

# Mercerization of Wood: Formation and Reversibility of Na-cellulose I in Reaction Wood\*<sup>1</sup>

Nam-Hun KIM\*<sup>2†</sup> and Dae-Young Kim\*<sup>3</sup>

## ABSTRACT

The phase transformation from cellulose I into cellulose II in woods by way of Na-cellulose I was examined by x-ray diffraction analysis.

The formation of Na-cellulose I in woods increased with the increase of treating time in alkali solution. When compression wood was treated with 20% NaOH solution at room temperature for 1 day, the x-ray diagram showed only Na-cellulose I. On the other hand, the x-ray diagram of tension wood showed a mixture of cellulose I and Na-cellulose I. Cellulose I of tension wood could not be transformed completely into Na-cellulose I even after 10-day treatment, but was transformed into Na-cellulose I after 30-day treatment. Na-cellulose I of compression and tension woods was converted to the cellulose I pattern and the mixture of cellulose I and cellulose II, respectively, after washing with water and drying at 20°C.

Cellulose I regenerated from Na-cellulose I in wood could not be converted to cellulose II by delignification. Thus, it revealed that the delignification of the alkali-treated wood did not affect their cellulose structures.

From the results, therefore, it can be concluded that lignin in woods prevents the formation of the stable Na-cellulose I and the conversion from cellulose I to cellulose II. This means that the conversion of chain polarity of wood cellulose hardly occurs during mercerization because cellulose microfibrils are fixed by lignin which not to be intermingled.

*Keywords* : Cellulose I, Cellulose II, Compression wood, Mercerization, Na-cellulose I, Tension wood

## 1. INTRODUCTION

The solid state conversion of crystal structure from cellulose I to cellulose II occurs during mercerization by way of Na-cellulose I, and the crystal transformation of cellulose I to cellulose II has been known to be irreversible. The pro-

bable mechanism has been proposed with the chain polarity transformation. Namely, the parallel packing in cellulose I must be transformed into the antiparallel in cellulose II (Blackwell *et al.* 1978; Sarko 1978).

An important study on the transformation mechanism of cellulose I into cellulose II was

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\*2 College of Forest Sciences, Kangwon National University, Chuncheon 200-701, Korea

\*3 College of Life Resources Sciences, Dongguk University, Seoul 100-715, Korea

† Corresponding author : Nam-Hun Kim (kimnh@kangwon.ac.kr)

performed by Chanzy and Roche (1975, 1976). They found in *Valonia* cellulose that cellulose I (shish) could be converted to cellulose II (kebab). From this fact, they assumed that during mercerization the chain folding might occur and the chain polarity changed from the parallel to antiparallel packing. Thereafter, Okano and Sarko (1985), and Nishimura and Sarko (1987) reported the possible mechanism of mercerization that the transformation of cellulose I into cellulose II occurred at the stage when Na-cellulose I was formed by the intermingling of "up" and "down" cellulose chains.

On the other hand, Fink *et al.* (1982, 1985) suggested that Na-cellulose was not converted completely to cellulose II in the range of 10% to 15% sodium hydroxide, and they concluded that part of Na-cellulose I could be obviously reconverted to cellulose I but that the Na-cellulose I formation was not considered a fully irreversible process.

Recently, Kim *et al.* (1990, 1991) confirmed that Na-cellulose I could not be reconverted to cellulose I and the incomplete Na-cellulose restricted by lateral compression stress could be reconverted to cellulose I.

Up to now, however, the question on the transformation mechanism from cellulose I to cellulose II has not been fully solved. Especially, the mercerization of wood cellulose has less been studied in comparison with those of other materials such as cotton, ramie and *Valonia*. Regarding the mercerization of wood cellulose, Revol and Goring (1981) suggested that lignin in wood cell walls might prevent the intermingling process during alkali swelling. On the other hand, Murase *et al.* (1988) in the examination of the ultrathin sections of G-layer by the selected area method of electron diffraction suggested that lignin hardly prevented the alkali swelling of cellulose in wood but restrained the intermingling of cellulose chains by

alkali swelling and the crystallization of cellulose II.

Nevertheless, it is likely to be clear that lignin in wood plays an important role in the transformation of cellulose crystal structure during mercerization. Especially, the lignin contents of wood cell walls would affect the degree of mercerization of wood cellulose. Interestingly, Lonikar *et al.* (1986), however, concluded that the lattice conversion of cellulose was affected by wood species, the extraction of hemicellulose during alkali swelling and sample condition but almost not by the lignin contents of woods.

From these points of view, it is an interesting subject to compare compression wood with tension wood in the mercerization characterization, because lignin (Timell 1986; Blanchette *et al.* 1994) and cellulose (Norberg and Meier 1966; Timell 1969; Blanchette *et al.* 1994) contents are respectively higher in compression wood and tension wood than in normal wood. The waste woods of an oak decayed by white rot fungi, which has a low lignin content (Blanchette 1991), were also used.

The purpose of this study, therefore, is to describe a series of experimental results based on x-ray diffraction analysis, which were conducted to investigate the formation and reversibility of Na-cellulose I, and the role of lignin in wood during alkali swelling.

## 2. MATERIALS and METHODS

### 2.1. Materials

Three types of wood samples were used. These samples were as follows: 1) cellulose-rich sample (tension wood of *Quercus mongolica*); 2) lignin-rich sample (compression wood of *Pinus koraiensis*); and 3) lignin-poor sample (*Quercus mongolia* biodegraded by a white rot fungus). The samples were taken from the reaction,

lateral, and opposite parts of the wood discs. The lignin-poor sample decayed by white rot fungi at air for 5 years was given by The Institute of Forestry, Kangwon-do. The specimens for x-ray diffraction analysis were prepared in the dimensions of 20 mm (L, longitudinal direction), 10 mm (T, tangential direction) and 1 mm (R, radial direction).

## 2.2. Methods

### 2.2.1. Mercerization and Delignification

The samples with the dimensions of 10 mm (L), 1 mm (T) and 1 mm (R) were prepared for mercerization. They were treated with 20% NaOH solution (w/v) until their X-ray diffraction diagrams showed the complete conversion to Na-cellulose I. Thereafter, the samples were thoroughly washed with distilled water, and dried. All of the procedures were carried out at room temperature. The mercerized blocks, then, were delignified at 40°C for 8 days by sodium chlorite solution, containing 2 g of NaClO<sub>2</sub> and 1.3 g of acetic acid in 100 ml of distilled water.

### 2.2.2. X-ray Diffraction

X-ray diffraction diagrams were recorded using a vacuum camera mounted on a Rigaku 2100V, which is equipped with an x-ray tube. Na-cellulose samples for X-ray diffraction were put in a glass capillary ( $\phi=1.0$  mm) to keep samples wet. X-ray beam was collimated in a 0.25 mm diameter pinhole.

## 3. RESULTS and DISCUSSION

### 3.1. Formation of Na-cellulose I in Wood

When compression wood was treated with

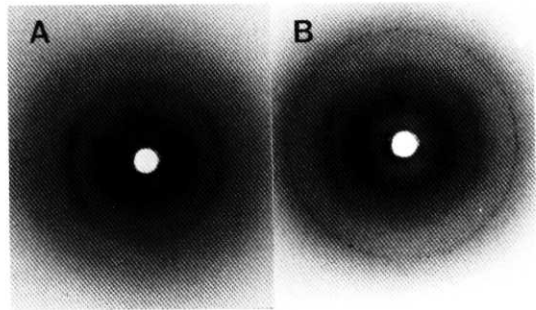


Fig. 1. X-ray diffraction diagrams of Na-cellulose I obtained from compression wood treated with 20% NaOH solution for 1 (A) and 10 (B) days.

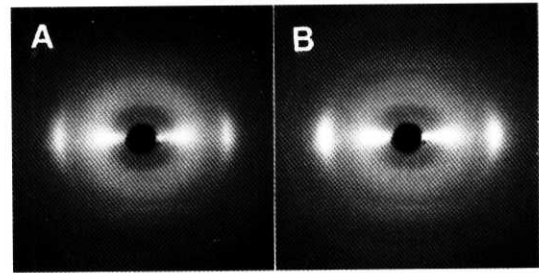


Fig. 2. X-ray diffraction diagrams of Na-cellulose I obtained from opposite (A) and lateral (B) woods of softwood treated with 20% NaOH solution for 1 day.

20% NaOH solution for 1 day, the X-ray diagram showed only Na-cellulose I (Fig. 1A). The X-ray diagram (Fig. 1B) after alkali swelling for 10 days was characterized by a little sharper peak than that in the diagrams of Na-cellulose I treated for a shorter period. Formation of Na-cellulose I in the opposite and lateral woods of softwood exhibited the same pattern with that in compression wood (Fig. 2A, B). That is, Na-cellulose I from compression, opposite and lateral woods of softwood was completely formed in one day treatment.

In hardwood, cellulose I of opposite and lateral woods was also converted easily to Na-cellulose I in one day treatment. On the other hand, when tension wood was immersed in 20% NaOH solution for one day, cellulose was par

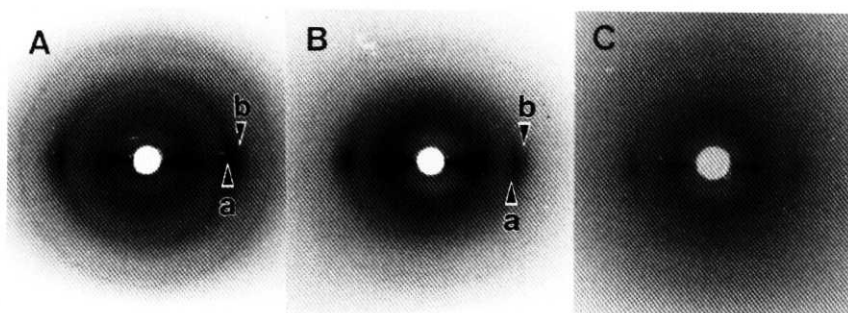


Fig. 3. X-ray diffraction diagrams of cellulose I + Na-cellulose I (A, B) and Na-cellulose I (C) obtained from tension wood treated with 20% NaOH solution for 1, 10 and 30 days. Note : a and b of diagrams indicate reflections of Na-cellulose I and cellulose I, respectively.

tially transformed into a Na-cellulose I, existing a mixture of Na-cellulose I and cellulose I (Fig. 3A). Cellulose I was clearly remained in the tension wood sample even after 10 days treatment (Fig. 3B). But cellulose I of tension wood was completely converted to Na-cellulose I after 30 days treatment (Fig. 3C). Therefore, even though rich in cellulose, the conversion of cellulose I to Na-cellulose I was proceeded slowly in tension wood, differently from the other samples.

Certainly, formation of Na-cellulose I in wood increased with increasing alkali swelling duration, and did not depend on the lignin content. It can be concluded that lignin in wood has no influence on the formation of Na-cellulose I, though it may restrict the physical swelling behavior of wood cells.

### 3.2. Transformation from Na-cellulose I into Cellulose I and/or II

As stated above, X-ray diagrams from all the wood samples treated with 20% NaOH solution for 1 to 30 days showed the reflections of Na-cellulose I. After washing compression wood samples with distilled water and drying at 20°C, Na-cellulose I was transformed into cellulose I (Fig. 4A). That is, Na-cellulose I of compression wood could be reconverted to cellulose I by

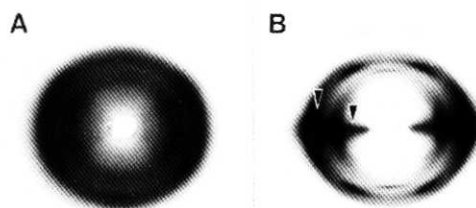


Fig. 4. X-ray diffraction diagrams of compression wood (A) and tension wood (B) washed and dried after treating 20% NaOH solution for 10 days. Note : Arrow of diagram (B) indicates (200) reflection of cellulose II.

washing and drying. In tension wood after washing and drying, however, the X-ray diagram showed a mixture of cellulose I and cellulose II (Fig. 4B). It, thus, can be presumed that a trace of cellulose II in tension wood is originated in the gelatinous layers of cell walls.

Fig. 5 shows the x-ray diagram of the decayed woods washed and dried after mercerization. Significantly, the X-ray diagram after 1 day treatment showed a mixture of cellulose I and cellulose II (Fig. 5A), and complete conversion to cellulose II after the mercerization for 10 days (Fig. 5B).

At present, therefore, it is clear that lignin in wood prevents the conversion from cellulose I to cellulose II. This means that the conversion of the chain polarity of wood cellulose hardly

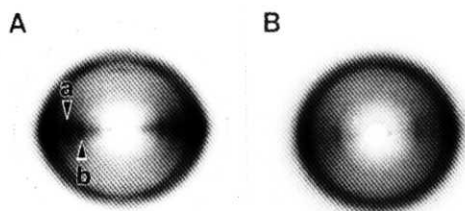


Fig. 5. X-ray diffraction diagrams of decayed wood washed and dried after treating 20% NaOH solution for 1 (A) and 10 (B) days. Note : a and b of diagram A indicate reflections of cellulose I and cellulose II, respectively.

occurs during mercerization because cellulose microfibrils are fixed by lignin which not to be intermingled.

### 3.3. Effect of Delignification

Fig. 6 shows the x-ray diagrams of delignified samples after mercerization. Before and after the delignification of wood samples, the x-ray diagrams exhibited no change in the reflection of cellulose. That is, the diagrams presented cellulose I pattern in compression wood (Fig. 6A), a mixture of cellulose I and II in tension wood (Fig. 6B), and only cellulose II in the decayed wood (Fig. 6C). Therefore, the cellulose

I regenerated from Na-cellulose I in wood could not be converted to cellulose II during delignification.

From the above results, we could see that the transformation from cellulose I into Na-cellulose I easily occurred in woods during mercerization, except for tension wood. It seems that the formation of Na-cellulose I is related to the characteristics of wood, such as density, species, part of wood, *etc.* Washing and drying of the Na-cellulose I samples showed different results: cellulose I in all samples of softwood and the opposite and lateral woods of hardwood; a mixture of cellulose I and cellulose II in tension wood; and only cellulose II in the decayed wood. Especially, in the decayed wood samples (lignin poor samples) cellulose I could be easily converted to Na-cellulose I and converted to cellulose II by washing and drying. Therefore, the chain polarity of cellulose I in woods is hardly changed during mercerization because lignin prevents the intermingling of cellulose chains in neighboring microfibrils. Accordingly, Na-cellulose I in lignified cell walls may have the same polarity with cellulose I.

Now, we suggest another possible mechanism, which can explain the reversible mechanism from Na-cellulose I to cellulose I as proposed

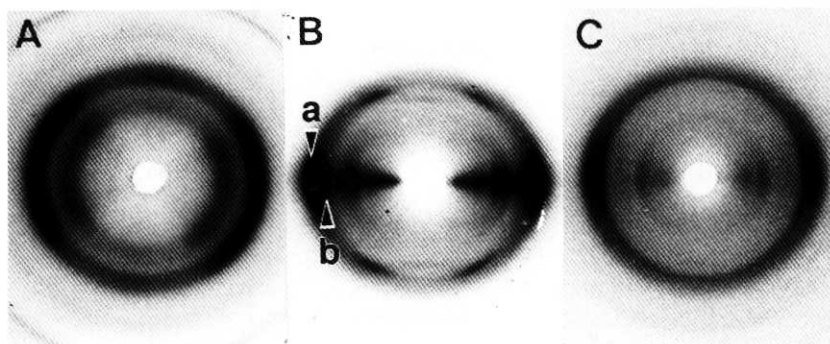


Fig. 6. X-ray diffraction diagrams of compression wood (A), tension wood (B) and decayed wood (C) delignified with a sodium chlorite solution after mercerization for 10 days. Note : a and b of diagram B indicate reflections of cellulose I and cellulose II, respectively.

in our previous reports (Kim *et al.* 1990, 1991). Namely, cellulose I in wood is easily transformed into a metastable sodium cellulose, which has an incomplete composition of NaOH and H<sub>2</sub>O, compared to the complete Na-cellulose I (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> : NaOH : H<sub>2</sub>O = 1 : 1 : 3 reported by Sakurada and Okamura(1937) and Sobue *et al.*(1939)) because when wood cellulose is swollen by alkali solution, lignin in cell wall is packed around the microfibrils, so that the penetration of Na<sup>+</sup> ion into cellulose chains is prevented, and then the formation of complete sodium cellulose and the swelling of cellulose chains are restricted. Thereafter, the metastable sodium cellulose can be regenerated to cellulose I by washing and drying. Otherwise, if the complete Na-cellulose I in wood is once formed during alkali swelling, it can be transformed into cellulose II after delignification.

#### 4. CONCLUSIONS

Crystal transformation from cellulose I into cellulose II in wood via Na-cellulose I was examined by x-ray diffraction analysis.

The x-ray diagram of the compression wood treated with 20% NaOH solution at room temperature for 1 day shows only Na-cellulose I. Tension wood exhibited a mixture of cellulose I and Na-cellulose I in the same treatment conditions. Cellulose I of the tension wood could not be transformed completely into Na-cellulose I even in 10-day treatment but into Na-cellulose I in 30-day treatment. Thereafter, when compression and tension woods were washed with distilled water and then dried at 200°C, the pattern of cellulose I and a mixture pattern of cellulose I and cellulose II appeared, respectively.

Delignification for the alkali treated wood samples did not have any effects on the cellulose structures.

It can be concluded that lignin in wood prevents the formation of the stable Na-cellulose I and the conversion from cellulose I to cellulose II. This means that the conversion of chain polarity of wood cellulose hardly occurs during mercerization because cellulose microfibrils are fixed by lignin which not to be intermingled.

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