spectrometer (UV-1700). The spectrum of a cuvette filled with water was used as a reference and to correct the transmittance of the slurry or dispersion sample.

Microscopic Observations. Slurries or dispersions of TEMPO-oxidized celluloses in water were observed using a photomicroscope (Olympus BX50) equipped with a phase-contrast lens (Olympus UPlanFLN-PH), cross-polarizers in some cases, and a digital camera (Olympus PD20). A 10 μL aliquot of the 0.01% (w/v) cellulose dispersion was mounted on a glow-discharged carbon-coated electron microscopy grid. The excess liquid was absorbed by a filter paper, and one drop of 2% uranyl acetate negative stain was added before drying. Excess solution was blotted out with a filter paper and allowed to stand for drying by natural evaporation. The sample grid was observed at 100 kV using a JEOL electron microscope (JEM 2000-EXII). All micrographs were taken on Fuji FG films.

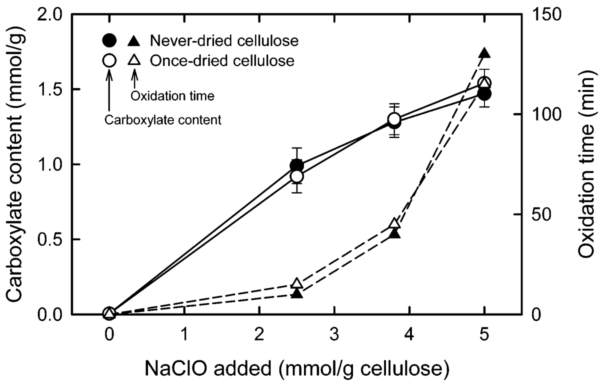

Figure 1. Associations between NaClO added to the TEMPO-mediated oxidation and either the carboxylate content of the oxidized cellulose or the oxidation time. Never-dried and once-dried celluloses were used as the starting materials.

Flow Properties. A Thermo HAAKE rotational rheometer (RheoStress 600) was used to examine the flow properties of the 0.1% cellulose/water slurry after being stirred. The cellulose/water dispersion (410 μL) was transferred to the titan cone−plate sensor system with a 2° cone angle and a 35 mm diameter. Measurements were carried out at 24 °C for 3 min. Flow curves were recorded by HAAKE rheometer software (RheoWin version 3.14). Viscosity of the 0.1% cellulose/water slurry was calculated from shear stress at 114 s^{-1} using the Newtonian equation for viscosity: viscosity (η) = shear stress (τ)/shear rate ($d\gamma/dt$).

Results and Discussion

TEMPO-Mediated Oxidation of Never-Dried and Once-Dried Celluloses. Figure 1 shows associations between the amount of NaClO added as the co-oxidant and either the carboxylate content of the TEMPO-oxidized cellulose or the oxidation time for never-dried and once-dried celluloses used as the starting materials. Here, 1 mol of the C6 primary hydroxyl group is converted to 1 mol of C6 carboxylate group via C6 aldehyde by consuming 2 mol of NaClO.[35] The amount of carboxylate groups formed from the primary hydroxyl groups of cellulose increased with the amount of NaClO added.[35,40] Correspondingly, the oxidation time also increased. Even though the increased carboxylate content due to the increase in added NaClO of 3.8−5.0 mmol per gram of cellulose was only 0.2−0.3 mmol/g, the oxidation time remarkably increased from 40−45 min to 115−130 min. In the case of the TEMPO-mediated oxidation of native celluloses, the regioselective oxidation to form the carboxylate groups on the surface of each cellulose fibril proceeds from the regions accessible to the reaction with the oxidized TEMPO molecules (i.e., 1-oxopiperidinium ions), maintaining the original fibrous morphology.[37,38] It seems likely that some cellulose fibril surfaces resistant to the oxidation exist in the cellulose fibers, resulting in longer oxidation time. The results in Figure 1 revealed that there were no significant differences in carboxylate content or oxidation time between the never-dried and once-dried celluloses. Some aldehyde groups are also formed from C6 primary hydroxyl groups of native

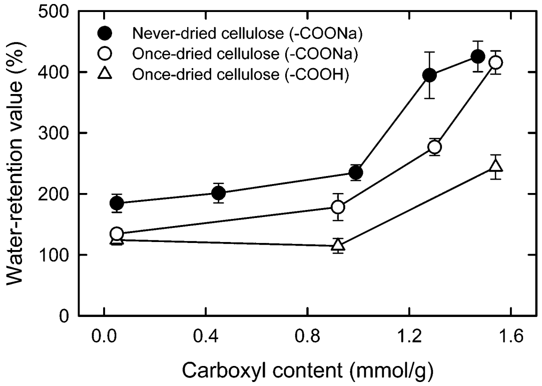

Figure 2. WRVs of the TEMPO-oxidized celluloses with different carboxylate contents.

celluloses by TEMPO-mediated oxidation.[35,39,40] However, these aldehyde groups had no influence, particularly on the cellulose nanofiber preparation. The detailed associations between oxidation conditions and the amounts of aldehyde groups formed in the TEMPO-oxidized celluloses have been described in previous papers.[35,39,40]

The TEMPO-mediated oxidation with the addition of 5.0 mmol NaClO (per gram of cellulose) was applied to the never-dried cellulose at pH 9.5, 10, and 10.5. The time required for oxidation was 285, 130, and 195 min, respectively, while the carboxylate contents were almost equal between the oxidized celluloses prepared at each pH. Indeed, TEMPO-mediated oxidation to convert the primary hydroxyl groups of polysaccharides to carboxylate ones is pH-dependent.[42] Also, in the case of TEMPO-mediated oxidation of native cellulose, the pH of the reaction clearly influences the efficiency or the time required for oxidation. The optimum pH was found to be 10 for shortening the oxidation time.

Figure 2 shows WRVs of the TEMPO-oxidized celluloses with different carboxylate contents. WRVs reflect the degree of swelling of TEMPO-oxidized celluloses in water, and are influenced by the content and distribution of hydrophilic carboxylate groups introduced and specific surface areas or degrees of fibrillation of the celluloses. Therefore, it is natural that the WRV increased with increasing the carboxylate content of the TEMPO-oxidized celluloses. In the range of the carboxylate content from 0.05 to 1.3 mmol/g, the WRV of the oxidized product prepared from the never-dried cellulose was higher than that prepared from the once-dried cellulose, even at similar carboxylate contents. It is well-known that once-dried cellulose or pulp fibers exhibit decreased accessibility to water swelling, cellulase degradation, or chemical reactions by increased hydrogen bonds or decreased specific surface areas.[43−45]

On the other hand, both the never-dried and once-dried celluloses turned to the oxidized products having similar WRVs of more than 400%, when the carboxylate contents reached approximately 1.5 mmol/g. Even at such high WRVs, however, the morphology of the cellulose fibers was mostly unchanged at the micron-scale level before and after the oxidation (Figure 3). The high WRV with little morphological change is characteristic of TEMPO-oxidized native celluloses. The oxidation of the primary hydroxyl groups occurs only on the surfaces of fibrils in cellulose fibers,[37,38] and this regioselective oxidation probably resulted in such specific water-absorption behavior without any significant changes in the fibrous morphology. When the sodium carboxylate groups in the TEMPO-oxidized cellulose were converted to free carboxyl ones by ion-exchange, the WRV drastically decreased (Figure 2).[44−46]

Stirring of TEMPO-Oxidized Cellulose Fiber/Water Slurries. When a 0.1% slurry of the TEMPO-oxidized cellulose fibers in water was further agitated with a magnetic stirrer at 1500 rpm, remarkable swelling was observed with the stirring time. The phase-contrast microphotographs in Figure 4 show that the TEMPO-oxidized cellulose fibers are swollen in water, partly forming balloon structures, which are swollen states of wood cellulose fibers often observed during the dissolution process in cellulose solvents such as 8% lithium chloride/*N*,*N*-dimethylacetamide, copperammonium hydroxide, copperethylene-diamine, and phosphoric acid.[47−48] As the stirring continued, the partly swollen fibers turned to more swollen and small fragments, and finally disappeared to provide almost transparent dispersions.

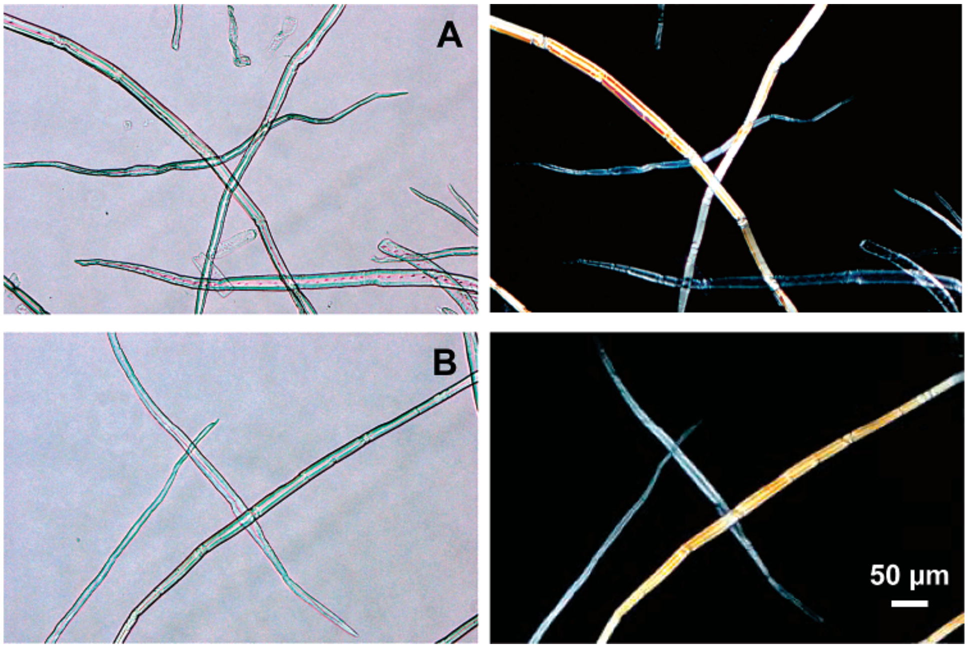

Figure 3. Optical microphotographs of the original (A) and TEMPO-oxidized (B) celluloses with carboxylate contents of 0.05 and 1.5 mmol/g, respectively. Images were taken with or without cross-polarizers.

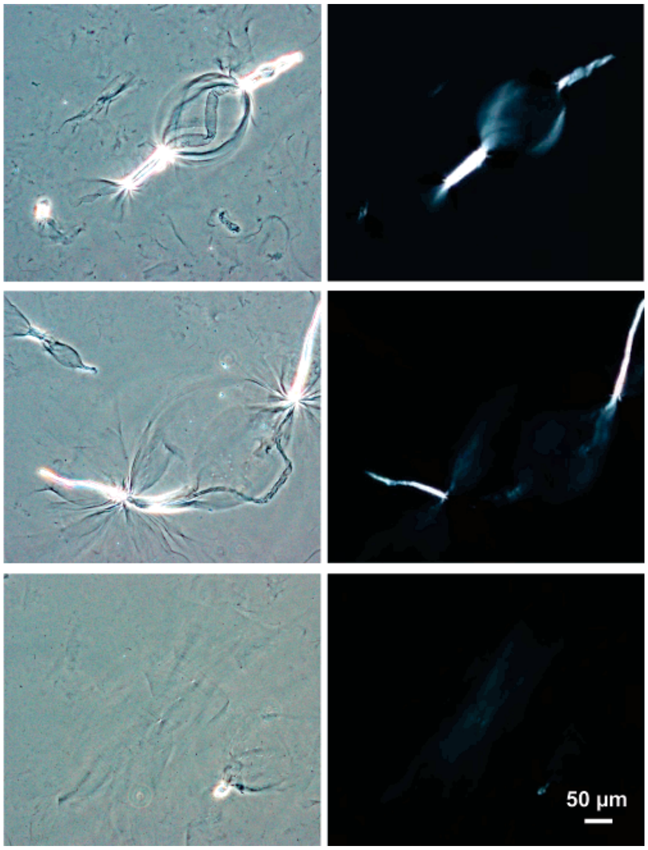

Figure 4. Phase-contrast microphotographs of swollen states of the TEMPO-oxidized cellulose (carboxylate content 1.5 mmol/g) in water during stirring treatment. Images were taken with or without cross-polarizers.

The weight-ratios of bulk cellulose in the slurries or dispersions recovered by centrifugation at 12 000 gravity for 30 min were 82, 74, 35, and 3% after stirring of the 0.1% oxidized cellulose/water slurries or dispersions (25 mL) at 1500 rpm for 12 h, 1 day, 3 days, and 10 days, respectively; 97% of the oxidized cellulose was transferred to the supernatant fraction by stirring for 10 days (Figure 5). Here, the TEMPO-oxidized cellulose with the carboxylate content of 1.5 mmol/g was used. When the 0.1% oxidized cellulose/water slurry (100 mL) was agitated at 12 000 rpm using a domestic blender, more than 97% of the oxidized cellulose was transferred to the supernatant fraction within 20 min. About 93% of the oxidized cellulose was transferred to the supernatant fraction within 2 min when the slurry (25 mL) was disintegrated using an ultrasonic homogenizer. Hence, the blender or ultrasonic treatments are more effective for converting the TEMPO-oxidized cellulose fibers into almost transparent dispersions in water for practical use. Mechanical damage may, however, occur on the TEMPO-oxidized celluloses during such harsh mechanical treatments.[41] Without stirring, the original state at 0 h in Figure 5 was maintained, even after allowing the suspension to stand for at least several months at room temperature.

Figure 6 shows photographs of a 0.1% slurry of the original cellulose and 0.1% dispersions of TEMPO-oxidized celluloses with various carboxylate contents after stirring in water for 10 days. Clear sedimentation in water was observed for the original cellulose fibers at the bottom of the bottle. The TEMPO-oxidized cellulose with the carboxylate content of 1.0 mmol/g, which was prepared from the never-dried cellulose, was homogeneously dispersed in water. However, the transparency was less high. When the TEMPO-oxidized cellulose with the carboxylate content of 0.9 mmol/g, which was prepared from the once-dried cellulose, was used, partial sedimentation of the cellulose fibers was still observed. Hence, even with similar carboxyl contents (i.e., 1.0 and 0.9 mmol/g), the dispersion behavior of the TEMPO-oxidized cellulose fibers in water after stirring was different between the never-dried and once-dried celluloses used as the starting materials in the TEMPO-mediated oxidation.

On the other hand, similar transparent dispersions were obtained from the slurries of the TEMPO-oxidized celluloses prepared from both the never-dried and once-dried celluloses, when their carboxylate contents increased to about 1.5 mmol/g. The weight-ratios of solid cellulose determined by centrifugation at 12 000*g* for 30 min were less than 3% for both these dispersions; more than 97% of the oxidized celluloses were transferred to the supernatant fraction by stirring for 10 days. Hence, there are no intrinsic differences in preparing almost transparent TEMPO-oxidized cellulose/water dispersions between the never-dried and once-dried celluloses used as the starting materials, as long as the carboxylate contents in the oxidized products reached about 1.5 mmol/g.

UV−vis transmittance spectra of the dispersions of the TEMPO-oxidized celluloses are presented in Figure 7. The transmittance is wavelength-dependent, as light scatters more when the wavelength approaches the diameter of the particles.[49] When the carboxylate content was about 1.5 mmol/g, almost transparent dispersions were obtained for the TEMPO-oxidized celluloses by stirring in water for 10 days, irrespective of the never-dried and once-dried celluloses used as the starting materials in the TEMPO-mediated oxidation. Thus, the carboxylate content is the key factor influencing the dispersion

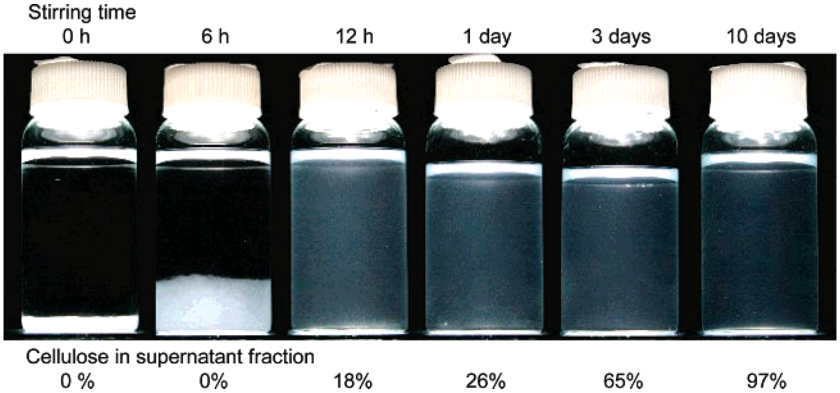

Figure 5. Changes in the dispersion state of the TEMPO-oxidized cellulose in water with increased stirring time. Carboxylate content of the oxidized cellulose was 1.5 mmol/g. The weight-ratio of cellulose present in the supernatant fraction was determined after centrifugation at 12 000*g* for 30 min. Photos were taken 1 day after stirring.

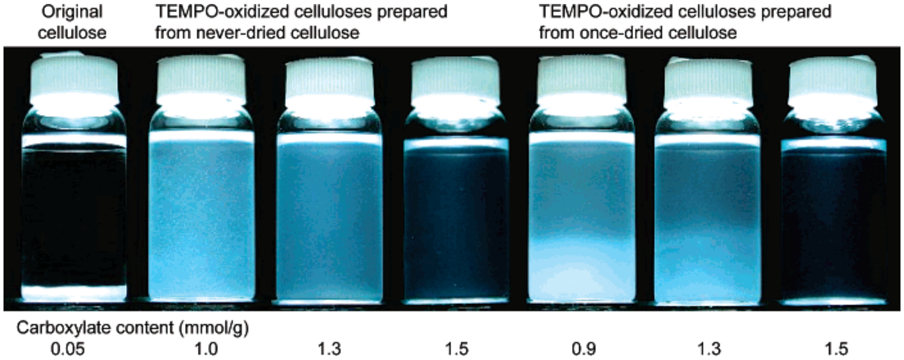

Figure 6. Dispersion states of the TEMPO-oxidized celluloses with different carboxylate contents. Each dispersion was prepared by stirring in water for 10 days. Photos were taken 1 day after stirring.

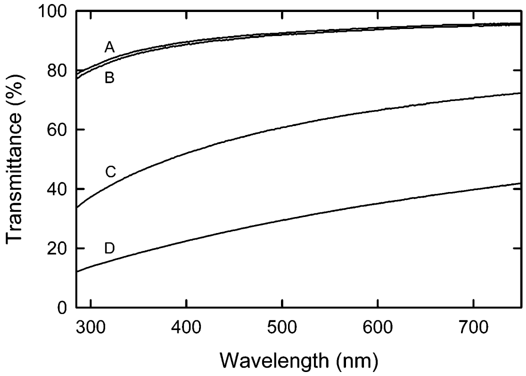

Figure 7. UV−vis transmittance of the TEMPO-oxidized cellulose/water dispersions. The oxidized celluloses with different carboxylate contents were prepared from never-dried (A,C,D) and once-dried (B) celluloses. Carboxylate contents were 1.5 (A), 1.5 (B), 1.3 (C), and 1.0 mmol/g (D).

behavior of the oxidized celluloses by stirring in water, and not the difference between the never-dried and once-dried celluloses used as the starting materials. Once such transparent dispersions of the TEMPO-oxidized celluloses in water were obtained, the transparencies were maintained for more than 6 months at about 4 °C in a refrigerator.

TEM Observations of the TEMPO-Oxidized Cellulose Fibrils. Figure 8 shows TEM images of the fibrils of TEMPO-oxidized celluloses with carboxylate contents of 0.9 and 1.5 mmol/g, which were prepared from the once-dried cellulose. Cellulose fibrils clearly formed lateral aggregates for the oxidized cellulose with the low carboxylate content. Hence, these oxidized cellulose/water dispersions had a low light-transmittance, even after the mechanical treatment (Figures 6 and 7). On the other hand, the TEMPO-oxidized cellulose with the carboxylate content of 1.5 mmol/g was mostly converted to individual cellulose fibrils with nearly uniform lateral size of 3−4 nm. The small width makes the dispersion almost transparent. However, kinks were partly observed in the TEM image, indicating that the cellulose nanofibers experience some mechanical damage during stirring. On the basis of the unit cell size of the plant cellulose crystal form (cellulose I_β[11,50]), the cellulose nanofibers 3−4 nm in width consist of approximately 30−50 cellulose chains in the cross-section of each cellulose nanofiber.

The TEM observation revealed that the length of most of the cellulose nanofibers obtained was a few microns. The cellulose chain length can be calculated from the size of anhydroglucose unit (0.518 nm) and the degree of polymerization.[51] The calculated weight-average contour length of the cellulose chains was about 870 nm, which is shorter than the length of the cellulose nanofibers observed in Figure 8. Thus, each cellulose nanofiber consists of a few cellulose chains along the longitudinal direction.

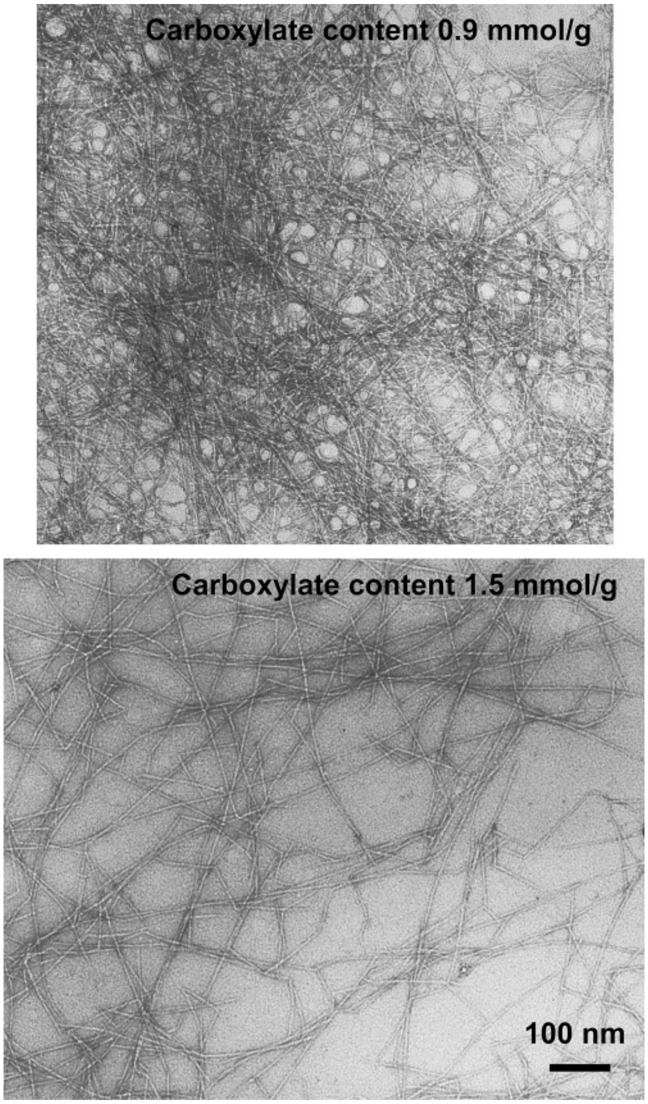

Figure 8. TEM images of dispersions of the TEMPO-oxidized celluloses with carboxylate contents of 0.9 and 1.5 mmol/g. Images were taken after stirring in water for 10 days.

With the assumption that each cellulose nanofiber has a square cross-section 3−4 nm across each side, the ratio of the oxidized glucose unit (i.e., the anhydroglucuronic acid unit) to the total units on the cellulose fibril surface is calculated from the carboxylate content and the unit cell size of cellulose I_β (the *d*-spaces of the 110 and 1-10 planes were about 0.53 and 0.61

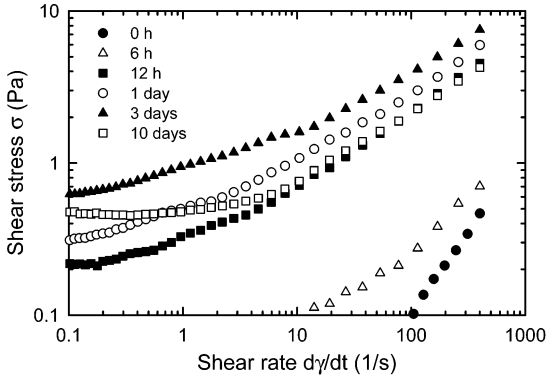

Figure 9. Associations between shear rate and shear stress of the TEMPO-oxidized cellulose/water slurries stirred for 0−10 days.

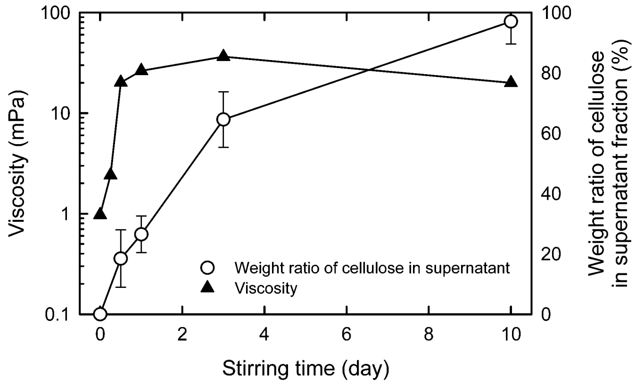

Figure 10. Associations between stirring times of a 0.1% slurry of the TEMPO-oxidized cellulose with a carboxylate content of 1.5 mmol/g and either its viscosity or the weight ratio of cellulose present in the supernatant faction after centrifugation at 12 000*g* for 30 min.

nm, respectively).[11,50] Since mostly individualized cellulose nanofibers were obtained from the TEMPO-oxidized celluloses with a carboxylate content of about 1.5 mmol/g, this carboxylate content was used in the calculation. The obtained ratio was approximately 0.5: one of every two anhydroglucose units of the cellulose fibril surface was oxidized to the anhydroglucuronic acid unit by the TEMPO-mediated oxidation. Because the primary hydroxyl group of every one of two anhydroglucose units on the cellulose fibril surface faces the outer side, or, inversely, that of every one of two anhydroglucose units on the cellulose fibril surface faces the inside cellulose crystallite, the calculated ratio 0.5 revealed that almost all the primary hydroxyl groups of cellulose fibril surfaces in the cellulose fibers, which face the outer side and are accessible to the reaction with the oxidized TEMPO molecules, are oxidized to carboxylate groups by the TEMPO-mediated oxidation. This oxidation level is needed to prepare the mostly individualized and long cellulose nanofibers in water.

The cellulose nanofibers obtained in this study originate from crystalline cellulose fibrils forming hierarchal structures in plant cell walls. The TEMPO-mediated oxidation selectively introduces anionic carboxylate groups on the surface of each cellulose fibril with high densities under mild conditions. On the basis of the unit cell size of cellulose I_β,[11,50] the density of the primary hydroxyl groups of anhydroglucose units facing the outer side on each cellulose fibril is 3.4 groups/nm^2 or 0.54 C/m^2. This characteristic point of the TEMPO-mediated oxidation of native cellulose makes it possible to prepare such long and individualized cellulose nanofibers, which have the same crystallinity as that of the original cellulose (i.e., ∼70%), maintaining the stable dispersion states.

Flow Properties of the Cellulose Nanofiber/Water Dispersions. Flow properties or viscosities of the TEMPO-oxidized cellulose/water slurries or dispersions were evaluated in terms of the stirring time, which reflects the degree of dispersion of the TEMPO-oxidized cellulose fibrils in water by stirring. Figure 9 depicts flow curves of the 0.1% slurries with different stirring times. The dispersions exhibited pseudo-plastic flows after stirring for 12 h. The dispersion obtained by stirring for 10 days clearly showed yield stress in the flat region at lower shear rates, which is often observed with gel-like structures.

Figure 10 shows associations between the stirring time of the 0.1% TEMPO-oxidized cellulose slurries or dispersions and either the weight percentage of the oxidized cellulose present in the supernatant fractions after centrifugation at 12 000*g* or the viscosity of the whole slurry or dispersion. Viscosity of the 0.1% slurry significantly increased by stirring for 12 h, although only about 20% of the oxidized cellulose was present in the supernatant fraction, resulting from strong swelling of the TEMPO-oxidized cellulose fibers in water at this stage (Figure 4). When the cellulose slurry was stirred for 3−10 days, the viscosity slightly decreased. The partial aggregates of cellulose nanofibers present in the dispersion after stirring for 3 days may have disappeared and mostly converted to individual cellulose nanofibers in water by stirring for 10 days.

Conclusion

Mostly individualized cellulose nanofibers dispersed in water can be obtained by TEMPO-mediated oxidation of native cellulose and successive mechanical treatment of the oxidized cellulose in water. The TEMPO-mediated oxidation of native cellulose at pH 10 is optimum for shortening the oxidation time. The cellulose nanofibers obtained were 3−4 nm in width and a few microns in length. This small lateral size of the cellulose nanofibers makes it possible to provide almost transparent and highly viscous dispersions. Almost all the primary hydroxyl groups facing the outer side of each cellulose fibril (i.e., about one of every two glucose units of the cellulose chains on the cellulose fibril surface) need to be oxidized to the carboxylate ones by the TEMPO-mediated oxidation in order to obtain mostly individualized cellulose nanofiber/water dispersions. The carboxylate groups formed on each cellulose nanofiber surface in a high density (ca. 3.4 groups/nm^2 or 0.54 C/m^2) allow for quite stable dispersions. Both never-dried and once-dried celluloses give similar cellulose nanofiber/water dispersion when the conditions described above are satisfied. Because the original cellulose crystallinity is maintained during TEMPO-mediated oxidation and the successive stirring, cellulose nanofibers with crystallinities of 65−95% can be obtained using this method.

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