Effect of Crosslinking on the Torsional and Tensile Behaviour of Cotton Fibres

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Torsional rigidity as well as torsional and tensile moduli of cotton were determined before and after crosslinking with formaldehyde (HCHO) and dimethylol dihydroxyethyleneurea (DMDHEU). The single fibre torsional pendulum method was adopted for determining the torsional properties, while the tensile load-extension curve obtained on the Instron was used for finding the tensile modulus. The tests were carried out in both conditioned (65% RH) and wet states. While the crosslinking in DMDHEU resulted in considerable increase in torsional rigidity, no such change seemed to accompany HCHO treatment. Torsional modulus did not change with HCHO treatment, but showed an apparent fall as a result of DMDHEU treatment, when this modulus was calculated on the basis of the increased cross-sectional area of the modified fibre. However, if the dimensional change is ignored and the cross-sectional area of the untreated fibre is used in the calculations, this modulus shows an increase. With both the treatments, the tensile modulus is found to register a fall. The results are discussed in the light of known ideas on fibre structure and deformation mechanism.

The resistance of fibres to twist about their axes is governed by the torsional rigidity. This fibre property has direct influence on many important characteristics of the yarn. It influences the liveliness of the yarn, its diameter, tendency to snarl and pliability. The torque in the yarn initiates the curling of knitted fabrics. Further, the draping quality of the fabric, as well as its crease resistance, depend on the torsional behaviour of the constituent fibres. In cotton, both the tensile and torsional strains show similar trends. Both are time-dependent and are affected by humidity and temperature and by fibre characteristics, such as fineness and diameter. A combined study of these two mechanical properties may throw further light on the peculiar morphology of the cotton fibre and its behaviour after chemical modifications.

Following the classical work by Peirce, Meredith and some other workers determined the torsional rigidity of various fibres, such as cotton, jute, wool, rayon and many synthetic fibres. Some workers have established the dependence of torsional rigidity on temperature and humidity. Demonstrating the use of a device for measuring the period of torsional oscillations at elevated temperatures and ambient pressures, Orr and Grant have shown that the shear modulus of cotton decreases with increase in temperature. While in all the above studies the determination was made by the torsional pendulum method using single fibres, some workers have measured the rigidity on fibre bundles by the same method. Although the use of bundles is time-saving, it has some limitations, as pointed out by Cheng and Duckett. The importance of torsional rigidity in the spinning performance of fibres has also been studied.

The above studies have been mainly on fibres in their raw state. It is well known that chemical treatments, such as mercerization and crosslinking, affect many fibre properties. Strength and elongation suffer a reduction in the case of cotton fibre, while its crease recovery improves on crosslinking with resins. However, very little information is available on the effect of crosslinking on the torsional behaviour of cotton fibres. It has been reported that the shear modulus of cotton is enhanced by resin treatments and that it decreases as the humidity increases. In this work, however, measurements were made on very few fibres. It has been felt that a more thorough study of the effect of crosslinking on the torsional as well as tensile behaviour of cotton would lead to a better assessment of the technological value of these treatments. In the present work, tensile and torsional measurements were made before and after crosslinking with formaldehyde (HCHO) and dimethylol dihydroxyethyleneurea (DMDHEU). The effect of wetting the modified fibre has also been studied.

Experimental Procedure

Torsional pendulum—The torsional pendulum consists of a rod suspended by the experimental fibre, the other end of which is clamped to a rigid support. The period \( T \) of torsional oscillations of the fibre is governed by its torsional rigidity \( r \), defined as the torque required to produce one turn per unit length.
The two are related by the equation

$$\tau = \frac{8\pi^3 I I}{T^2}$$  \hspace{1cm} (1)

where $l$ is the length of the fibre; and $I$, the moment of inertia of the rod about the axis of suspension. The torsional rigidity can also be expressed in terms of the torsional modulus $(n)$ of the material as

$$\tau = \epsilon n A^2$$  \hspace{1cm} (2)

where $A$ is the area of cross-section of the fibre; and $\epsilon$, the shape factor, which, in the case of a fibre of circular cross-section, is equal to unity. From Eqs. (1) and (2),

$$n = \frac{8\pi^3 I I}{\epsilon (4\pi T)^2}$$  \hspace{1cm} (3)

In the present work, the rod was a piece of copper wire of 9.5 mm length and 1.0 mm cross-sectional diameter. The wire carried in its middle a thin metal strip to which one end of the fibre was attached with an adhesive. The combined moment of inertia of the wire together with the metal strip about the suspension axis was 0.0038 g-cm$^2$. The other end of the fibre was held by a clamp. The length of the fibre under torsion could be kept nearly constant for all the specimens by using a special mounting device. The actual length of the fibre was measured with the aid of a cathetometer after suspending the pendulum in an enclosure. The cathetometer was also used for viewing the motion of the rod during measurement of the period of oscillation. On account of damping due to internal friction, it was possible to observe only five successive oscillations at a time. Five sets of five oscillations each were timed for every fibre specimen to arrive at the mean period. This was done only after allowing the fibre to initially execute 20-30 oscillations so as to remove any possible effects of secondary creep. For each sample, 75 single fibres were tested for the period of oscillation.

Cross-sectional measurements—Fibre cross-sections were prepared by a procedure employing Hardy microtome with collodion as the embedding medium. For obtaining cross-sections in the wet state, the fibre bundle was immersed in water for 10 min, gently squeezed to remove the adhering water and then embedded in collodion. The sections cut with the microtome were irrigated with drops of water after being placed on a microscope slide. In this case, water acted as the mounting medium, while in the case of dry fibre cross-section, liquid paraffin was used. For estimating the cross-sectional area and shape factor, 100 fibre cross-sections were observed for each sample. The area and perimeter were measured by using planimeter and map measurer respectively. The shape factor was calculated using the formula

$$\epsilon = \frac{4\pi A}{P^2}$$

where $A$ is the area of cross-section; and $P$ its perimeter. Substituting the average value of the area of cross-section, shape factor and period of oscillation in Eq. (3), the rigidity modulus was calculated.

For determining the tensile modulus, single fibres were mounted with 1 cm test length on the Instron tensile tester. Each specimen was first subjected to cyclic extension between 0 and 2% of the initial length and the load-elongation curve was traced after it became reproducible. The tensile modulus was obtained from the slope of the initial part of the load-elongation curve.

Preparation of samples—Kier boiled and dewaxed cotton (Sujata) was subjected to a sequence of three mercerizations in the slack state. This treatment was carried out to enhance the accessibility, as well as to obtain fibres of high circularity which would render the results of torsional measurements more accurate. The thrice-mercerized fibre is hereafter referred to as the 'control' sample.

The crosslinking agents used were HCHO and DMDHEU. Treatment in HCHO was carried out by the Form W process at a concentration of 16% for two intervals, namely 3 min and 40 min. These two samples are hereafter referred to as 'HCHO (3 min)' and 'HCHO (40 min)'. With DMDHEU, the crosslinking was carried out at two concentrations, namely 18 and 25% by the conventional pad-dry-cure method. Though these concentrations are higher than the levels employed commercially for easy-care finishing of fabrics, they were so chosen as to effect drastic structural changes in the fibre. Crosslinking was carried out on samples in the fibre form, contrary to the usual practice, in which the treatment is done on a fabric and then fibres are carefully removed from the treated fabric. Although treatment of the fabric is very convenient, it can lead to heterogeneity in the degree of crosslinking among the constituent fibres. The heterogeneity could result from the inevitable differences in the wet pick-up of individual fibres after padding, as well as from the migration of resin during drying. For resin treatment on fibres, a fibre tuft of about 4 cm width, held at one end between a pair of jaws, was immersed in DMDHEU for 10 min. The tuft was carefully placed on the roller surface and dislodged from jaws before padding. To ensure homogeneity in wet pick-up among different fibres, it is necessary that the tuft is originally very uniform in thickness. Padding
was followed by drying at 80°C for 7 min and curing at 160°C for 3 min. The sample was mounted again on the jaws and later washed thoroughly with a mild detergent.

Bound formaldehyde was estimated by Roff's method, while nitrogen estimation in the case of DMDHEU-treated sample was made by the infrared method based on the absorbance of C=O band at 1710 cm\(^{-1}\). Use was made of a standard calibration graph showing the relationship between N\% obtained by chemical determination (Kjeldahl method) and absorbance at 1710 cm\(^{-1}\) of a range of samples prepared under standard conditions.

Results and Discussion

The results of tests carried out on the control (mercerized) and crosslinked fibres in both dry and wet states are summarized in Table 1. The confidence intervals are also indicated in the case of elasticity indices obtained in the dry state.

Cross-sectional area—The cross-sectional area increases on resin treatment, the increase being higher when the treatment is given under conditions in which crosslinking is expected to be severe. Wetting further increases the area (Table 1). It is interesting that HCHO-treated fibre swells considerably on wetting, while the DMDHEU-treated sample shows very little increase in the cross-sectional area. This is so because in the latter case, the reagent molecules are able to bridge adjacent lamellae, which are in a collapsed state when the treatment is carried out in the dry state. The formation of interlamellar linkage through DMDHEU molecules has been demonstrated by electron microscopy. The resin molecules linking the lamellae are thus able to inhibit distension of the fibre when it is subsequently wetted. In the case of HCHO treatment, which takes place under wet condition, only elementary fibrils and microfibrils are crosslinked and not the layers. Water molecules entering into such a structure can swell the fibre to a greater extent by pushing apart the unbridged layers, leading to a greater increase in the cross-sectional area.

Variability of data—The elasticity parameters, like other physical characteristics of cotton, show high dispersion among individual fibres. The values of CV\% for \(\tau\) were 24, 49, 48, 54 and 47 for the control and the four crosslinked samples in the order in which they appear in Table 1. The CV\% values for \(n\) were 31, 21, 25, 27 and 20. The CV\% is found to be generally much higher for \(\tau\) than for \(n\). The torque required for twisting a fibre is high for a fibre with large cross-sectional area and hence the variability of cross-sectional area among different fibres in the sample would lead to a large dispersion of the \(\tau\) values. On the other hand, the torsional modulus characterizes the fibre “structure” alone and is independent of the “form” of the fibre (Eq. 2) and hence the dispersion in its values is not influenced by the variability of cross-sectional area. While the CV\% of \(\tau\) for the control sample is lower than that (34) reported by Meredith, that of \(n\) is higher than the value (22) reported by him. It may be noted that Meredith’s data pertained to raw cotton and were based on measurement of only 10 fibres, whereas in the present work the control sample was mercerized cotton and 75 fibres were tested.

In Table 1, the 95% confidence limits have also been indicated for the elasticity parameters obtained in the dry state. These limits are obtained as ± \(t\sigma/\sqrt{n}\), where \(t = 2; n = 75\); and \(\sigma\) is the standard deviation.

In the case of tensile modulus, the CV\% values obtained in the present case were 47, 42, 42, 44 and

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Bound HCHO/ nitrogen content</th>
<th>Cross-sectional details</th>
<th>Torsional rigidity (\times 10^{12}) dynes/cm(^2)</th>
<th>Torsional modulus, (\times 10^{10}) dynes/cm(^2)</th>
<th>Tensile modulus, (\times 10^{10}) dynes/cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>—</td>
<td>163 219 1.3</td>
<td>3.19±0.02 1.37±0.18 1.37 0.57</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
</tr>
<tr>
<td>HCHO (3 min)</td>
<td>1.93</td>
<td>168 291 1.7</td>
<td>3.23±0.45 1.37±0.12 1.45 0.41</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
</tr>
<tr>
<td>HCHO (40 min)</td>
<td>2.65</td>
<td>174 273 1.6</td>
<td>3.01±0.43 1.37±0.12 1.38 0.35</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
</tr>
<tr>
<td>DMDHEU (18%)</td>
<td>1.5</td>
<td>203 265 1.3</td>
<td>3.53±0.50 1.02±0.16 1.59 0.39</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
</tr>
<tr>
<td>DMDHEU (25%)</td>
<td>2.6</td>
<td>283 318 1.1</td>
<td>5.34±0.72 0.79±0.10 2.39 0.25</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
<td>1.63±0.02 1.37±0.18 1.37 0.57</td>
</tr>
</tbody>
</table>
could, therefore, lead to increased torsional rigidity, fibres. The difference may perhaps be attributed to treated samples, showing that the structural rigidity while such a change may not take place in wet cross-

Torsional rigidity—Torsional rigidity has registered an increase on crosslinking with DMDHEU, while no such change seems to accompany HCHO treatment. The increase in torsional rigidity on DMDHEU treatment suggests that the fibre now requires a higher torque for a given amount of twist. This result is consistent with the microscopic observation referred to earlier that resin treatment in the dry state results in linkage between adjacent lamellae and that such a linkage fails to occur in the wet treatment. It is easy to imagine that in a cotton fibre, constituted as it is by a set of concentric cylindrical sheets of cellulose, the restoring torque is provided by forces linking adjacent layers. In the untreated fibre, these forces are provided by hydrogen bonds, while in the dry crosslinked fibre, the reagent crosslinks take their place, the latter being presumably stronger. Crosslinking in the dry state could, therefore, lead to increased torsional rigidity, while such a change may not take place in wet crosslinking (HCHO), which is essentially intralamellar.

Torsional modulus—The values of torsional modulus \( n_d \) given in Table 1 are lower than those reported by Peirce\(^1\) and Meredith\(^2\) for raw cotton fibres. The difference may perhaps be attributed to structural changes brought about by slack mercerization.

Crosslinking seems to result in a fall in the torsional modulus \( n_d \), though its effect is not evident with HCHO treatment. The reason for the fall in the value of \( n_d \) in spite of a pronounced increase in the value of \( r \) as with DMDHEU treated fibres apparently results from the fact that the reaction is accompanied by an increase in cross-sectional area. Thus, by virtue of the increase in cross-sectional dimension, the fibre appears 'softer', notwithstanding the increase in the number of valence linkages which would normally enhance the restoring torque in a twisted fibre.

The role of increase in cross-sectional area in bringing down the torsional modulus to a level below that of untreated fibre can be understood from the values of the modulus recalculated on the basis of the treated as well as the untreated fibre cross-sectional areas. Both these moduli (denoted by \( E_d \) and \( E_n \) respectively) are reduced by crosslinking treatments. It is significant that even after correction for the increase in area, the tensile modulus of the treated fibre is lower than that of the untreated fibre. The change in the value of tensile modulus thus shows a trend different from that found in the value of torsional modulus \( (n_d') \) which, as discussed earlier, either remains steady (HCHO) or registers an increase (DMDHEU) after crosslinking.

While literature\(^{28-30}\) contains a profusion of data establishing increase in tensile modulus with the degree of crosslinking in regenerated cellulosic fibres, very little information of this type is available in the case of cotton. Woo et al.\(^29\) observed a decrease in the value of this modulus when cotton was crosslinked with HCHO. No attempt was, however, made by these workers to explain the fall in the value of modulus, which appeared somewhat contrary to expectation. It would seem that any transverse link, either hydrogen bond or covalent crosslink between perfectly oriented molecular chains, would be subjected to only small strains during tensile deformation of the fibre, particularly at low extensions\(^{31-34}\). During torsion, on the other hand, the crosslinks disposed in the radical direction would be called upon to bear a considerable amount of stress. Thus, while the crosslinking reaction could bring about an increase in torsional rigidity and torsional modulus as found in the present study with DMDHEU resin in the conditioned state, the longitudinal modulus should remain unchanged or should show only a small increase. It has, however, not been possible to give an adequate explanation for the decrease in the value of this modulus when fibres are resin treated.

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References
2 Meredith R J Text Inst 45 (1954) T489.
4 Chamberlin N H & Khera M P J Text Inst 43 (1952) T123.
9 Skelton J J Text Inst 56 (1965) T443.
17 Chakrabarti B K Indian Text J 60 (1950) 310.
24 Tovey H Text Res J 31 (1961) 185.
33 Flory P J J Am chem Soc 78 (1956) 5222.
34 Flory P J Science 124 (1956) 53.