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Alkali-Swollen Morphology of Native Cellulose Fibers[*1]

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ABSTRACT

The behavior of ramie fibers and some wood elements in the early stage of alkali swelling was examined. When the fibers were treated with alkali solution, they significantly shrank in length and swelled in wall thickness. Ramie fibers showed a shrinkage averaging 23% in length and a swelling averaging 92% in width in 100 seconds treating time. Dimensional changes showed different fashion in each element of woods. The tracheids of latewood especially in *Pinus densiflora* and *Larix kaempferi* woods swelled intensively and showed balloon swelling, but in the case of *Cryptomeria japonica,* it was hardly observed. The swelling morphology of libriform fibers was similar to that of tracheids. The walls of vessel elements and parenchyma cells also swelled considerably in thickness but, no balloon swelling was found in both elements. The differences of swelling in different elements can be interpreted in terms of the differences of organization and/or chemical components of the cell walls.

Keywords : ramie fiber, wood elements, alkali swelling, alkali-cellulose, ballon-swelling

1. INTRODUCTION

It has been reported that the alkali-induced conversion from cellulose I to cellulose II is governed by the swelling of fibers (Warwicker *et al.*, 1971: Nishiyama *et al.*, 2000). It was also found that, in wood, the degree of mercerization of cellulose depended on the duration of swelling (Kim, 2005).

Treating native cellulose fibers with certain aqueous solutions, such as sodium hydroxide, causes the swelling in wall thickness and the shrinkage in length. For the swelling morphology of native fibers in alkali or acid solutions, balloon swelling and mushroom-head swelling had been known (Hosoi *et al.*, 1958; Warwicker, 1971). Balloon swelling has been illustrated with the common feature of native fibers due to bursting of primary wall (Warwicker, 1966) or primary wall and secondary wall (S_1) (Wardrop and Dadswell, 1950) while mushroom-head was attributed to a cut fiber (Saito, 1939). To test the effect of primary wall, Rollins and Tripp (1954) examined quantitatively and reported that raw cotton fibers in 18% sodium hydroxide solutions shrank by 3% in length and swelled by 20% in width, but cotton freed of non-cellulosic materials by extraction shrink by 40% in

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length and swelled by 60% in width.

From the above results, it is clear that primary wall and outer layer (S_1) of secondary wall have restriction effect for the swelling behavior, consequently the fiber wall would swell imperfectly.

During alkaline swelling, cellulose I can be transformed to alkali-celluloses of different crystal structures. Namely, the swelling behavior of cellulose fibers in the early stage of alkali treatment is considered to be a consequence of the formation of alkali-cellulose (Kolpark and Blackwell, 1978; Revol and Goring, 1981; Kim *et al.*, 1989; Nishiyama and Okano, 1998; Dinand *et al.*, 2002; Kim and Kim, 2003). However, the transformation would be restricted or slowly progressed by the influence of primary wall and S_1 layer.

The study on dimensional changes of cellulose fibers is considered to be an important object to solve mercerization mechanism in connection with the formation of alkali-cellulose (Kim *et al.*, 1989; Nishiyama and Okano, 1998). Therefore, in this study, to understand the alkali swelling behavior of wood cellulose, dimensional changes of ramie fibers and some wood elements in alkali solution are measured quantitatively, and the swelling morphology is observed.

2. EXPERIMENTAL

2.1. Materials

Purified native ramie fibers *(Boehmaria nivea* Gaud.) and some commercial species which include *Cryptomeria japonica*, *Larix kaempferi* and *Pinus densiflora* in softwoods, and *Fagus crenata* and *Zelkova serrata* in hardwoods were used.

2.2. Methods

Defibrilation of the wood elements was carried out using Schultze's solution. Ramie fibers, and tracheids and parenchyma cells in softwoods, and wood fibers, vessel elements and parenchyma cells in hardwoods were treated with 3.5 N sodium hydroxide solutions which is an effective alkali concentration for mercerization (Kim *et al.*, 1989). Length and width of the various fibers, before and after alkaline swelling, were measured using a combined system of ocular and objective micrometers under optical microscope (Olympus BH-2), and their micrographs were obtained. Each result is the mean of 50 sample measurements.

3. RESULTS and DISCUSSION

3.1. Alkali-swollen Morphology of Ramie Fibers

Ramie fibers treated with the solution of 3.5 N sodium hydroxide showed in considerable changes in the morphology of the fibers: a shrinkage averaging 20% in length and a swelling averaging 92% in width for quite a short period. The shrinkage and swelling started simultaneously just after immersion in the alkaline solution. Especially after 20~30 sec, fibers showed fast movement and then stopped the contraction after 50~100 sec. Figure 1 shows the longitudinal shrinkage of ramie fibers at various concentrations of sodium hydroxide solution. The shrinkage decreased with increasing concentration and the shrinkage maximum was observed at 3 N sodium hydroxide solution. It can be explained that the differences of fiber swelling in different concentrations were affected by the degree of hydration during alkali treatment (Zeronian, 1985). In our previous report (Kim *et al.*, 1989), we examined the con-

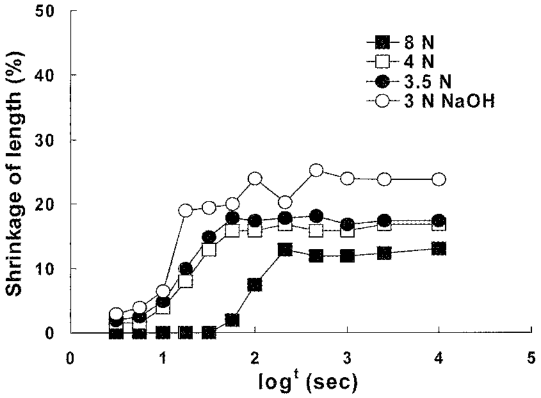


Fig. 1. Longitudinal shrinkage of ramie fibers in different concentrations of sodium hydroxide solution.

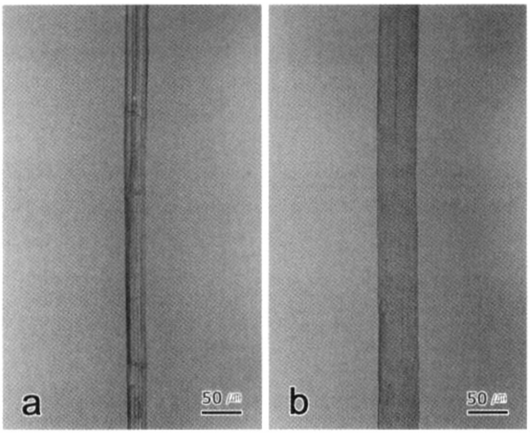


Fig. 2. Optical micrographs of untreated (a) and treated (b) ramie fiber with 3.5 N sodium hydroxide solution.

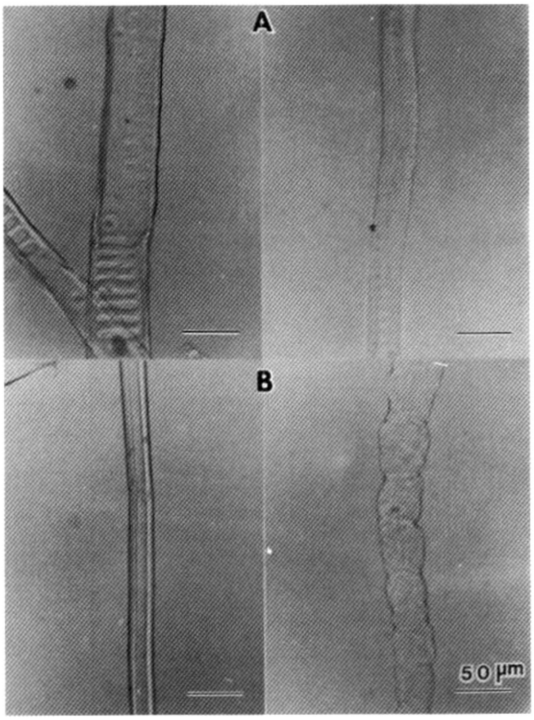
siderable changes of the morphology of ramie fibers during alkali swelling. Nishiyama & Okano (1998) reported that the observed twisting and changes in the cross-sectional shape of the fibers could be explained as a geometrical alteration caused by lateral expansion of coiling fibrils.

As shown in an optical micrograph of a native ramie fiber (Fig. 2), we can identify the cell wall thickness, but a fiber after complete alkaline treatment has a homogeneous appearance, suggesting that the swelling of the wall was so extensive that even the lumen was occupied completely by the swollen wall. Kim *et al.* (1989) reported that the formation of Na-cellulose I in the early stage of alkali swelling kept pace with the swelling behavior of the fibers, and that the morphological changes of fiber walls after alkali treatment might be intimately connected with the formation of Na-cellulose I.

3.2. Alkali-swollen Morphology of the Elements in Softwoods

When tracheids were placed in the solution of 3.5 N sodium hydroxide, the wall swelled. Swelling took place in the inward of the wall. Swelling morphology of latewood tracheids of *Pinus densiflora* as well as *Larix kaempferi* was characterized with balloon swelling (Fig. 3), but in the case of *Cryptomeria japonica,* it was hardly observed. Balloon swelling occurred predominantly at wounded regions of cell wall. It means that the network of fibrils of the primary wall plays a part in restricting swelling of the cell wall (Wordrop and Dadswell, 1950; Warwicker, 1971). Dimensional changes of tracheids are shown in Table 1. The length of earlywood tracheids shrank more than that of latewood: that is, 25～30% in earlywood and 11～12.5% in latewood.

The diameter of earlywood tracheids decreased by 25～31%, whereas that of the tracheids in latewoods increased by 17～40%. Swelling was most noticeable in the wall thickness. Namely, the wall thickness in earlywood increased by about 110%, and in latewood by about 200%, except for *Cryptomeria japonica* by 96%. The increase in the diameter and wall thickness of *Pinus densiflora* and *Larix kaempferi* latewoods caused by balloon swelling was greater than that of *Cryptomeria*



(untreated) (treated)

Fig. 3. Optical micrographs of untreated and treated tracheids in earlywood (A) and latewood (B) of *Pinus densiflora*.

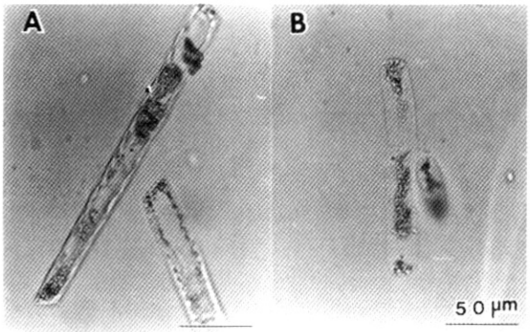


Fig. 4. Optical micrographs of untreated (A) and treated (B) parenchyma cells in *Larix kaempferi.*

japonica.

Swelling morphology of parenchyma cells was simple and balloon swelling was not observed. Fig. 4 shows the parenchyma cells of *Larix kaempferi* wood before and after alkaline swelling. Dimensional changes differed from among the species as shown in Table 2. Especially, the diameter of *Pinus densiflora* and *Cryptomeria japonica* woods decreased by 20～45%, whereas, that of *Larix kaempferi* wood increased slightly. Length and diameter of axial parenchyma cells shrank more than those of ra-

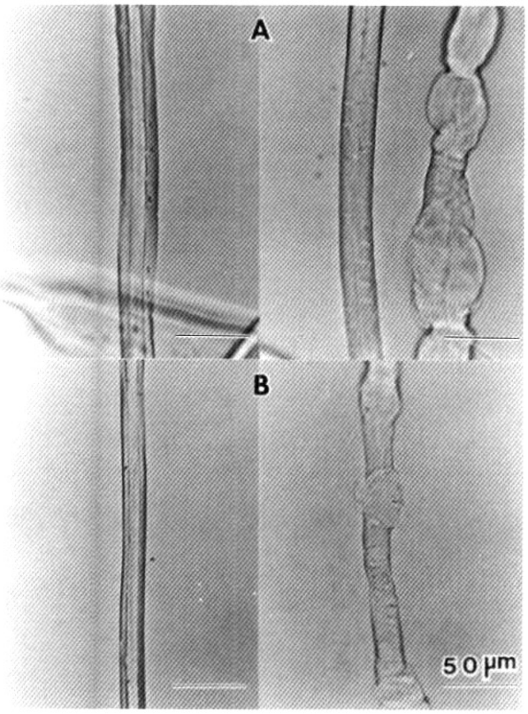
Table 1. Dimensional changes of tracheids in 3.5 N sodium hydroxide solution

Species		*Pinus densiflora*		*Larix kaempferi*		*Cryptomeria japonica*	
		EW	LW	EW	LW	EW	LW
Length (mm)	Before	3.70±0.50	4.80±0.65	3.20±0.45	4.20±0.60	2.80±0.30	3.70±0.52
	After	2.60±0.40	4.20±0.50	2.40±0.35	3.70±0.45	2.0±0.20	3.30±0.40
Swelling (%)		-30.0	-12.5	-25.0	-12.0	-29.0	-11.0
Diameter (μm)	Before	56.0±3.20	30.0±4.80	80.0±9.00	33.0±3.00	49.0±8.80	23.0±2.64
	After	42.0±2.50	42.0±5.50	56.0±3.00	45.0±5.00	34.0±1.50	27.0±2.5
Swelling (%)		-25.0	40.0	-30.0	36.4	-31.0	17.0
Wall thickness (μm)	Before	2.90±0.60	6.50±1.00	2.70±0.60	6.00±1.00	2.10±0.50	5.60±1.00
	After	6.00±1.00	20.00±2.00	5.50±1.50	17.00±2.50	4.50±1.00	11.00±2.00
Swelling (%)		107.0	208.0	104.0	183.0	114.0	96.0

* EW: Early-wood, LW: Late-wood

Table 2. Dimensional change of the parenchyma cells in softwoods at 3.5 N sodium hydroxide solution

Species		*Pinus densiflora*	*Larix kaempferi*	*Cryptomeria japonica*	
		Ray	Ray	Axial	Ray
Length (μm)	Before	149.0±49.6	199.60±65.60	270.0±46.4	114.0±13.6
	After	120.0±40.4	137.60±50.80	147.0±16.4	91.0±6.0
Swelling (%)		-19.5	-31.10	-45.5	-37.0
Diameter (μm)	Before	24.6±4.6	17.6±3.0	21.0±5.0	15.0±3.0
	After	13.6±3.6	18.6±2.0	11.5±2.2	12.0±1.4
Swelling (%)		-44.7	5.7	-45.0	-20.0
Wall thickness (μm)	Before	2.0±0.5	2.0±0.5	2.0±0.5	2.0±0.5
	After	6.0±1.5	7.0±1.5	4.0±1.0	5.0±1.5
Swelling (%)		200.0	250.0	100.0	150.0



(untreated) (treated)

Fig. 5. Optical micrographs of untreated and treated libriform fibers in *Fagus crenata* (A) and *Zelkova serrata* (B).

dial parenchyma cells, but the wall swelled more in their thickness.

3.3. Alkali-swollen Morphology of the Elements in Hardwoods

The swelling morphology of the libriform fibers of *Fagus crenata* and *Zelkova serrata* was similar to that of tracheids, as shown in Fig. 5. The fibers of these species showed both balloon swelling and uniform swelling. In earlier study, Baily and Kerr (1935) used the term 'ring-bead type swelling' for 'balloon swelling' of libriform fibers. Dimensional changes of the elements in hardwoods are shown in Table 3. Swelling of the fibers of *Zelkova serrata* was greater than that of *Fagus crenata*. Swelling behavior of fiber tracheids in *Fagus crenata* was similar to that of libriform fibers, except for the absence of balloon swelling.

The swelling morphology of vessel elements of *Fagus crenata* is shown in Fig. 6. The wall of vessel elements in *Fagus crenata* swelled remarkably by 166~200%, and the swelling of the parenchyma cell walls of both species was

Table 3. Dimensional changes of the elements in hardwoods at 3.5 N sodium hydroxide solution

Species		*Fagus crenata*				
Elements		Libriform fibers	Fiber tracheids	Vessel elements		Parenchyma cells
				EW	LW	
Length (mm)	Before	1.02±0.19	0.69±0.05	0.48±0.05	0.45±0.06	0.19±0.04
	After	0.68±0.08	0.48±0.05	0.31±0.03	0.30±0.03	0.14±0.02
Swelling (%)		-33.3	-30.4	-35.4	-33.3	-26.3
Diameter (μm)	Before	25.60±3.50	27.0±5.5	900.0±10.0	40.0±6.0	22.0±3.5
	After	21.60±3.02	20.0±3.0	50.0±6.0	25.0±3.5	18.0±2.0
Swelling (%)		-15.6	-26.0	-44.4	-37.5	-18.2
Wall thickness (μm)	Before	7.0±1.5	4.0±1.0	1.5±0.5	2.0±0.5	2.0±0.5
	After	10.0±2.0	8.0±2.0	4.0±1.0	6.0±1.0	5.5±1.0
Swelling (%)		43.0	100.0	166.6	200.0	175.0

Species		*Zelkova serrata*			
Elements		Libriform fibers	Vessel elements		Parenchyma cells
			EW	LW	
Length (mm)	Before	1.493±0.211	0.281±0.091	0.232±0.020	0.211±0.033
	After	1.104±0.193	0.203±0.024	0.152±0.020	0.144±0.040
Swelling (%)		-26.1	-27.8	-34.5	-31.8
Diameter (μm)	Before	11.30±2.22	210.0±28.4	70.0±11.4	13.6±2.2
	After	13.50±2.40	132.0±22.8	62.0±8.0	16.6±3.0
Swelling (%)		19.50	-37.0	-31.0	22.0
Wall thickness (μm)	Before	5.0±1.0	3.0±0.5	4.0±1.0	2.0±0.5
	After	10.0±2.0	5.0±1.0	7.0±2.0	4.0±1.0
Swelling (%)		100.0	66.6	75.0	100.0

* EW: Early-wood, LW: Late-wood

also great. However, the vessel elements and the parenchyma cells did not show balloon swelling.

Consequently, it was considered that the differences of swelling in various elements can be interpreted in terms of the differences of organization and/or chemical components of the cell walls.

4. CONCLUSIONS

When the fibers were treated with alkali solution, they would be shrunk in length and swollen in wall thickness. Dimensional changes show different fashion in each element. The tracheids of latewood and libriform fibers swelled intensively, and showed balloon swelling. The

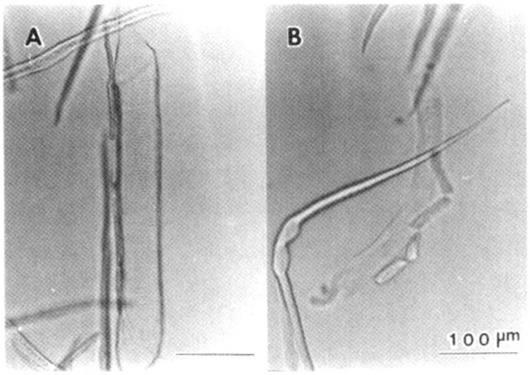


Fig. 6. Optical micrographs of untreated (A) and treated (B) vessel elements in *Fagus crenata*.

walls of vessel elements and parenchyma cells also swelled considerably in thickness, but, no balloon swelling was found in both elements. The differences of swelling in different elements can be interpreted in terms of the differences of organization and/or chemical components of the cell walls. Although the movement of the fibers treated with alkali solution might be explained in terms of osmotic phenomena, it was considered that this behavior was intimately connected with the formation of Na-cellulose I.

REFERENCES

1. Baily, I. W. and T. Kerr. 1935. The visible structure of the secondary wall and its significance in physical and chemical investigations of tracheary cells and fibers. Journal of the Arnold Arboretum 16(3): 273~300 (with plates 140~149).
2. Dinand, E., M. Vignon, H. Channzy, and L. Heux. 2002. Mercerization of primary wall cellulose and its implication for conversion of cellulose I → cellulose II. Cellulose 9: 7~18.
3. Hosoi, H., K. Katahara, and N. Migita. 1958. Researches on the swelling of fibers. III. Mokuzai Gakkaishi 4(2): 60~66.
4. Kim, N. H. 2005. An investigation of mercerization in decayed oak wood by a white rot fungus (Lentinula edodes). Journal of Wood Science 51: 290~294.
5. Kim, N. H. and D. Y. Kim. 2003. Mercerizarion of wood: Formation and reversibility of Na-cellulose I in reaction wood. Mokchae Konghak 31 (6): 1~7.
6. Kim, N. H., J. Sugiyama, and T. Okano. 1989. The behavior of cellulose fibers in the early stage of alkalineswelling. Mokuzai Gakkaishi Vol. 35(5): 387~391.
7. Kolpak, F. J. and J. Blackwell. 1978. Mercerization of cellulose: 2. The morphology of mercerized cotton cellulose. Polymer 19: 132~135.
8. Nishiyama, Y. and T. Okano. 1998. Morphological changes of ramie fiber during mercerization. Journal of Wood Science 44: 310~313.
9. Nishiyama, Y., S. Kuga, and T. Okano. 2000. Mechanism of mercerization revealed by X-ray diffraction. Journal of Wood Science 46: 452~457.
10. Revol, J. F. and D. A. I. Goring. 1981. On the mechanism of the mercerization of cellulose in wood. Journal of Applied Polymer Science 26: 1275~1282.
11. Rollins M. L. and V. W. Tripp. 1954. Optical and electron microscopic studies of cotton fiber structure. Textile Research Journal 24: 345~357.
12. Saito, G. 1939. Das verhalten der zellulose in alkalilösungen. Kolloid-Beihefte 49: 365~453.
13. Wardrop, A. B. and H. E. Dadswell. 1950. The swelling behavior of conifer tracheids and the concept of a skin substance. Australian Pulp and Paper Industry Technical Association Proceedings 4: 198~221.
14. Warwicker, J. O. 1971. Swelling. Cellulose and cellulose derivatives. Bikales, N. M. and L. Segal, eds., Wiley and Sons Inc.: 325~379.
15. Warwicker, J. O., R. Jeffries, R. L. Colbran, and R. N. Robinson. 1966. A review of the literature on the effect of caustic soda and other swelling agents on the fine structure of cotton. Shirley Institute Pamphlet No.93. St Ann's Press: 55~70.
16. Zeronian, S. H. 1985. Intracrystalline swelling of cellulose. Cellulose Cehmistry and Its Applications. Nevell, T. P. and Zeronian, S. H., eds. Ellis Horwood Ltd.: 159~180.