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NOTE

Effect of coexisting salt on TEMPO-mediated oxidation of wood cellulose for preparation of nanocellulose

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Abstract The influence of coexisting salt in 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation of wood cellulose in water at pH 10 for 100 min was investigated, in which Na_2SO_4 was partly used in place of NaBr in the conventional TEMPO/NaBr/NaClO oxidation system. The amount of NaBr could be reduced from 1 to 0.2 mmol/g-wood cellulose by adding 0.4 mmol/g Na_2SO_4. This introduced a carboxylate content of ~1.2 mmol/g, which is sufficient to prepare TEMPO-oxidized cellulose nanofibrils (TOCNs) by mechanical disintegration of the oxidized cellulose in water. When no NaBr was used and Na_2SO_4, Na_2SO_3, NaCl or CH_3COONa was instead used as a coexisting salt in TEMPO/NaClO oxidation, the oxidized celluloses had carboxylate contents of 0.6–0.8 mmol/g, which are insufficient to prepare TOCNs with nanofibrillation yields >55%. The viscosity-average degrees of polymerization of the resulting TEMPO-oxidized celluloses were in the range 420–450, indicating that depolymerization of cellulose is not governed by the carboxylate content of the TEMPO-oxidized cellulose but rather by the oxidation time.

Keywords TEMPO · Oxidation kinetics · Coexisting salt · Carboxylate content · Nanofibrillation

Introduction

2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation is widely used to introduce carboxylate groups into polysaccharides (de Nooy et al. 1995). When oxidation is applied to native celluloses, C6-carboxylate groups are position-selectively formed on the crystalline cellulose microfibril surfaces. In the conventional method, wood celluloses or bleached kraft pulps are oxidized using the TEMPO/NaBr/NaClO system in water at pH 10. When the oxidized celluloses have more than 1 mmol/g C6-carboxylate groups, TEMPO-oxidized wood cellulose nanofibrils (TOCNs) ~3 nm wide with high aspect ratios (>150) are obtained by gentle mechanical disintegration in water (Saito et al. 2006a, b, 2007; Isogai et al. 2011).

In the TEMPO/NaBr/NaClO system, NaBr used as a catalytic coexisting salt enhances the oxidation rate by formation of NaBrO from NaClO (de Nooy et al. 1995; Isogai and Kato 1998; Isogai et al. 2011; Pääkkönen et al. 2015). Yui et al. (2014) reported that in TEMPO-mediated oxidation of cotton fabrics to provide a hydrophilic nature and deodorant functions to cotton underclothes, the TEMPO/Na_2SO_4/NaClO system is better than the conventional system to introduce carboxylate groups of ~0.3 mmol/g in

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terms of the mechanical properties, soft texture, and color stability during thermal laundry drying. This result indicates that NaBr can be partly replaced by Na_2SO_4, which is less expensive than NaBr, in TEMPO-mediated oxidation of wood cellulose to prepare TOCNs.

In TEMPO-mediated oxidation and bromide-free TEMPO-mediated oxidation, the effect of coexisting salt on the structures of the oxidized polysaccharides has been reported (Bragd et al. 2000, 2001, 2002; Chang et al. 2008; Jiang et al. 2000; Lai et al. 2013), in terms of environmental and cost aspects. In this study, we added Na_2SO_4 with NaBr at various molar ratios to investigate the effect of the coexisting salt on TEMPO-mediated oxidation of wood cellulose.

Experimental

Materials

A softwood bleached kraft pulp with α-cellulose content of ~90% was supplied by Nippon Paper Industries Co. Ltd. (Tokyo, Japan) in a never-dried state with water content of ~80%. The pulp was demineralized according to a previously reported procedure (Shinoda et al. 2012). All of the reagents were laboratory grade (Wako Pure Chemicals, Tokyo, Japan), and used without further purification. Ion-exchanged water with electric conductivities <0.2 μS/cm was used in the whole experiments.

TEMPO-mediated oxidation of wood cellulose

Never-dried wood cellulose corresponding to 1 g dry weight was suspended in water (100 mL) containing TEMPO (0.1 mmol) and a designated amount of a salt or salt mixture, that is, various molar ratios of NaBr and Na_2SO_4. An aqueous solution containing 5 mmol NaClO was added to the cellulose slurry to start TEMPO-mediated oxidation. Oxidation of wood cellulose was performed in water for 100 min at pH 10 and room temperature (Shinoda et al. 2012). The amount of 0.5 M NaOH consumed to maintain the slurry at pH 10 was monitored by a pH stat (AUT-501, DKK-TOA, Japan). The oxidized celluloses were repeatedly washed with water by filtration, and then stored at 4 °C in a refrigerator. Part of the oxidized celluloses was freeze-dried, and the carboxylate and aldehyde contents were determined by the electric conductivity titration method (Saito and Isogai 2004).

DP_v measurement

The oxidized celluloses containing small amounts of C6-aldehyde groups were further oxidized with $NaClO_2$ in water at pH 4.5 (Shinoda et al. 2012) followed by thorough washing thoroughly with water by centrifugation at 3000×*g* for 5 min. The TEMPO-oxidized and $NaClO_2$-oxidized cellulose (0.04 g) obtained after freeze-drying was dissolved in 0.5 M copper ethylenediamine (20 mL) by stirring for 30 min. The intrinsic viscosities of the solutions were measured at 25 °C using a capillary viscometer. The values were converted to viscosity-average degrees of polymerization (DP_v) using the previously reported equation $[\eta] = 5.7 \times DP_v$ (Shinoda et al. 2012).

Mechanical fibrillation

The never-dried TEMPO-oxidized cellulose was suspended in water at 0.1% w/v (40 mL), and the slurry was then mechanically disintegrated under previously reported conditions (Shinoda et al. 2012). Light transmission spectra of the TOCN dispersions without removal of the unfibrillated fraction were recorded using an ultraviolet–visible (UV–vis) spectrometer (JASCO V670, Tokyo, Japan). The as-prepared TOCN dispersions were centrifuged at 3000×*g* for 5 min to remove the unfibrillated fraction, and the supernatants were observed between cross-polarizers. The nanofibrillation yield was calculated from the dry weight of the unfibrillated fraction collected by centrifugation (Takaichi et al. 2014).

Results and discussion

Carboxylate contents and DP_v values of the TEMPO-oxidized celluloses

The weight recovery ratios of all of the TEMPO-oxidized celluloses were greater than 95%. Figure 1a shows the carboxylate and aldehyde contents and DP_v values of the TEMPO-oxidized celluloses prepared with various NaBr:Na_2SO_4 molar ratios. Because one mole of Na_2SO_4 has two sodium cations and one divalent sulfate anion, the amount of added Na_2SO_4

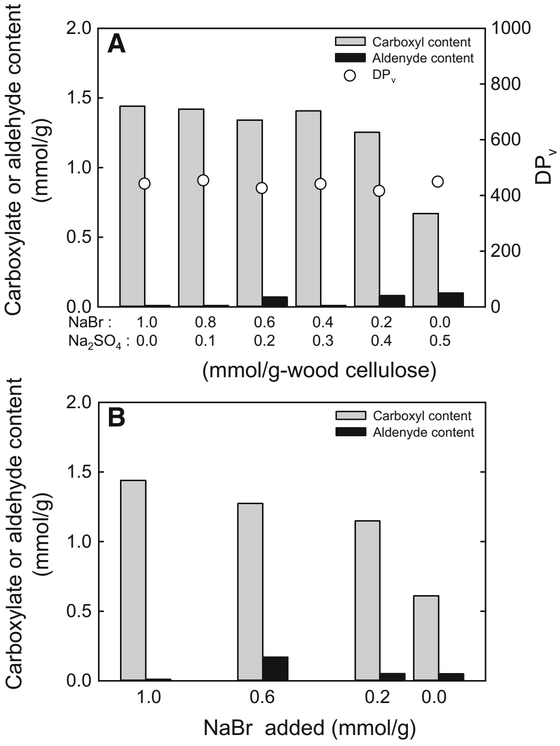

Fig. 1 Carboxylate and aldehyde contents and DP_v values of TEMPO-oxidized celluloses prepared with **a** the TEMPO/NaBr/Na_2SO_4/NaClO system at various NaBr:Na_2SO_4 molar ratios and **b** the TEMPO/NaBr/NaClO system with various amounts of NaBr. All of the experiments were performed for 100 min in water at pH 10

was adjusted to be half that of the replaced amount of NaBr. Hence, the total amounts of valences originating from NaBr and Na_2SO_4 were adjusted to the same between the TEMPO/NaBr/NaClO and TEMPO/NaBr/Na_2SO_4/NaClO systems in this study. When the amount of added NaBr was 0.2 mmol/g-wood cellulose and that of Na_2SO_4 was 0.4 mmol/g-wood cellulose, the carboxylate content was still high (1.25 mmol/g). The DP_v values decrease from 1270 for the original wood cellulose to 420–450 (Fig. 1a), and thus the DP_v value is hardly influenced by the NaBr:Na_2SO_4 molar ratio. Because the oxidation time was fixed at 100 min in this study, the decrease in DP_v may be mainly governed by the reaction time. There are small amounts of aldehyde groups (<0.1 mmol/g) in the oxidized celluloses prepared under Na_2SO_4-rich conditions, except for the oxidized cellulose prepared with a NaBr:Na_2SO_4 molar ratio of 0.6:0.2.

The reference data prepared for TEMPO-mediated oxidation without Na_2SO_4 are shown in Fig. 1b. The carboxylate content of the oxidized cellulose prepared without Na_2SO_4 is lower than that of the oxidized cellulose prepared with Na_2SO_4 at the same NaBr addition level. Thus, addition of Na_2SO_4 has a positive influence on formation of carboxylate groups. Because oxidized TEMPO or $TEMPO^+$ has a chemical structure similar to those of surfactants, the presence of salt in the oxidation medium may cause low solubility of $TEMPO^+$ in water, resulting in enhancement of covalent bond formation between the $TEMPO^+$ molecules and dissociated primary hydroxy groups of wood cellulose in the oxidation medium (Yui et al. 2014).

The carboxylate contents are similar (0.6–0.8 mmol/g) for the TEMPO/NaClO oxidation without NaBr but with Na_2SO_4, Na_2SO_3, NaCl, CH_3COONa, or no coexisting salt. Sodium acetate and NaCl gave the highest and lowest carboxylate contents of 0.8 and 0.6 mmol/g, respectively. Thus, significant amounts of carboxylate groups form in the oxidized celluloses without a co-existing salt. However, these carboxylate contents of 0.6–0.8 mmol/g are insufficient to prepare TEMPO-oxidized cellulose nanofibrils (TOCNs) by mechanical disintegration in water.

The consumption of 0.5 M NaOH during oxidation was monitored, and the results are shown in Fig. 2a. In Fig. 2b, these results are plotted as the relationship between the initial reaction time (t min) less than 40 min and the amount of 0.5 M NaOH consumed (Y mmol) according to the following equation:

$$Y = \exp[k(t - 10)] \qquad (1)$$

where k is the slope of each line. When oxidation was performed with NaBr:Na_2SO_4 molar ratios of 1:0 and 0.6:0.2, the k values are both 0.26 mmol/min. The k value is 0.22 mmol/min for the NaBr:Na_2SO_4 molar ratio of 0.2:0.3. When oxidation was performed with the molar ratio of 0:0.5, the k value decreases to 0.02 mmol/min. Thus, the presence of NaBr in the oxidation system clearly enhances the oxidation rate, as previously reported (de Nooy et al. 1995; Isogai and Kato 1998; Pääkkönen et al. 2015). However, the results in Figs. 1 and 2 indicate that regeneration of $TEMPO^+$, which can oxidize the C6-OH groups of cellulose to C6-carboxylate groups, steadily proceeds from reduced TEMPO or its hydroxy amine-type structure even without NaBr. The level of depolymerization of the TEMPO-oxidized celluloses does not correspond to their carboxylate content but to the

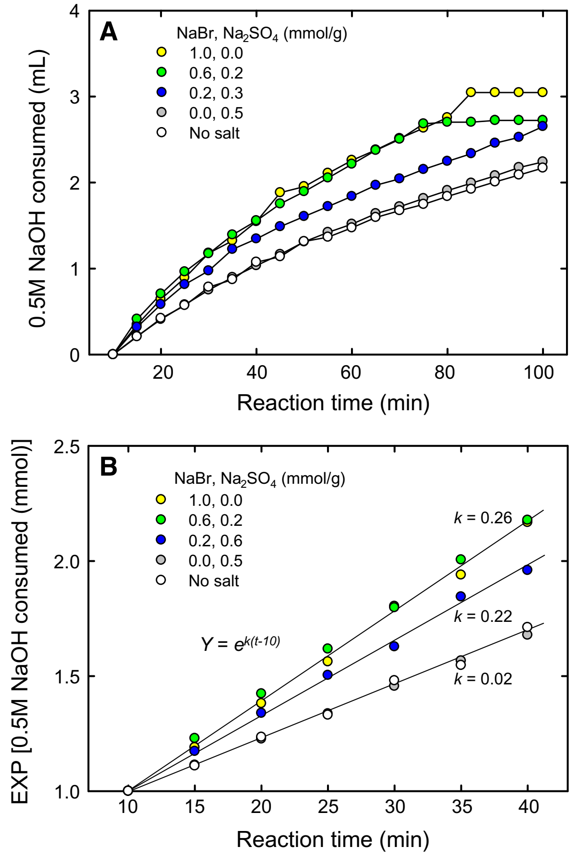

Fig. 2 **a** Relationships between the oxidation time and the amount of 0.5 M NaOH consumed in TEMPO/salt/NaClO oxidation of wood cellulose in water at pH 10 for different NaBr:Na_2SO_4 molar ratio, and **b** the data in **a** plotted according to Eq. (1)

oxidation time, indicating that some active species, such as OH radicals, formed as byproducts in the TEMPO/NaClO system in water mainly cause depolymerization of the oxidized celluloses (Shibata and Isogai 2003; Tamura et al. 2009; Coseri 2017).

Nano-dispersibility of the oxidized celluloses in water

The TEMPO-oxidized celluloses prepared under three conditions were selected (NaBr:Na_2SO_4 molar ratios of 1.0:0, 0.2:0.4, and 0:0.5). UV–vis spectra of 0.1% w/v dispersions of the celluloses after disintegration in water under the same conditions (without removing the unfibrillated fraction) are shown at the bottom of Fig. 3. Although the sample prepared with the NaBr:Na_2SO_4 molar ratio of 0.2:0.4 has a high carboxylate content of 1.25 mmol/g, its dispersion has low transmittance and a low nanofibrillation yield of 55%. However, the dispersions of samples A and B in Fig. 3 show birefringence after removal of the unfibrillated fraction by centrifugation. However, when the disintegration time was increased, both the nanofibrillation yield and the transparency increased to close to the values of sample A in Fig. 3. In contrast, a high nanofibrillation yield of TOCNs could not be obtained with sample C even after disintegration for a long time because of the low carboxylate content.

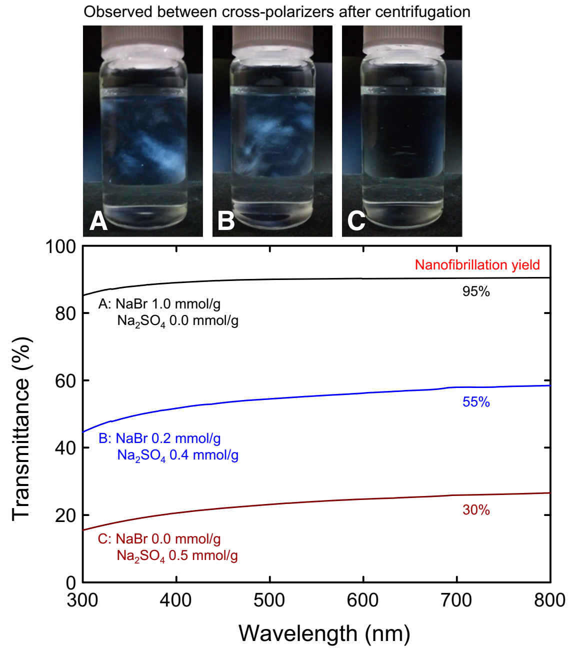

Fig. 3 UV–vis spectra of 0.1% w/v aqueous dispersions of TEMPO-oxidized celluloses prepared under different oxidation conditions but with the same disintegration conditions in water. The *photographs* show the dispersions between cross-polarizers after removal of the unfibrillated fraction by centrifugation

Conclusion

The amount of NaBr used in conventional TEMPO/NaBr/NaClO oxidation of wood cellulose to prepare TOCNs can be decreased and partly replaced by Na_2SO_4 to produce TEMPO-oxidized celluloses with similar carboxylate contents (>1.2 mmol/g). Because the presence of Na_2SO_4 with NaBr enhances formation of carboxylate groups in TEMPO-oxidized celluloses, the salting-out effect for $TEMPO^+$, which behaves like a surfactant, may be elicited in the TEMPO/NaBr/Na_2SO_4/NaClO system. All of the TEMPO-oxidized celluloses with different carboxylate contents have similar DP_v values, indicating that depolymerization of TEMPO-oxidized celluloses mainly depends on the oxidation time rather than the carboxylate content. Although a lower NaBr addition level causes a lower rate of formation of carboxylate groups, the added amount of expensive NaBr can be decreased by addition Na_2SO_4 to prepare TEMPO-oxidized celluloses for production of TOCNs.

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