On the Mechanism of the Mercerization of Cellulose in Wood

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Synopsis

When spruce wood was treated with 20% aqueous NaOH, only partial conversion of cellulose I to cellulose II took place. In contrast, complete conversion occurred when a low yield kraft pulp from the same wood was mercerized. This difference in behavior is interpreted in terms of restricted swelling of the wood in the mercerizing alkali; this treatment preserves some memory of meridional order. Differences in polarity of the molecules in cellulose I and cellulose II are also considered as a possible reason for the difficulty in mercerizing the cellulose in wood.

INTRODUCTION

The conversion of cellulose I to cellulose II in mercerization has been studied by a variety of methods.[1-4] Although not yet fully interpreted, the results of such research have helped to elucidate the ultrastructure of cellulose in its natural state. Virtually no work has been reported on the alkali-induced mercerization of the cellulose present in wood cell walls. The main reason for the lack of interest is that there is no commercial application of such a treatment. Also, the presence of lignin and hemicellulose in the wood will tend to make the results complex and difficult to interpret. Nevertheless, careful study of the behavior of wood in mercerizing systems could lead to a greater understanding of the ultrastructure of cellulose in the wood cell wall in relation to the morphology of the other major polymeric components of wood, viz., lignin and hemicellulose.

The purpose of the present work was to determine the crystallographic changes induced in the cellulose component of wood by mercerization in aqueous sodium hydroxide. Standard methods of x-ray analysis were used. As control, a low-yield wood pulp was studied in a similar manner. Care was taken to use wood containing fibers of low fibril angle. In this manner the disposition of the microfibrils with respect to the orientation of the specimen was fairly well defined. The results obtained were then interpreted in the light of certain new proposals concerning the molecular morphology of naturally occurring cellulose.

EXPERIMENTAL

A sample of black spruce wood with a fibril angle of between 0° and 10° was used for the study. Kraft pulp at a yield level of 47% from the same black spruce wood was used as a control. In preparing the pulp, the wood was handled in such a way that the original alignment of the fibers was not disrupted. During mercerization and subsequent x-ray analysis, care was taken to preserve the parallel orientation of the fibers.

Samples 0.5 mm square and few millimeters long were used. For the mer-

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cerizing treatment, the samples were impregnated under vacuum with an aqueous solution of 20% sodium hydroxide by weight (25 g NaOH + 100 g H_2O) at room temperature for 24 hr. After the alkali treatment, the samples were washed with distilled water at room temperature, again using vacuum impregnation. Washing was conducted until the wash water was neutral in pH.

X-ray diffraction patterns were recorded on flat film using a Warhus camera at room temperature. Ni-filtered CuK_α radiation (λ = 1.54 Å) was used. NaF powder was used as calibration standard.

Most samples were examined in the dry state. However, the alkali-soaked specimens were retained in special Lindeman glass capillaries.

RESULTS

The results for the wood pulp are given in Figure 1. The fiber diagram for the dry untreated wood pulp is shown in Figure 1(a). The well known pattern of cellulose I is clearly evident.

Figure 1(b) represents the same pulp after 24 hr in an aqueous solution of NaOH 20% by weight. The diagram shows that a complete penetration of the cellulose has been achieved, as indicated by the presence of a soda–cellulose complex.

Figure 1(c) is for the same sample after washing in water and drying. The fiber diagram obtained clearly corresponds to that of the cellulose II structure. The presence of cellulose I was virtually undetectable in the diffraction diagram of the mercerized wood pulp.

In Figure 2 the results for wood are given. The sequence of experiments was identical as that carried out with pulp. Figure 2(a) represents the fiber diagram of dry wood. It is, essentially, a rather diffuse cellulose I pattern. The broadness of the reflections is evident in the equatorial direction while the meridional direction exhibits finer lines. This phenomenon is attributed to long crystallites of cellulose being aligned along the fiber axis. The small lateral dimensions of these crystallites result in more diffuse equatorial reflections. The high degree of orientation of the cellulose chains along the fiber axis is indicated by the small arcing of the spots and confirms the low fibril angle of this wood. The poor quality of the pattern compared with Figure 1(a) is attributed to the presence of lignin and hemicelluloses which are removed in the case of pulp.

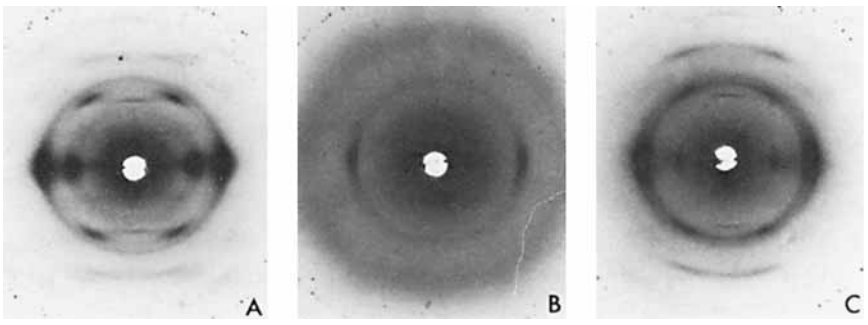

Fig. 1. X-ray fiber diffractograms of kraft fibers: (a) untreated; (b) treated with 20% aqueous NaOH for 24 hr (soda–cellulose); (c) after washing in water and drying.

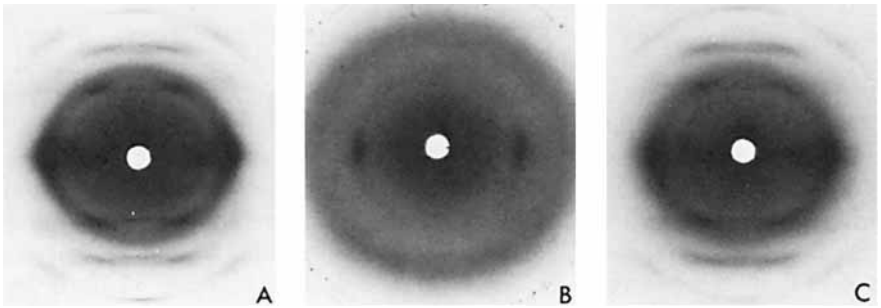

Fig. 2. X-ray fiber diffractograms of spruce wood: (a) untreated; (b) treated with 20% aqueous NaOH for 24 hr (soda–cellulose); (c) after washing in water and drying.

The almost complete absence of the cellulose I pattern in Figure 2(b) shows that the wood has been penetrated by the sodium hydroxide. However, the two equatorial reflections at 4.51 Å and 4.15 Å seen for the pulp have merged into one broad reflection with a *d*-spacing of 4.40 Å. Thus, the soda–cellulose intermediate formed in the wood is not as well defined as in the case of pulp. A further interesting feature in Figure 2(b) (more clearly seen in the original negatives) is the weak reflections 004, 002, and 012, which suggest the presence of vestiges of the cellulose I polymorph.

Figure 2(c) represents the fiber diagram after washing in water and drying. A mixture of cellulose I and cellulose II is detected and the ratio of cellulose II/cellulose I was estimated over several identical treatments to be between 40 and 60%.[5]

DISCUSSION

The results show that while wood pulp is readily mercerized, the cellulose in wood resists mercerization. What is the reason for this difference in behavior?

Jeffries and Warwicker[6] have shown that the alkali-induced conversion of cotton from cellulose I to cellulose II is governed by the swelling of the fiber. When the fiber is allowed to swell freely in the alkali, high conversion is obtained. If the swelling is restricted, the degree of mercerization is lower. In the literature we could find no comparison of the degree of swelling of whole wood and wood pulp fibers in mercerizing alkali. However, Stone and Scallan[7] have shown that on delignification of spruce wood in both kraft and sulfite pulping, the fiber saturation point increases from 0.5 ml/g for the wood to a value about three times as large for the pulps. Apparently, the swelling of the fiber wall in water increases markedly during delignification. It is, therefore, a plausible assumption that the cellulose in whole wood will swell less than the cellulose in the wood pulp in the mercerizing alkali.

We may now speculate on the way in which the degree of swelling affects the conversion of cellulose I to cellulose II. Two mechanisms will be considered. One is the effect of vestiges of cellulose I remaining in the wood during the mercerization. The second deals with the possibility that the conversion of cellulose I to cellulose II is accompanied by a change in the polarity of the chains.

"Meridional Memory"

The very weak meridional reflections seen in the soda–cellulose intermediate found with wood, Figure 2(b), are for cellulose I. No cellulose I reflections were found in the equatorial plane in spite of the fact that equatorial reflections are usually the strongest for cellulose I.[8,9] Thus, the alkali swelling of the wood seems to destroy the lateral order in the cellulose chains but allows some of the longitudinal order in the direction of the fiber axis to remain. When the alkali is washed out and the soda–cellulose reverts to cellulose, this "meridional memory" may promote some recrystallization to the cellulose I structure. With the wood pulp there is no trace of lateral or longitudinal order corresponding to cellulose I in the soda–cellulose. The disruption of the cellulose I lattice appears to be complete. In this case, conversion of soda–cellulose back to cellulose produces only cellulose II, which is the structure of lower energy.

Polarity

Blackwell et al.[1,2] have used x-ray fiber diffraction methods to determine the structure of native, regenerated, and mercerized celluloses. Their results showed that in native cellulose all chains have the same polarity, i.e., they are parallel. In contrast, these authors concluded that the chains in the regenerated and mercerized celluloses had alternating polarity, i.e., they are antiparallel. Thus, in the cellulose I crystal structure, all molecules run in the same direction while in cellulose II, the direction of each chain is opposite to that of its neighbors.

Cellulose I may be converted to cellulose II by solution and precipitation. Under these conditions, it is easy to visualize a change of chain polarity on regeneration. However, in the case of mercerization, as Blackwell et al.[1] point out, it is difficult to see how the extended chains of cellulose can reverse polarity without first going into solution. Blackwell et al. have suggested a mechanism by means of which the improbable concept of end-over-end rotation of complete cellulose molecules is avoided in the solid-state conversion of cellulose I to cellulose II. Quoting from their paper[1]:

> In the cellulose I crystallite, all the chains have the same polarity, but at a higher level of organization, the fibril is thought to contain crystallites of both polarities. Swelling of native cellulose was shown by Warwicker and co-workers[5,10] to involve separation of sheets of cellulose chains. Since cellulose II is the more stable structure, re-arrangement to recombine with a neighbouring "antiparallel" rather than a "parallel" sheet will be favoured on removal of the swelling agent.

In other words, Blackwell et al.[1] envisage that although in any one microfibril the cellulose chains are parallel, the microfibrils themselves are antiparallel in the sense that the chain in one microfibril points in a direction opposite to that of the chains in an adjacent microfibril.

The concept of antiparallel microfibrils in cellulose is a rather plausible one. Chafe[11] has proposed a geodesic hypothesis of wall formation in plant cells in which a microfibril is generated by a moving granule (enzyme complex) which travels up and down the long axis of the cell, laying down the microfibril in a path roughly corresponding to a geodesic line. If there is a steep fibril angle (as is common in the S2 layer of wood fibers), then alternate layers of microfibrils will be in approximately the same orientation with respect to the fiber axis. When the granule moves up the cell, it may be pictured as synthesizing cellulose mol-

ecules in parallel array which crystallize in the cellulose I structure. On the return journey down the cell, the granule will continue to produce a microfibril consisting of parallel chains of cellulose molecules, but now the chains will point in the direction opposite to that of the molecules in the microfibril synthesized when the granule moved up the cell. Thus, the cellulose molecules in adjacent microfibrils will often point in opposite directions. This type of molecular orientation is shown in Figure 3.

It is interesting to note that the arrangement shown in Figure 3 is supported by a recent suggestion by Preston[12] who wrote, "In this sense there must be two types of microfibril; as far as the basal plane is concerned, it is as though one kind is upside down with reference to the other."

Several years ago, Kerr and Goring[13] proposed the structure shown in Figure 4 for the plant cell wall. The microfibrils of cellulose are laid down in form of ribbons with the flat sides parallel to the middle lamella and with the length oriented in the direction of the fiber axis. The lignin and the hemicellulose are deposited between the microfibrils to give an interrupted lamellar structure as shown in Figure 4. Recently, this lamellated structure has been confirmed by electron microscopy for the S2 layer in softwoods,[14] hardwoods, and a grass.[15] It, therefore, seems likely that such a morphology will be found in the secondary wall of most lignified plant cells.

It should be noted that the model shown in Figure 4 is not inconsistent with the geodesic hypothesis proposed by Chafe,[11] and the arrangement shown in Figure 3 for the cellulose microfibrils alone is readily envisaged as yielding that shown in Figure 4 on biogenesis and intussusception of the lignin in wood.

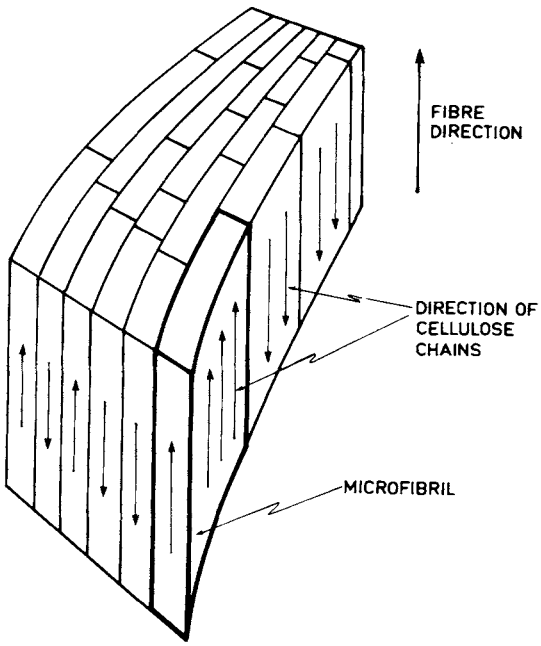

Fig. 3. Diagrammatic representation of the polarity of cellulose molecules in the microfibrils in the S2 layer. For clarity, the microfibril in the lower right-hand portion of the drawing is outlined more heavily.

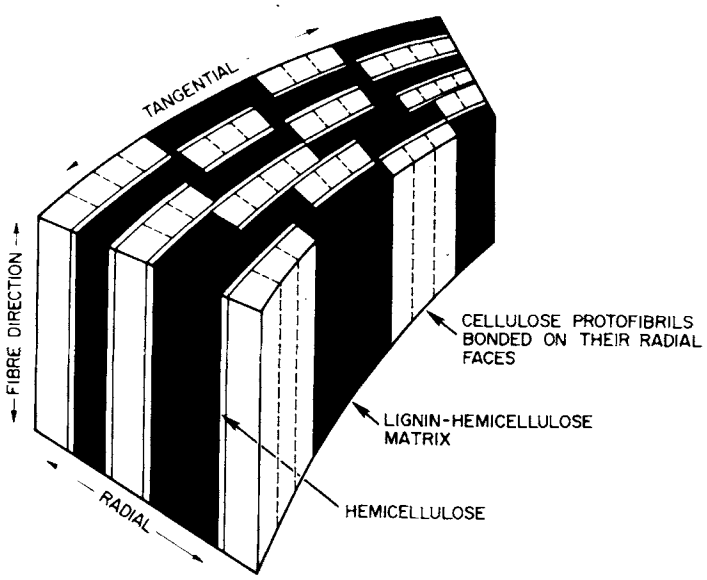

Fig. 4. Diagrammatic representation of the proposed interrupted lamella model for the ultrastructured arrangement of cellulose, hemicellulose, and lignin in the wood cell wall.[13]

If the above picture of the wood cell wall is correct, then the mechanism of mercerization proposed by Blackwell et al.[1] should not be effective for fully lignified fibers. The lignin layered between the microfibrillar ribbons will prevent the molecules in microfibrils of opposite polarity getting together during mercerization. Thus, if untreated wood is soaked in 20% alkali without removal of the lignin, the cellulose I/cellulose II transformation will be restricted. On the other hand, if the lignin is first removed and the resulting pulp fibers soaked in 20% alkali, the cellulose I structure is destroyed by swelling and the chains move apart under the action of the alkali. During this process, cellulose chains of opposite polarity may intermingle and on removal of the alkali, cellulose II is formed. A diagrammatic representation of this hypothesis is given in Figure 5.

The results obtained in the present work support the polarity mechanism only in part. This is because some transformation to cellulose II was observed. However, one would expect that even in the lignified fiber some cellulose microfibrils of opposite polarity will be adjacent to one another. In such cases, swelling with alkali could produce the intermingling of the chains required to give cellulose II even though lignin were present.

One of the consequences of the mercerization process for the cellulose fiber as shown in Figure 5 is that the microfibrillar structure of the natural fiber should change markedly on mercerization. Porter and Rollins[16] have shown that this is the case. These authors found that treatment of a cotton fiber with 5.0*M* sodium hydroxide caused the characteristic concentric array of ruptured lamellae to change to a more evenly dispersed arrangement of smaller microfibrillar aggregates. Manjunath and Venkataraman[17] also have observed fibrillar aggregation in cotton cellulose subjected to swelling treatments with alkali.

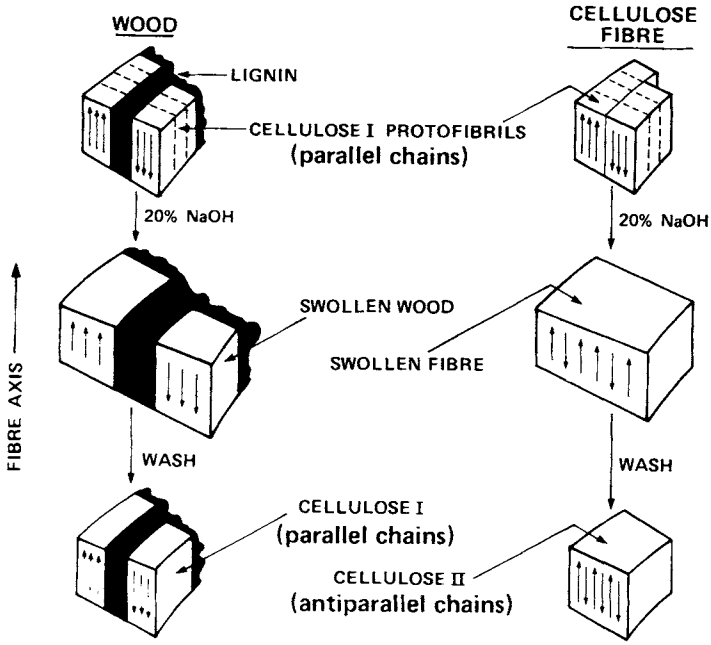

Fig. 5. Diagram showing how cellulose II is produced by alkali treatment of a delignified cellulose fiber and why formation of cellulose II is restricted in a lignified wood fiber.

CONCLUSIONS

The present work has shown that the cellulose I in wood is not as readily converted to cellulose II by treatment in alkali as is the cellulose I in wood pulp fibers. Two explanations are offered for this behavior. The first (preferred by J.-F. Revol) is that a vestige of the cellulose I crystal structure is retained in alkali-treated wood and this retards the conversion to cellulose II. The second explanation (preferred by D. A. I. Goring) is based on concepts of Blackwell et al.[1] concerning the polarity of the chains in cellulose I and II. We cannot say which, if either, of these are correct. It is quite clear, however, that there are still questions on the ultrastructure of cellulose in wood which need to be answered.

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