THE FINE STRUCTURE OF MERCERIZED AND CROSSLINKED COTTONS

D. V. Parikh and D. P. Thibodeaux
Southern Regional Research Center
New Orleans, LA

Abstract

A continuously recording X-ray diffractometer was used to study changes in the crystalline structure of cotton fibers subjected to a wide range of chemical and physical treatments. These included combinations of mercerization and bleaching and crosslinking utilizing either wet crosslinking with formaldehyde (Form W) or dry crosslinking with dimethylol dihydroxy ethylene urea (DMDHEU) or Citric Acid (CA). Results indicate that crosslinking of bleached cotton does not change the crystalline nature of cotton, but does increase its degree of crystallinity. Cellulose II structure in mercerized cotton is very similar to that observed in pure viscose (Fortisan). Crosslinking of mercerized cotton changes the crystalline nature of the fiber in that the degree of crystallinity of Cellulose II (mercerized cotton) is diminished while there is an appearance of certain Cellulose I (native cotton) characteristics.

Introduction

It has long been recognized through x-ray diffraction that cellulose, at least in part, is crystalline [11]. For native cotton cellulose, portions of the fiber are arranged in an orderly fashion or lattice. The fundamental repeating unit that makes up this lattice is referred to as the unit cell. A diagram of this unit cell as derived by Meyer and Misch [5] is reproduced in Figure 1. The cell is a monoclinic crystal with three principal planes of reflection shown as (002), (101), and (10$\underline{1}$).

As shown in Figure 2a, when a collimated beam of x-rays is incident on a sample with crystalline properties, certain portions of the beam are diffracted in preferential directions that are perpendicular to crystalline planes of symmetry. These diffracted x-rays form regular patterns as they impinge on a film sheet oriented normal to the direction (c-) of the incident beam. Film orientation is designated as the meridian (oriented vertically or in the b-direction) or as the equator (oriented horizontally or in the a-direction). When the specific sample is a bundle of cotton fibers parallel to the b-direction, a diffractogram similar to the one shown in Figure 2b results. Three major diffraction arcs are produced along the equator on either side of the center of the diffractogram. These correspond to reflections from the (101), 10$\underline{1}$), and (002) planes described in Figure 1.

Reprinted from the *Proceedings of the Beltwide Cotton Conference*
Volume 1:841-846 (2000)
National Cotton Council, Memphis TN

In 1957 Segal and Conrad published a review of the use of a continuously recording X-ray diffractometer to characterize the structure of chemically modified cellulose fibers [9]. Their setup is shown in Figure 3a depicting an x-ray beam incident on a sample diffracting a beam whose angular dependence is measured by a photomultiplier detector travelling along a goniometer. The angle between the incident x-rays and the sample surface is called θ. The angle between the detector position and the direction of the incident beam is 2θ. A plot of the angular dependence of the intensity of x-ray photons detected as a function of 2θ is shown in Figure 3b. The three peaks shown in this plot for native cotton Cellulose I correspond to the major equatorial diffraction arcs shown in Figure 2b. Specifically, these are (101) at $2\theta = 14.9^{o}$, (10$\underline{1}$) at $2\theta = 16.6^{o}$, and (002) at $2\theta = 22.7^{o}$.

Segal et al. [10] developed an empirical method for estimating the degree of crystallinity of native cellulose (Cellulose I). The amount of crystalline Cellulose I in the total cellulose can be expressed by the x-ray "crystallinity index" (*CI*) defined by

$$CI = 100\ [I_{002}/(I_{002} - I_{am})] \qquad (1)$$

Where I_{002} is the intensity of the principal Cellulose I peak at $2\theta = 22.7^{o}$ and I_{am} is the intensity attributed to amorphous cellulose given at $2\theta = 18^{o}$.

Thorough caustic mercerization causes significant distortion of the cellulose lattice as the cotton is converted from Cellulose I to Cellulose II. In his study of the fine structure of viscose rayon, Ingersoll [2] proposed a method for estimating the "radial intensity ratio" (RIR) or the amount of crystalline Cellulose II in the material (viscose rayon). An X-ray diffractogram for a very pure form of Cellulose II (obtained with Fortisan rayon) is shown in Figure 4. It is important to note that compared with Cellulose I, the (002) plane is shifted down to approximately 21.9^{o} while the (10$\underline{1}$) peak becomes much stronger and shifts to a higher value of $2\theta = 20.1^{o}$. Meanwhile, the (101) peak remains at about the same intensity but shifts to somewhat lower 2θ values (12.3^{o}). Ingersoll defined the "radial intensity ratio" (*RIR*) as:

$$RIR = \%\ \text{Cell (II)} = 100\ [I_{10\underline{1}}/(I_{10\underline{1}} - I_{am})] \qquad (2)$$

where $I_{10\underline{1}}$ is the intensity of the principal Cellulose II peak at $2\theta = 20.1^{o}$ and I_{am} is the intensity attributed to amorphous cellulose being the minimum of the X-ray intensity located between the (10$\underline{1}$) and (101) peaks which is at $2\theta = 13^{o}$.

One of the motivations for carrying out this study is that a search of the literature indicated there are several works on x-ray diffraction to study changes to cotton structure as a result of chemically treating with swelling or mercerizing agents

[1], [4], and [5]. Likewise, there is at least one reference utilizing this method to study the response of cotton to treatment with anticrease chemical crosslinking agents [6]. However, no reference could be found examining treatment of cotton with a combination of mercerizing, bleaching, and crosslinking. This work studies the influence of mercerizing cotton prior to bleaching and crosslinking.

Experimental

The cotton lint in this study had a length of 0.776", and a micronaire of 5.3. Mechanical processing through the SRRC pilot mill consisted of opening, cleaning, and carding of the cotton lint. From here on in this paper we will refer to this mechanically cleaned cotton lint as "natural fiber". Wet finishing of the natural fiber consisted of mercerization, bleaching, and crosslinking. With slack mercerization, the fiber length shrank and the micronaire increased to 6.9. The sequence of operation was: mercerization of natural fiber, bleaching of mercerized or nonmercerized natural fibers followed, finally, by crosslinking. Three crosslinking treatments were used: (a) Form W (to impart high wet recovery), (b) DMDHEU, and (c) CA.

Laboratory Mercerizing

An aqueous solution of 22% caustic (w/w) containing 1% surfactant (Dypenol 731NF, Dexter Chemicals) at 23 ^{o}F was used for mercerization. A 9" x 36" carded batt of the natural fiber was saturated with the caustic solution and allowed to soak for five minutes. Excess solution was then squeezed out on a padder followed by thorough washing in hot water at 95 ^{o}C, rinsing in room temperature water, and neutralizing with acetic acid. Use of an alkali stable surfactant and the removal of occluded air from the batt during the saturation in the mercerizing solution helped in wetting. The neutralized batt at pH 6.0 was given a spin finish in the last rinse before centrifuging and drying in an oven.

Laboratory Bleaching

Approximately 2.0 kg of the natural fiber were wetted out for 1 hour in a bucket filled with 3 liters of water containing 3.0 g of Basophen (1 g/l) (wetting agent from BASF). Wet fibers were put in a 40 liter reaction chamber similar to a conventional kier. Fiber to liquor ratio was 1:20. Steam heating (indirect heating) in the jacket of the chamber was carried out until it reached 90^{o}C and maintained at that temperature for 45 minutes. Bath liquor was drained. Fibers were washed twice in hot water at approximately 75^{o}C. Each wash was for ten minutes. Fibers were given a final rinse with acetic acid in water so that the pH of the fiber was in the range of 6.0- 6.5. Fibers were then given a soap finish (0.6% w/w) to aid subsequent carding. The fibers were then centrifuged and dried in a forced air oven at 80^{o}C [7].

Crosslinking

All crosslinking treatments were conducted on prepared batt made from the natural fiber (described above). Crosslinked (Form W and DMDHEU) fibers were finished with 0.6% (w/w) soap. Form W treatment was carried out for 40 minutes in a stainless steel tray under a hood with formulation containing 17.5% concentrated hydrochloric acid, 7.4% commercial grade formaldehyde per Reeves et al. [8]. Fibers (prepared batt) were washed sequentially in a copious supply of room temperature tap water, and hot tap water. The fibers were neutralized in soda ash solution. Fibers were finally rinsed with weak acetic acid to a pH of 6.0 to 6.5.

The prepared batt was immersed in DMDEU formulation for 10 minutes. The formulation consisted of 6% Hylite LF, 0.1% Triton X-100, 1% PEG 400, and 1.8% Magnesium Chloride hexahydrate. Wet pick-up was 110%. Fibers were dried in a forced air oven at 100 ^{o}C and cured at 160 ^{o}C for 3 minutes.

The CA formulation consisted of 7% citric acid, 0.1% Triton X-100, 1.5% PEG 400, 1.5% H PO, and 5% Sodium Hypophosphite monohydrate. Wet pick up was 100%. Fibers were dried at 85 ^{o}C and cured at 80 ^{o}C for 2.5 min.

Treatment Sequence

The sequence of treatments used in this study are summarized in Table I. Treatment sequence I eliminates mercerization. It starts out with natural cotton that is then bleached and finally crosslinked with any of the three crosslinking agents: Form W (wet), DMDHEU, or CA. Here, natural cotton is the control for bleached cotton and bleached cotton is control for the bleached/crosslinked fiber. Treatment sequence II includes mercerization. It starts out with natural cotton that is then mercerized, bleached, and finally crosslinked with any of the three crosslinking agents: Form W (wet), DMDHEU, or CA. In this case mercerized natural cotton is the control for mercerized/bleached cotton and mercerized/bleached cotton serves as control for the mercerized/bleached/ crosslinked fiber.

X-Ray Crystallography

X-ray diffraction data was obtained using a Rigaku Model D-Max B X-ray Diffractometer. The D-Max B is equipped with a water-cooled rotating copper anode producing Cu Ka X-rays using an accelerating voltage of 40 kV with a tube current of 80 mA. The goniometer scans a 2θ range between 8^{o} and 28^{o} with a scan rate of 1^{o}/min. Cotton fiber samples are prepared by Wiley milling into a powder that is passed through a 20-mesh screen and pressed with a 10-ton hydraulic press into a 10 x 25 mm pellet that is mounted at the center of the goniometer circle.

Results and Discussion

Treatments involved in this study were carried out as outlined in Table I. In Sequence I natural cotton is bleached and then crosslinked with one of the three agents. Diffractograms of both the natural and bleached cotton samples are shown in Figure 5. Both curves are typical of the Cellulose I pattern shown in Figure 3a. The amounts of crystalline Cellulose I for Sequence I (the non-mercerized cottons) as expressed by CI are given in Table II. Here the CI for both the natural and bleached cottons are both about 85%. In Figure 6 x-ray diffractograms of bleached cottons that has been crosslinked with Form W, DMDHEU, and CA, respectively, are shown. All three diffraction curves are similar to the Cellulose I patterns exhibited in Figures 3a and 5. Consulting Table II again, there is now a noticeable difference between the CI values for the bleached/Form W crosslinked fiber (84.5%) and those for the bleached/DMDHEU crosslinked fiber (91.3%) and the bleached/CA crosslinked fiber (91.4%). Summing up the results of Sequence I at this point, these treatments do not change the nature of the Cellulose I, but crosslinking with both DMDHEU and CA yields a somewhat higher level of Cellulose I crystallinity.

In Sequence II natural cotton is mercerized, bleached, and then crosslinked with one of the three agents. A diffractogram of the mercerized and bleached cotton is shown in Figure 7. The shape of this diffractogram indicates Cellulose II crystallinity similar to that for Fortisan (Figure 4) with the exception that region A is characterized by a slightly convex shape as compared with the same region for the Fortisan. The amounts of crystalline Cellulose II for Sequence II (the mercerized cottons) are expressed by RIR and are given in Table III. Here the RIR for Fortisan and the mercerized and bleached cotton are both of the order of 85%. In Figure 8, an x-ray diffractogram for the mercerized and bleached cotton that has been crosslinked with Form W is shown. There is no apparent difference in this plot compared to the plot for the mercerized and bleached fiber (Figure 8 with a typical Cellulose II pattern and the A region characterized by the same slightly convex shape). From Table III we see that the Cellulose II RIR crystallinity is slightly increased for Form W crosslinking to 86.5%. Results of crosslinking mercerized and bleached cotton with DMDHEU are shown in Figure 9. This diffractogram has the same general Cellulose II shape as was seen in Figures 4, 7, and 8; however, the height of the B - peak is further reduced with respect to the principal peak and in addition, doublet peaks appear in the A region which have similar 2 locations as seen for the 101 and 101- peaks in Cellulose I. Considering the data in Table III, the RIR (%) associated with crosslinking mercerized, bleached cotton with DMDHEU is reduced by almost 10% of crystallinity. The effects of crosslinking mercerized, bleached cotton with CA are shown in Figure 10. This diffractogram has the same basic shape as shown for crosslinking mercerized, bleached cotton with DMDHEU in Figure 9 with the doublet peaks appearing in the A region. Finally, considering the data in Table III, the RIR(%) associated with of crosslinking mercerized, bleached cotton with CA is also of the order of 76%.

This reduction of the Cellulose II crystallinity along with the appearance of the doublet peak in the A region (a characteristic of Cellulose I) for both DMDHEU and CA crosslinked, mercerized cottons indicate that there is some reversal back to Cellulose I as a result of this sequence of treatments. This would seem to be quite unlikely based upon current beliefs concerning the irreversibility of the mercerization process. One possible explanation for this phenomenon might be the fact that the DMDHEU and CA crosslinking caused an increase in the crystallinity index for the bleached cotton and that mercerization further increases the availability or potential for the conversion of amorphous cellulose to Cellulose I by application of the crosslinking agents. In effect, crosslinking would cause an increase of order of the Cellulose I form yielding the apparent mixture of Cellulose I and II.

Conclusions

1. Crosslinking of bleached cotton with either Form W, DMDHEU, or CA does not change the crystalline (Cellulose I) nature of cotton, but it does increase the degree of crystallinity of the cotton by about six percent.
2. The mercerization treatment procedures used in this study yield excellent conversion of Cellulose I to Cellulose II.
3. Crosslinking of mercerized cotton with Form W does not change the crystalline (Cellulose II) nature of the cotton nor its degree of crystallinity.
4. Crosslinking of mercerized cotton with either DMDHEU or CA changes the crystalline nature of the sample in that the degree of crystallinity of Cellulose II is diminished while there is an appearance of certain Cellulose I characteristics.

References

1. Aravindanath, S., Bhama-Iyer, P., and Sreenivasan, S., 1992. Layer Morphology and Relation to Swelling and Structure. I. Cotton Fibres Treated In Alkali Metal Hydroxides, J. Appl. Poly. Sci., 46, 2239-2244.
2. Ingersoll, H.G., 1946. Fine Structure of Viscose Rayon, J. Appl. Phys., 17, 924-939.
3. Lai, B.T. and Panda, B.C., 1976. Response of Cotton Fibres to Anticrease Chemical Finish – A Varietal Study by X-Ray Diffraction Method. Indian J. of Text. Res., 1, 102-103.

4. Lal, G. and Pande, 1975. X-Ray Diffraction Studies of Native and Mercerized Cotton Cellulose. Colourage, 22, 21-27.
5. Meyer, K.H. and Misch, L., 1938. Helv. Chim. Acta. 20, 232.
6. Niaz, A. and Tahir. K., 1989, Effect of Temperature of Alkali Solution on Mercerization. Text. Res. J., 59, 772-774.
7. Parikh, D.V., 1997. Bleaching Cotton Fibers For Nonwoven Applications, Book of Papers, AATCC International Conference and Exhibition Atlanta, GA., October 28-31, 1997, p. 131- 135.
8. Reeves, W.A., Perkins, R., and Chance, L., 1990. Cotton fabric with wet WRA produced with formaldehyde without excessive strength loss, Am Dyestuff Reporter, Sept 5, 1990, p.640.
9. Segal, L. and Conrad, C.M., 1957, Characterization of Cellulose Derivatives by Means of the X-Ray Diffractometer, Am Dyestuff Reporter, 59, 637-642.
10. Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M., 1959. An Empirical Method For Estimating The Degree of Crystallinity of Native Cellulose Using The X-Ray Diffractometer, Text Res J, 29, 786-794.
11. Ward, K., Jr. 1955. Chemistry and Chemical Tecnology of Cotton, Interscience Publishers, Inc., New York, 27-28.

Table I. Coding for Treatment Sequences Used in this Study

Non-Mercerized (I)	Mercerized (II)
Natural Fiber	Natural Fiber
Bleached	Mercerized
Crosslinked with Form W	Bleached
Crosslinked with DMDHEU	Crosslinked with Form W
Crosslinked with CA	Crosslinked with DMDHEU
	Crosslinked with CA

Table II. The amount of crystalline Cellulose I for non-mercerized cottons (Sequence I) as given by the Crystallinity Index [1/]

Cotton Treatment	CI (%)
Natural	85.3
Bleached	85.6
Bleached/Form W	84.5
Bleached/DMDHEU	91.3
Bleached/CA	91.7

[1/] Calculated using Equation 1.

Table III. The amount of crystalline Cellulose II for mercerized cottons (Sequence II) given by the Radial Intensity Ratio [2/]

Cotton Treatment	R I R (%)
Fortisan	85.2
Merc/Bleach	85.0
Merc/Bleach/Form W	86.5
Merc/Bleach/DMDHEU	76.7
Merc/Bleach/CA	75.6

[2/] Calculated using Equation 2.

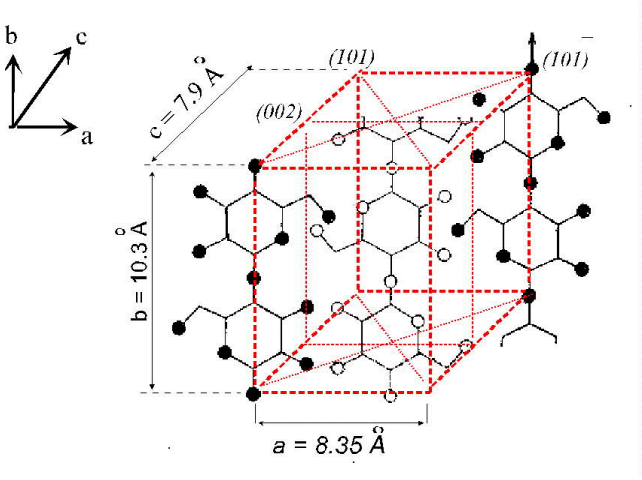
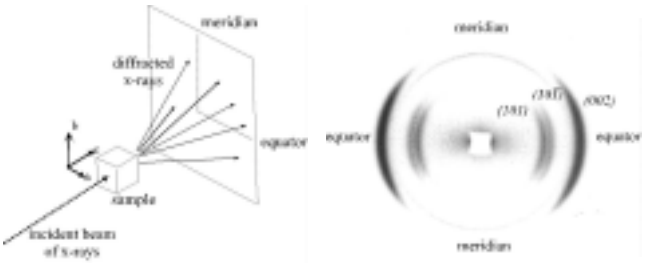
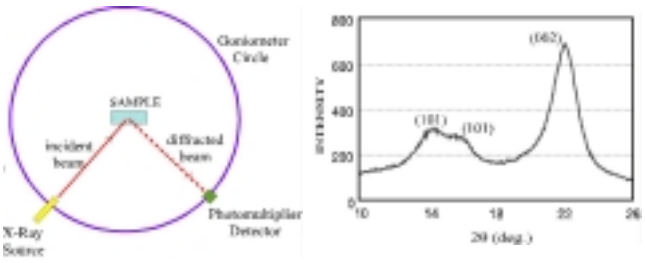


Figure 1. A diagram of the unit cell of Cellulose I as derived by Meyer and Misch [5].



(a) (b)

Figure 2. (a) An illustration of the diffraction of a collimated beam of x-rays incident on a crystalline sample. (b) A diffractogram for Cellulose I indicating that certain portions of the beam are diffracted in preferential directions perpendicular to planes of symmetry.



(a) (b)

Figure 3. (a) An x-ray beam is shown incident on a sample diffracting a beam whose angular dependence is measured by a photomultiplier detector travelling along a goniometer. (b) A plot of the angular dependence of the intensity of x-ray photons detected as a function of 2θ, the angle between the detector position and the direction of the incident beam.

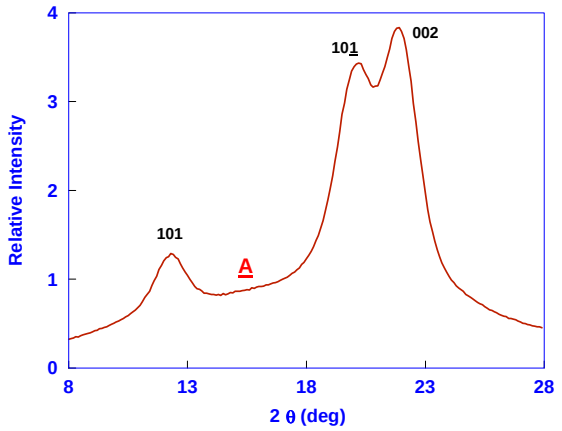


Figure 4. X-Ray Diffractogram of Fortisan Viscose Rayon

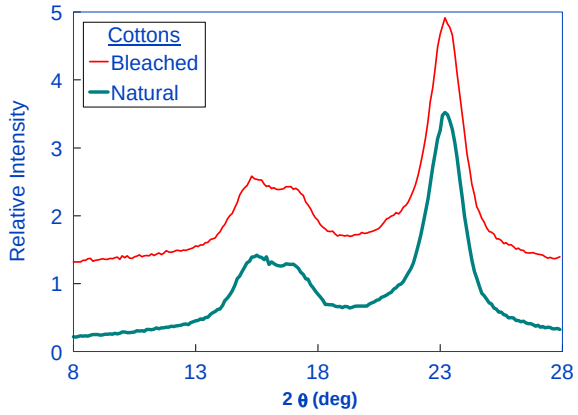


Figure 5. X-Ray Diffractograms of Natural and Bleached Cottons

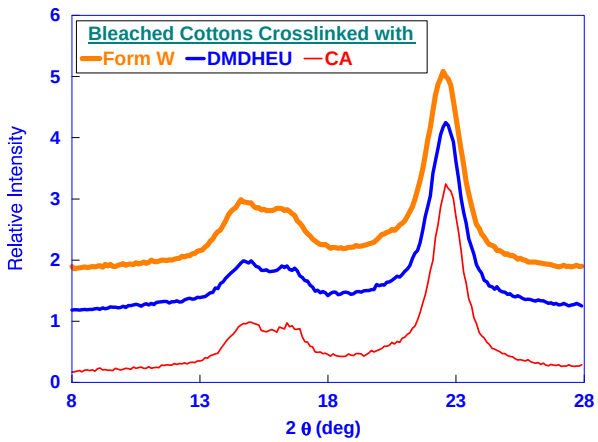


Figure 6. X-Ray Diffractograms of Bleached Cottons Crosslinked with Form W, DMDHEU, and CA, respectively.

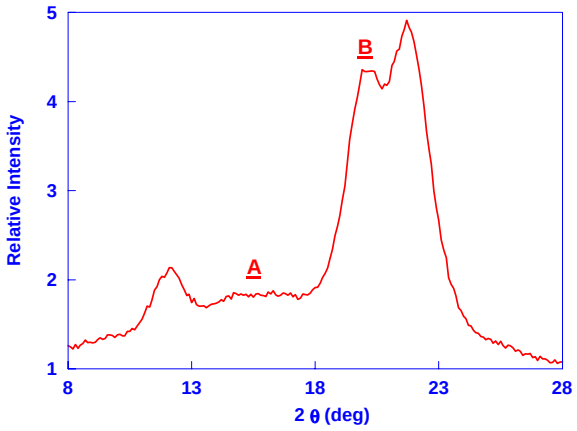


Figure 7. X-Ray Diffractogram of Mercerized/Bleached Cotton.

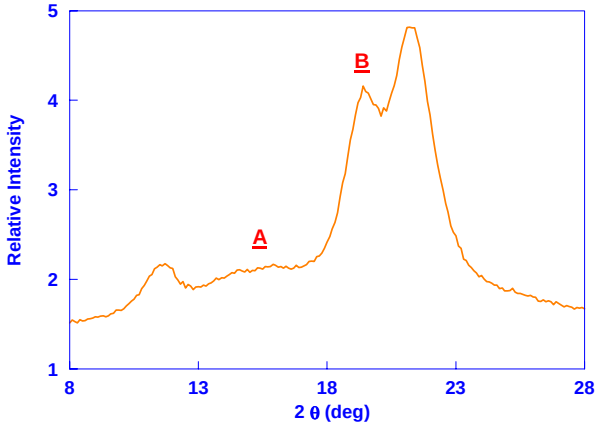


Figure 8. X-Ray Diffractogram Of Mercerized and Bleached Cotton Crosslinked with Form W

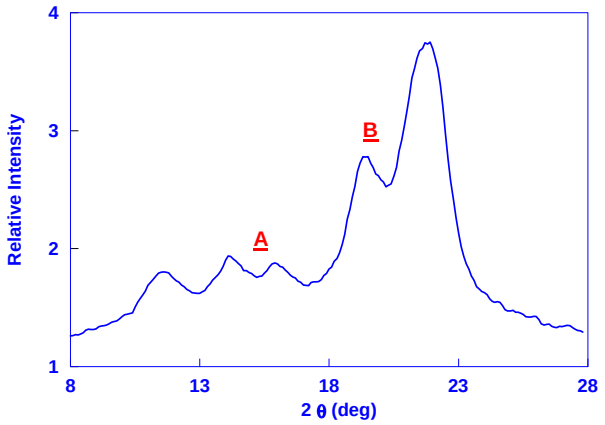


Figure 9. X-Ray Diffractogram Of Mercerized Bleached Cotton Resulting From Crosslinking With DMDHEU

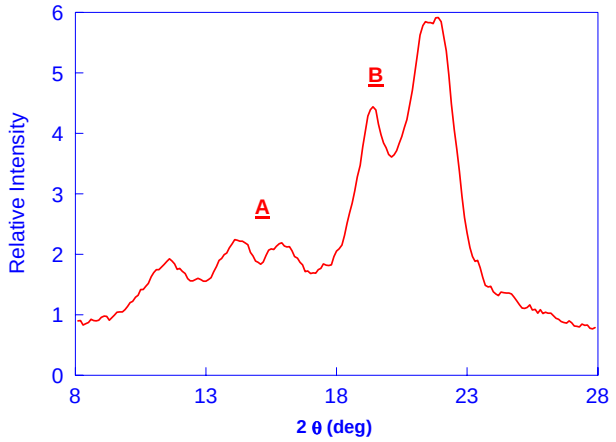


Figure 10. X-Ray Diffractogram Of Mercerized Bleached Cotton Resulting From Crosslinking with Citric Acid (CA).