CHAPTER 3

MEASUREMENT OF DEGREE OF CRYSTALLINITY AND CRYSTALLITE ORIENTATION

INTRODUCTION

Meaning of Crystallinity:

Electron microscopic work has made it clear that the cotton fibre is made up of layers or growth rings and that each growth ring is composed of an array of spiralling fibrils. The spectrum of physical and chemical properties exhibited by the cotton fibre leads one to infer that in places, the fibrils are highly ordered arrangements of chain molecules, whereas, elsewhere, they may "fringe" or branch out into sub-fibrils or individual chains. In this process, they may lose all vestiges of lateral order or crystallinity. The term "degree of crystallinity" or just "crystallinity" is used in this thesis to denote the fraction of the fibrous material which is organized with sufficient lateral order to be termed "crystalline" according to X-ray diffraction or some other criterion. Strictly speaking, the highly ordered region should be termed "paracrystalline" rather than crystalline. This is because, apart from limitations in the dimensions of such regions, there are also likely to be distortions which disturb short-range as well as long-range order. In particular, strong thermal distortions are likely in a structure which is held together by covalent bonds only in one direction. Mass order distribution curves\(^{(1)}\) indicate that natural cellulose has essentially a bimodal spectrum of order. It
is therefore assumed as a simplification for purposes of X-ray analysis that there are only two types of order, namely crystalline and amorphous. The X-ray diffraction pattern of cotton should therefore be quantitatively explained in terms of two-phase model of micro-crystallites embedded in an amorphous matrix of cellulose chain molecules. The chemical methods of estimating proportions of ordered disordered structure also give similar results. The portion of the fibrous material which is "non-accessible" to the chemical used is analogous to the "crystalline" fraction. The proportion of such "non-accessible" part will obviously depend on the chemical used and hence the degree of crystallinity thus obtained from chemical methods is quite arbitrary in nature. The X-ray diffraction technique based on two-phase theory is also somewhat arbitrary. Nevertheless, it is a widely acknowledged method and has been used in the present investigations.

Molecular Orientation:

In fibres, the crystallites or in general the chain molecules are not aligned exactly parallel to the fibre-axis. The overall orientation of the molecules has a marked influence on the physical properties of fibres. For example, it gives rise to optical anisotropy or birefringence. The ratio of the birefringence of the fibre to that of the ideal fibre of the same density, in which all chain molecules are aligned parallel to the fibre-axis, is called the "optical orientation factor" (generally denoted by $I_0$). It is an index obtained from
"crystalline" as well as less ordered regions in the fibre. The "crystallite orientation factor" or "X-ray orientation factor" (generally denoted by $f_X$) is related to the effective orientation of "crystallites" alone, with respect to the fibre-axis. In the present work "crystallite orientation factor", obtained by using standard X-ray diffraction techniques, is used as a rough measure of "orientation".

The work presented in this chapter is based on experimental techniques and theoretical methodology developed in this Laboratory and elsewhere. No originality is claimed either in regard to techniques or results. However, the parameters of fine structure obtained by X-ray methods will be constantly used as a background to the discussions of mechanical properties.

PART I

MEASUREMENT OF CRYSTALLINITY

The crystalline nature of the cellulose fibres was established as early as 1913, by using X-ray diffraction techniques. Since then various methods have been used to determine the degree of crystallinity in high polymers. Detailed reviews have been published by Krimm and Tolansky, Nichols, and Ellefson et al. In all these methods the basic assumption is that the "sharp" X-ray diffraction peaks are due to the crystalline or say well ordered regions.
METHOD USED IN THE PRESENT INVESTIGATIONS

The method employed in the present thesis is based on work done in our Laboratory and is fully described elsewhere\(^{(6-10)}\).

For the sake of completeness, it is summarised as follows:

It is assumed that cellulose can be prepared as purely crystalline cellulose I (by acid hydrolysis of purified cotton fibres in 1N HCl for 24 hours at 60° C) and in purely amorphous form (by prolonged dry ball-milling). Let C and A be the diffracting powers of unit masses of these standards at a common angle \(2\theta\), while S is the diffracting power of a sample of intermediate crystallinity. It is assumed that we can express S as a linear combination of C and A in properly weighted proportions:

\[
S = fC + (1 - f)A \\
\text{i.e. } (S - A) = f(C - A)
\]

By taking the diffractograms of the materials, it is possible to get a large number of pairs of observations \((S - A), (C - A)\) for different values of \(2\theta\). The regression equation of \((S - A)\) on \((C - A)\) will give a good estimate of \(f\), which is called the degree of crystallinity\(^{(10)}\).

The method can be extended to cases like mercerized cotton, where the lattices of both cellulose I and II are present\(^{(6)}\). There are several factors which may affect determinations of
crystallinity by this method. Some of these factors are corrections of various types and another, more important, factor is the degree of approach of the experimental "crystalline standard" to a truly microcrystalline powder of cellulose. On this last account, the values of "degree of crystallinity" obtained by the present method may lose their absolute significance, as is indeed the case with all methods available hitherto. Nevertheless, the values are still very useful as comparative measures between different samples of swollen cotton.

EXPERIMENTAL TECHNIQUES

(a) Instrumental:

The instrument used to record the diffracted X-ray intensities was a standard Philips diffractometer of the focussing reflection type. This diffractometer was used in conjunction with a Philips stabilized-current X-ray generator having a conventional normal focus X-ray tube with copper target.

(b) Crystallinity determinations:

About 115 mg. of the fibre sample was cut with a pair of sharp scissors until it was reduced to a fine powder. This powder was packed into a rectangular space (2 x 1 x 0.1 cm) in the specimen holder and compressed into a slab. The specimen holder with the slab of cellulose material was then mounted in place on the diffractometer so that at any inclination of the specimen holder, only the cellulose was in the X-ray beam.

The angular range over which most of the wide angle X-ray
diffraction occurs is from $2\theta = 10^\circ$ to $40^\circ$. Accordingly, intensities were recorded over this region at suitable intervals. In all the cases, the counts were measured for one minute. These were then corrected for the cosmic ray background by subtraction after correcting for count losses due to the dead time of the counter. The dead time correction was by means of the formula:

$$N_a = \frac{N_0}{1 - N_0 T}$$  \hspace{1cm} (3)

where $N_a$ and $N_0$ are the actual and observed counts per second respectively and $T$ is the dead time of the counter in seconds. (In this case $T = 180 \mu\text{sec.}$). The corrected intensity data were then normalized so that the areas under the intensity curves between the angles $2\theta = 10^\circ$ to $40^\circ$ were the same for all samples (standards as well as treated and untreated samples). These corrected and normalized intensity data were then used for estimating degree of crystallinities by eq. (2).

PART II
MEASUREMENT OF CRYSTALLITE ORIENTATION

Sisson and Clark\textsuperscript{(12)} were the first to develop and apply the X-ray method for the quantitative estimation of orientation of crystallites in cellulose fibres. The method used by them was based on the assumption that the intensity distribution of the equatorial arcs is related to the orientation of the crystallites with respect to the fibre-axis. The intensity distribution was
measured using micro-densitometer. Various methods were used (13, 14, 15) to determine the orientation in terms of intensities along the equatorial arcs. Segal et. al. (16) were the first to use a Geiger counter to measure the aximuthal intensity distribution of the diffracted X-ray beam. Similar methods were used by some other workers (17, 18) also. Many empirical parameters have been used (12, 13, 14, 16, 18, 19, 20, 21) to describe quantitatively the crystallite orientation in fibres. These methods include the method of "half maximum angle" (18, 19, 20).

METHOD USED IN THE PRESENT INVESTIGATIONS

The orientation factor $f_\theta$, as defined by Hermans (21) was evaluated by an analysis of the aximuthal intensity distribution of equatorial reflections from fibres (22). The relevant formulae are:

$$f_\theta = 1 - 3 \sin^2 \delta$$

(4)

for fibres having cellulose I lattice, and

$$f_\theta = 1 - 3/2 \left( \sin^2 \beta + \sin^2 \gamma \right)$$

(5)

for fibres having cellulose II lattice.

Where generally

$$\sin^2 \theta = \int_{\pi/2}^{\pi/2} I(\theta) \cos \theta \cdot \sin^2 \theta \, d\theta$$

(6)
In eq. (6), $I(\tilde{\delta})$, $I(\tilde{\beta})$, and $I(\tilde{\gamma})$ refer to the corrected intensity as a function of the azimuthal angle for the (002), (103) and (101) reflections respectively.

EXPERIMENTAL TECHNIQUES

The experimental techniques and other details are described by Badhakrishnan et al. (23). However, they are briefly given as follows:

A parallel bundle of fibres was fixed on a specimen holder prepared specially for this purpose. This bundle was rotated very slowly (one revolution per hour) around the incident well collimated X-ray beam as the axis. The diffracted beam was detected by a Geiger counter tube. The output from the counter was fed to the commercial Philips X-ray diffractometer. Thus automatic scans of the $I(\tilde{\delta})$, $I(\tilde{\beta})$ and $I(\tilde{\gamma})$ were recorded. The recorded scans were smoothed out and a visually estimated background was subtracted at each azimuthal angle. The corrected intensities were used to evaluate the orientation factor $f_x$. The integrals such as given by eq. (6) were evaluated numerically by Simpson's rule.

RESULTS AND DISCUSSIONS

The crystallinities and crystallite orientation factors (sometimes called X-ray orientation factor) of all the samples are given in Table I. The effect of swelling and stretching treatments on crystallite orientation factor ($f_x$) is shown in Fig. 1. Swelling even without stretch generally appears to increase the orientation of
<table>
<thead>
<tr>
<th>Swelling Conditions (Symbols used in graph)</th>
<th>Stretch</th>
<th>X-ray parameters</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Karnak Dewaxed (N)</td>
<td>-</td>
<td></td>
<td>68</td>
<td>0.70</td>
</tr>
<tr>
<td>Karnak Cotton swollen in NaOH 24%, 27°C, 1 hour (N)</td>
<td>- 15.0</td>
<td>50</td>
<td>46</td>
<td>0.71</td>
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<td></td>
<td>+ 5.0</td>
<td>64</td>
<td>53</td>
<td>0.88</td>
</tr>
<tr>
<td>Karnak Cotton swollen in EDA 78%, 27°C, 1 hour (E)</td>
<td>- 4.0</td>
<td>44</td>
<td></td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>+ 5.0</td>
<td>49</td>
<td></td>
<td>0.80</td>
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<tr>
<td>Karnak Cotton swollen in ZnCl₂ 65%, 35°C, 45 minutes (Z₁)</td>
<td>0.0</td>
<td>22</td>
<td></td>
<td>0.92</td>
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<tr>
<td></td>
<td>+ 3.5</td>
<td>26</td>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td>Karnak Cotton swollen in ZnCl₂ 65%, 35°C, 15 minutes (Z₂)</td>
<td>-</td>
<td>56</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>+ 3.5</td>
<td>51</td>
<td></td>
<td>0.77</td>
</tr>
</tbody>
</table>
FIG. 1. EFFECT OF STRETCH ON X-RAY ORIENTATION FACTOR
the fibre, probably on account of deconvolution effects. The increase is more when stretch is applied to the fibre in the presence of the swelling agent, as is to be expected. The extent of increase also seems to be dependent on the nature of the swelling agent and the conditions of swelling. In the case of swelling in ZnCl₂, there seems to be some saturation in orientation at stretches beyond the original length (0.0% stretch). Crystallinity, on the other hand, is generally lowered by these swelling agents. With each swelling agent, an increase of stretch appears to increase somewhat the "degree of crystallinity" though the effect is feeble and erratic. In the case of NaOH, there is a marked re-formation of the Cellulose I lattice when the swollen fibres are stretched and washed. These results have been observed earlier (7, 24). Looking at Table 1, it will be seen that the highest orientation (points Z₁, Z₁) is secured along with the lowest crystallinity and conversely, the raw fibre (R) has the highest crystallinity and lowest orientation factor. But this reciprocal relationship is not maintained at the intermediate crystallinities, as shown by the group of points N, E and Z₂. In other words, the extent of decrystallization seems to have no clear-cut bearing on the extent of reorientation.
REFERENCES


(ii) Krimm, S. and Tobolsky, A.V. J. Polymer. Sci. 7 57 (1951)


