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Oxidation of bleached wood pulp by TEMPO/NaClO/NaClO₂ system: effect of the oxidation conditions on carboxylate content and degree of polymerization

Abstract Oxidation of bleached wood pulp by the TEMPO/NaClO/NaClO₂ system was carried out at pH 3.5–6.8 and 25°–60°C with different amounts of NaClO, and investigated in terms of effects of the reaction conditions on carboxylate content and degree of polymerization (DP) of the oxidized pulp. Oxidation was accelerated by the addition of NaClO, when carried out at pH 6.8 and 40°–60°C. Addition of NaClO of more than 0.5 mmol per gram of the pulp was effective to accelerate the oxidation. Carboxylate content of pulp oxidized under such conditions increased to approximately 0.6 mmol/g within 6 h. Although DP of the oxidized pulp gradually decreased with oxidation time, no significant differences in DP of oxidized pulps were found at oxidation temperatures between 25° and 60°C, and DP values of more than 900 were maintained after oxidation for 54 h at 60°C.

Key words Cellulose · Microfibril · TEMPO · Oxidation · Carboxyl

Introduction

Many fundamental or technological studies have been directed to oxidation of cellulose with a view to developing the material properties of cellulose by formation of aldehyde and/or carboxyl groups.[1–5] However, most of the oxidation methods reported earlier must be carried out under conditions that are harsh for cellulose and inevitably were accompanied by substantial degradation of the cellulose and various side reactions.[6–9] In the past decade, the catalytic oxidation method using stable nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has become one of the promising procedures for oxidation of cellulose.[10–14] Catalytic oxidation using TEMPO has thus far been applied to cellulose under weakly alkaline conditions at pH 9–11, in conjunction with NaBr and NaClO as a cocatalyst and a primary oxidant, respectively (TEMPO/NaBr/NaClO system), and the C6 primary hydroxyls of cellulose are selectively oxidized.[10–12]

When regenerated or mercerized celluloses are used as starting samples for TEMPO/NaBr/NaClO oxidation, all the C6 hydroxyls of cellulose are oxidized to carboxyls, and water-soluble β-(1→4)-linked polyglucuronic acids (cellouronic acids) are quantitatively obtained.[10] In the case of native celluloses such as bleached wood pulp and cotton, oxidation occurs only at the surface of cellulose microfibrils, maintaining the fibrous morphology of the pulp.[15–18] This beneficial surface oxidation of the pulps led to development of a novel environmentally friendly mechanism for improving wet-paper strength and of metal ion adsorbents having a high exchange capacity.[19–22] In addition, because carboxyl groups formed on the microfibril surfaces have anionic charges in water, which produce repulsive effects between the microfibrils, oxidized pulp can be fully disintegrated in water to individual microfibrils by mild mechanical treatment.[23,24] Films of the individualized microfibrils are transparent and flexible and exhibit high tensile strength, low coefficients of thermal expansion, and extremely high oxygen barrier properties.[25]

However, substantial depolymerization of cellulose during oxidation is inevitable even when using the TEMPO/NaBr/NaClO system. Degrees of polymerization of regenerated celluloses, ranging from 220 to 680, decreased to 40 during the oxidation,[26,27] and degrees of polymerization of bleached wood pulps and cotton linters also decreased eventually to 200–300.[12,15] Depolymerization mechanisms of cellulose during oxidation have been proposed as follows: (1) the β-elimination of glycoside bonds at the C6 aldehydes formed as intermediates in the oxidation of primary hydroxyls to carboxyls, occurring under alkaline conditions,[28] and (2) active species such as hydroxyl radicals formed in situ, in turn attacking the glycoside bonds of cellulose.[29]

In the latest studies about the TEMPO-mediated oxidation of cellulose, we found that depolymerization of cellulose during oxidation was substantially inhibited by using the TEMPO/NaClO/NaClO₂ system under weakly acidic

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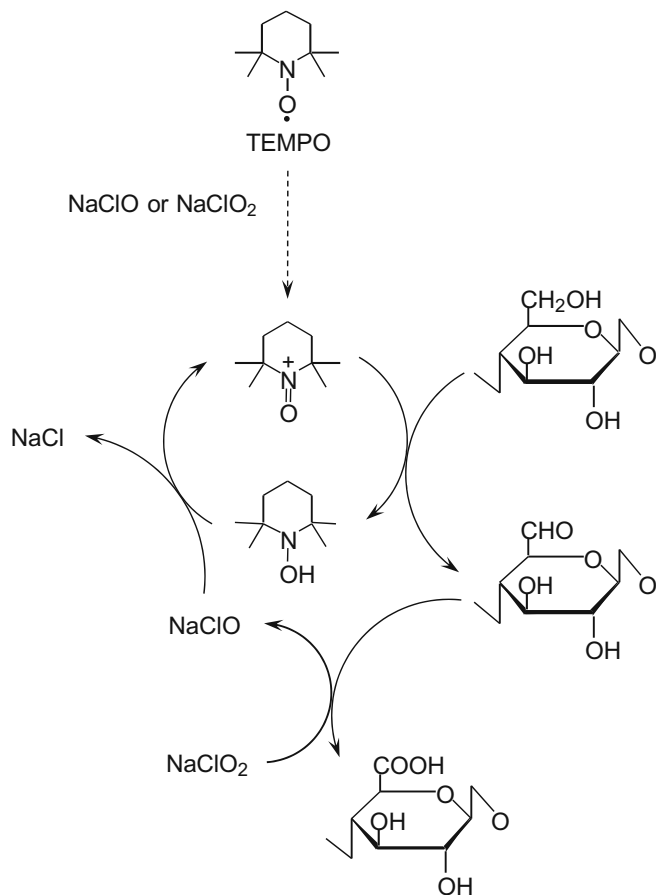e-mail: asaitot@mail.ecc.u-tokyo.ac.jp

Fig. 1. Catalytic cycle of the TEMPO(2,2,6,6-tetramethylpiperidine-1-oxyl)/NaClO/NaClO$_2$ system for oxidation of cellulose

conditions (Fig. 1).[30–32] In the TEMPO/NaClO/NaClO$_2$ system, a primary oxidant is NaClO$_2$, and a catalytic amount of NaClO is added to start the catalytic cycle. Because the C6 aldehydes formed as intermediates are immediately oxidized to carboxyls by NaClO$_2$ under weakly acidic conditions, the depolymerization of cellulose by β-elimination is avoided.

In the present study, oxidation of bleached wood pulp by the TEMPO/NaClO/NaClO$_2$ system was carried out under various reaction conditions to investigate in more detail the effects of the oxidation conditions on carboxylate content and degree of polymerization.

Materials and methods

Materials

A commercial hardwood bleached kraft pulp was provided by a Japanese pulp company as never-dried wet pulp with about 80% water content. The pulp was purified with 0.3% NaClO$_2$ in acetate buffer at pH 4.8 and 60°C for 1 h, and this treatment was duplicated until the pulp became completely white. The pulp was then washed with water by filtration and stored at 4°C. The cellulose content of the pulp was 90%, and the remainder was mostly xylan. TEMPO,

sodium chlorite, a 2 M sodium hypochlorite solution, and other chemicals were of laboratory grade (Wako Pure Chemicals, Japan), and were used without further purification.

Oxidation of bleached wood pulp by TEMPO/NaClO/NaClO$_2$ system

The pulp (1 g) was suspended in 0.1 M sodium phosphate buffer (90 ml, pH 6.8) or 0.1 M acetate buffer (90 ml, pH 3.5 or 4.8) dissolving TEMPO (0.016 g, 0.1 mmol) and sodium chlorite (80%, 1.13 g, 10 mmol) in an airtight flask. The 2 M sodium hypochlorite solution (0.5 ml, 1.0 mmol) was diluted to 0.1 M with the same 0.1 M buffer used as the oxidation medium, and was added at one step to the flask (in some experiments, the oxidation was carried out without addition of sodium hypochlorite solution). The flask was immediately stoppered, and the suspension was stirred at 25°, 40°, or 60°C for a designated time (2–54 h). After cooling the suspension to room temperature, the TEMPO-oxidized celluloses were thoroughly washed with water by filtration. The oxidized pulps were recovered in yields of more than 98% by filtration for all the conditions examined.

Determination of carboxylate content

Carboxylate contents of the oxidized pulps were determined by the electric conductivity titration method. The freeze-dried sample (0.3 g) was suspended in water (55 ml), and sufficiently stirred to be well dispersed. After 0.01 M NaCl (5 ml) was added, the pH value of the suspension was set to 2.8 with 0.1 M HCl. A 0.05 M NaOH solution was added at 0.1 ml/min up to pH 11 using a pH stat. Carboxylate content of the sample was determined from the conductivity and pH curves.[15]

DPv measurement

Intrinsic viscosities of the oxidized pulps were obtained by a capillary viscometer using 0.5 M copper ethylenediamine (cuen) as the solvent, and these values were converted to viscosity average degrees of polymerization (DPv) by the reported method.[33]

Results and discussion

Oxidation of bleached wood pulp by the TEMPO/NaClO$_2$ system

The catalytic cycle of the TEMPO/NaClO/NaClO$_2$ system starts by oxidation of TEMPO to the oxoammonium ion with NaClO or slowly with NaClO$_2$ (see Fig. 1).[32] In the cycle, the oxoammonium ion oxidizes the C6 primary hydroxyls of cellulose to aldehyde and is reduced to the hydroxylamine. The aldehydes are immediately oxidized to
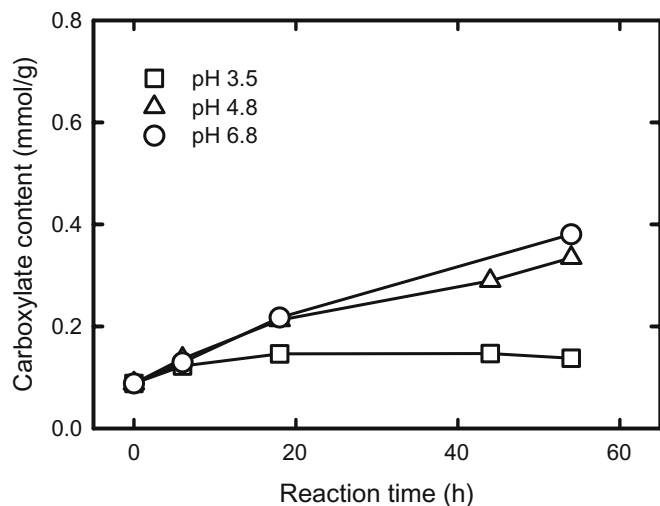
Fig. 2. Influence of pH on the oxidation of bleached wood pulp by the TEMPO/NaClO$_2$ system at 40°C

Fig. 3. Influence of temperature on the oxidation of bleached wood pulp by the TEMPO/NaClO$_2$ system at pH 6.8

carboxyls with NaClO$_2$, and then NaClO generated in situ from NaClO$_2$ oxidizes the hydroxylamine, again to the oxoammonium ion.

The oxidation of pulp was first carried out only with TEMPO and NaClO$_2$ (TEMPO/NaClO$_2$ system), without addition of NaClO, to simplify the oxidation system. Figure 2 shows the influence of pH of the reaction medium on oxidation of pulp by the TEMPO/NaClO$_2$ system. Carboxylate content of the pulps oxidized at pH 4.8 and 6.8 similarly increased with increasing reaction time, although the oxidation rates were slow. At pH 3.5, almost no increase in carboxylate content was shown even after 54 h of reaction time. Oxidative activity of NaClO$_2$ is known to increase at lower pH, although decomposition of NaClO$_2$ to chlorine dioxide and chlorate is also accelerated in an acidic medium.[34–36] For this reason, oxidations with NaClO$_2$ are generally carried out at pH 4–5. However, in contrast to the activity of NaClO$_2$, oxidation of alcohols with the oxoammonium ion of TEMPO in acidic medium has been reported to be a significantly slower process at low pH,[37,38] which might have caused almost no increase in carboxylate content of the pulp oxidized at pH 3.5 by the TEMPO/NaClO$_2$ system.

Oxidation of pulp by the TEMPO/NaClO$_2$ system was also investigated to clarify the effect of reaction temperature on carboxylate content of the oxidized pulp (Fig. 3). Oxidations were carried out at pH 6.8 and 25°–60°C. As expected, oxidation at 60°C gave the highest oxidation rate within the range examined. A similar tendency was observed in oxidation at pH 4.8 (data not shown). Influence of temperature on degree of polymerization of the oxidized pulp is described later in this article.

Oxidation of bleached wood pulp by the TEMPO/NaClO/NaClO$_2$ system

Concerning the oxidation system with addition of NaClO, the TEMPO/NaClO/NaClO$_2$ system, we have already
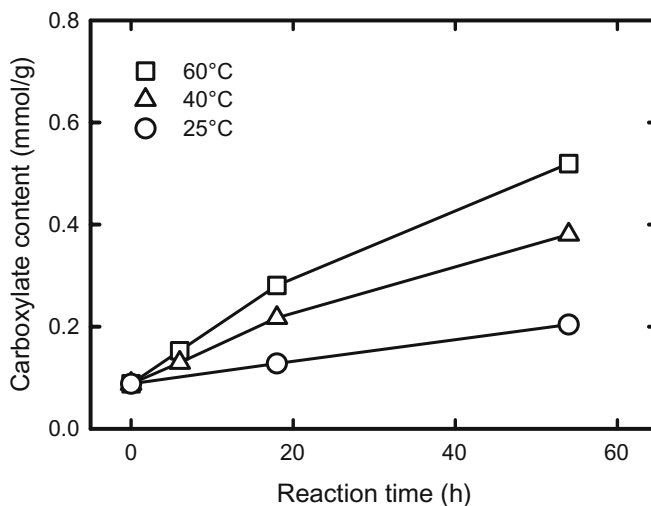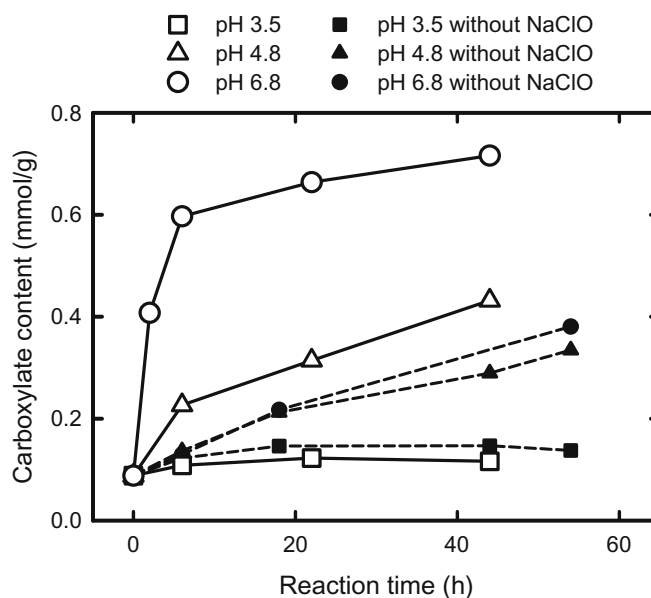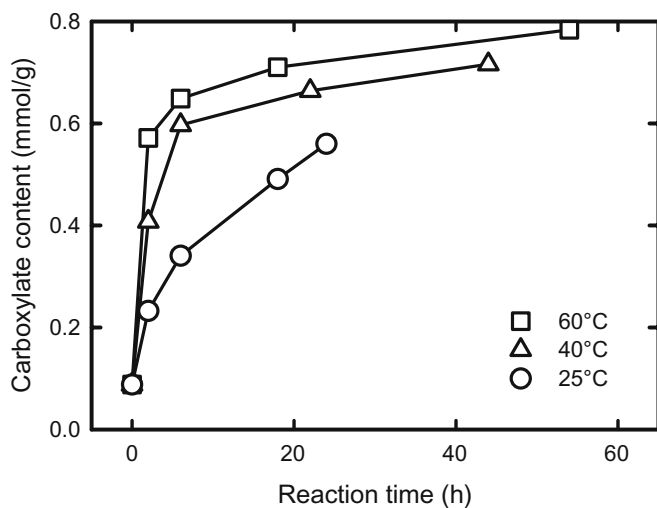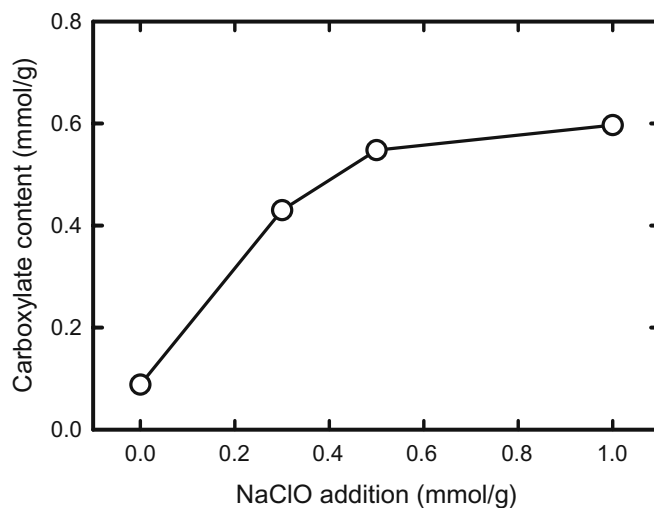

Fig. 4. Influence of pH on the oxidation of bleached wood pulp by the TEMPO/NaClO/NaClO$_2$ system at 40°C. Carboxylate content of the pulps oxidized by the TEMPO/NaClO$_2$ system was also plotted for comparison

reported the influence of pH on the oxidation of pulp at 60°C.[30] In this article, discussion focuses on the effect of adding NaClO on oxidation efficiency. Figure 4 shows carboxylate content of pulp oxidized at 40°C by the TEMPO/NaClO/NaClO$_2$ system at different pH values. For comparison, carboxylate content of pulp oxidized by the TEMPO/NaClO$_2$ system (see Fig. 2) was also plotted in Fig. 4. Similar to oxidation by the TEMPO/NaClO$_2$ system, almost no carboxyls formed at pH 3.5 even with addition of NaClO. However, at pH 6.8 oxidation was greatly accelerated by the addition of NaClO, and carboxylate content reached approximately 0.6 mmol/g for 6 h; addition of NaClO at pH 4.8 also slightly accelerated the oxidation. In fact, the effect

Table 1. Influence of temperature on degrees of polymerization (DPv) of bleached wood pulps oxidized by TEMPO/NaClO/NaClO$_2$ system at pH 6.8

	Temperature (°C)	Time (h)	Carboxyls (mmol/g)	DPv
Original bleached wood pulp	–	–	0.09	1320
Oxidized bleached wood pulp	25	24	0.56	970
	40	22	0.66	1050
	40	44	0.72	920
	60[a]	6	0.65	1100
	60[a]	18	0.71	1030
	60[a]	54	0.78	910

[a] Cited from Saito et al. (2009)[30]

Fig. 5. Influence of temperature on the oxidation of bleached wood pulp by the TEMPO/NaClO/NaClO$_2$ system at pH 6.8. Data at 60°C are cited from Saito et al. (2009)[30]

Fig. 6. Effect of NaClO addition on oxidation of bleached wood pulp by the TEMPO/NaClO/NaClO$_2$ system at pH 6.8. Carboxylate content of pulps oxidized for 6 h with different amounts of NaClO added was measured

of NaClO addition in the TEMPO/NaClO/NaClO$_2$ system was improved at higher pH. Although formation of the oxoammonium ion of TEMPO with NaClO is quite fast in a weakly acidic medium,[39] oxidation of alcohols or the C6 primary hydroxyls with oxoammonium ions is a significantly slower process at low pH.[37,38]

Figure 5 shows the influence of temperature on oxidation by the TEMPO/NaClO/NaClO$_2$ system at pH 6.8. Oxidation rapidly proceeded at 60°C,[30] and carboxylate content increased to approximately 0.6 mmol/g for 2 h. Oxidation at 40°C gave a carboxylate content of 0.4 mmol/g for 2 h and of 0.6 mmol/g for 6 h. The carboxylate content of 0.6 mmol/g corresponds to approximately 11% of the C6 primary hydroxyls to be oxidized in the original pulp. After 6 h of oxidation, carboxylate content gradually increased at both 40° and 60°C.[30] Despite addition of NaClO, oxidation at 25°C was slow, and carboxylate content was lower than 0.6 mmol/g even after 24 h of oxidation. Thus, a temperature higher than 40°C was needed for efficient oxidation of the pulp by the TEMPO/NaClO/NaClO$_2$ system at pH 6.8.

In Table 1, DPv values of the pulps oxidized at different temperatures are listed, corresponding to some of the results in Fig. 5.[30] Although DPv of the oxidized pulp gradu- ally decreased with oxidation time by some oxidative deg- radation of cellulose,[6,7,30] no significant differences in the DPv of the oxidized pulp were found at oxidation tempera- tures between 25° and 60°C, and DPv values of more than 900 were maintained for all the pulps oxidized under the various conditions examined.

The effect of the amount of NaClO added was also studied. In Fig. 6, carboxylate contents of the pulp oxidized at pH 6.8 and 40°C for 6 h are plotted against the amount of NaClO added. Even a small amount of NaClO, which, however, corresponded to 3–10 moles per mole of the cata- lytic TEMPO added, was highly effective for the accelera- tion of oxidation, and the carboxylate content nearly reached a plateau at the addition of 0.5 mmol NaClO per gram of the pulp.

Occurrence of two side reactions for NaClO is plausible during oxidation in this system: disproportionation of hypo- chlorite to chlorate, and decomposition of hypochlorite to chlorine. Although disproportionation of hypochlorite to chlorate is known to occur gradually at pH 5–7,[40] oxidation of TEMPO or N-hydroxyl-TEMPO to the corresponding oxoammonium ion by hypochlorite proceeds more rapidly within a few minutes.[39] Thus, hypochlorite ions might be consumed primarily for oxidation of TEMPO and N-

hydroxyl-TEMPO to oxoammonium ions rather than disproportionation under the conditions used in this study. Decomposition of hypochlorite to chlorine is enhanced in water at lower pH.[40] The quite low carboxylate content of the pulps oxidized at pH 3.5 in Fig. 4 supports the presence of this side reaction. Moreover, even at pH 6.8, addition of a certain amount of NaClO was needed for efficient oxidation of C6 primary hydroxyls of the pulp to carboxyls (Fig. 6). Therefore, part of the hypochlorite might be lost as chlorine under the conditions used. However, because the oxidation was carried out in a closed vessel, both hypochlorite ions and chlorine molecules might exist as an equilibrium state in the solution, thus resulting in achievement of oxidation of C6 primary hydroxyls of cellulose to carboxyls, when suitable conditions were adopted for the oxidation.

Conclusions

When bleached wood pulp was oxidized with NaClO₂ and a catalytic amount of TEMPO under weakly acidic conditions, the oxidation became more accelerated by the addition of NaClO at pH 6.8 and 40°–60°C. The addition of more than 0.5 mmol NaClO per gram of the pulp was effective to accelerate the oxidation. Carboxylate content of the pulp oxidized under such conditions increased to approximately 0.6 mmol/g within 6 h. The carboxylate content of 0.6 mmol/g corresponds to approximately 11% of the C6 primary hydroxyls to be oxidized in the original pulp. Although DPv of the oxidized pulp gradually decreased with reaction time, no significant differences in the DPv of the oxidized pulps were found between oxidation temperatures at 25°, 40°, and 60°C, and the DPv values of more than 900 were maintained for all the pulps oxidized under various conditions examined.

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