Mercerization and crimp formation in jute

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The mercerization effects of aqueous NaOH solution of varying concentrations on the isolated ultimate cells and the fibre strands of jute have been studied. It is observed that the treatment with higher concentration of alkali (12% and above) results in a decrease in crystallinity index and deterioration in overall molecular orientation along with the change in crystalline lattice from cellulose I to cellulose II. The changes in the supermolecular structure and morphology of cellulose in the ultimate cells appear to be mainly responsible for the development of crimp in jute. A qualitative mechanism for the three-dimensional crimp formation in jute has also been discussed in terms of rearrangement of internal molecular forces in cellulose on mercerization.

1 Introduction
The mercerization of jute fibre by treatment with strong aqueous sodium hydroxide solution at room temperature is a well-known process for the diversification of its end-uses. It has been reported that the mercerization of jute fibre is accompanied by loss in weight, longitudinal shrinkage, decrease in breaking strength and an increase in extension at break. The most important feature is the development of crimp in the fibre. An X-ray study has shown that there is a partial conversion of native cellulose I lattice to cellulose II. Jute differs from the pure cellulosic fibres like cotton and ramie in that it contains a considerable amount of non-cellulosic materials of which lignin and hemicellulose are the most important. The characteristic features of jute originate from these lignin and hemicellulose molecules which probably form some complex cross-bonding with the cellulose molecules. The fibre strand is multicellular and consists of ultimate cells (av. length, ~ 2 mm and av. width, ~ 20 µm) cemented together with non-cellulosic materials. It has been reported that in mercerized jute the ultimate cells shrink longitudinally and the cell wall thickness increases along with a decrease in lumen width. The development of crimp in fibre has been related by different workers to non-uniform dissolution of cementing materials, swelling of ultimate cells and differential shrinkage of cellulose I and cellulose II structures. In the present work, the effect of alkali of varying concentrations on both ultimate cells and fibre strands of jute has been studied in detail for a better understanding of mercerization and crimp formation.

2 Materials and Methods
2.1 Materials
Jute fibre strands of both capensis (JRC 212) and olitorius (JRO 632) varieties were taken from the middle portion of the reeds. The fibres were cleaned, suitably combed and then treated with various concentrations of aqueous NaOH solution at room temperature (~ 30°C) following the procedure described earlier. The treated samples were washed, air dried and used for the study.

The ultimate fibre cells of both the jute varieties were separated following the method described earlier. These isolated ultimate cells were then treated with different concentrations of alkali as described above. The treated ultimate cells were washed till free of alkali and then air dried or preserved in glycerol for further studies.

2.2 Methods
2.2.1 IR Studies
The IR spectra of the samples were measured by KBr disk technique using a Shimadzu IR 440 spectrophotometer following the procedure described earlier.

2.2.2 Measurement of Crimp Frequency
The crimp frequency in the fibre was measured following the procedure described earlier.

2.2.3 Measurement of Sonic Velocity in Fibre Strand
The sonic velocity measurements were carried out...
using a dynamic modulus tester (PPM-5). From the slope of spacing between the transducers versus transit time curves the sonic velocity \( (c) \) was calculated. Ten fibres were taken for each sample and for each fibre, the average of ten slopes was determined. The dynamic modulus \( E \) in g/den was calculated by the following equation:
\[
E = 11.3 \, c^2
\]
where \( c \) is the sonic velocity in km/s.

2.2.4 Measurement of Cell Dimensions
Cell width, lumen width and length of the ultimate cells were measured using a projection microscope as described elsewhere\(^8\)\(^-\)\(^10\).

2.2.5 SEM Studies
Fibres and ultimate cells were mounted on the aluminium stubs using a conducting adhesive tape and then coated with a thin silver film (~200 \( \AA \) thickness) in a vacuum coating unit. These samples were observed on a Hitachi scanning electron microscope (model S430) and representative photographs were taken.

3 Results and Discussion
Figs 1 and 2 show respectively the variations in the absorbance of the IR bands near 895 cm\(^{-1}\) (\( \beta \)-linkage) and 1425 cm\(^{-1}\) (CH\(_2\) symmetrical deformation), measured as a ratio to CH stretching band near 2900 cm\(^{-1}\) with the concentration of alkali. These bands are sensitive to the change in lattice from cellulose I to cellulose II. It is seen that though the absorbance values of ultimate cells and fibre strands of jute differ quantitatively, the nature of variation is similar in both the cases. The quantitative difference in the absorbance values may be attributed to the non-cellulosic constituents such as lignin and hemicellulose present in the jute fibre strand. However, it is observed that the major change in the absorbance of these bands occurs above 12% of NaOH concentration. Table 1 shows the change in IR crystallinity index of the ultimate cells and fibre strands with the alkali concentration. The crystallinity index (C.I.) was calculated by the absorbance ratios \( a_{1425} \) cm\(^{-1}/a_{2900} \) cm\(^{-1}\) (O’Connor et al.\(^14\)) and \( a_{1370} \) cm\(^{-1}/a_{2900} \) cm\(^{-1}\) (Nelson and O’Connor\(^13\)). Nelson and O’Connor argued\(^15\) that the absorbance ratio \( a_{1370} \) cm\(^{-1}/a_{2900} \) cm\(^{-1}\) can be applied to both cellulose I and cellulose II and also to samples containing mixed lattice as the band near 1370 cm\(^{-1}\) (CH bending vibrations) depends on the crystallinity and not on the lattice type. However, in jute fibre, both cellulose and xylan may contribute to this band\(^6\). It is interesting to observe that the C.I. value is lower in the case of fibre strands compared to that in case of ultimate cells (Table 1). This may be due to the presence of non-cellulosic constituents like lignin and hemicellulose in the fibre strands. For both ultimate cells and fibre strands of jute, the C.I. value decreases with the increase in alkali concentration. The decrease in C.I. value appears to be associated with the change in crystalline lattice from cellulose I to cellulose II as observed above (Figs 1 and 2).

Table 1—Infrared crystallinity index of alkali-treated jute

<table>
<thead>
<tr>
<th>NaOH conc. %</th>
<th>IR crystallinity index</th>
<th>Crimp frequency No./cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultimate cells</td>
<td>Fibre strands</td>
</tr>
<tr>
<td>a(<em>{1370}) cm(^{-1})/a(</em>{2900}) cm(^{-1})</td>
<td>a(<em>{1425}) cm(^{-1})/a(</em>{2900}) cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.570</td>
<td>1.712</td>
</tr>
<tr>
<td>8</td>
<td>0.572</td>
<td>1.761</td>
</tr>
<tr>
<td>10</td>
<td>0.574</td>
<td>1.735</td>
</tr>
<tr>
<td>12</td>
<td>0.516</td>
<td>1.539</td>
</tr>
<tr>
<td>14</td>
<td>0.512</td>
<td>0.848</td>
</tr>
<tr>
<td>16</td>
<td>0.504</td>
<td>0.743</td>
</tr>
<tr>
<td>18</td>
<td>0.504</td>
<td>0.717</td>
</tr>
</tbody>
</table>

Table 1 further shows that there is practically no crimp in the fibre below 12% NaOH treatment, but the
crimp frequency increases with the further increase in NaOH concentration. It is evident from the IR spectra of ultimate cells (Fig. 3) that the hydroxyl band reduces and shifts slightly towards higher wave number on mercerization. This apparently indicates weakening or breaking of some hydrogen bonds.

Table 2 shows that the sonic velocity and dynamic modulus values are slightly higher for *olitorius* variety compared to that for *capsularis* variety. The sonic velocity in fibres is related to the state of overall molecular orientation with respect to fibre axis. The considerable decrease in both sonic velocity and dynamic modulus at higher NaOH concentrations (18% and 25%) indicates the overall disorientation of molecular chains on mercerization. The marginal decrease in sonic velocity at lower NaOH concentration (8%) may be due to the disorientation of molecular chains as a result of intercrystalline swelling.

The dimensional changes in the ultimate cells of both *capsularis* and *olitorius* jute with increasing concentration of alkali are shown in Table 3. The cell length and the lumen width decrease while the cell wall thickness increases with the increase in alkali concentration as expected. Table 3 also shows a decrease in the cell width at the lower NaOH concentration (8%). This may be due to the dissolution of nitrogenous solid residues often present within the lumen.

### Table 2—Sonic velocity (c) and dynamic modulus (E) in alkali-treated jute fibres

<table>
<thead>
<tr>
<th>NaOH conc.</th>
<th><em>capsularis</em> jute</th>
<th><em>olitorius</em> jute</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>c, km/s</td>
<td>E, g/den</td>
</tr>
<tr>
<td>0</td>
<td>5.05</td>
<td>288.18</td>
</tr>
<tr>
<td>8</td>
<td>4.27</td>
<td>260.03</td>
</tr>
<tr>
<td>18</td>
<td>3.21</td>
<td>116.44</td>
</tr>
<tr>
<td>25</td>
<td>2.76</td>
<td>86.08</td>
</tr>
</tbody>
</table>

### Table 3—Dimensions of alkali-treated ultimate cells of jute

<table>
<thead>
<tr>
<th>Jute sample</th>
<th>NaOH conc.</th>
<th>Cell length</th>
<th>Cell width</th>
<th>Lumen width</th>
<th>Cell wall thickness</th>
<th>Change in cell length</th>
<th>Change in cell wall thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>capsularis</em> variety</td>
<td>0</td>
<td>1.98</td>
<td>15.2</td>
<td>3.0</td>
<td>6.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.80</td>
<td>14.9</td>
<td>2.3</td>
<td>6.3</td>
<td>-9.1</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>1.68</td>
<td>15.9</td>
<td>1.5</td>
<td>7.2</td>
<td>-15.2</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.60</td>
<td>15.6</td>
<td>1.2</td>
<td>7.2</td>
<td>-19.2</td>
<td>18.0</td>
</tr>
<tr>
<td><em>olitorius</em> variety</td>
<td>0</td>
<td>1.95</td>
<td>16.0</td>
<td>3.8</td>
<td>6.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.85</td>
<td>15.3</td>
<td>3.0</td>
<td>6.2</td>
<td>-5.1</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>1.73</td>
<td>15.9</td>
<td>1.7</td>
<td>7.1</td>
<td>-11.3</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.63</td>
<td>15.7</td>
<td>1.6</td>
<td>7.1</td>
<td>-16.4</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Fig. 3—IR spectra of ultimate cells of jute showing change in the hydroxyl band on mercerization [(a) raw, and (b) mercerized]
depicted. This is evidently due to removal of some non-cellulosic constituents by the action of alkali. Fig. 4b also shows that the dissolution of cementing materials between the ultimate cells is non-uniform. Fig. 5 shows the surface topography of untreated and mercerized jute fibres at higher magnification. The mercerized jute fibre shows less surface debris and more clear fibrillar structure as compared to untreated fibre. It also shows less compact structure of fibrils as compared to untreated fibre, probably due to swelling.

The isolated ultimate cells before and after mercerization treatment are shown in Figs 6a and 6b respectively. The untreated cells are mostly straight in nature.
with the tapered ends. However, mercerized ultimate cells are mostly curved in nature. This crimped nature of the mercerized ultimate cells indicates that the formation of crimp in jute is mainly associated with the swelling of cellulose\(^{11}\). The fibrillar structure of untreated and mercerized ultimate cells at higher magnification is shown in Figs 7a and 7b respectively. As expected, the fibrillar structure is more clear in ultimate cells as compared to that in fibres. In the untreated ultimate cells, the fibrillar structure consists mostly of straight fibrils running along the fibre axis while in the mercerized ultimate cells it is comparatively distorted. It may be noted that cellulose II is thermodynamically more favoured structure than native cellulose I (ref. 11). Stockmann\(^{16,19}\) reported that elementary fibrils have built-in stresses in native cellulose. As
Cellulose Chain

Longitudinal force due to relaxation of stress

Twisting force due to conformational change

Transverse force due to swelling

Fig. 8—Internal molecular forces in cellulose on intracrystalline swelling and conversion from cellulose I to cellulose II

discussed above, the intracrystalline swelling due to NaOH causes a reduction in the interaction between the adjacent cellulose chains. Thus, the relaxation of stresses and the disorientation of molecular chains may cause the longitudinal shrinkage of fibrils. Further, during conversion from cellulose I to cellulose II, the chain conformation is reported\textsuperscript{20,21} to change from the bent (cellulose I) to the bent and twisted form (cellulose II). These changes in internal forces may produce a supermolecular texture, leading to the distorted fibrillar structure as observed above.

It may be concluded from the above observations that the intracrystalline swelling of cellulose and the change in lattice from cellulose I to cellulose II seem to be the essential prerequisites for the formation of crimp. Swelling and change in lattice from cellulose I to cellulose II may cause a rearrangement of internal molecular forces as shown in Fig. 8. These forces mainly include the longitudinal forces due to stress-relaxation and shrinkage, twisting forces due to change in conformation of molecules and the transverse forces due to change in lateral packing of chain molecules. The above rearrangement of molecular forces together with the differential transverse swelling\textsuperscript{10} of cell wall due to the variation in cell wall thickness along the length of the ultimate cell may lead to the development of a three-dimensional crimp in jute. Moreover, in partially crystalline jute, shrinkage will be more prominent in the amorphous regions than in the comparatively rigid crystalline regions of cellulose. Thus, a lower crystallinity and smaller crystallite size in the cellulose structure of jute may lead to a better crimp curvature.

4 Conclusions
Mercerization and crimp formation in multicellular jute fibre depend essentially on the change in supermolecular structure and morphology of cellulose in the ultimate cells. The alkali of concentration below 12% affects mainly the non-cellulosic constituents adhering to the ultimate cells and may cause intercrystalline swelling of cellulose structure without developing any crimp. At higher concentrations, alkali penetrates the crystalline structure of cellulose, resulting in the change in lattice from cellulose I to cellulose II, decrease in the crystallinity, deterioration in overall molecular orientation and development of crimp in fibre. The IR crystallinity index decreases and crimp frequency increases with the increase in alkali concentration. The development of three-dimensional crimp in jute may be attributed mainly to the rearrangement of internal molecular forces which is caused by longitudinal shrinkage due to stress relaxation and molecular disorientation, twisting of chain molecules due to change in conformation on conversion from cellulose I to cellulose II, and the transverse forces due to the change in the lateral packing of molecular chains. In the partially crystalline cellulose structure of jute, a low crystallinity along with the change in lattice from cellulose I to cellulose II may give better crimp curvature or frequency.

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References
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