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Yoshiharu Nishiyama · Takeshi Okano

Morphological changes of ramie fiber during mercerization

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Abstract Morphological changes of ramie fibers due to swelling in alkali solution were investigated. 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 the unmercerized ramie fiber showed an S-helix structure. The fibril angle of ramie fibers was estimated to be 3°. Although the swollen fiber untwisted to some extent on washing with water, the shape of the twisted ribbons as observed by scanning electron microscopy was retained even after drying. Concentrated 8N NaOH produced only a moderate change in morphology, whereas swelling with 3.5N NaOH at 0°C expanded the cross sections about 30 times over the initial ones accompanied by a drastic change in the shape of the fiber.

Key words Cellulose · Mercerization · Ramie · Swelling

Introduction

Aqueous sodium hydroxide solution of high enough concentration is known to swell even the crystalline part of cellulose and lead to a polymorph of cellulose II after washing and drying. This alkaline treatment of natural cellulose fibers with successive washing and drying, called mercerization, has long been investigated and has been applied to the industry for more than a century.[1]

Y. Nishiyama (✉) · T. Okano
Department of Biomaterial Science, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo 113-8657, Japan
Tel. +81-3-3812-2111; Fax +81-3-5684-0299
e-mail: aa56159@hongo.ecc.u-tokyo.ac.jp

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The mercerized cellulose gives practically the same diffraction as those regenerated from solution and is claimed to have an anti-parallel packing on the basis of X-ray diffraction analysis.[2] However, the mechanism of chain rearrangement in the swollen state is still controversial.[3] The swollen structure also form polymorphs that include ions and water molecules in their unit cells.[4] Direct evidence of the mechanism of crystalline conversion is difficult to obtain, and the poor crystallinity of cellulose II prevents clear discussion on the chain polarity.

Understanding the swollen state of cellulose is essential to the conversion among cellulose polymorphs and chain polarity and to controlling the higher-order structure. Alkali-swollen cellulose can be considered a physical gel for which thermodynamic interpretation of phase transitions has been investigated during the last few decades; one example is methylcellulose gel.[5] The macroscopic behavior of swelling of cellulose fibers is not simple because of its anisotropic structure. In this study, we tried to distinguish the effect of fiber structure and thermodynamic behavior. We report here the morphological changes that can be attributed mainly to fiber structure and the lateral expansion of individual fibrils.

Material and methods

Purified native ramie (Boehmaria nivea Gaud.), donated by Teikoku Boseki KK., was used in this study.

Observation by optical microscopy

Cross sections of the fiber were prepared by embedding a bundle of fibers in epoxy resin and cutting them to a desired thickness with a microtome equipped with a glass knife. The resin was removed with a 14% methanol solution of sodium methylate. The sections were washed with and kept in methanol before use.

The sections were placed in an indented glass slide allowing the methanol to evaporate, and aqueous solutions of

caustic soda were added. Changes in their shape and dimensions were observed with a light polarized microscope. The effects of washing with water and then drying were observed in the same manner.

Cross sections were prepared with a thickness ranging from 5 to 50 μm. Thinner sections were used only to observe the initial state because such thin sections curl on swelling. Thicker sections were useful for observing the swelling behavior.

Ramie fibers cut into 2 cm long pieces were placed on a glass slide and alkali solution was added. Light microscope observation was carried out without a cover glass to prevent any restriction.

X-ray diffraction

X-ray diffraction diagrams were prepared of a bundle of about 20 fibers held stretched in a vacuum camera mounted on a Rigaku RU-200HB with a rotating anode X-ray generator operating at 40 kV and 80 mA. An inclined X-ray diffraction of 17.3° (theta angle for 004) was used to observe the azimuthal distribution of 004 reflection, which directly reflects the distribution of microfibril orientation. The diffraction diagrams stored on an imaging plate (Fuji imaging plate HRV) were read with an imaging plate reader RAXIS IID. The azimuthal intensity distribution of 004 reflection showed only one peak due to the disorientation of the fibrils. A gaussian distribution was assumed for the disorientation, and the fibrillar angle was calculated by deconvoluting the intensity profile into two gaussian profiles of the same shape by the least-squares method.

SEM observation

Fibers were peeled with forceps in water under the microscope to confirm that the fiber was composed of layers. To estimate the fibril angle, fibers were split with a needle along the fiber length. Mercerization of fibers was carried out in a slack condition. All samples were freeze-dried with *t*-butyl alcohol and coated with Pt using an ion sputter. Observation was done with a field emission scanning election microscope (SEM) (S-4000) using an accelerating voltage of 20 kV.

Results and discussion

Fibril angle of ramie

Ramie cell walls appeared to consist of layers, and the microfibrils were oriented nearly parallel to the fiber axis with a small deviation in the S-helix direction (Fig. 1a–c). Warwicker[6] had previously concluded that ramie samples exhibited an S-helix of 6°. Figure 2 shows the X-ray diffraction diagram obtained from an inclined sample from which the half-width of the 004 arc can be determined to be about 10°. The profile of the arc could be resolved into two

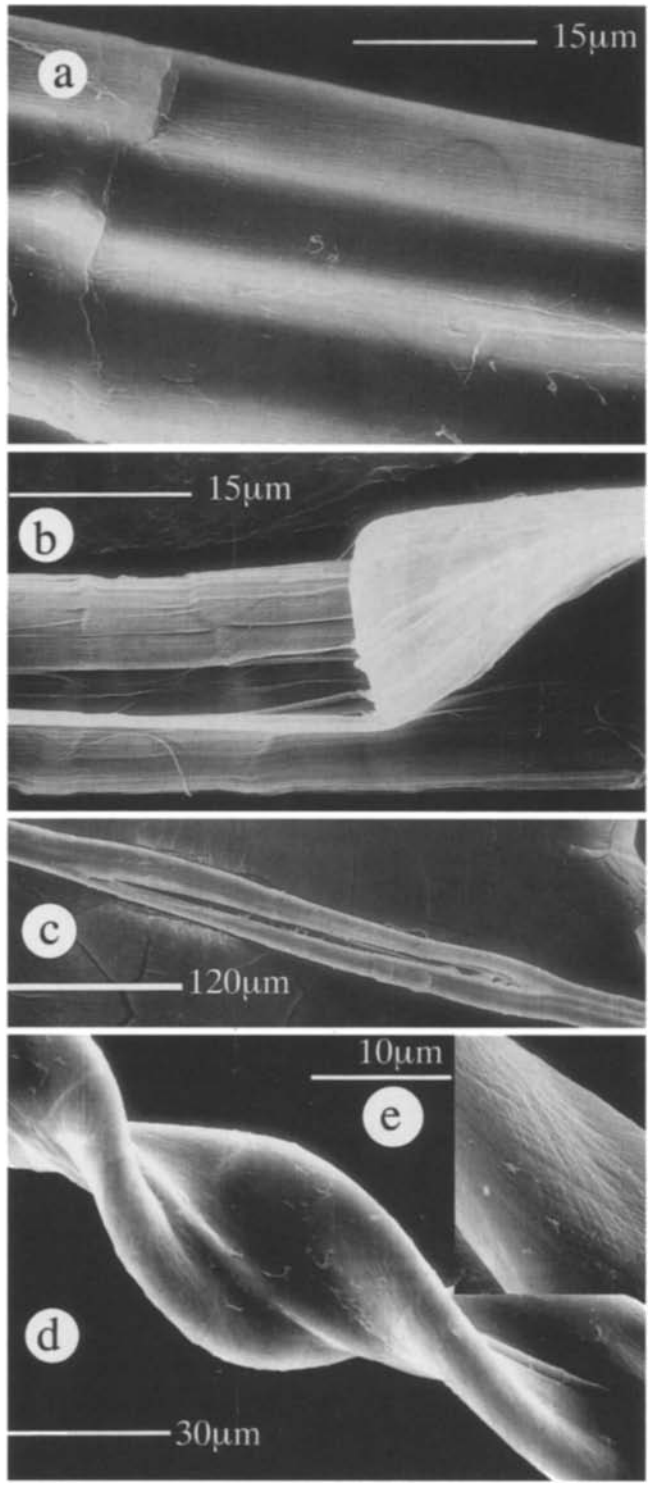

Fig. 1. Scanning electron micrographs of ramie fibers. **a** Surface of a purified native ramie. Fibril direction is slightly deviated from parallel. **b** Concentric layers can be peeled off with a pair of forceps, exposing almost the same structure inside. **c** Scratched with a needle along the fibril direction, the S-helix can be observed. **d** After slack mercerization in 3.5 N aqueous NaOH at 0°C. **e** Condition are the same as in **d**. Crossing structure can be observed

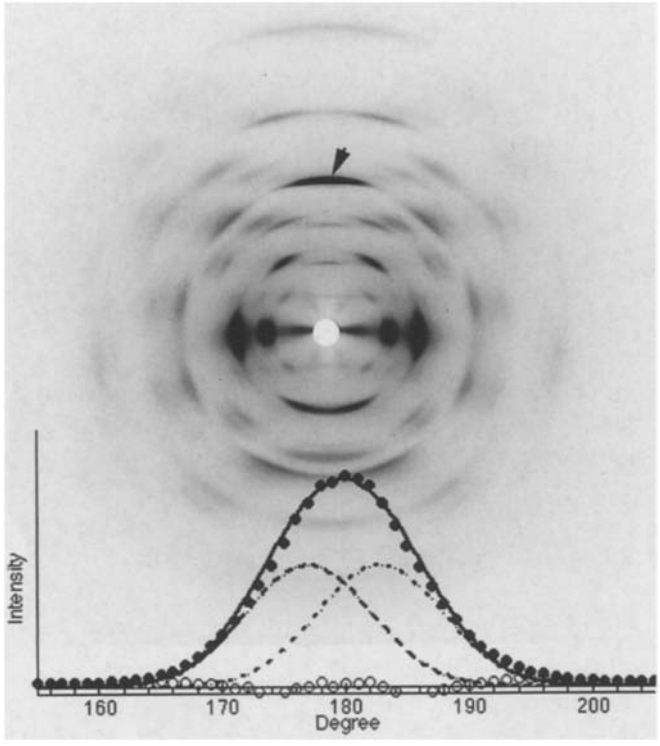

Fig. 2. X-ray diffraction diagram of ramie fibers inclined about 17.3° relative to vertical, and the azimuthal profile of its 004 reflection (*arrowhead*). *Filled circles*, observed intensity; *thick line*, calculated profile as a sum of two gaussian functions (*dashed lines*); *circles*, difference of calculated and observed data

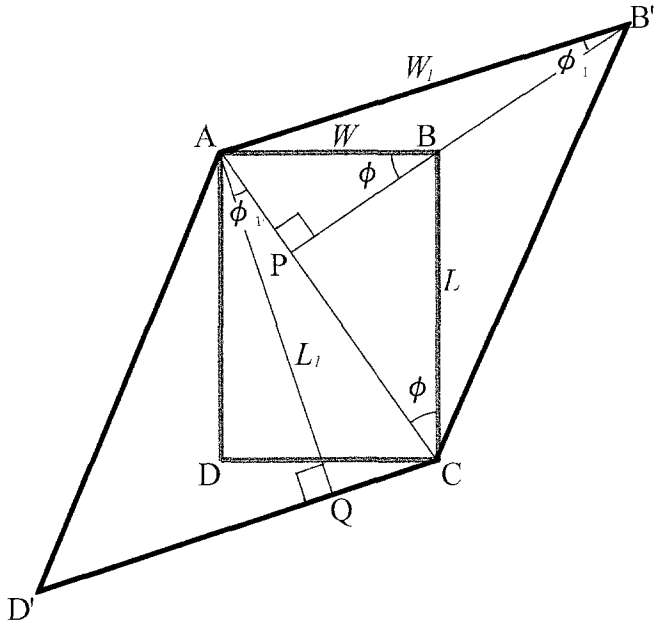

Fig. 3. Expansion of the ramie cell wall. *ABCD* is a section cut and opened one turn of the wall with fibril angle ϕ, width W, and helix pitch L. Assuming a lateral expansion of fibrils by rate α, the expanded section is expressed with suffix *1*

gaussian curres at a distance of 5.8°. Therefore, the fibril angle was determined to be approximately 3°. The scanning electron micrographs of the ramie fiber (Fig. 1a–c) revealed the fiber to have a structure of S-helix, or left-handed helix (coiling in the counter direction is denoted as Z-helix). Light microscopy with varying focusing distances confirmed this coiling direction.

Uncoiling of a fiber

When a fiber was soaked in a caustic soda solution under slight tension exerted by a small attached rod, the rod rotated clockwise as seen from the top; the fibers twisted right-handed. This can be interpreted as lateral expansion of individual fibrils in an S-helix.

The expansion of a thin layer of the cell wall simplified as a cylinder is illustrated in Fig. 3. We approximate the structure of the fiber to be a cylinder of infinite small thickness with a fibrillar orientation of ϕ. The section cut at length L, corresponding to one turn of the fibril, is presented as the orthogonal ABCD. Here, AB = CD = W, and BC = DA = L

On swelling, assuming that the swelling takes place only perpendicular to the microfibril direction, the section becomes parallelogramic AB′CD′ at a swelling ratio α. Under this assumption, we can calculate the width and fibril angle after swelling, and the rotation of the fiber on swelling. P and Q in Fig. 3 are the feet of orthogonal projections from point B′ to line AC and from point A to line CD′, respectively.

Because AB′ and CD′ are parallel, $\angle$ACQ = $\angle$CAB′, which means that ΔPAB′ and ΔQAC are similar figures. Here PB = $L\sin\phi$, PB′ = αPB, and AP = $W\sin\phi$; thus the fibril angles ϕ in the initial state and ϕ_1 in the swollen state are expressed as follows:

$$\tan\phi = \frac{\mathrm{AB}}{\mathrm{BC}} = \frac{W}{L} \tag{1}$$

$$\tan\phi_1 = \frac{\mathrm{QC}}{\mathrm{AQ}} = \frac{\mathrm{AP}}{\mathrm{PB'}} = \frac{W\sin\phi}{\alpha L\sin\phi} \tag{2}$$

$$= \frac{W}{\alpha L} \tag{3}$$

The width and length of the section in the swollen state are AB′ and AQ, respectively,

$$W_1 = \mathrm{AB'} = \frac{\mathrm{PB'}}{\cos\phi_1} = \frac{\alpha L\sin\phi}{\cos\phi_1} \tag{4}$$

$$= W\sqrt{\frac{\tan^2\phi + \alpha^2}{\tan^2\phi + 1}} \tag{5}$$

$$L_1 = \mathrm{AQ} = \frac{L\cos\phi_1}{\cos\phi} \tag{6}$$

The twisting of the fiber corresponds to the shift of D′ from D. This is QD′. Thus the number of rotations r per unit length of the fiber can be calculated by

$$r = \frac{D'Q}{W_1} \cdot \frac{1}{L_1} \tag{7}$$

$$= \frac{W_1 - L\sin\phi_1}{\cos\phi L W_1} \tag{8}$$

$$= \frac{\frac{1}{L} - \sin\phi}{W_1 \cos\phi} \tag{9}$$

$$= \frac{\tan\phi}{W}\left\{1 - \frac{\tan^2\phi + 1}{\tan^2\phi + \alpha^2}\right\} \tag{10}$$

Hence, one can see that a fiber in an S-helix twists in the right-hand direction, and the fibril angle becomes small. The values of $= 2.5°$–$4.0°$ and $W = 60$–$100\,\mu m$ are compatible with the observed rotation of about one rotation per 1 mm of fiber length.

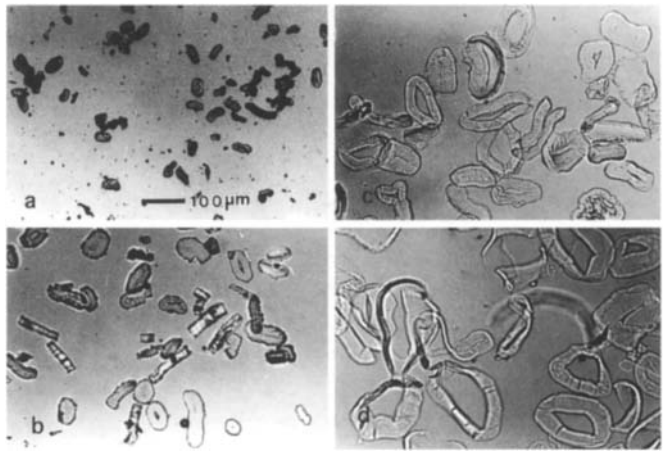

Fig. 4. Cross sections of ramie fibers. **a** Native. **b** Swollen in 8 N aqueous NaOH at room temperature. **c** Swollen in 3.5 N aqueous NaOH at room temperature. **d** Swollen in 3.5 N aqueous NaOH at 0°C. The scale is identical

Effect of thickness of the cell wall

Although the fiber untwisted to some extent by subsequent washing, the twisted shape was retained even after washing and drying. SEM images revealed the mercerized fiber to be like a twisted ribbon (Fig. 1d). The above geometrical explanation cannot explain this irreversibility. Furthermore, the fibrils on the surface of mercerized ramie exhibited a Z-helix (Fig. 1d). The above calculation only predicted the fibril angle to become smaller, not to revert.

Here the thickness of the cell wall should be taken into account. Assuming a constant value of the fibril angle for all layers, Eq. (9) indicates that the potential for twisting is proportional to the inverse of the diameter of a lamella cylinder. Hence, a shearing force develops between the cylinders, resulting in the outer layer twisting more and the inner layer twisting less than expected from the diameter and fibril angle. Above a certain swelling ratio, the outer layer begins to form a Z-helix, whereas the inner layer must be still in S-helix; This crossing structure could be confirmed by careful observation with SEM (Fig. 1e).

Further twisting results in squeezing of the fiber by the outer layer, which can be in the shape of the cross sections after swelling. The cross sections of fibers exhibited various shapes and sizes. The thickness of the wall ranged from 5 to 12 μm (Fig. 4a). Changes of the cross sections on swelling were dependent on both temperature and the alkali concentration (Fig. 4b–d). At a higher swelling ratio, thin-walled shapes were observed (Fig. 4d), perhaps because of the squeezing mentioned above. The change in the shape of cross sections can also originate from the helical structure of the fibrils and their lateral expansion.

Temperature and concentration dependence

When treated with 3.5 N NaOH at 0°C, the thickness of the wall increased about five times over the original one and the circumference of the wall about six times, making the area 30 times larger. The other extreme is treatment with 8 N NaOH, which produced an area only about four times larger. This dependence on temperature and concentration where the swelling is maximum at around 3.5 N/0°C is consistent with previous reports.[6] Attention should be paid to the fact that the swelling process was irreversible; once expanded, the cross section did not shrink after raising the temperature or the NaOH concentration. Hence the alkali swollen cellulose fiber is not in thermodynamic equilibrium. The twisted shape was more pronounced when it was treated in extreme swelling conditions (e.g., 3.5 N/0°C) than in lesser swelling conditions, although the width of the fiber almost recovered to the initial size of the untreated fiber after drying.

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