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Ultraviolet Microscopic Study on Lignin Distribution in the Fiber Cell Wall of BCTMP

Seung-Lak Yoon and Yasuo Kojina*

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ABSTRACT

Bleached chemithermomechanical pulp (BCTMP) was produced from CTMP of Betula maximowicziana Regel by two staged ozone-hydrogen peroxide bleaching in order to improve the optical properties of high yield pulp. This pulp was used for the evaluation of optical properties improvement, chemical characteristics of lignin in fiber and the relationship between lignin and optical properties in fiber cell wall.
Hydrogen peroxide treatment improved the brightness, but the post color number (PC No.). There was little improvement on optical properties by ozone treatment, but this could be improved more by using two staged ozone-hydrogen peroxide bleaching.
The hydrogen peroxide treatment did not make any change on chemical characteristics of lignin in cell wall, but by ozone treatment, it was found that the non-aromatic conjugated structure was existed in the surface of cell wall, but this could be removed by hydrogen peroxide treatment in two staged ozone-hydrogen peroxide treatment. Therefore, the optical properties was significantly improved, due to the removal of non-aromatic conjugated structure.

Keywords : birch, CTMP, BCTMP, fiber cell wall, ozone treatment, delgnification, hydro gen peroxide bleaching

1. Introduction

One of disadvantages in high yield pulp with high lignin content was that in the exposure of light, the pulp becomes yellow-colored, and then gradually decolorized due to the presence of lignin, ultraviolet-sensitive phenolic compound. Among them, the Leuco chromophores in lignin are gradually changed and transformed to various chromophores by ultraviolet.

* Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, JapanDepartment of Forest Products Engineering, Jinju National University, Jinju 660-758, Korea

It was reported that, compared with some kinds of high yield pulp, ozone treated CTMP for the purpose of the improvement of optical properties contains a little lower content of lignin (1), and could be used for the papers with low decolorizing, especially for the sources of printing papers. However, deciduous CTMP treated with ozone did not show any improvement on brightness and post color number, while showed the strength improvement (2,3). This was due to the presence of a little content of lignin in the fiber, which contained a susceptible chromophore by ultraviolet. Since the improvement of optical properties was not obtained by the treatment only ozone, hypersulfite gas, sodium chloride, and hydrogen peroxide were used together with ozone. The result showed that the ozone-hydrogen peroxide was effective on the brightness and strength properties with reducing PC No (4,5). Several treatments such as ozone-hydrogen peroxide, NaOCl-ozone, and ozone treatment after short time NaOCl impregnation were reported else where (6,7).

The most influencing factor for optical properties in high yield pulp was considered to lignin content in fiber. During the delignification in high yield pulp by ozone treatment, lignin was gushing out from the surface of fiber to inner side of cell wall. In contrast, there was no lignin gushing out by hydrogen peroxide treatment, since the lignin distribution in fiber, after and before treatment was not differentiated in pattern. However, by two staged ozone- hydrogen peroxide treatment, there was a different pattern on lignin distribution.

In this research, three kinds of deciduous BCTMP were produced by bleaching CTMP by one staged ozone, one staged hydrogen peroxide, and two staged ozone-hydrogen peroxide treatments, respectively. The produced pulp was used for the evaluation of optical properties improvement, chemical characteristics of lignin in fiber cell wall, and the relationship between lignin distribution and optical properties.

2. Materials and Methods

2.1 Materials

The species was 135 years old birch(Betula maximowicziana Regel), and the chemical composition was shown on Table 1.

Table. 1. Chemical composition of birch

Alcohol-benzene extractives (%)	Klason lignin (%)	Holocellulose (%)
1.3	22.7	76.5

2.2 CTMP manufacture

Chemical pretreatment of 400 g of chip was performed by the bisulfite condition indicated on Table 2. The pulp yield was 89.0%, and the refining was carried out by using Asplund defibrator (D-type) according to the conditions on Table 3.

Table 2. Cooking conditions and pulp yield

Chemical	Maximum temperature (℃)	Heating time(min)	Cooking time(min)	Yield (%)
3%-$NaHSO_3$	145	60	15	89.0

Table 3. Refining conditions of CTMP

Temperature (℃)	Preheating time (min)	Refining time (min)
135	4	3

2.3 Ozone Treatment

The used ozone generator was O-3-2 type of Japan Ozone Co. with 100 voltage, and 100 L/hr of oxygen supply. The produced amount of ozone was 3.8 g per hour. The pulp samples were treated with ozone for 30 min.

Table 4. Conditions of H_2O_2 treatment

H_2O_2 addition (%)	pH	Pulp concentration (%)	Temperature (℃)	Treatment time (hr)
1, 2, 4	11	10	70	2

2.4 Hydrogen peroxide bleaching

The conditions for hydrogen peroxide bleaching were shown on Table 4. Hydrogen peroxide, 5% of sodium silicate, 0.05% of magnesium sulfate were added to pulp, and adjusted to pH 11 with sodium hydroxide. The treatment was carried out on the basis of 10% of pulp consistency, as shown on Table 4.

2.5 Brightness and post color number (PC No.)

The brightness was measured by JIS P 8123, and the PC No. was calculated by the difference of brightness calculated before and after decolorizing paper at 100℃ for 24 hrs.

2.6 UV microscope observation

The samples for UV microscope observation were obtained from CTMP, ozone and hydrogenperoxide treated fiber, ozone- hydrogen peroxide treated fiber, and impregnated fiber with Epon resin. The lignin distribution in cell wall was observed at 280 nm by UV microscope HPM-01 of Carl Zeiss Co. The UV spectrum at specific part of cell wall in wood fiber wall was measured at 250 to 300 nm by Carl Zeiss UMSP 80 Microscopic Spectrophotometer.

3. Results and Discussion

3.1 Yield and lignin content of hydrogen peroxide and ozone treated pulp

The pulp yield and lignin contents of CTMP (89.0% yield) treated with hydrogen peroxide, ozone, and two staged ozone-hydrogen peroxide bleaching are were shown in Table 5.

The yield of CTMP treated with 1% hydrogen peroxide was not changed, but those with 2%, and 5% ones were reduced by approximately 5%. In contrast, in the case of ozone treatment, the yield was reduced by 19%. Treatment of CTMP with ozone followed by hydrogen peroxide decreased by 4% pulp yield, when compared with only ozone treatment. The yield was significantly reduced by ozone treatment, but was not by hydrogen peroxide treatment.

In general, the hydrogen peroxide was usually used in the bleaching of GP, and TMP which contained high lignin. The hydrogen peroxide in bleaching stages resulted in an increasement of brightness, due to oxidation and degradation of lignin chromophore. Therefore, the delignification amount from pulp was not expected.

Table 5. Yield and lignin concentrations of BCTMP, treated with H_2O_2 and O_3

Pulp	Yield(%)	Lignin(%)
CTMP	89.0	15.0
CTMP-1% H_2O_2	88.5	13.5
CTMP-2% H_2O_2	83.6	12.9
CTMP-4% H_2O_2	82.7	12.6
CTMP-O_3	70.3	3.3
CTMP-O3-1% H_2O_2	66.7	2.3
CTMP-O3-2% H_2O_2	66.3	2.3
CTMP-O3-4% H_2O_2	65.4	1.8

3.2 Optical properties of hydrogen peroxide, and ozone treated pulp

The brightness, and PC No. of CTMP (89.0% yield) treated with hydrogen peroxide, ozone, and two staged ozone-hydrogen peroxide bleaching are shown in Table 6.

Table 6. Optical properties of BCTMP treated with H_2O_2 and O_3

Pulp	Brightness(%)	PC No.
CTMP	33.7	5.8
CTMP-1% H_2O_2	38.3	7.4
CTMP-2% H_2O_2	44.5	8.7
CTMP-4% H_2O_2	52.4	8.3
CTMP-O_3	39.0	4.4
CTMP-O_3-1% H_2O_2	46.9	1.8
CTMP-O_3-2% H_2O_2	55.1	1.3
CTMP-O_3-4% H_2O_2	65.7	1.0

The brightness of pulp was increased by hydrogen peroxide treatment, and was proportional to the increase hydrogen peroxide content. The brightness was increased by 52.4% at 4% hydrogen peroxide treatment, while there was no significant brightness improvement by ozone treatment. However, two staged ozone-hydrogen peroxide treatment made an remarkable improvement on brightness. For example, the brightness of CTMP treated with 4% hydrogen peroxide was 52.4%, while that with two staged ozone-hydrogen peroxide (4%) was increased to 65.7%.

By hydrogen peroxide bleaching, the PC No. was increased, while by ozone treatment it was decreased. However, it was significantly decreased by ozone-hydrogen peroxide treatment.

In order to improve the optical properties of CTMP, two staged ozone-hydrogen peroxide treatment was very effective. The PC No. was reduced to 1.0 by 4% hydrogen peroxide bleaching after ozone treatment. Therefore, the decolorizing problem of CTMP may be solved by this process. It was necessary to speculate the lignin distribution and optical properties after each treatment.

3.3 Chemical characteristics on remained lignin after treatment

Previously, the delignification processes of CTMPs treated with hydrogen peroxide, ozone treatment, and two staged ozone-hydrogen peroxide bleaching were determined by UV microscope [1, 3]. In order to evaluate the chemical characteristics of lignin remained in fiber, the UV spectrum of fiber cell wall depending on treatment was measured at 250 to 300 nm by microscopic spectrophotometer.

The UV spectra at specifically cut parts of CTMP fiber, which was treated with 4% hydrogen peroxide, are shown in Fig. 1. Photographs of cross-cut fiber were taken at 280 nm by UV microscope. The dark part adsorbing wave length of 280 nm was considered as lignin, and the other white part indicated that there was no lignin.

In CTMP (yield 89.0%), the cell wall was surrounded by complex inter-cell layer, and espe-

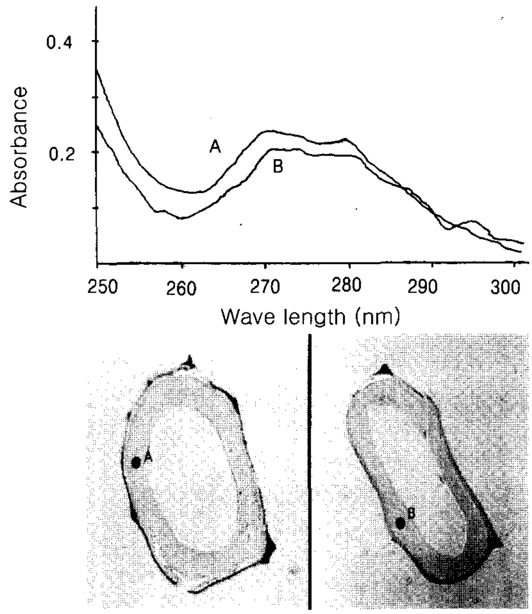
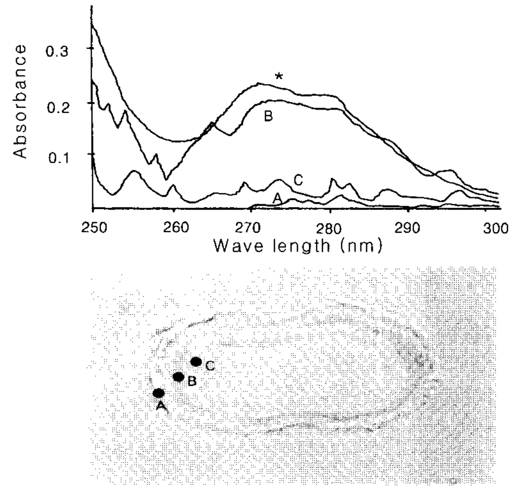


Fig. 1. UV spectra of areas in the cell wall of CTMP and BCTMP treated with hydrogen peroxide.



*:A of Fig. 1.

Fig. 2. UV spectra of areas in the cell wall of BCTMP treated with hydrogen peroxide after ozonation.

cially, there was strong adsorption at the corner of cell wall, and at the inner part of cell wall, indicating the uniform lignin distribution. In the case of 4% hydrogen peroxide bleaching, the pulp did not show any symptom of delignification, and the lignin distribution was uniform. This phenomenon was similarly occurred depending on the addition of hydrogen peroxide (1, 2, and 4%), referring that the delignification from fiber was not occurred. It was pointed out by Spitter (8) that the lignin content reduction in high yield pulp by hydrogen peroxide bleaching was very minimal by 2 to 3%. This bleaching process showed lower delignification degree with higher brightness, deserving as preservative bleaching process.

The UV spectra of CTMP, before and after hydrogen peroxide treatment showed similar adsorption bands at 270, and 280 nm, indicating that the lignin in fiber was not changed by hydrogen peroxide bleaching because the identical lignin was still present before and after treatment.

The UV spectra of specifically cut parts of CTMP fiber, which have been treated with 4% hydrogen peroxide after ozone treatment, were shown in Fig. 2. By ozone treatment in this process, the lignin was gushing out from the surface of fiber to the middle part of cell wall [1, 9], and then by hydrogen peroxide treatment, the lignin was only remained in middle part of cell wall because the lignin from lumen was already gushing out. This phenomenon was similarly shown in each concentration of hydrogen peroxide (1,3), and was reported that ozone and alkali solution could penetrate into the pit of cell wall during hydrogen peroxide bleaching. The UV spectra of fiber cell wall treated with ozone, and hydrogen peroxide treatment, respectively, showed different adsorption band. There were two bands at 250 to 270 nm at C area (in photograph) where did not contain lignin, presuming the presence of non-aromatic conjugated structure. However, there was no adsorption band at A area, assuming the absence of non-aromatic conjugated structure, which might be related to the PC No. There were also two adsorption bands at 270 to 280 nm, and 250 to 270 nm at B area, where contained lignin.

Usually, the lignin in fiber from CTMP was not chemically changed, but by hydrogen peroxide treatment after ozone treatment, it was first changed by ozone, and then gushing out by hydrogen peroxide. Therefore, it could be classified to two regions, lignin containing region and non-lignin containing region. In the lignin containing region, the lignin was chemically changed, and so this could be the important factor for improving the optical properties.

3.4. Relationship between lignin in fiber and optical properties

The UV spectra of lignin from CTMP and hydrogen peroxide treated fiber were similar, the refore there was different brightness with similar PC No. (Table 6). In addition, The fibers from CTMP and ozone treated pulp had similar optical properties, but the lignin in fiber showed different distribution and chemical characteristics. In ozone treated fiber, there was non- aromatic conjugated structure in non-lignin containing region.

In two staged ozone-hydrogen peroxide bleaching, there was no adsorption band at 250 to 270 nm at A area, where did not contain lignin (Fig. 2). This indicated that the non-aromatic conjugated structure, one of chromophores, was absent. This could contribute for improving the optical properties of ozone- hydrogen peroxide bleached pulp.

4. Conclusions

In order to improve the optical properties of high yield pulp, two staged ozone-hydrogen peroxide bleaching was carried out, and the following results were evaluated the improvement of optical properties, chemical characteristics of lignin in fiber, and the relationship between lignin and optical properties in fiber cell wall.

Peroxide treatment improved brightness, but the PC No. was not. There was little improvement on optical properties by ozone treatment, but this could be improved more by using two staged ozone-hydrogen peroxide treatment.

The hydrogen peroxide treatment did not make any change on chemical characteristics of lignin in cell wall, but by ozone treatment, the non-aromatic conjugated structure was existed in the surface of cell wall, but this could be removed by hydrogen peroxide treatment in two staged ozone-hydrogen peroxide treatment. Therefore, the optical properties were significantly improved, due to the removal of non-aromatic conjugated structure.

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