Studies on the Structure of Never-Dried Cotton: Part I—Physical Characteristics of Cotton Dried under Controlled Conditions

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The physical and morphological characteristics of never-dried cotton, cotton dried under controlled conditions and nature-dried cotton have been examined. On drying in nature, the never-dried cotton fibres get transformed into a convoluted, bean-shaped and collapsed structure from the state of unconvoluted, tubular structure with circular cross-section. In this process, the physical characteristics of cotton could be improved over the nature-dried cotton by drying the cotton under controlled conditions. The effectiveness of different methods of drying in retaining the physical characteristics of cotton in the never-dried state lies in the following order: never-dried cotton > freeze-dried cotton > cotton dried by solvent exchange > cotton dried at 300°C > cotton dried at 100°C > cotton dried at 25°C > nature-dried cotton.

Several studies have been reported on never-dried cotton. These studies were devoted mainly to cotton in the never-dried state. Earlier X-ray studies on never-dried cotton fibres taken from developing bolls showed little or no evidence of crystallinity, whereas some crystallization was found to take place on applying tension to the never-dried cotton fibres. These workers proposed that crystallization takes place when the boll starts self-opening and fibres undergo initial dehydration. However, studies made in this laboratory have shown the presence of crystallinity even in the young fibres (35 days old). This finding has been further substantiated by Ingram et al.

Material — Cotton of Kalyan variety belonging to Gossypium herbaceum var. frutescens Delite and grown in the outskirts of Ahmedabad was used. The matured (65 days old) cotton bolls were opened under water and fibres were removed carefully from the seeds. The fibres were used either immediately without any treatment or after purification.

The chemicals and solvents used were of analytical reagent grade. Methanol was distilled before use.

Purification of never-dried cotton — When the standard method of purifying cotton fibres was followed, the never-dried cotton fibres developed a light brown colour during the final extraction with ethanol. This method of purification was, therefore, modified. The modified method of purification involved the extraction of cotton first with ethanol for 18 hr, then with chloroform for 16 hr and again with ethanol for 18 hr. The purified cotton wet with ethanol was washed with distilled water several times and then stored in 10% methanolic distilled water.

Removal of superficial water from the never-dried cotton fibres — The never-dried cotton fibres stored in methanolic water were washed with plenty of distilled water to remove ethanol completely from them. The never-dried cotton fibres were put in a syringe up to a given mark. A slight pressure was applied slowly on the fibres in the syringe up to another mark to remove superficial water from never-dried cotton fibres. The method was standardized by performing several preliminary experiments. This procedure of removing superficial water from the never-dried cotton fibres was followed in all the experiments in which wet fibres were used.

Drying of never-dried cotton fibres by freeze drying — About 2 g of the never-dried cotton fibres were taken in a 250 ml round bottomed flask fitted with a standard ground glass joint. The excess water was drained out and cotton was spread as uniformly as possible all along the inner surface of the flask. The flask was then placed in liquid air to freeze the water associated with never-dried cotton fibres. The flask was then evacuated at 10^{-5} mm of Hg till the fibres were completely dry. The dried fibres were removed from the flask and stored in a conditioned room maintained at 25°C and 65% RH.

Drying of never-dried cotton fibres at different temperatures — Superficial water from never-dried cotton fibres was removed. A constant ratio of 1:4
for cotton to water was maintained in all the cases before drying. The fibres were dried at different temperatures in the range 25°-300°C using the apparatus shown in Fig. 1. The fibres were put on the pan. The pan with the cotton sample was lowered into the cylindrical oven, maintained at the desired temperature. At each temperature, the fibres were dried for a period just sufficient for complete drying. Care was taken to avoid thermal degradation by excessive heating of the fibres.

Drying of never-dried cotton by solvent exchange technique — The never-dried cotton fibres were dried by the solvent exchange technique described by Merchant. About 1 g of never-dried cotton was dispersed in about 100 ml methanol. After half an hour the cotton was again squeezed lightly and transferred to methanol. This process was repeated 5-6 times and finally the fibres were dispersed in dry methanol. Methanol was then replaced by dry organic liquid (e.g. benzene, n-hexane, n-heptane and cyclohexane). The fibres were dried at the critical temperature of the organic liquid. Precautions were taken to remove the liquid completely without excessive heating. The dried samples were stored in a conditioned room maintained at 25°C and 65% RH.

Measurements of physical characteristics — The physical characteristics of fibres were measured by the ASTM procedures. The fibres before measurements were conditioned at 65% RH and 25°C. The characteristics measured were: maturity, effective length, gravimetric fineness, micronaire value, elastic recovery, strength and extensibility of single fibres. In the case of single fibre tests, which were performed on the Instron tensile tester, 100 single fibres were taken in each case and effective gauge length was kept at 1 cm. Single fibre elastic recoveries were measured at 2% extension of fibres.

Photomicrographs for longitudinal view of the single fibres — Fibres were isolated from the sample and were laid flat over a microscopic glass slide and immersed in paraffin oil. Photographs were taken through the optical microscope. Longitudinal photomicrographs of the various fibre samples obtained are shown in Figs. 2-10.

Photomicrographs of fibre cross-section — The combed fibre bundle was coated with an epoxy resin and dried. The dried bundle was mounted on a hand microtome. The cross-sections were obtained by cutting the fibre bundle with a sharp razor blade. The cross-sections obtained were mounted on a glass slide, immersed in liquid paraffin and examined through an optical microscope.

The photomicrographs of cross-sections of nature-dried and never-dried cotton fibres dried under different conditions are shown in Figs. 11-15.

Examination through transmission electron microscope—An important part of the electron microscopy experiments is the preparation of replicas. Preliminary experiments were carried out to test the suitability of a known method for preparing replicas of cotton fibre surfaces. Modification of the standard method was necessary, since the never-dried cotton fibres should not dry out during the period of setting the fibre impression on polystyrene film. The modified method of preparing the replicas was as follows. A solution of polystyrene was prepared by dissolving 5 g low molecular weight polystyrene and 1 g dibutyl phthalate in 100 ml xylene. A microscopic glass slide was dipped in the polystyrene solution. The glass slide was then allowed to dry in air till a hard film was formed on the glass. The fibre profiles of never-dried cotton fibres were separated under water. The glass slide coated with polystyrene film was dipped into the water containing the fibre profiles of never-dried cotton fibres. The fibre profiles were collected under water over the polystyrene coated glass slide. Another clean glass slide was dipped into the water and two glass slides were clamped together with rubber tubing clamps. The clamping was done to sandwich the fibre profiles between the two glass slides with enough tension. The temperature of the water was raised to 50°C while the glass slides were in position. This temperature was maintained for about 1 hr. The water was then cooled to room temperature. The glass slides were removed from the water and separated. The polystyrene impression was transferred to a shadow casting device and carbon was evaporated on it. A positive impression of carbon was formed. Chromium metal was then evaporated over the carbon deposited film.

The carbon-chromium coated layers were cut into several squares of about 4 × 4 mm size. The squares were then floated over distilled water by carefully dipping the slide into the water. The polystyrene layer was dissolved by keeping each square separately in xylene for about 24 hr. Each carbon-chromium replica was examined by placing on a screen grid through an electron microscope at various magnifications ranging from ×1050 to ×10,000. Figs. 16-22 show electronmicrographs of the surfaces of never-dried and nature-dried fibres and fibres dried under controlled conditions.

Results and Discussion

The never-dried cotton fibres from the green cotton
Fig. 2 — Longitudinal view of never-dried cotton. Fig. 3 — Longitudinal view of nature-dried cotton. Fig. 4 — Longitudinal view of cotton dried at 300°C. Fig. 5 — Longitudinal view of cotton dried at 200°C. Fig. 6 — Longitudinal view of cotton dried at 100°C. Fig. 7 — Longitudinal view of cotton dried at 25°C.
bolls which are still wet with the boll moisture exhibit cylindrical shape and have a circular cross-section (Fig. 2). However, on drying in nature, the fibres lose their tubular shape and assume a ribbon-like structure (Fig. 3) that twists in different directions to form convolutions having bean-shaped cross-section. The longitudinal shapes of the fibres dried at different temperatures are shown in Figs. 4-7. It is seen that fibres dried at 300°C have a cylindrical shape almost similar to that of never-dried cotton fibres. This shape is also retained when the fibres are dried by freeze drying or by solvent exchange techniques using benzene (Figs. 8-10). Similar results are obtained when other solvents, namely n-hexane, cyclohexane, n-heptane, DMSO, DMF, pyridine and THF are used.

From the present study it was found that the degree of collapse depends upon the nature of the liquid used for the exchange. The degree of collapse is found to decrease in the order: \( H_2O > DMSO > pyridine > THF > benzene \). Thus, the structural collapse is maximum in water and minimum in benzene.

It is also seen from Figs. 4-7 that the structural collapse decreases as the temperature of drying is increased. In other words, the fibres dried at 25°C are collapsed and are similar to those of nature-dried cotton, whereas the fibres dried at higher temperature are cylindrical. The degree of collapse is found to decrease in the order: fibres dried at 25°C > dried at 100°C > dried at 200°C > dried at 300°C.

The cross-sections of never-dried cotton fibres dried at different temperatures are shown in Figs. 11-15. It is seen that the cross-section of fibres dried at 25°C is of bean shape and is similar to that of nature-dried cotton, but the fibres dried at 300°C are nearly circular. This tends to suggest that as the temperature of drying is increased, the cross-section approaches that of never-dried cotton. Further, the cross-section of never-dried cotton fibres dried by freeze drying, shown in Fig. 15, is circular and is very similar.
Fig. 11 — Cross-sectional view of cotton dried at 300°C
Fig. 12 — Cross-sectional view of cotton dried at 200°C
Fig. 13 — Cross-sectional view of cotton dried at 100°C
Fig. 14 — Cross-sectional view of cotton dried at 25°C
Fig. 15 — Cross-sectional view of freeze-dried cotton
to that of never-dried cotton. It is further found that the circular cross-section of never-dried cotton can also be retained by solvent exchange drying of never-dried cotton. However, the cross-section of nature-dried cotton wetted with water and then dried by solvent exchange was bean-shaped. This suggests that during drying of the cotton fibres in natural surroundings after the opening of the cotton bolls, certain irreversible changes take place which lead to collapse of the fibres. These changes are most probably caused by interfibrillar hydrogen bonds which cannot be broken by just wetting with water.

Electronmicrographs of never-dried and nature-dried cottons are shown in Figs. 16 and 17. It is seen that the surface of never-dried cotton is smooth and uniform and the presence of ridges or grooves is not noticed. On the contrary, the surface of nature-dried cotton is not uniform and possesses ridges parallel to one another. The surface characteristics of fibres dried under different conditions are shown in Figs. 18-22. It is seen that the surface of fibres dried at 300°C is smooth and uniform like that of never-dried cotton. However, the presence of ridges or grooves becomes visible as the temperature of drying is lowered. Ridges and non-uniformity of the fibre surface become prominent in the sample dried at 25°C. The electronmicrograph of cotton fibres dried by the freeze drying technique shows surface almost similar to that of never-dried cotton, except at the edge marked with the arrow in Fig. 22. The marked edge shows uneven pull. This may be caused by the high vacuum applied during freeze-drying.

The physical characteristics of never-dried cotton dried at different temperatures and of nature-dried cotton are given in Table 1. It is seen that the breaking strength properties of fibres dried under controlled conditions are superior to those of nature-dried cotton. The breaking strength of freeze-dried cotton is about 40%, higher than that of nature-dried cotton. It is also seen that the percentage elongation decreases as the strength of the fibre increases. Further, the percentage elongation bears a direct relationship with the number of convolutions per unit length of the fibre or the extent of collapse of the fibre upon drying. The number of convolutions introduced per unit length of the fibre is found to decrease with increase in the temperature of drying.

In other words, the number of convolutions is minimum in the fibre sample dried at 300°C and maximum in the sample dried at 25°C. However, the freeze-dried sample showed the lowest number of convolutions per unit length of the fibre.

Thus, it is possible to improve the physical characteristics of cotton fibres by allowing the fibres to dry at optimum temperatures. From the present study, it may be concluded that so far as the retention of surface and morphological characteristics of the original cotton fibres is concerned, the different methods can be arranged in the following order: never-dried > freeze-dried > dried at 300°C > dried at 200°C > dried at 100°C > dried at 25°C > nature-dried cotton.

<table>
<thead>
<tr>
<th>Sample particulars</th>
<th>Breaking strength (g)</th>
<th>Extension %</th>
<th>Elastic recovery at 2% stretch (%)</th>
<th>Number of convolutions per mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature-dried cotton (control)</td>
<td>5.2</td>
<td>8.0</td>
<td>85.5</td>
<td>5.6</td>
</tr>
<tr>
<td>Never-dried cotton dried at 25°C</td>
<td>5.5</td>
<td>7.9</td>
<td>84.0</td>
<td>4.3</td>
</tr>
<tr>
<td>100°C</td>
<td>5.8</td>
<td>7.0</td>
<td>84.0</td>
<td>4.5</td>
</tr>
<tr>
<td>200°C</td>
<td>6.6</td>
<td>6.8</td>
<td>82.0</td>
<td>3.8</td>
</tr>
<tr>
<td>300°C</td>
<td>6.6</td>
<td>6.8</td>
<td>82.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Never-dried cotton dried by freeze drying technique</td>
<td>7.2</td>
<td>5.7</td>
<td>77.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Fig. 18 — Electronmicrograph of cotton dried at 300°C (x 2500)
Fig. 19 — Electronmicrograph of cotton dried at 200°C (x 2500)
Fig. 20 — Electronmicrograph of cotton dried at 100°C (x 2500)
Fig. 21 — Electronmicrograph of cotton dried at 25°C (x 2500)
Fig. 22 — Electronmicrograph of freeze-dried cotton (x 2500)
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References