Structural Change in Mercerized Cotton Fibers on Cellulase Treatment

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ABSTRACT: Cotton fibers treated with liquid ammonia and sodium hydroxide were hydrolyzed with crude cellulase. The structural change in the fibers due to the cellulase treatment was examined in relation to the apparent affinity of Congo Red. The cellulose III crystalline structure collapsed and generated intermediate-molecular-ordered regions on cellulase treatment. Adsorption of Congo Red occurred on the crystallite surfaces of cellulose II and cellulose III that was transformed from cellulose II. The fiber, the dominant crystallite phase of which was cellulose III that was transformed from cellulose II, had a considerably increased apparent affinity after cellulase treatment. The intermediate structure on the crystallite surface was associated with the adsorption of Congo Red in the cases of cellulose II and cellulose III. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1675–1680, 2001

Key words: cotton fiber; cellulase; hydrolysis; crystallinity; crystallite; affinity of Congo Red; intermediate-molecular-ordered region

INTRODUCTION

Liquid ammonia (ammonia) treatment renders high resilience and good shape retention in cotton fabrics,[1] whereas sodium hydroxide treatment provides cotton fabrics with a deep shade and a good luster. On the other hand, cellulase treatment is markedly effective for improving the mechanical and aesthetic properties of cellulose fabrics. Therefore, the combination of cellulase and alkaline treatments is promising for improving the performance of cotton fabrics.

We reported that crystalline regions of cotton fibers, which were mercerized with ammonia and sodium hydroxide, were hydrolyzed by cellulase treatment in the first step of hydrolysis.[2] We also elucidated that water sorption was closely related to the surface of the crystallites, irrespective of the fiber species treated with cellulase.[2]

It is well known that the crystalline structure of cellulose I is transformed to those of cellulose III[1] and cellulose II[3] by ammonia and sodium hydroxide treatments, respectively. The structural transformation of cellulose III to cellulose I and that to cellulose II by respective treatments with hot water and sodium hydroxide were very effective in improving the softness of cotton fabrics.[4] We studied the structural changes in the mercerized cotton fibers caused by cellulase treatment, using infrared spectroscopy, X-ray diffraction, and a method involving the apparent affinity of Congo Red.

The extent of the ordered regions evaluated by infrared spectroscopy has a better correlation

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with the accessibility obtained by water sorption than with the crystallinity evaluated by the X-ray method.[5] The accessibility obtained by water sorption corresponds to the number of hydroxide groups, which are sufficiently free from neighboring molecules.[5] The criterion of fine structure for the accessibility evaluated by water sorption and the ordered regions evaluated by infrared measurement is at the molecular level or short-distance order rather than at the level of larger units of the crystallites in the X-ray method.[5]

The dyeing of Congo Red occurs in disordered regions which have enough space to adsorb large molecules of the dye. The adsorption of direct dyes such as Congo Red requires planar and linear configurations of cellulose molecules in order for the dye molecule to be proximate to the polymer chain.[6] This suggests that the structure of the short-distance order detected by infrared adsorption is an effective dyeing site of Congo Red.

The structure of short-distance order, detected as crystalline regions by infrared measurement,[5] is divided into two regions: One exists outside of well-grown crystallites and has an intermediate-molecular-ordered structure. The other is included in well-grown crystallites detected by the X-ray method. The intermediate-molecular-ordered structure outside the crystallites is an important subject in the study dealing with the structural changes in cotton fibers caused by cellulase treatment.

The amount of bound water, which was estimated from the exotherm peak of different scanning calorimetry, was decreased by cellulase treatment.[7] The cellulase-treated cuprammonium rayon fiber increased the peak temperature of tan δ,[8] based on the segmental movement of the cellulase chain in disordered regions. The intermediate-molecular-ordered structure plays a role in reducing the amount of bound water, which is a measure of the accessibility, and in increasing the peak temperature of tan δ to restrict the movement of the cellulose chain.

We also focused our attention on the influence of the sequence of combined treatment, which consists of ammonia (sodium hydroxide) treatment and subsequent sodium hydroxide (ammonia) treatment. We observed that the subsequent treatment had a marked effect on the final fiber formation, even though the crystallinity and affinity of Congo Red are dependent on the first treatment.

EXPERIMENTAL

Materials

The cotton fibers were purified in the same manner described in our previous article.[2] The fiber (original 1 fiber) was dipped in liquid ammonia for 2 s, then squeezed and dried for 10 s at 130°C in a hot drum. It was then steamed for 1 min to completely eliminate ammonia.[2] The original 1 fiber was treated with an 18% sodium hydroxide solution at 20°C for 10 min and then rinsed thoroughly in water. Mercerization treatment was performed in the relaxed state. The unprocessed fiber described in our previous article[9] was also examined (original 2 fiber).

The crude cellulase (Meiselase) used was kindly offered by Meiji Seika Ltd. (Tokyo, Japan); it is from *Trichoderna viride.* The carboxymethylcellulase activity of the cellulase was 233,000 units/g, determined in the same manner as that in our previous article.[10] One unit of carboxymethylcellulase was defined as the amount of enzyme which liberates 10 μg glucose equivalents per 10 min.

Cellulase Treatment

The fibers were treated with an enzyme concentration of 0.2% (w/v) 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 it in boiling water after the treatment. Weight-loss values were obtained by comparing fabric weights before and after treatment.

X-ray Diffraction Measurement

The crystallinity and the crystallite size were measured using an X-ray diffractometer (SRA M18XHF; MAC Science Co.) under the same conditions as those in our previous article.[2] Crystallinity was defined as the ratio of the integrated crystallite scattering intensity to the total scattering intensity ranging from 10 to 26°. The dominant crystalline phase of the ammonia-treated fiber and the sodium hydroxide- and subsequently ammonia-treated fibers is cellulose III, whereas that of the sodium-hydroxide-treated fiber and the ammonia- and, subsequently, sodium hydroxide-treated fiber is cellulose II, as described previously.[2] It was confirmed that the crystalline phase of the original fiber is cellulose I.

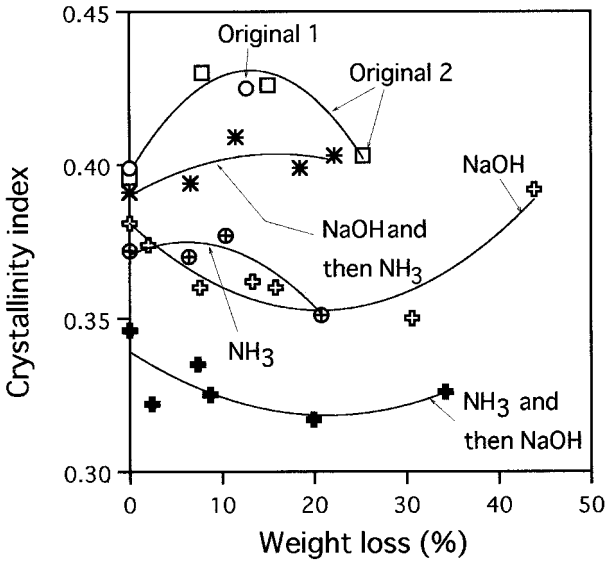

Figure 1 Change in crystallinity index with increasing weight loss for mercerized fibers after cellulase treatment. The reagents indicated were used for mercerization treatment.

Dyeing Method

The fibers were dyed to equilibrium with Congo Red at 80°C. Other dyeing conditions were described previously.[10] The apparent affinity (affinity) of Congo Red to cotton fibers was calculated in the same manner described previously,[10] based on the assumption that the effective volume term for the dyeing of cotton fiber is 0.22 L/kg. The change in the apparent affinity calculated reflects the change in the amount of the inner surface of the fibers in which dye adsorption takes place.

Measurement of Infrared Spectrophotometry

The adsorptivity ratio of 1372–2900 cm^{-1} was obtained as the crystallinity index,[5] using an infrared (IR) spectrophotometer (FTS-30, Bio-Rad Co.). Measurement was performed by means of a diffuse reflection method[11] using a mixture of cut fiber segments and potassium bromide. The absorptivity ratio was estimated according to the literature.[5]

RESULTS AND DISCUSSION

Collapse of Crystallites

The relationship of the crystallinity index to the weight loss of the fibers examined is shown in Figure 1. The crystallinity index of the original 2 fiber first increased, reached a maximum, and then decreased with an increasing weight loss. The crystallinity index of the ammonia-treated fiber and the sodium hydroxide- and subsequently ammonia-treated fiber first increased and then reached a maximum in a manner similar to that shown by the original 2 fiber with an increasing weight loss. The amount of the increase of the sodium hydroxide- and subsequently ammonia-treated fiber was greater than that of the ammonia-treated fiber. In contrast, the crystallinity index of the sodium hydroxide-treated and the ammonia- and subsequently sodium hydroxide-treated fibers first decreased, reached a minimum, and then increased with an increasing weight loss.

The crystallinity index versus crystallinity plots for the fibers treated with cellulase are shown in Figure 2. The crystallinity index increased with decreasing crystallinity for the ammonia-treated fiber and the sodium hydroxide- and subsequently ammonia-treated fiber. Cellulase treatment generally decreased the crystallinity and increased the crystallinity index of these fibers.

It was found that cellulase treatment of the ammonia-treated fiber and the sodium hydroxide-

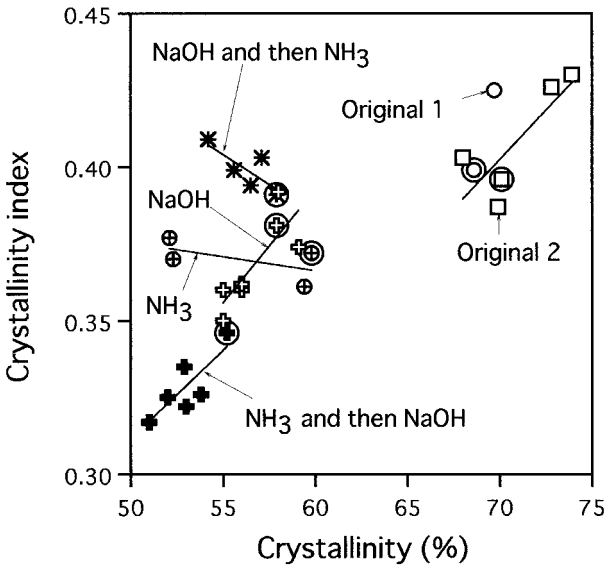

Figure 2 Relationship between crystallinity index and crystallinity for fibers mercerized using the reagents indicated. The encircled plots correspond to fibers which were not treated with cellulase. A straight line of the original fibers was obtained based on all data of the two original fibers.

and subsequently ammonia-treated fiber caused the cellulose III crystalline structure to collapse, such that the extent of the intermediate-molecular-ordered structure outside the crystallites was increased, which was detected as an increase of the crystallinity index. The initial increase of the crystallinity index with weight loss shown in Figure 1 was caused by the collapse of crystalline regions in both the ammonia-treated fiber and the sodium hydroxide- and subsequently ammonia-treated fiber.

The negative slope of the crystallinity index versus the crystallinity of the ammonia-treated fiber was smaller than that of the sodium hydroxide- and subsequently ammonia-treated fiber. This indicated that the amount of transformation of the well-ordered structure to the intermediate-molecular-ordered structure was greater for the sodium hydroxide- and subsequently ammonia-treated fiber than for the ammonia-treated fiber.

The sodium hydroxide-treated fiber and the ammonia- and subsequently sodium hydroxide-treated fiber exhibited a decrease in both the crystallinity index and the crystallinity during cellulase treatment. This trend suggested that the crystallites of these fibers were hydrolyzed with no collapse during cellulase treatment. The positive slope of the crystallinity index versus the crystallinity of the ammonia- and subsequently sodium hydroxide-treated fiber was almost the same as that of the sodium hydroxide-treated fiber. It was found that the cellulose II crystalline structure formed from cellulose III was hydrolyzed in a manner similar to that of cellulose II formed from cellulose I.

Cellulase treatment of the original fibers increased both the crystallinity and the crystallinity index. This is because the hydrolysis occurred only in the disordered regions, as indicated by the initial increase in crystallinity. It was assumed that the initial increase in the crystallinity index was not caused by the collapse of the crystalline regions, but was due to the increase in the proportion of the crystalline regions, compared to the disordered regions for the original fibers. This was consistent with the assumption that the cellulose I structure is more stable under cellulase treatment than are the cellulose II and III structures.[2]

Affinity of Congo Red

The affinity of Congo Red was plotted against the weight loss of the cellulase-treated fibers and compared with the original fibers in Figure 3. The affinity of the dye for the original fibers decreased with increasing weight loss because of the decrease in the extent of disordered regions. In addition, the affinity of the dye for the mercerized fibers decreased with increasing weight loss, except for the sodium hydroxide- and subsequently ammonia-treated fibers, for which the affinity of the dye increased on cellulase treatment.

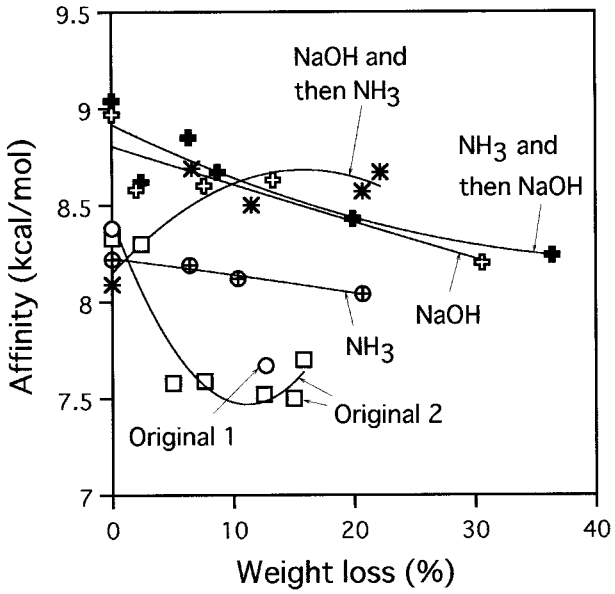

Figure 3 Affinity of Congo Red with increasing weight loss of fibers mercerized using the reagents indicated.

The relationship between the affinity of the dye and the crystallinity index is shown in Figure 4. The affinity of the dye for the original fibers exhibited a tendency to decrease with an increasing crystallinity index. This was due to the increase in the proportion of crystalline regions compared with disordered regions.

In contrast, the affinity of the dye increased with an increasing crystallinity index for all alkali-treated fibers. Concretely, the sodium hydroxide-treated and the ammonia- and subsequently sodium hydroxide-treated fibers decreased in both the affinity of the dye and the crystallinity index after cellulase treatment, in contrast with the decrease in the extent of crystalline regions, as shown in Figure 2. The cellulase treatment clearly increased both the affinity of the dye and the crystallinity index of the sodium hydroxide- and subsequently ammonia-treated fiber.

It was concluded that the adsorption of the dye in the mercerized fibers was closely related to

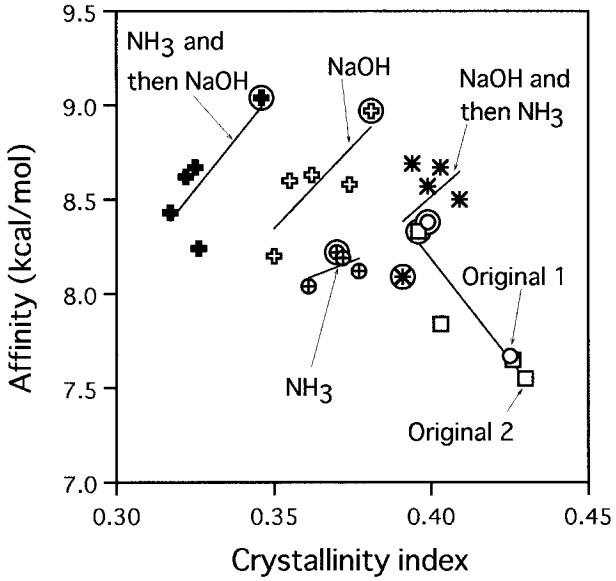

Figure 4 Affinity of Congo Red against crystallinity index of fibers mercerized using the reagents indicated. Encircled plots correspond to fibers which were not treated with cellulase. A straight line of the original fibers was obtained based on all data of the two original fibers.

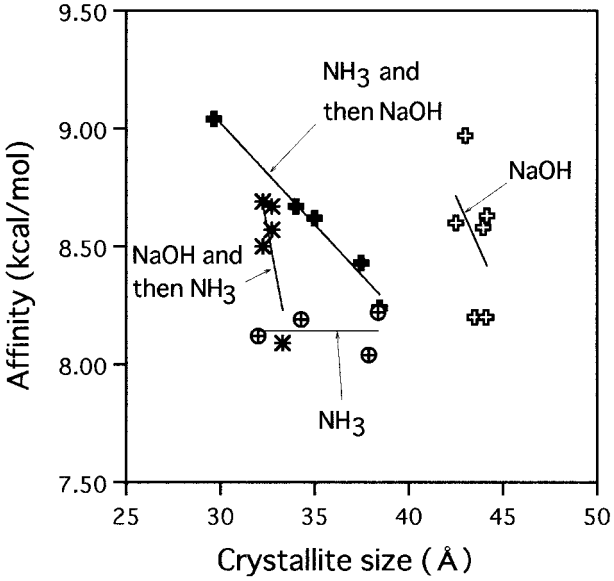

Figure 5 Change in affinity of Congo Red with crystallite size due to cellulase treatment for fibers mercerized using the reagents indicated.

intermediate-molecular-ordered regions on the crystallite surface. This is because Congo Red was preferably adsorbed in planar and linear configurations of cellulose molecules related to the crystallinity index on the crystallite surface.

It was reported that the sodium hydroxide- and subsequently ammonia-treated fiber was much more effective for achieving a soft fabric hand compared with the ammonia-treated fiber.[12] The cellulose III crystallite surface of the sodium hydroxide- and subsequently ammonia-treated fiber was easily changed into intermediate-molecular-ordered regions on cellulase treatment. The surface regions of cellulose III may have a possible role in the improvement of the fabric softness mentioned above.

The relationship between the affinity of Congo Red and the crystallite size is shown in Figure 5. Because dye adsorption took place in the disordered regions and the crystalline regions are not directly related to the adsorption of Congo Red in the original fibers, the data for the original fibers are not shown in this figure.

Small crystallites are thermodynamically unstable and it is thought that their surfaces easily adsorb dye molecules. The mercerized fibers, except for the ammonia-treated fiber, exhibited a decrease in the affinity with increasing crystallite size, as shown in Figure 5. This trend is reasonable and indicates the occurrence of dye adsorption on the crystallite surfaces in these fibers.

Slopes of the affinity of Congo Red plotted against the crystallite size for mercerized fibers are shown in Table I. The slopes of water sorption plotted against the crystallite size for mercerized fibers were calculated based on our previously reported results[2] and are also shown in Table I. It was clear that the dye adsorption of the sodium hydroxide- and subsequently ammonia-treated fi-

Table I Regression Coefficients of the Linear Relationship of Affinity of Congo Red and Water Sorption to Crystallite Size for Mercerized Cotton Fibers

	Regression Coefficient	
Fibers	Affinity of Congo Red	Water Sorption
Ammonia	0.011	0.083
Sodium hydroxide	−0.063	−1.063
Sodium hydroxide and then ammonia	−0.421	1.301
Ammonia and then sodium hydroxide	−0.057	−0.227

ber exhibited a decrease with increasing crystallite size. This trend of dye adsorption was different from that of water sorption, which increased with increasing crystallite size.[2] The contradiction is because the molecular size of Congo Red is much larger than that of a water molecule. It was assumed that the surfaces of large crystallites of cellulose III, which were formed from cellulose II and treated with cellulase, were finely split and easily penetrated by water molecules but not by Congo Red molecules. This trend was probably greater with larger crystallites.

The dependence of dye adsorption on the crystallite size of the ammonia-treated fiber was weak, similar to water sorption,[2] compared with the other mercerized fibers, as shown in Table I. The extent of disordered regions was thought to contribute considerably to dye adsorption and water sorption for the ammonia-treated fiber.

CONCLUSIONS

Four mercerized cotton fibers were treated with crude cellulase. The cellulose III crystalline structure progressively collapsed and generated intermediate-molecular-ordered regions. This trend was considerable for cellulose III transformed from cellulose II. Cellulose II crystallites were hydrolyzed with no collapse of the crystalline structure. Adsorption of Congo Red occurred on the crystallite surfaces of cellulose II and cellulose III transformed from cellulose II, while the crystalline regions of the original fiber were unrelated to dye adsorption. The extent of the intermediate-molecular-ordered structure on the crystallite surface was closely related to the amount of Congo Red adsorption for all mercerized fibers.

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