

# Induced Crystallization of Cellulose in Never-Dried Cotton Fibers\*

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## SYNOPSIS

In the present investigation, we have made a systematic study of the induced crystallization in never-dried cotton fiber, by allowing it to desiccate under different conditions of humidity and temperature. The resulting structural changes have been followed using x-ray diffraction and infrared absorption techniques. A slow rate of drying coupled with a high temperature was more conducive for maximum crystallization. Analysis of the effect of temperature on the induced crystallization showed possible existence of a thermal transition in cellulose around 30°C. The induced crystallization brought about by slow drying as well as those produced using intercrystalline swelling agents, have been shown to be resulting from a proper channelization of the interfibrillar mobility existing in the never-dried fibers.

## INTRODUCTION

Cotton fibers as present in the unopened bolls, often referred to as never-dried fibers have stimulated a lot of research interest. It is believed that a study with this form of cellulose can lead to an understanding of the mode of fiber development, including the growth and packing of cellulose chains and the mechanism of cellulose biosynthesis.<sup>1-5</sup> The imperfect arrangement of the unassociated protofibrils<sup>6,7</sup> which constitutes the cell-walls of the never-dried fibers facilitates easy access to chemical reagents. The high reactivity and accessibility of the never-dried fibers, have been amply demonstrated by studies on dye uptake<sup>7-10</sup> crystalline order,<sup>7,9,11-14</sup> chemical modifications,<sup>7,15</sup> and fixation<sup>16-20</sup> of this native biological state. Further, the high reactivity of this cellulose enables an easy method of bioconversion of cellulose to sugars.<sup>21</sup>

Although, opinions differ<sup>9,11-14</sup> as to the extent and nature of order of cellulose in the never-dried fibers, it is generally agreed<sup>7,12,15,22</sup> that decrease in

accessibility and increase in density are suggestive of some fibrillar aggregation during the initial dehydration of the never-dried fibers. However, the nature of removal of water plays a significant role in this fibrillar aggregation and collapse of the fibers which is almost tubular in the never-dried state. A fast dehydration leads to a sudden collapse of the fiber resulting in the development of convolutions and regions of stress-concentration along the length.<sup>14,23</sup> Removal of water by solvent exchange method<sup>12,23,24</sup> prevents the formation of convolutions or twists and retains the tubular nature of the fiber. Investigations into the fine structure of solvent-dried fibers is hindered to some extent by the presence of entrapped solvents.<sup>7</sup> On the contrary, it is believed that a slow dehydration from the never-dried state may lead to a uniform stress distribution and also at the same time alter the nature of crystallization resulting from agglomeration of elementary fibrils. In the present investigation, an attempt is made to channelize the high internal mobility<sup>25</sup> of the structural elements in the never-dried fibers, by slow dehydration under specific conditions of temperature and humidity and thus modify the extent of crystallization.

By suitable combinations of temperature and humidity, drying periods ranging from a few hours to a few hundred hours were obtained. Extent of crystallization in these differently dried fibers were as-

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certained by using x-ray and infrared techniques. Results are discussed below along with the data obtained for induced crystallization by techniques other than slow drying.

## EXPERIMENTAL

### Materials

Bolls collected 40 days postanthesis from the 1985–86 season and transported from the field to the laboratory by preserving in 5% aqueous formaldehyde were used throughout the study. Bolls were washed several times just before use and were slit open after placing them in a tray containing distilled water. The fibers were separated from the seeds with caution as not to subject the fibers to any pulling force. About 10 bolls were opened at a time, a portion from the same being used as the control for the set. For each set of drying experiments, fibers were obtained from the preserved bolls while the sample dried in normally from the same lot was taken as the control.

### Methods

#### *Drying Tests*

Saturated solutions of salts capable of giving relative humidities varying from 10–98% rh<sup>26,27</sup> were prepared and used to give different drying times. Depending on the temperature at which the solutions were maintained, humidity too showed some variations. However, this effect is not important in the present context as we are interested only in the drying period for each relative humidity (irrespective of the actual humidity). Drying to constant weight at any relative humidity was done by keeping the samples in desiccators containing saturated solutions of different salts. Using an incubator chamber, desiccators could be maintained at any preselected temperature to an accuracy of  $\pm 0.5^\circ\text{C}$ . Samples were maintained over any specific humidity and temperature until successive weights became constant, after which, they were transferred over to 65% rh and were left for a minimum of 24 h before attempting any measurement.

#### *Acid Hydrolysis*

About 2 g each of the water-wet sample was treated with 1 *N*, 2 *N*, and 4 *N* HCl at 3 different temperatures, viz. 30°C (15 days), 70°C (4 h), and 98°C (30 min). A couple of the slowly dried samples were

also treated with 4 *N* acid at boil for 30 min so as to measure the gravimetric weight loss.

#### *Treatment With Iodine and Intercrystalline Swelling Agents*

About 1 g of the never-dried fiber was treated with 0.2 *M* iodine solution at 42.5°C for a period of 24 h. Wet fibers were also treated with intercrystalline swelling agents such as 9% NaOH (w/w), dimethyl sulfoxide (DMS) and dimethyl formamide (DMF) for about 30 min. After the specified treatment the samples were washed with water several times. A portion from each of the treated fibers was dried in air at 30°C and 65% rh, while the other portions were dried slowly by placing them in a desiccator containing saturated solution of potassium dichromate maintained at 42.5°C.

#### *X-ray Measurements*

All fibrous samples (previously conditioned overnight in 65% rh) were cut in a Wiley mill fitted with a 40-mesh screen. Radial intensity scans of the packed powder in the reflectance mode for the  $2\theta$  range 10° to 40° were obtained using Philips X-ray Generator fitted with recording accessories. From the diffractometer tracings crystallinities were calculated by using the method of Chidambareswaran et al.<sup>28</sup> Half width at the 50% intensity for the (200) reflection ( $\beta_{1/2}$ ) was measured in the usual way (the conventions for the first setting for monoclinic unit cell have been followed here).

#### *Infrared Measurements*

Two milligrams of the Wiley-cut powder was mixed with 200 mg of KBr and ground thoroughly in an agate mortar for about 5 min. The mixture was transferred to the KBr die and pressed at a load of 10 tons for about 5–6 min, evacuation being on all the time. The transparent pellet obtained was scanned for the following specific regions: 1600–1200  $\text{cm}^{-1}$  and 1100–700  $\text{cm}^{-1}$ , with a Perkin-Elmer Model 457 Infrared Spectrophotometer using slow speed and normal slit. Index I given by O'Connor and coworkers<sup>29</sup> was measured after drawing appropriate base lines for the peaks at 1429  $\text{cm}^{-1}$  and 893  $\text{cm}^{-1}$ .

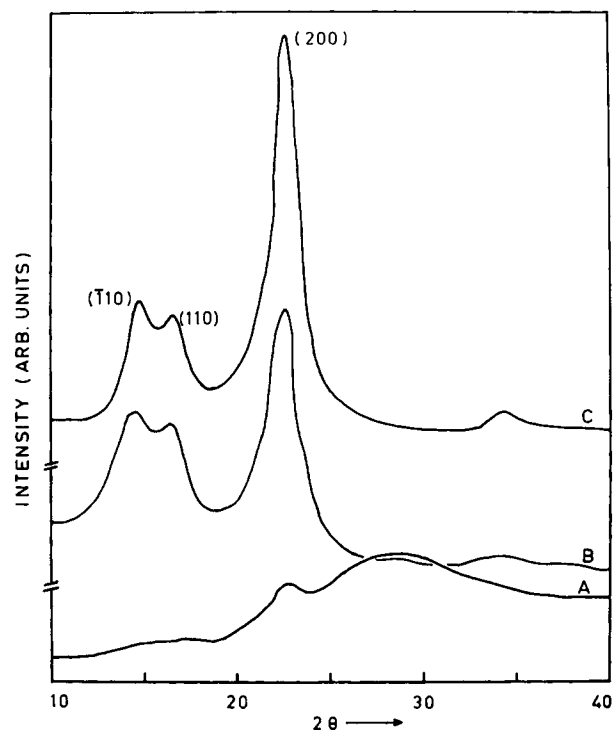
#### *Bundle Tenacity Measurements*

Bundle tenacities (both at nominal zero gauge and 3.2-mm gauge lengths) and extension corresponding

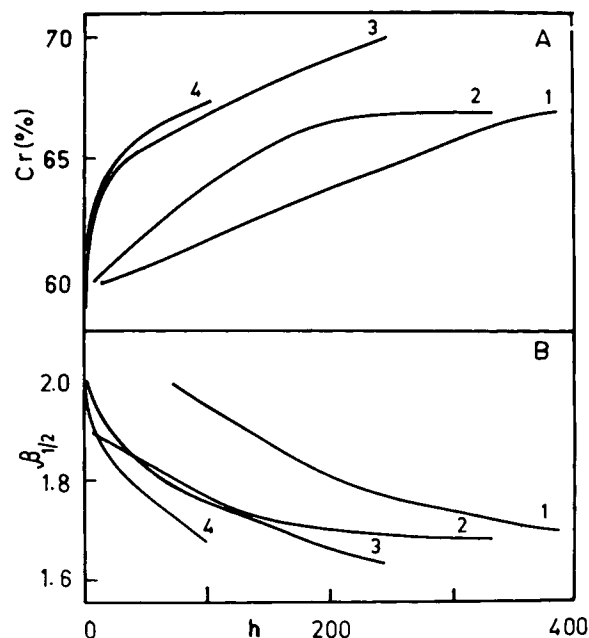
to break using 3.2-mm gauge length were measured in a Stelometer employing standard procedures.<sup>30</sup>

## RESULTS AND DISCUSSION

Normalized x-ray diffractograms for the water-wet, never-dried fibers, normal-dried fibers, and slow-dried fibers (dried at 42.5°C) are depicted in Figure 1(A), (B), and (C). Note the higher peak heights for (200), ( $\bar{1}10$ ), and (110) and the better resolution for the ( $\bar{1}10$ ) and (110) region for the slow-dried fibers (pattern C) indicative of higher crystallization achieved by the slow-drying process. X-ray crystallinities of the samples dried at different temperatures and humidities (i.e., for different drying periods) are shown in Figure 2(A) along with  $\beta_{1/2}$  values [Fig. 2(B)]. It may be noted that for any temperature, slowest drying (obtained by keeping the samples over higher humidities) produced maximum crystallization. However, fibers obtained after the same drying time but with higher temperature and over higher humidities had higher crystallinities. Initial fast drying (over 0% rh) at various temperatures (starting points in the graph) produced only a little variation in crystallinity. Variations in half width



**Figure 1** X-ray diffraction patterns of (A) never-dried, (B) normal-dried, and (C) slow-dried cotton fibers.

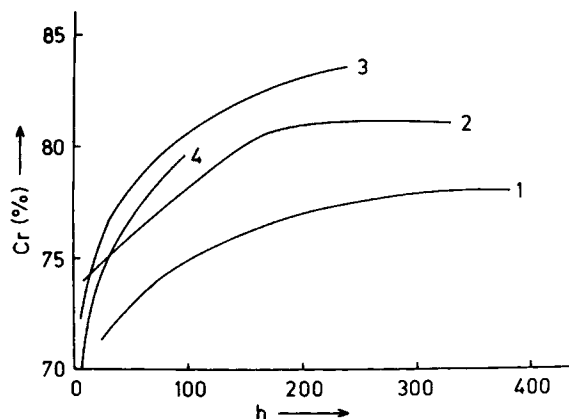


**Figure 2** Effect of drying time (h) on crystallization. (A) crystallinity (Cr %), (B) half-width  $\beta_{1/2}$  of (200) reflection. 1—17.5°C, 2—30°C, 3—42.5°C, 4—55°C.

for the various drying times and temperatures [Fig. 2(B)] indicates that the slowest dried sample at any temperature had the lowest width suggestive of more perfect crystallites. However, slowest drying coupled with higher temperature ( $\approx 200$  h, 42.5°C) resulted in higher crystallinity and crystallite size.

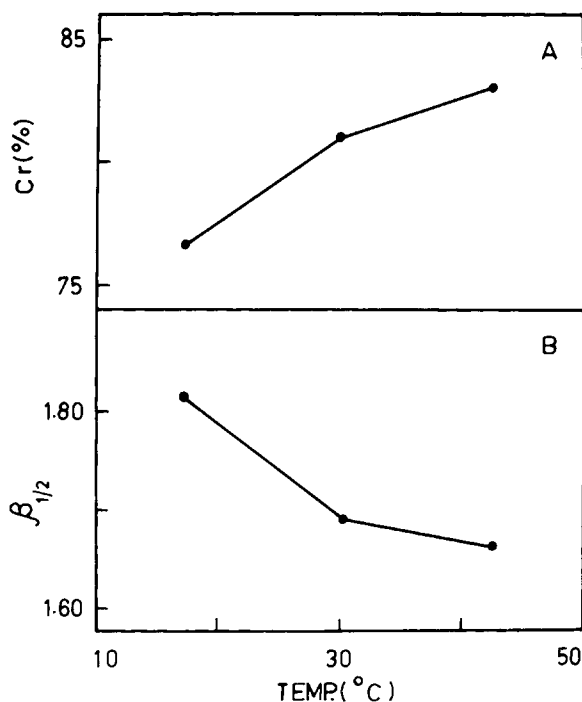
Figure 3 depicts a plot of infrared crystallinity with time, obtained by using Index I, for the differently dried samples. This index is based on the ratio of intensities of 1429  $\text{cm}^{-1}$  and 893  $\text{cm}^{-1}$  bands. The values obtained for this index were converted to absolute crystallinities by using the method of standards described earlier.<sup>31</sup> It is evident from Figure 3 that Ir crystallinities also show an increase with drying time. Further, slowest drying at a slightly higher temperature gave the maximum crystallization quite in line with the observations made by the x-ray technique.

In Figure 4(A) and (B), we have the plots of Ir crystallinity and  $\beta_{1/2}$  with temperature for a 200-h-dried sample. X-ray crystallinity and  $\beta_{1/2}$  are inter-related parameters and while the former measures the quantum of crystalline (well-ordered) regions, the latter depends on the perfection of the crystallites as well. The lesser the value of  $\beta_{1/2}$ , more perfect the crystallites would be. Note from Figure 4 that while crystallinities show increase,  $\beta_{1/2}$  shows a decrease and a change of slope is evident in both the



**Figure 3** Effect of drying time (h) on infrared crystallinity (Cr %) 1—17.5°C, 2—30°C, 3—42.5°C, 4—55°C.

plots. While measuring the temperature dependence of certain properties of cellulosic materials a change of slope around 25°C has been observed<sup>32-36</sup> and this is attributed to some thermal transition in cellulose. Since our measurement of crystallinities were limited to temperatures of 17.5°, 30°, and 42.5°C, the change in slope occurred at 30°C. Figure 4(A) indicates that the process of crystallization is slightly slowed down beyond the transition temperature.



**Figure 4** Effect of drying temperature (°C) on crystallization. (A) Ir crystallinity (Cr %), (B) half-width  $\beta_{1/2}$  of (200) reflection.

Decrease in  $\beta_{1/2}$  also slows down beyond 30°C [Fig. 4(B)]. We could not extend these measurements to 55°C as the sample drying time was much lower than 200 h even when kept over saturated solution of potassium dichromate. Beyond the transition temperature, the mobility of the structural elements are expected to increase leading to a lowering of the rate of crystallization. At the same time this additional mobility could enable the cellulosic chains to position favorably, such that during desorption, more stable interfibrillar arrangements could be achieved ultimately leading to the attainment of higher net three-dimensional order.

The induced crystallization observed and discussed here in never-dried fibers cannot be directly compared to polymer crystallization from melt or dilute solutions. Even in cellulose crystallization from solutions, only very low molecular weight material ( $DP \approx 30$ ) can form lamellar crystals.<sup>37</sup> In solution crystallization we start with a homogeneous phase and the crystallization is triggered by suitable conditions. Even in this case, when the DP of the material is high crystallization occurs leading to the formation of 3.5 nm elementary fibrils.<sup>38</sup> Never-dried fibers, are often compared to a gel, however, the polymerized fibrous material (elementary fibrils) is already present in the system and it is far from homogeneous. Some kind of association should already exist between chains leading to the formation of the so-called elementary fibrils. What is absent is the association or agglomeration (interfibrillar bonding) between these protofibrils which ultimately coalesce to form microfibrils. The influence of environmental or drying conditions in affecting this coalescence is what we are concerned with. The high mobility of the fibrillar elements in the never-dried state provides sufficient room for an ordered aggregation when the conditions are favorable and hence fibers dried under normal conditions show different extents of crystallization from that, from which water was removed under controlled conditions.

**Table I** Gravimetric Weight Loss Data Obtained During Acid Hydrolysis of Never-Dried Fibers, Dried Under Different Conditions

Temperature and Duration of Drying	Crystallinity (%) Dried Fibers	% Weight Loss
30°C, 8 h	60	42
42.5°C, 265 h	70	33

Hydrolysis conditions: 4N HCl, boil, 30 min.

**Table II Bundle Tenacity (g/t) Data on Differently Dried Samples**

Conditions of Drying	Bundle Tenacity (g/t)		Breaking Extension, <i>E</i> (%)
	Zero Gauge ( <i>T</i> <sub>0</sub> )	3.2-mm Gauge ( <i>T</i> <sub>3</sub> )	
1. Room temperature and humidity	39.6	25.2	5.6
2. Slowest drying			
(a) 17.5°C	40.7	28.3	4.4
(b) 30°C	42.6	28.3	4.6
(c) 42.5°C	38.3	23.4	5.7
(d) 55°C	39.2	26.2	5.4

Additional evidence for the induced crystallization is obtained from data on gravimetric weight loss measurements given in Table I. Note the difference in weight loss, almost 9% less, observed for the slowly dried sample compared to the normally dried sample. The weight loss seems to show almost good correspondence with crystallinity; the higher the crystallinity, the lower the weight loss. In this connection, it is interesting to recall the results of Battista<sup>39</sup> who observed lower weight loss during severe hydrolysis of a sample, which had already been subjected to a very mild hydrolysis treatment that induced crystallization.

Table II gives the tenacity and breaking extension (%) values for the slowest dried samples at different temperatures. It is heartening to note that the higher

crystallinity induced by the slow drying did not affect the tenacity and extension values adversely. Tensile properties of the cotton fibers depend on various other factors, and crystallinity has the minimum influence<sup>40</sup> on the tensile behavior of fibers, which is further confirmed with this observation.

It is interesting to note that, the usual treatments, i.e., acid hydrolysis, swelling with intercrystalline reagents, etc. which promote crystallization in cellulose, could not increase the crystallinity in the never-dried fibers beyond that obtained by the process of gradual drying. This is evident from the data given in Tables III and IV. In fact, treatment with intercrystalline swelling agents and iodine were less effective in inducing crystallization in never-dried fibers and to observe sufficient crystallization the

**Table III Fine Structural Data on Never-Dried Fibers Subjected to Acid Hydrolysis**

Hydrolysis Conditions			Crystallinity (%)		
Concentration	Temperature (°C)	Time	X-ray Data		
			<i>C</i> <sub>r</sub>	<i>β</i> <sub>1/2</sub>	<i>I</i> <sub>r</sub>
1 <i>N</i>	30°	15 days	63	1.75	78.1
	70°	4 h	69	1.75	72.3
	98°	30 min	70	1.70	82.3
2 <i>N</i>	30°	15 days	69	1.73	79.0
	70°	4 h	67	1.80	77.2
	98°	30 min	71	1.65	80.0
4 <i>N</i>	30°	15 days	67	1.73	78.8
	70°	4 h	70	1.70	80.7
	98°	30 min	73	1.70	76.8

**Table IV Fine Structural Data on Never-Dried Fibers Treated With Intercrystalline Swelling Agents**

Treatment	Conditions of Drying	Crystallinity (%)		
		X-ray Data		
		$C_r$	$\beta_{1/2}$	Ir
1. None	Room temperature and humidity	60	1.90	74.0
2. (a) DMF	Room temperature and humidity	66	1.68	73.9
(b) DMSO	Room temperature and humidity	63	1.75	76.3
3. None	42.5°C; Slow drying	70	1.70	88.6
4. (a) DMF	42.5°C; Slow drying	67	1.60	87.6
(b) DMSO	42.5°C; Slow drying	68	1.60	85.8
(c) 9% NaOH	42.5°C; Slow drying	68	1.65	—
(d) 0.2 M $I_2$ , 30°C	42.5°C; Slow drying	70	1.70	88.6

fibers had to be dried slowly after treating with the reagents. Even the combined treatment could not take the crystallinity to values above that obtained by slow drying only, while  $\beta_{1/2}$  values were slightly lower. This indicates a higher perfection in the crystalline regions arising from the combined treatments.

## CONCLUSIONS

1. Crystallization produced in the never-dried fibers during the first drying is very much dependent on the conditions of drying.
2. Under suitable slow drying conditions, about 10–15% additional crystallization could occur over that observed by normal drying.
3. A slow drying coupled with a higher temperature seems to be more conducive for crystallization.
4. Crystallization obtained by processes other than slow drying could seldom achieve a higher value than that obtained by slow drying.
5. The present results (temperature-crystallization plots) indicate the possible existence of a thermal transition in cellulose around 30°C which is in keeping with the observations made by earlier workers based on other temperature-dependent parameters, i.e., specific volume, birefringence, etc.

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