

Effects of Ozone and Chlorine Dioxide on the Chemical Properties of Cellulose Fibers

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ABSTRACT: The effects of ozone and chlorine dioxide on the structure of hardwood cellulose fibers were studied by chemical methods. Chlorine dioxide had very little effect on the cellulose degree of polymerization (DP_v), although 40–50% of the chlorine dioxide charged was consumed. By contrast, ozonation of the cellulosic fibers resulted in a substantial reduction in the cellulose DP_v . Increasing the ozone charge increased the extent of cellulose degradation. At an ozone charge of approximately 3 wt % (20 mol equiv/100 g of fiber), a 40% reduction in DP_v , as measured by cupriethylenediamine viscosity, was observed. A comparison of the cellulose DP_v values obtained for ozonated cellulose fibers reduced with sodium borohydride before the viscosity measurements increased confirmed that the primary reaction of

ozone with the cellulose fibers was glycosidic bond cleavage, with only a small amount of cellulose oxidation taking place. A functional group analysis of the ozonated cellulose fibers revealed a slight increase in the amount of carbonyl groups introduced into the fibers. In addition, carbon dioxide was detected, which combined with the lack of change in the carboxyl group content, indicated that the oxidation mechanism likely occurred in a three-step process: formation of the carbonyl groups, followed by oxidation to carboxyl groups, and finally, decarboxylation resulting in glycosidic bond cleavage. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1219–1223, 2004

Key words: viscosity; fibers; degradation; biopolymer

INTRODUCTION

In recent years, concerns over the environmental impact of bleaching chemicals used in the production of paper have increased. Laws have placed limits on the amount of chlorinated organic waste that can be released into receiving waters.¹ The use of elemental chlorine is unquestionably being phased out simply because it does not meet new environmental standards.

Chlorine dioxide, ozone, and hydrogen peroxide are among the most important chemicals used in the production of wood-free paper. As a result, totally chlorine-free and elemental-chlorine-free bleaching processes have been and continue to be developed. However, in the optimization of new bleaching sequences, it is important to understand what happens to the main component of the pulp, the cellulose, during the different bleaching stages and how the chemical properties of the cellulose are affected.

Chlorine dioxide is one of the most important chemicals used today for the bleaching of chemical pulps. Chlorine dioxide reacts readily with lignin and does not react to any significant extent with carbohydrates.² The degradation of lignin is due to the combination of both chlorination and oxidation, especially at higher charges of chlorine dioxide. Although some reports exist regarding the behavior of cellulose model compounds toward chlorine dioxide,^{3,4} little data exists with regard to the behavior of cellulose itself. Reportedly, chlorine dioxide reacts primarily with the aldehyde groups of reducing end units, oxidizing them to carboxyl groups. In the absence of carbonyl groups, chlorine dioxide oxidizes the C-2 carbon and, subsequently, the C-3 carbon of the glycopyranoside ring, which leads to the formation of a 2,3-diketone and, eventually, to the formation of a 2,3-dicarboxylic acid. However, it is nearly impossible to prevent the formation of hypochlorous acid and, thus, the formation of molecular chlorine in chlorine dioxide reaction systems.⁵ The reactions with carbohydrates may be artifacts of other more reactive compounds produced in the system.

Ozone reacts with carbohydrates by causing the cleavage of glycosidic linkages and by oxidizing alcohol groups to carbonyl groups and terminal aldehyde groups to carboxyl groups.⁶ It has been postulated that the poor selectivity of ozone is due to the formation of a large number of hydroxyl radicals ($\cdot OH$),

This article is dedicated to R. D. Gilbert on the occasion of his 83rd birthday.

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TABLE I
Chemical Composition of Bleached Hardwood Cellulose Fibers

	Composition (%)
α -Cellulose	93.4
Carbohydrates	
Arabinan	0.2
Xylan	22.4
Mannan	0.4
Galactan	< 0.1
Glucan	72.2
Lignin	< 0.1

which react with both lignin and carbohydrates.⁷ However, it has also been reported that the poor selectivity of ozonation is not due to the hydroxyl radicals but mainly to molecular ozone itself.^{8,9} Another reason for cellulose depolymerization is the fact that alkali-labile carbonyl groups formed during the ozone stage undergo certain β -alkoxy eliminations during subsequent alkali stages.¹⁰

In this article, we discuss the effects of the reactions of chlorine dioxide and ozone on the chemical structure of cellulose derived from fully bleached hardwood kraft pulp.

EXPERIMENTAL

Materials and supplies

Cellulose

A fully bleached commercial hardwood kraft pulp was used in this study. Before any treatment, the pulp was acidified with 4N H₂SO₄ (Aldrich, Milwaukee, WI) to pH 2, filtered, and washed repeatedly with acid water (pH 2) until all fines were removed. The pulp was then dewatered to approximately 35–40 wt % solids and fluffed. The chemical composition was determined according to standard methods (TAPPI T249 cm-85; Table I).

Chemical treatments

Ozone oxidation

Ozone treatments were performed at room temperature in a rotating spherical reactor. Cellulose fiber (10

g, oven-dried weight) (International Paper, Tuxedo Park, NY) was mixed with 30 mL of deionized water adjusted to a pH of about 4.5 with 1N H₂SO₄ (Aldrich). The gas flow was 1 L/min. The ozone concentration in oxygen was set at 1.5 wt % as determined by iodometric titration. The times of ozonation were set to 10, 20, 30, and 45 min to introduce the quantities of ozone needed. At the end of the reaction, the cellulose fibers were filtered and reneutralized by repeated washing with deionized water.

Chlorine dioxide oxidation

Chlorine dioxide was produced by the reaction of 80% stabilized sodium chloride (Acros, Fairlawn, NJ) with 1.5 equiv of potassium persulfate (Aldrich) in distilled water at room temperature. The resulting solution was stripped with ultra high purity (UHP)-nitrogen. The nitrogen gas containing the stripped chlorine dioxide was passed through a column of sodium chlorite and then scrubbed in cold high performance liquid chromatography (HPLC) water pH-adjusted to 4 with 0.1 wt % aqueous sulfuric acid. The resulting chlorine dioxide stock solution was greater than 98% pure, as determined by iodometric titration. The chlorine dioxide reactions were performed in polyethylene bags at 70°C. Cellulose fiber (10 g) was mixed with 90 mL of acidified deionized water. The pH was adjusted to about 3 with sodium hydroxide (0.1N). After the reaction had progressed for a set time interval, the reaction solution was filtered, and the cellulose fibers were neutralized by repeated washing with deionized water.

Sodium metaperiodate oxidation

Periodate oxidation was performed at room temperature with various concentrations of sodium metaperiodate (Aldrich). In a typical reaction, 10 g (oven-dried weight) of cellulose fiber was weighed into a 250-mL amber reaction vial and diluted to about 2 wt % with an acidic periodate solution. The vial was then sealed and mixed for 2 h in the absence of light. At the end of the reaction, the cellulose fibers were carefully washed with ethylene glycol to eliminate any sodium periodate and washed repeatedly with methyl alcohol

TABLE II
Viscosity Results for the Reaction of Hardwood Cellulose Fibers with Ozone, Chlorine Dioxide, and Sodium Periodate

	Cellulose fiber	ClO ₂			O ₃			IO ₄ ⁻			
Applied charge (mol equiv/100 g)	—	3.0	7.5	30.0	4.5	9.0	20.0	8.0	60.0	300	
Consumed (mol equiv/100 g)	—	1.2	3.5	15.8	2.2	4.5	6.7	9.9	—	—	
DP _v	1390	1410	1400	1390	1100	1040	960	800	1320	1210	720
DP _v ^{Red}	1510	1460	1400	1400	1330	1180	1150	1050	1400	1410	1380

TABLE III
Functional Group Analyses of the Hardwood Cellulose Fibers Reacted with Ozone,
Chlorine Dioxide, and Sodium Periodate

	Cellulose fiber	ClO ₂			O ₃				IO ₄ ⁻		
Applied charge (mol equi/100 g)	—	3.0	7.5	30.0	4.5	9.0	13.0	20.0	8.0	60.0	300
Carbonyl content (mol equi/100 g)	3	2	2	2	6	13	16	16	3	60	70
Carboxyl content (mol equi/100 g)	4.8	5.6	5.5	5.6	4.5	4.8	4.8	4.8	5.0	4.7	4.8
CO ₂ evolved (mol equi/100 g)	—	—	—	—	0.6	1.0	1.6	2.6	—	—	—

and water. The cellulose fiber was then neutralized by repeated washing with deionized water.

Sodium borohydride reduction

All reductive treatments were carried out at room temperature for 16 h. Accordingly, 5 mg of sodium borohydride (Aldrich) was added to a suspension of 3 mg of cellulose fiber in 100 mL of deionized water (pH = 10). After the remaining sodium borohydride was decomposed with 1.0N acetic acid (Aldrich), the reduced cellulose fibers were recovered and neutralized by repeated washing with deionized water.

Cellulose characterization

Carbonyl and carboxyl groups were determined with the method of Lewin and Epstein.¹¹ Viscosity was measured according to TAPPI T254 cm-85. The degree of polymerization (DP_v) was calculated from the viscosity values.¹² The relationship between the viscosity (V) measurements and DP_v were determined as follows: DP_v = [0.75(954 log V - 325)]^{1.105}.

RESULTS AND DISCUSSION

Effect of oxidative treatment on the chemical properties of hardwood cellulose

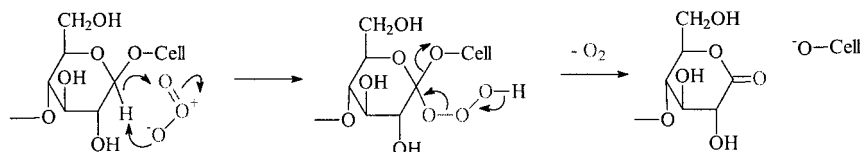
The results obtained from the reaction of the hardwood cellulose fibers with ozone (O₃) and chlorine dioxide (ClO₂) are listed in Tables II and III. As expected, the consumption of O₃ was higher than that of ClO₂ (Table II). The consumption of O₃ was approximately 50% for all of the chemical charges applied, whereas ClO₂ consumption was as low as 40% and increased to 50% with increasing applied chemical charges.

Viscosity measurements were used to determine DP_v of the cellulose fibers before and after chemical treatment. As shown in Table II, increasing the concentration of applied O₃ dramatically increased the calculated DP_v from 1340 in the original cellulose fibers to 800 in the cellulose fibers exposed to a 20 mol equiv/100 g O₃ charge. This corresponded to a reduction of about 40% in the cellulose DP_v and was consistent with the observed consumption of O₃. By contrast, no change in viscosity was observed in the fibers treated with ClO₂; increasing the charge of ClO₂ from 3.0 to 30 mol equiv/100 g did not have any effect on the cellulose DP_v.

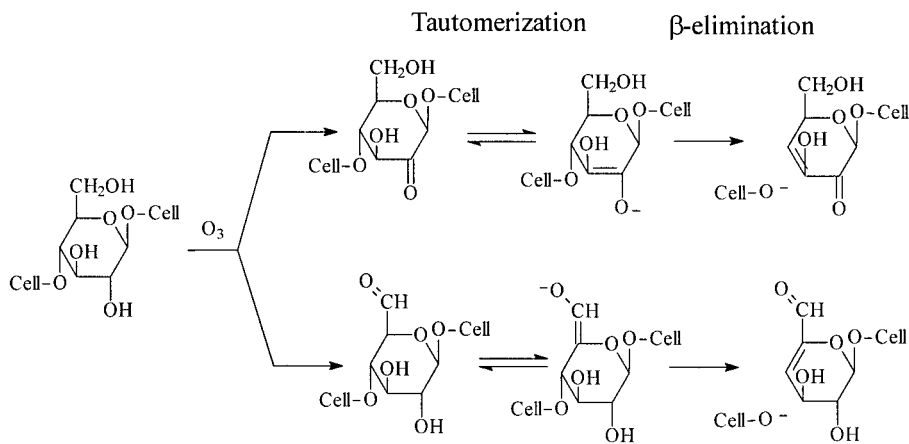
In the oxidation of carbohydrates with O₃, two primary reactions reportedly take place: the cleavage of the glycosidic linkage (Scheme 1) and the oxidation of the primary and secondary hydroxyl groups (Scheme 2).¹³ Glycosidic bond cleavage occurs via an insertion mechanism, with the subsequent formation of a corresponding lactone.¹⁴ A decrease in DP_v occurs and manifests in an observed decrease in the viscosity.

Similarly, the oxidation of various hydroxyl groups to carbonyl groups and further to carboxyl groups also affects the observed viscosity. The carbonyl groups are extremely alkali sensitive, which facilitates bond cleavage via a series of keto-enol tautomers and β elimination (Scheme 2).¹⁵

It has been reported that the large decrease in DP_v accompanying the O₃ oxidation of cellulose is the result of the viscosity test conditions, wherein the alkali-sensitive carbonyl groups introduced into the cellulose facilitate glycosidic bond cleavage.¹⁶ For that reason, the cellulosic samples were reduced with sodium borohydride before the viscosity measurements. As shown by the degree of polymerization after reduction (DP_v^{Red}) values listed in Table II, the reduction of the cellulose after oxidation increased the observed



Scheme 1



Scheme 2

viscosity. However, a substantial reduction in DP_v^{Red} was still observed for the O_3 -treated samples; a 30% decrease in DP_v^{Red} was observed compared to a 40% decrease in DP_v before reduction. These results suggest that the primary reaction affecting the observed DP_v in the reaction of O_3 with carbohydrates under the conditions used in this study was glycosidic bond cleavage and not oxidation followed by alkali-induced elimination reactions.

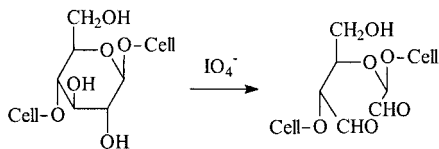
Although it is only a minor reaction, the oxidation of cellulose by O_3 is well-documented.^{7,9,13,17-19} Although O_3 reacts preferentially at the C-6 position, O_3 oxidations at the C-2 and C-3 positions also occur.²⁰ However, the oxidation of each position and the effect of viscosity and DP_v have not been thoroughly studied. To better understand the O_3 oxidation process, cellulose fibers were oxidized with sodium periodate (IO_4^-). IO_4^- oxidation is a highly specific reaction that is widely used in the structural analysis of carbohydrates.²¹ Specifically, IO_4^- oxidation converts 1,2-dihydroxyl (glycol) groups to paired aldehyde groups without significant side reactions. In the reaction with cellulose, the corresponding 2,3-dialdehyde cellulose is readily obtained (Scheme 3).²² As expected IO_4^- oxidation resulted in a substantial decrease in the cellulose DP_v ; in fact, it was very similar to that observed for the O_3 -oxidized cellulose fibers (Table II). However, on reduction, the calculated DP_v^{Red} was practically the same as for the original cellulose fiber.

Further information about the oxidation of cellulose was obtained by functional group analysis. The vari-

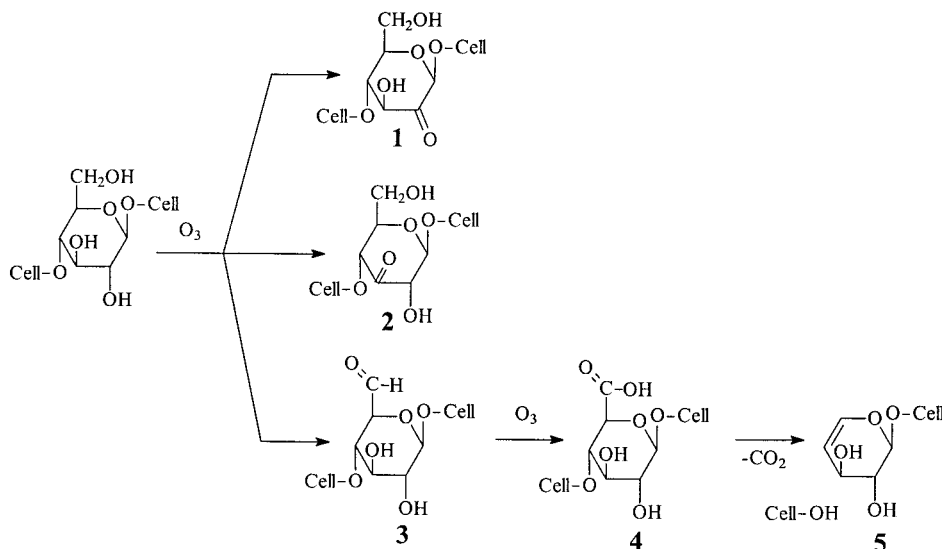
ous oxidized cellulose fibers revealed differences in the carbonyl and carboxyl group contents (Table III). As with the viscosity results, the ClO_2 -reacted cellulose fibers showed very little change. A slight decrease in the carbonyl content (~ 1 mol equiv/100 g) was accompanied by an increase in the carboxyl content of about 1 mol equiv/100 g. By contrast, in the O_3 -reacted cellulose fibers, an increase in the carbonyl content was observed, wherein an increase in the concentration of O_3 resulted in an increased number of carbonyl groups formed. A maximum of about 16 mol equiv/100 g, or about 30 carbonyl units per cellulose molecule ($DP_v^{\text{Red}} \approx 1150$), was obtained at a 13 mol equiv/100 g O_3 charge. However, a further increase in the O_3 charge to 20 mol equiv/100 g did not increase the carbonyl content further.

No change in the carboxyl group content was detected in the O_3 -reacted cellulose fibers (Table III). These results are consistent with those reported in the literature.²³ However, a substantial amount of carbon dioxide (CO_2) was detected, and the amount of CO_2 formed during the reaction of the cellulose fibers increased with increasing O_3 charge. The quantity of carbon dioxide formed and the lack of change in the carboxyl group content indicated that the ozonation mechanism likely occurred in a three-step process. The first step was the formation of the carbonyl groups, the second step was the oxidation of the carbonyl groups to carboxyl groups, and the third step was decarboxylation. Interestingly, the steady state of the carboxyl group content indicated that the rate of oxidation of the carbonyl groups to carboxyl groups was likely slower than the oxidation of the alcohol groups to carbonyl groups but was approximately the same as decarboxylation.

Finally, on the basis of model compound studies²⁰ and the results obtained from IO_4^- oxidation, it is likely that the oxidation to carbonyl groups and subsequently to carboxyl groups occurred at the C-6 po-



Scheme 3



Scheme 4

sition. Moreover, in addition to direct glycosidic bond cleavage, as outlined in Scheme 1, some glycosidic bond cleavage likely occurred as a result of a decarboxylation process, specifically the decarboxylation of the C-6 position with concurrent β elimination (Scheme 4, bottom pathway).

CONCLUSIONS

In the reaction of hardwood cellulose fibers with ClO₂, very little change in the chemical structure was detected. Although nearly 50% of the ClO₂ was consumed, no change in DP_v was observed. An approximate 1 mol equiv/100 g decrease in carbonyl content was accompanied by an appropriate increase in the carboxyl content. By contrast, O₃ had a dramatic effect on the cellulose fiber structure. At a charge of about 3 wt % O₃, a 40% reduction in cellulose DP_v was measured. An increase in the carbonyl content was observed, and a substantial amount of CO₂ was detected, both increasing with increasing O₃ charge. The quantity of CO₂ formed and the lack of change in the carboxyl group content suggested an ozonation mechanism involving a three-step process of successive oxidation and subsequent decarboxylation wherein the rate of oxidation of the carbonyl groups to carboxyl groups was likely slower than the oxidation of the alcohol groups to carbonyl groups but was approximately the same as decarboxylation. On the basis of the DP_v values and the functional group analysis, the primary reaction of O₃ with cellulose was the hydrolysis of the glycosidic bond at the C-1 position. However, the detection of CO₂ supported a glycosidic bond hydrolysis mechanism involving the C-4 position through a successive oxidation mechanism of the

C-6 hydroxyl group, culminating in glycosidic bond cleavage via decarboxylation.

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