Chemical and Chemi-mechanical Processes for Degumming of Ramie Fibre and Their Characterization by XRD, FT-IR and Microscopic Methods

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Decorticated Ramie collected from Ramie Research Station, Sorhorg, Assam, India were degummed, using both chemical and chemi-mechanical processes. Microstructural and morphological properties of these degummed fibres were studied by XRD, FT-IR and microscopic methods. The crystallinity percentages were found to be 28 and 27 per cent for the samples chemically treated (M), and chemi-mechanically treated (M1), respectively. The crystallite sizes were found to be increased in the directions normal to both (002) and (040) reflection planes for the samples M and M1 from that of decorticated ramie without treatment (R). Results indicate that these degummed fibres are suitable for use as a raw material for fibre and pulp-paper industries.

Introduction

Ramie (Boehmeria nivea) locally in Assam known as Reha. indigenous to China, Indonesia, and India is an important fibre yielding plant. Although it is cultivated as source of fibre since ancient time, it remains a comparatively underdeveloped crop because of non-availability of high-yielding varieties, improved agronomic practices, pest and disease management and efficient fibre extracting machine. This fibre, on the other hand, cannot be retted like jute, and mesta by ordinary water retting because of gum content adhering in the plants1. Variations of ramie in the decorticated state contain gum that may vary from 19 to 30 per cent of the weight of the dry fibre2,3. The physical properties of the fibres at various states of degumming have been studied2-4. Thus, degumming of ramie fibre is important. Some significant studies on degumming of ramie fibre have been carried out in this laboratory using chemical and chemi-mechanical processes. The study describes the chemical and chemi-mechanical processes for degumming of ramie fibres and their evaluation using XRD, FT-IR, and microscopic techniques.

Materials and Methods

Ramie plants were collected from Ramie Research Station, Sorhorg, Assam, India. The stem portion after removing the leaves and roots were used. The material was kept 1h in water at room temperature (25 ± 2 °C) and then cleaned. The upper portion of the cortex was removed and decorticated materials thus obtained were combed along the axis of the fibre with sharp teeth of plastic comb (sample-R). Table I shows different two selective experimental conditions for chemical and chemi-mechanical processes used for degumming the fibre. The sample (M) was prepared from raw ramie fibre (R) using 2 per cent sodium carbonate solution with 0.2 per cent non-ionic surfactant as cooking chemical and heated for 3h at 100 ± 5 °C. The materials thus obtained was washed with water to remove the adhering chemicals. The fibre was then bleached with hot peroxide solution at 70 °C for one and a half h. It was washed and used for the study. The fibre sample (M1) was prepared from the raw ramie fibre(R). The fibre thus obtained was soften with boiling water for 2 h and passed through iron rollers twice so as to flatten the materials. The fibre was then treated in a solution of 0.3 per cent non-ionic surfactant containing 10 per cent peroxide (at pH 10-12 for 24 h at 25 ± 2 °C). The fibre sample was washed and used for study.

Fibre Morphology

The length (L), diam (D) and wall thickness (W) of degummed fibres were determined under a
Table 1 — Experimental conditions for degumming the ramie fibres

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Soften with H2O</th>
<th>Chemically treated</th>
<th>Temperature, °C</th>
<th>Time, h</th>
<th>Bleaching</th>
<th>Mechanically treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>No</td>
<td>Yes</td>
<td>100 ± 5</td>
<td>3</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>M1</td>
<td>Yes</td>
<td>Yes</td>
<td>25 ± 2</td>
<td>24</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Dokural photomicroscope (JEOL, Japan) at different magnifications.

**XRD Study**

**Determination of Cristallinity**

The degree of crystallinity ($Kc$) was determined from the ratio of the integrated crystalline scattering to the total scattering, both crystalline and amorphous, and is given by:

$$Kc = S^2 l_c(S) ds / S^2 l(S) ds,$$

... (1)

Crystallinity per cent = $Kc$ x 100,

where $l(S)$ is the intensity of coherent x-ray scattered from a specimen (both crystalline and amorphous); $l_c(S)$, the intensity of coherent x-ray scattered from the crystalline region; and $S$, the magnitude of the reciprocal lattice vector and is given by:

$$S = (2 \sin \theta) / \lambda,$$

... (2)

where $\theta$ is one-half of the angle of deviation of the diffracted rays from the incident x-ray and, $\lambda$ the x-ray wavelength.

**Determination of Crystallite Size**

The mean crystallite size of a powder compound of relatively perfect crystalline particles can be determined with the familiar Scherrer equation:

$$L = K \lambda / \beta \cos \theta,$$

... (3)

where $\lambda$ is X-ray wavelength, $\theta$ is half the peaks of diffraction angle, $L$ is crystallite size, $\beta$ is the breadth of the pure diffraction profile on the scale in radians, $K$ is constant ($=0.89$). Crystallite sizes were calculated in the directions normal to the (002) and (040) reflection planes. The instrumental broadening was determined using the calibration curve method given elsewhere. Both, Cauchy and Gaussian methods were used for correcting the experimental reflection profiles for instrumental broadening as given below:

**Cauchy profile:**

$$\beta = B - b,$$

**Gaussian profile:**

$$\beta^2 = B^2 - b^2,$$

where $B$ = The breadth of experimental profile, $b$ = The breadth of instrumental line broadening, and $\beta$ = The integral breadth of pure line profile.

X-ray diffraction data were collected using a computer controlled x-ray diffractometer (Type JDX-11P3A, JEOL, Japan) with pulse-height analyzer and scintillation counter with scintillator NaI(Tl) single crystal. The measurements were made by the reflection technique using high-precision vertical type goniometer model DX-GE-2PC which can stably hold the specimen holder surface horizontally allowing measure of micro-volume specimens. The samples were rotated to record X-ray diffraction intensities from various lattice planes -(002), (040) etc.

**Determination of Crystallinity by IR Method**

Degree of crystallinity ($Kc$) from IR spectrometric measurement was calculated from the following relationship:

$$Kc = Ac/Aa,$$

... (4)

where $Aa$ and $Ac$ are absorbance at a given frequency ($cm^{-1}$). The absorbance $A$ was calculated according to the Beer-Lambert Law:

$$A = \log (I_o / I),$$

... (5)

where $I_o$ is the intensity of the incident IR radiation and $I$ is the IR radiation transmitted through the sample. IR spectra were recorded on Perkin Elmer IR spectrometer (237-B) in KBr discs.

**Results and Discussion**

The gum content of the sample (R) was found to be varied from 22-27 per cent. After degumming it was found to be 4-5 per cent for M and 5-6 per cent...
for M1. Thus the gum can be removed 81 per cent for M and 77 per cent for M1. Table 2 shows the characteristic morphological properties of chemically (M) and chemi-mechanically (M1) degummed ramie fibres. The data were statistically analysed. The average length (143 mm) of chemi-mechanically degummed fibres (M1) were found to be greater than those of chemically treated fibres (M). The flexibility coefficient, rankel ratio and slender ratio for M1 were found to be 34.33, 0.87, and 2750, respectively, while these values were 46.1, 0.58, and 2750, respectively, for M. Thus the flexibility coefficient in the case of M1 was found to be lower than that of M but rankel ratio and slender ratio were significantly higher than M. The ratio of cell wall thickness to lumen width, as well as ratio of cell wall thickness to fibre width for M1, were found to be significantly higher value than that of M.

X-ray diffraction and IR patterns are shown in Figure 1 and 2. Table 3 gives the d-spacings and crystallinity data, as determined by X-ray and IR methods, and Table 4 shows crystallite size and number of unit cells of the samples M, M1, and R. The XRD patterns were compared with that of native cellulose with unit cell dimensions \(a = 8.35\), \(b = 10.28\), \(c = 7.96\), \(\beta = 78^\circ\) and system monoclinic.\(^8\) The X-ray diffraction patterns indicate that the fibre was a typically native cellulose consisting of both crystalline and amorphous phases in ratio 7:18 for M, 3:8 for M1 and 1:3 for R. The percentages of crystallinity of the fibres were found to be higher values for both M and M1 compared with that of R, which is, however, supported by crystallinity index as obtained by IR method. The crystallite sizes and number of unit cells in the directions normal to both (002) and (040) reflection planes were determined for their quantitative comparison. The crystallite sizes in the directions normal to both (002) and (040) reflection planes were found to be higher values for both M and M1 than that of R. It is, however, much more significant for M1 in the direction normal to the (040) reflection plane. However, it may be mentioned that the main portion of the gum removed from ramie fiber is of the nature of glucan, a polysaccharide, and the association of the gum with the crystalline structure would be expected to change the dimension of the crystalline repeating unit.\(^9\) As the removable

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### Table 2—Morphological properties of ramie fibre

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fibre length, (L, \text{mm})</th>
<th>Diam. mm</th>
<th>(\frac{\text{Ratio of cell wall thickness to fibre width, } W}{\text{cell wall thickness to lumen width}})</th>
<th>Flexibility coefficient</th>
<th>Rankel ratio</th>
<th>Length/width ratio (L/W) (Slenderness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>110</td>
<td>0.04</td>
<td>0.54</td>
<td>0.57</td>
<td>46.1</td>
<td>0.58</td>
</tr>
<tr>
<td>M1</td>
<td>143</td>
<td>0.04</td>
<td>0.65</td>
<td>0.93</td>
<td>34.33</td>
<td>0.87</td>
</tr>
<tr>
<td>R</td>
<td>145</td>
<td>0.05</td>
<td>0.60</td>
<td>0.76</td>
<td>33.30</td>
<td>0.90</td>
</tr>
</tbody>
</table>
gum resides in the amorphous region and does not take part in the formation of the crystalline regions, the gum by its presence restricts the alignment of the chain molecules and this gives rise to strains in the crystalline regions\(^3\). On removal of the gum, the restrictive force being withdrawn, the molecular chains are free to rearrange. In the process, the crystallites are apt to increase their lateral size. It may be noted that there are reasons to suppose that the Gaussian form is more appropriate for broad profile and Cauchy form for narrow ones. Polymers reflection profiles, in general, are nearly always broad so that the pure Gaussian assumption is applicable\(^10\).

Cellulose has a high degree of molecular cohesion and it absorbs gases, liquids, and solids. The decrease in the crystallinity of cellulose is, however, accompanied by increased elongation, increased moisture regain and increased chemical reactivity\(^11\). Cellulose, having the highest percentage of amorphous material, exhibits maximum swelling, since water preferentially enters the amorphous regions. Thus, it can be inferred that the chemically treated fibre (M) has less swelling effect than that of chemi-mechanically treated (M1) and raw fibre (R).

Also, crystallite size and crystal perfection effect the total percentage of the hydroxylic lie in the crystal surface. It increases with decreasing crystallite size and decreasing crystal perfection of crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X-ray powder diffraction data (d spacings in Å)</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>5.948(28); 5.35 (24); 4.303 (17); 3.594 (100); 2.638 (5); 2.579(4)</td>
<td>28; 0.792</td>
</tr>
<tr>
<td>M1</td>
<td>5.929(8); 5.375(19); 4.314(25); 3.877 (100); 2.649 (4); 2.576 (13)</td>
<td>27; 0.647</td>
</tr>
<tr>
<td>R</td>
<td>5.948(17); 5.359(22); 4.314 (30); 3.885(100); 2.649(11); 2.572 (13)</td>
<td>25; 0.539</td>
</tr>
</tbody>
</table>

* Compared with the data JCPDS Card No. 3-2089, b The figures in parenthesis indicate relative intensity

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Crystallite sizes in 002 and 040 plane direction as determined from XRD patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>002 – plane direction</td>
</tr>
<tr>
<td></td>
<td>Cauchy correction</td>
</tr>
<tr>
<td>M</td>
<td>50.09 (7)*</td>
</tr>
<tr>
<td>M1</td>
<td>48.70 (6)</td>
</tr>
<tr>
<td>R</td>
<td>41.63 (5)</td>
</tr>
</tbody>
</table>

* The figures in parenthesis indicate the number of unit cells
From X-ray results, it can be inferred that the chemically treated fibre (M) has higher moisture sorption capacity in the direction normal to the (040) reflection plane than that of chemi-mechanically treated fibre (M1). As the crystallinity data obtained from these degummed ramie fibres are comparable to those of Populus Deltoids, wood pulp fibres, these degummed ramie fibres are likely to be commercially useful for fibre and pulp-paper industries.

**Conclusion**

The crystallinity percentage were found to be 28, 27 and 25 per cent respectively for the ramie samples chemically treated (M), chemi-mechanically treated (M1) and without treatment (R), respectively. The crystallite sizes were found to be increased in the directions normal to both (002) and (040) reflection planes for the samples M and M1 from that of R. In the direction normal to the (040) reflection plane the chemi-mechanically process is found to be more effective in changing the crystallite size, while it is less effective in the direction normal to the (002) reflection plane. Thus, both the chemically and chemi-mechanically degumming processes were found to be effective on microstructure of degummed ramie fibre. Results indicate that these degummed fibres are suitable for use as a raw material for fibre and pulp-paper industries.

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**References**