

Hydrolysis of Mercerized Cotton Fibers Due to Cellulase Treatment

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ABSTRACT: Cotton fibers mercerized under the relaxed state were hydrolyzed with crude cellulase. The mercerization treatment examined included ammonia treatment, sodium hydroxide treatment, and two combined treatments using ammonia and sodium hydroxide. Crystalline regions of the mercerized fibers were hydrolyzed in the first step of hydrolysis. In this step, ammonia treatment decreased the crystallite size to a great extent due to the hydrolysis of the cellulose III crystalline phase. Cellulase treatment rendered the crystallite surface highly accessible to water molecules. The crystalline phase was closely related to water sorption of cellulase-treated fibers. The sequence of treatment had an influence on the fiber structure in the case of the combined mercerization treatment with ammonia and sodium hydroxide. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 364–370, 2000

Key words: cotton fiber; ammonia treatment; crystallinity; crystallite size; water sorption; crystalline phase

INTRODUCTION

The mercerization treatment using liquid ammonia (ammonia) and sodium hydroxide confers softness to cotton fabrics. Cotton fabrics are provided with large resilience and good dimensional stability due to ammonia treatment and with deep shade due to sodium hydroxide treatment. Because dye and finishing reagents easily penetrate into the treated cotton fibers, ammonia treatment was developed as pretreatment to realize dimensional stability.^{1,2}

Ammonia treatment eliminates large pores and leads to the formation of hydrogen bonds in

the disordered regions of the cotton fiber, whereas sodium hydroxide treatment leads to a small degree of crystallinity and the relaxation of disordered regions. Ammonia treatment of cotton fibers was reported to increase water-sorption and equilibrium-dye uptake.³ The crystalline phase of cotton fibers was changed from cellulose I to cellulose III by ammonia treatment^{1,2,4} and to cellulose II by sodium hydroxide treatment.⁵

Cellulase treatment is markedly effective for improving the mechanical and aesthetic properties of cellulose fabrics.⁶ Therefore, the combined treatments of cellulase and alkali are expected to be useful for improving the performance of cotton fabrics. Crude cellulase secreted by fungi contains hydrolytic enzymes such as endoglucanase and exoglucanase, which preferably attack disordered and crystalline regions, respectively.⁷ This study

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dealt with the structural changes in mercerized cotton fibers due to cellulase treatment in connection with the roles of the cellulase complex in the hydrolysis.

EXPERIMENTAL

Materials

Original cotton fibers (original 1) were Soxhlet-extracted for 10 h with benzene and ethanol successively and then repeatedly washed with distilled water. Mercerization was performed in the relaxed state. The fibers were dipped into liquid ammonia for 2 s, squeezed, and dried for 10 s at 130°C in a hot drum. Then, they were steamed for 1 min to completely eliminate ammonia. The fibers were treated with an 18% sodium hydroxide solution at 20°C for 10 min and then rinsed thoroughly in water. The unprocessed fiber described in a previous article⁸ was also examined (original 2). Mercerized fibers tested in this study were ammonia-treated fiber, sodium hydroxide-treated fiber, sodium hydroxide- and, subsequently, ammonia-treated fiber, and ammonia- and, subsequently, sodium hydroxide-treated fiber.

The crude cellulase (Meiselase) used was a kind gift from Meiji Seika Ltd. (Tokyo, Japan) and is from *Trichoderma viride*. Carboxymethylcellulase activity of the cellulase was 233,000 units/g, which was determined by the same manner as that reported previously.⁹ One unit of carboxymethylcellulase activity was defined as the amount of enzyme which liberates 10 μ g glucose equivalents per 10 min.

Cellulase Treatment

The fibers were treated with an enzyme of 0.2% (v/v) concentration at 40°C and pH 4.5. The liquor-to-sample ratio was 1:100. The treatment solution containing the substrate was inactivated by immersing in boiling water after the treatment. Weight loss was obtained by comparing fabric weights before and after treatment.

Weight loss of the fibers caused by cellulase treatment is plotted against treatment time in Figure 1. Weight loss was larger in the order of the sodium hydroxide-treated fiber, the ammonia- and, subsequently, sodium hydroxide-treated fiber, the ammonia-treated fiber, the sodium hydroxide- and, subsequently, ammonia-treated fi-

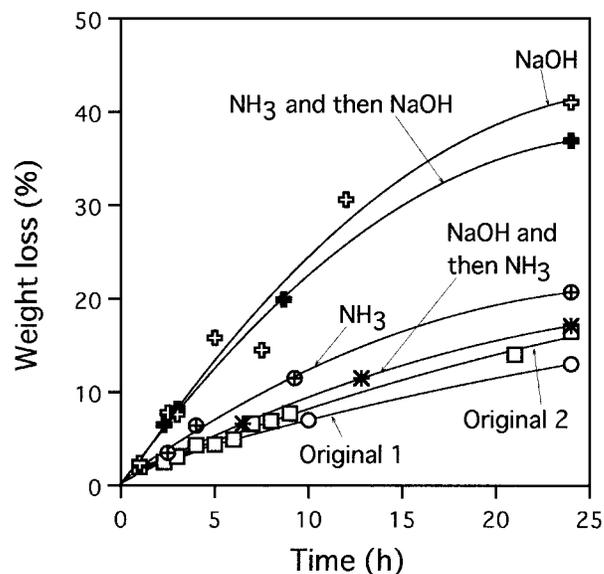


Figure 1 Plots of weight loss against treatment time given by cellulase treatment. Cotton fibers mercerized with the reagents indicated were examined. Original 1 was starting material of mercerization treatments.

ber, and the original fibers, at a given treatment time.

X-ray Diffraction Measurement

An X-ray diffractometer (SRA M18XHF; MAC Science Co.) was used to obtain the crystallinity and the crystallite size under conditions similar to those reported previously.⁸ The X-ray patterns obtained are shown in Figure 2. The cellulose I crystalline phase of the original fiber was changed to cellulose II and cellulose III due to sodium hydroxide and ammonia treatments, respectively. In the case of combined mercerization treatments, the subsequent treatment determined the crystalline phase of the fibers. All the mercerized fibers contained a small amount of cellulose I.

Crystallinity was represented by the ratio of integrated crystallite scattering intensity to total scattering intensity ranging from 10 to 26°. Crystallite size was calculated according to Scherrer's equation, assuming that the scattering intensity of each reflection obeys the Lorentzian distribution. Crystallite size was obtained from the reflection of the (002) plane except for the sodium hydroxide-treated and ammonia- and, subsequently, sodium hydroxide-treated fibers, for which the crystallite size was calculated from the (10 $\bar{1}$) plane of cellulose II.

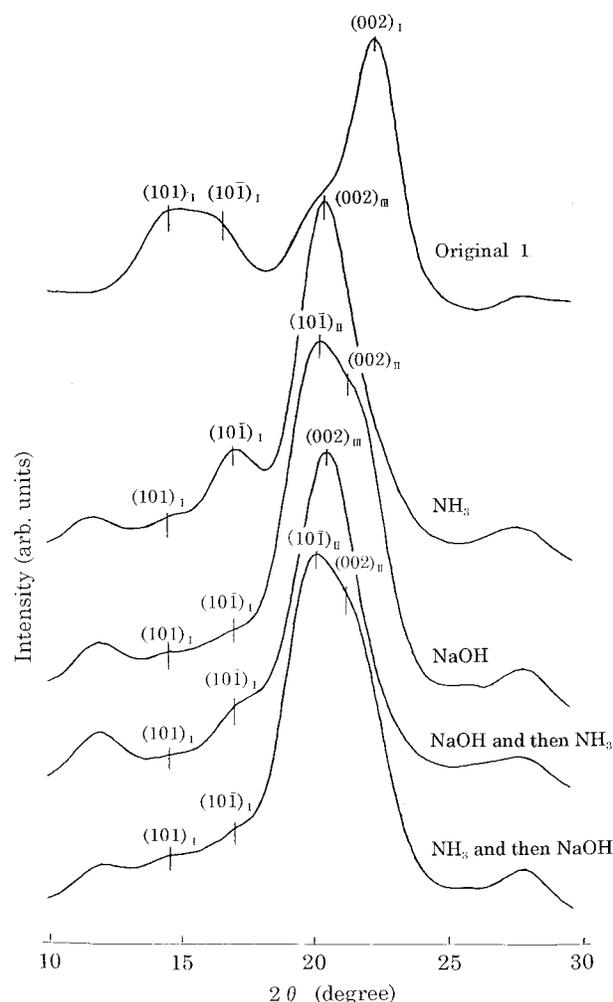


Figure 2 X-ray diffraction patterns of cotton fibers mercerized with the reagents indicated.

The X-ray characteristics of the fibers examined are summarized in Table I. The crystallinity and the crystallite size decreased with the ammo-

nia and sodium hydroxide treatments. This is in agreement with the results in the literature.¹⁰

Dyeing Method

The fibers were dyed to equilibrium with Congo Red at 80°C. Other dyeing conditions were as described previously.⁹ The effective volume term of dyeing (V) for the treated fibers was calculated in the same manner as that described previously.⁹ It was assumed that the affinity of Congo Red for the cellulose molecule was constant and the V of the original fibers was 0.22 L/kg. V represents the inner surface of the fiber accessible to the dye molecule and a measure of the number of the disordered regions.

Measurement of Water Sorption

Equilibrium water sorption of the fibers was measured after keeping the fibers at a relative humidity (RH) of 95% and a temperature of 20°C for more than 3 weeks. Water sorption of the fibers is also shown in Table I. The order of magnitude of the water sorption agreed with that reported in the literature.³ Water sorption is, therefore, a measure of the internal volume of the fibers.

RESULTS AND DISCUSSION

Hydrolysis of the Crystalline Region

The relationship between the crystallinity and the weight loss of the fibers examined is shown in Figure 3. The original 2 fiber exhibited an increase in crystallinity initially and then reached maximum crystallinity with increasing weight loss. This indicates that the disordered region of

Table I Characteristics of Cotton Fibers Examined

Mercerization	Crystallinity (%)	Crystallite Size (Å)	Crystalline Phase ^a	Water Sorption (%)
Untreated (original 1)	68.7	45.7	I	12.3
Untreated (original 2)	70.1	43.4	I	12.5
NH ₃	59.8	38.4 ^b	III	14.8
NaOH	57.9	43.0 ^c	II	18.4
NaOH and then NH ₃	57.1	33.3 ^b	III	17.0
NH ₃ and then NaOH	55.2	29.6 ^c	II	19.0

Mercerization was performed on the original 1 fiber.

^a Dominant phase.

^b From cellulose III.

^c From cellulose II.

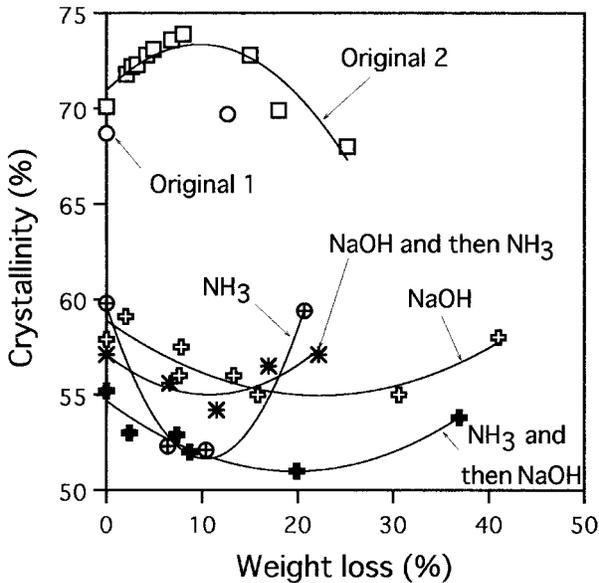


Figure 3 Changes in crystallinity with weight loss of mercerized fibers due to cellulase treatment. The reagents indicated were used in the mercerization treatment.

the original fiber was preferably hydrolyzed in the first step of hydrolysis. In contrast, all the mercerized fibers exhibited an initial decrease in crystallinity, reached a minimum, and then increased with increasing weight loss, even though the weight loss at minimum crystallinity depended on the mercerization treatment.

Generally, weight loss by cellulase for the fibers with lower crystallinity was larger at a given treatment time (Fig. 1 and Table I). This trend indicates that the disordered regions contributed to the hydrolysis by cellulase for all the fibers examined. In addition, a considerable number of crystalline regions of all the mercerized fibers were hydrolyzed by cellulase in the first step of hydrolysis, as shown in Figure 3. A greater number of crystalline regions were hydrolyzed in the phase of decreasing crystallinity, compared to the phase of increasing crystallinity; for all the mercerized fibers. The cellulase used contained exoglucanase, which preferably attacks crystalline regions.⁶ It was suggested that the crystalline regions in the mercerized fibers were more accessible to exoglucanase than were those in the original fibers.

The change in the X-ray diffraction pattern of the ammonia-treated fiber due to cellulase treatment is shown in Figure 4. The (002) reflection of

cellulose I became discernible as a distinct shoulder on the right side of the (002) plane of cellulose III after cellulase treatment. This indicates that cellulose I was more difficult to hydrolyze than was cellulose III with cellulase treatment.

It was reported¹¹ that the cellulose III structure was transformed into the cellulose I structure by treatment in boiling water and into the cellulose IV structure by heat treatment. This indicated that cellulose III is a thermodynamically unstable structure. In this regard, cellulose III is thought to be more reactive to cellulase than is cellulose I.

The weight loss at minimum crystallinity for the ammonia-treated fiber and the sodium hydroxide- and, subsequently, ammonia-treated fiber was smaller than that for the sodium hydroxide-treated fiber and the ammonia- and, subsequently, sodium hydroxide-treated fiber (Fig. 3), indicating that cellulose III is more easily hydrolyzed than is cellulose II.

Figure 5 shows the change in crystallite size with weight loss of the original and mercerized fibers. The crystallite size of the ammonia-treated fiber and the sodium hydroxide- and, subsequently, ammonia-treated fiber decreased ini-

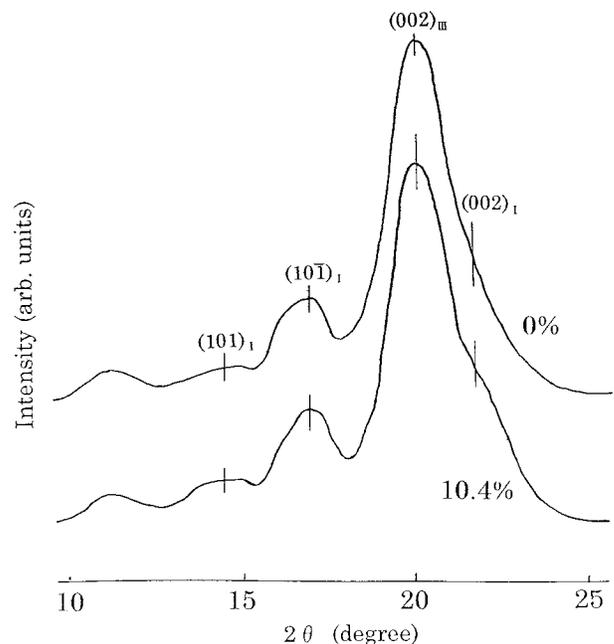


Figure 4 X-ray diffraction patterns of ammonia-treated fiber subjected to cellulase treatment. The fiber with 10.4% of weight loss was compared with the original fiber.

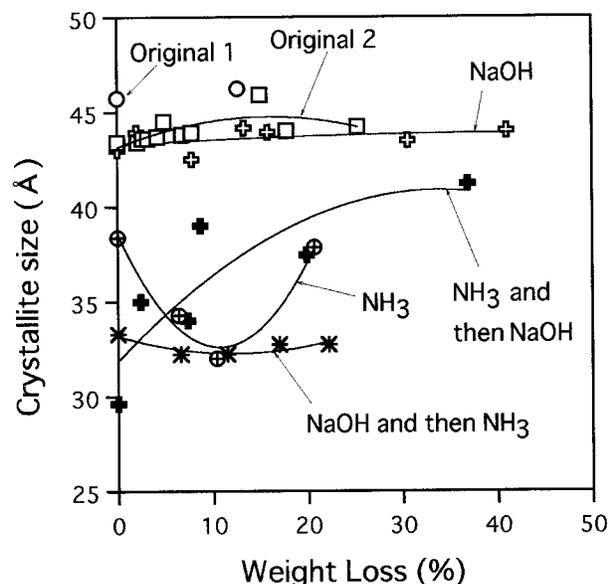


Figure 5 Change in crystallite size with weight loss of mercerized fibers due to cellulase treatment. The reagents indicated were used in the mercerization treatment.

tially to reach a minimum at approximately 10% weight loss. The weight loss at the minimum crystallite size is almost the same as that at minimum crystallinity for the fibers mentioned above (see Fig. 3). On the other hand, the crystallite size of the sodium hydroxide-treated fiber and the ammonia- and, subsequently, sodium hydroxide-treated fiber exhibited no minimum with weight loss, similar to the original fiber.

For the ammonia-treated fiber, the initial marked decrease in crystallite size was consistent with that in crystallinity (Figs. 3 and 5). It is presumed that a considerable number of crystalline regions collapsed, leading to a decrease in

both the crystallinity and the crystallite size for this fiber.

The occurrence of minimum crystallinity for the sodium hydroxide-treated fiber and the ammonia- and, subsequently, sodium hydroxide-treated fiber could be explained by the hydrolysis of microcrystallites in the disordered matrix. It is assumed that the hydrolysis of these microcrystallites did not contribute to the decrease in crystallite size as a whole.

The change in the V ratio of the ammonia-treated and sodium hydroxide-treated fibers relative to the V of the original fibers is shown in Table II. Fibers with minimum or maximum crystallinity were chosen for comparison. The original and the sodium hydroxide-treated fibers were found to exhibit a more marked decrease in V than that of the ammonia-treated fiber (B/A in Table II). This suggests that the latter exhibited a greater decrease in the crystalline regions than that of the former during cellulase treatment.

The initial decrease in crystallinity was smaller for the sodium hydroxide- and, subsequently, ammonia-treated fiber than for the ammonia-treated fiber, while minimum crystallinity occurred at the same weight loss for these fibers. The sodium hydroxide-treated fiber had a larger crystallite size than that of the ammonia- and, subsequently, sodium hydroxide-treated fiber regardless of weight loss, while these two fibers increased in crystallite size with weight loss. In the case of the combined treatment of ammonia and sodium hydroxide, as mentioned above as examples, the first treatment influenced the final fiber structure, even though the following treatment played a dominant role on the final fiber structure formation.

Table II Change in Effective Volume Term for Dyeing of Mercerized Fibers Due to Cellulase Treatment

Mercerization	Weight Loss (%)	Volume Ratio		
		Control A	Treated B	B/A
Original 1	12.7	1.00	0.70	0.70
Original 2	13.2	1.00	0.77	0.77
NH ₃ (from original 1)	10.4	0.91 ^a	0.87	0.95
NaOH (from original 2)	13.5	1.42 ^a	1.25	0.88

Change is represented as relative values.

^a Value relative to each original fiber.

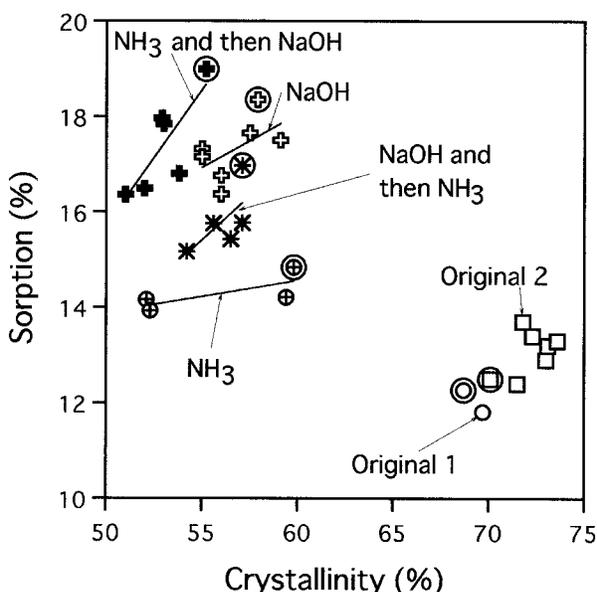


Figure 6 Change in water sorption with crystallinity of mercerized fibers due to cellulase treatment. The reagents indicated were used in the mercerization treatment. Encircled symbols refer to fibers that were not treated with cellulase.

Water Sorption

The change in the water sorption of the fibers given by the cellulase treatment was plotted against the crystallinity in Figure 6. Water sorption had a tendency to decrease with increasing crystallinity for the six fibers that were not treated with cellulase. This trend is reasonable because water sorption occurred mainly in the disordered regions.

Cellulase treatment decreased both the crystallinity and water sorption of the mercerized fibers; in contrast, the original fibers, in general, increased in crystallinity and water sorption during cellulase treatment, based on all data of the original fibers, that is, cellulase treatment resulted in the anomalous behavior that water sorption increased with increasing crystallinity for all of the fibers examined. Water sorption hardly occurred in the interior of well-ordered crystallites. This led us to the assumption that cellulase treatment rendered the crystallite surface highly accessible to water molecules. This was because the crystallite surface became thermodynamically unstable due to cellulase treatment.

The plots of water sorption against crystallite size are shown in Figure 7. Water sorption was

found to increase with increasing crystallite size of cellulose III, which was the dominant crystalline phase in the ammonia-treated fiber and the sodium hydroxide- and, subsequently, ammonia-treated fiber. In contrast, water sorption decreased with increasing crystallite size for cellulose II, which was the dominant crystalline phase in the sodium hydroxide-treated fiber and the ammonia- and, subsequently, sodium hydroxide-treated fiber. Cellulose I of the original fibers showed the same trend as that of cellulose II, indicating that the crystalline phase was closely associated with water sorption for cellulase-treated fibers.

Small crystallites are thermodynamically unstable and are thought to absorb much water. Thus, the trends of the crystalline phases except for cellulose III were reasonable. The trend of cellulose III, which was inconsistent with the above explanation, confirmed that the crystalline structure of cellulose III is thermodynamically unstable in itself.

CONCLUSIONS

Cotton fibers mercerized with ammonia and sodium hydroxide were treated with crude cellulase. The crystalline regions of the mercerized fibers were hydrolyzed in the first step of the treatment. The

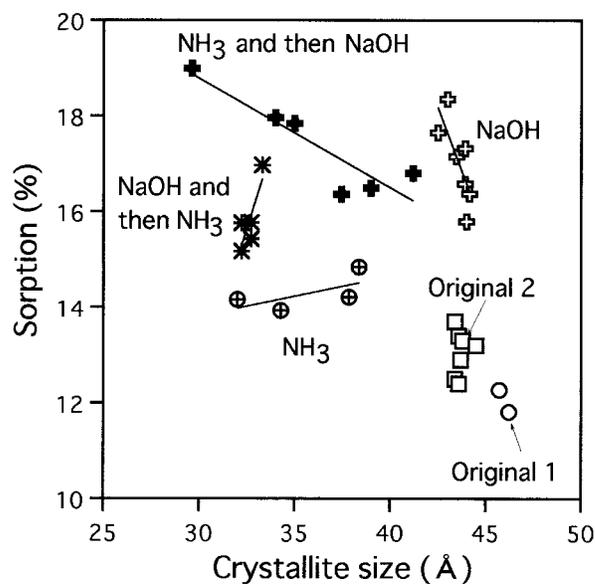


Figure 7 Change in water sorption with crystallite size due to cellulase treatment for fibers that were mercerized using the reagents indicated.

crystalline structure of cellulose III in the ammonia-treated fiber was easily hydrolyzed by cellulase. Cellulase treatment made the crystallite surface highly accessible to water molecules. The crystalline phase was closely related to water sorption for cellulase-treated fibers. The sequence of treatment influenced the fiber structure in the case of the combined mercerization treatment with ammonia and sodium hydroxide.

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