Anisotropy of X-ray structural parameters of the three phase model in cellulose I

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Anisotropy of X-ray structural parameters of the three phase model proposed by Mitra and Mukherjee (ref.2), has been investigated in the case of cellulose fibres of ramie, hemp and jute. The structural parameters have been determined separately from each of the observable equatorial reflections. It has been found that the parameter degree of crystallinity as defined in the model is in fact anisotropic at least in the samples studied. The parameter degree of paracrystallinity introduced by Mitra and Mukherjee was also found to be anisotropic. Several important correlations between the structural parameters have been drawn. It has been observed, in agreement with the recent findings of Hosemann and Balta Calleja (ref.10) that the greater the paracrystalline distortion, the smaller the 'paracrystallite size'.

Keywords Anisotropy; crystallinity; paracrystallinity; distortion; crystallite size

INTRODUCTION

Recently Mitra and Mukherjee[1,2] have shown that fibrous polymers, in comparison with previous current theories which point to these polymers being composed of small crystallites embedded in a matrix of amorphous materials, can be better represented as a conglomeration of small domains which are crystalline amorphous and paracrystalline. The structural characteristics of this model have been described in terms of the following parameters: degree of crystallinity (x_c), degree of paracrystallinity (x_p), degree of amorphity (x_a), crystallite/paracrystallite size (P) and degree of distortion (g) of the paracrystalline region. The parameters x_c, x_p and x_a quantitatively determine the crystalline, paracrystalline and amorphous phases respectively. 'P' represents the average size of the crystalline or paracrystalline regions and 'g' or 'D' gives a measure of the average distortion in the paracrystalline regions. This set of parameters defining the proposed 3-phase model of Mitra and Mukherjee[2] (hereafter will be termed as M–M parameters) has been discussed in detail and an elaborate methodology of their determination has been described. Measurements utilizing this methodology have been carried out on samples of fibrous polymers using one reflection viz. (002) only. Since this represented only partial information of the fibrous polymer, it has been considered necessary to extend these measurements to all available equatorial reflections. The present work describes determination of the M–M parameters mentioned above for ramie, hemp and jute for (002), (101) and (10$\bar{1}$) reflections separately. These three reflections were the observable equatorial reflections with the samples under study.

EXPERIMENTAL

The samples of ramie, hemp and jute were first cleaned and delignified. The samples where then finely powdered

to remove the orientation and were also rotated while the intensity distribution was recorded. Powder photographs were taken[2] to ensure randomness of the orientations of the fibrils comprising the samples. The intensity distribution was then recorded using a symmetrical reflection technique with the help of a Philips diffractometer. CuKα radiation at 35 KV, 10 ma along with a balanced Ni–Al filter was used in obtaining the diffraction patterns. Fibre diffraction equatorial reflections were recorded using a specially made fibre sample holder for the diffractometer. For recording the meridional reflections from the fibre diffraction a different type of attachment[3] is needed and this was not attempted. It can be seen from the powder patterns[2] (*Figures 1, 2 and 3* in ref. 2) that the reflections (020) and (021) do not appear. This is because these reflections overlap with the much stronger equatorial reflections in the same angular range $(2\theta \sim 16°)$ and hence cannot be distinguished in the powder pattern. Intensity measurements were taken using G.M. counter employing fixed-count step counting. Quartz powder was used as the instrumental standard.

The observed intensity was corrected for the Lorentz factor, the polarization factor and the absorption factor. Background was corrected using the method described by Mitra and Mishra[4]. The overlapped profiles were separated by the method of Mitra and Bhattacharjee. (002), (101) and (10$\bar{1}$) reflections were taken for analysis of variance and integral breadth.

A program was written for computing variance with range and was run in a Riyad–1030 Computer.

Figures 1, 2 and *3* show the observed equatorial reflections of ramie, hemp and jute after all corrections as mentioned above. *Figures 4, 5* and *6* show the variance range functions of the (002), (101) and (10$\bar{1}$) profiles of ramie, hemp and jute. The three profiles corresponding to the three different crystallographic directions were used to determine the corresponding structural parameters in those directions. These parameters have been shown in *Tables 1–6*.

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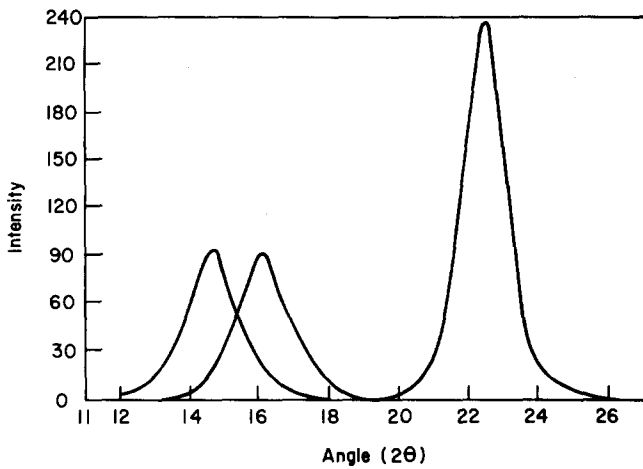
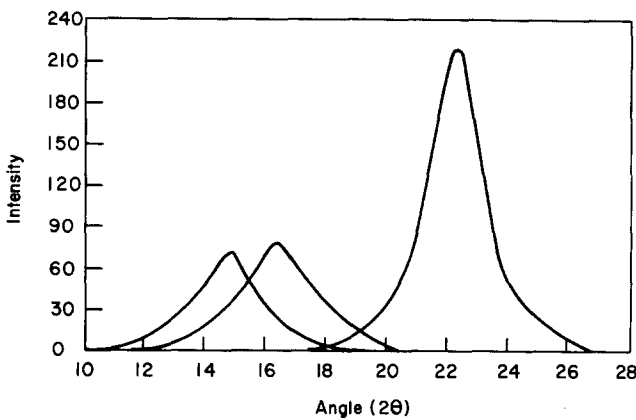*Figure 1* Corrected and separated overlapped profiles of Ramie

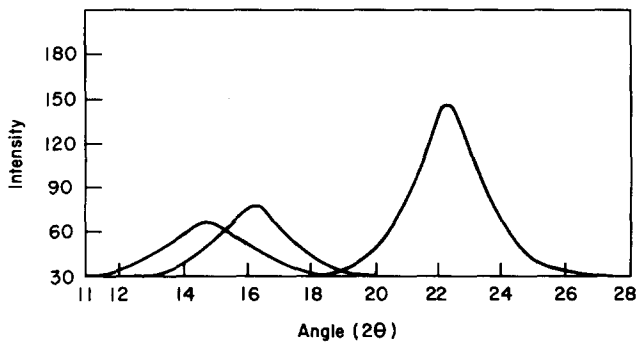*Figure 2* Corrected and separated overlapped profiles of Hemp

Figure 3 Corrected and separated overlapped profiles of Jute

on the other hand is found to have the least regularity in its chain arrangements as it has a maximum amorphous content together with a large degree of distortion. A comparative study of the M–M parameters thus shows ramie to be the more favoured fibre.

The degree of crystallinity parameter has always been taken to be isotropic by all the previous workers. No
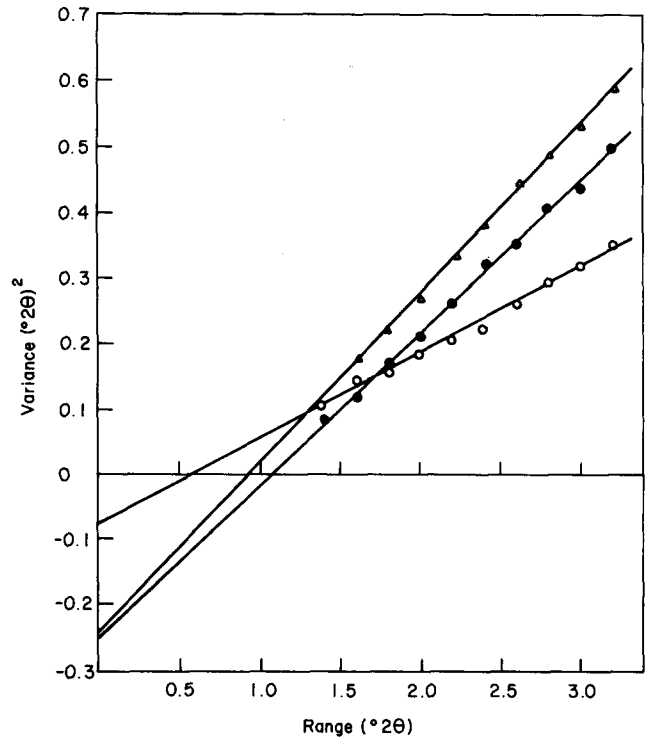
Figure 4 Variance–range function of the (002) profiles of (○) ramie, (●) hemp and (△) jute
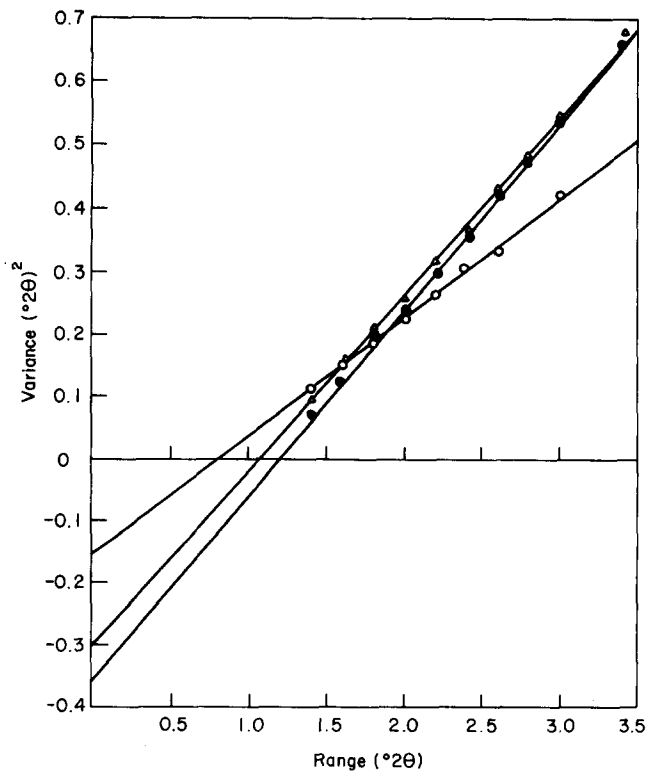
Figure 5 Variance–range function of the (101) profiles of (○) ramie, (●) hemp and (△) jute

RESULTS AND DISCUSSIONS

The M–M parameters indexing each of the samples studied reveals the nature of the arrangements of the molecular chains in them. The factors that reveal regularity in chain arrangements are essentially degree of crystallinity and degree of distortion. From *Tables 1–3*, it can be observed that ramie has the largest degree of crystallinity and largest crystallite size with the smallest degree of distortion. This leads us to the conclusion that the arrangements of the cellulose chains are of a much more regular manner in ramie than in hemp or jute. Jute

Figure 6 Variance–range function of the (10$\bar{1}$) profiles of (○) ramie, (●) hemp and (△) jute

Table 4 Anisotropy of the degree of distortion (g) and para-crystallite size (P_p)

Parameter	Ramie	Hemp	Jute
$g(002):g(10\bar{1}):$ $g(101)$	0.76:0.93:1	0.85:0.95:1	0.68:0.84:1
$P_p(002):P_p(10\bar{1}):$ $P_p(101)$	1:0.73:0.70	1:0.77:0.77	1:0.84:0.67

Table 5 Anisotropy of the degree of crystallinity (x_c) and crystallite size (P_c)

Parameter	Ramie	Hemp	Jute
$x_c(002):x_c(10\bar{1}):$ $x_c(101)$	1:0.86:0.70	1:0.94:0.87	1:0.75:0.62
$P_c(002):P_c(10\bar{1}):$ $P_c(101)$	1:0.73:0.78	1:0.77:0.77	1:0.95:0.91

Table 6 Anisotropy of the degree of paracrystallinity (x_p) and paracrystallite size (P_p)

Parameters	Ramie	Hemp	Jute
$x_p(002):x_p(10\bar{1}):$ $x_p(101)$	0.88:0.99:1	0.97:0.98:1	0.90:0.97:1
$P_p(002):P_p(10\bar{1}):$ $P_p(101)$	1:0.73:0.70	1:0.77:0.77	1:0.84:0.67

Table 1 Structural parameters along (002) direction

Parameter	Remie	Hemp	Jute
Degree of crystallinity $(x_c\%)$	14	8	8
Degree of paracrystallinity $(x_p\%)$	31	25	30
Degree of amorphity $(x_a\%)$	55	57	62
Degree of distortion $(g\%)$	4.4	5.5	5.0
Paracrystallinity/crystallite size $(P$ Å$)$	44	26	22

Table 2 Structural parameters along (101) direction

Parameter	Ramie	Hemp	Jute
Degree of crystallinity $(x_c\%)$	10	7	5
Degree of paracrystallinity $(x_p\%)$	35	36	33
Degree of amorphity $(x_a\%)$	55	57	62
Degree of distortion $(g\%)$	5.8	6.5	7.4
Paracrystallite/crystallite size $(P$ Å$)$	31	20	20

Table 3 Structural parameters along (10$\bar{1}$) direction

Parameter	Ramie	Hemp	Jute
Degree of crystallinity $(x_c\%)$	12	7.5	6.0
Degree of paracrystallinity $(x_p\%)$	33	35.5	32
Degree of amorphity $(x_a\%)$	55	57	62
Degree of distortion $(g\%)$	5.4	6.2	6.2
Paracrystallite/crystallite size $(P$ Å$)$	32	20	21

previous workers have pointed out the anisotropic nature of this parameter. The present results show for the first time that the degree of crystallinity parameter is in fact anisotropic, at least in the samples studied. It has also been observed that the proposed new degree of paracrystallinity parameter is also different in different directions. The present analysis thus throws new light on the understanding of the structural variations in a polymer. The variations of the parameters, the degree of crystallinity and the degree of paracrystallinity give information regarding the extent of chain folding, chain ends and chain regularity in the various directions within a polymer. The anisotropy of the M–M parameters in the three directions for the cellulose samples studied have been shown in *Tables 4–6*. It has been observed that anisotropy of the degree of crystallinity parameter (x_c) is at a maximum for jute. The ratio of the parameter x_c in the three directions studied is given by 1:0.75:0.62 for jute whereas for ramie and hemp are given by 1:0.86:0.70 and 1:0.94:0.87 respectively. From the results shown in *Tables 5* and *6*, two significant conclusions can be made. The crystallite size is found to increase with increase in the value of the degree of crystallinity (*Table 5*). It can further be concluded that the larger the degree of paracrystallinity, the smaller is the paracrystallite size (*Table 6*).

From anisotropic variations in the degree of crystallinity and crystallite sizes as shown in *Table 5*, it can be observed that these parameters are larger for the (002) reflection compared with the (101) or (10$\bar{1}$) reflections. Also the degree of distortion for the (002) reflection is always found to be smaller compared with the values for the (101) or (10$\bar{1}$) reflections. The same conclusion has also been drawn from the line profile analysis of the cellulose

fibres using paracrystalline theory by Mitra and Mukherjee[5].

It is evident from *Tables 4, 5* and *6* that the anisotropy in some of the M–M parameters in the directions studied are not large. This is due to the fact that the directions considered are transverse to the fibre axis and the planes involved viz. (101), 10$\bar{1}$) and (002) are oriented randomly within any one fibre. The observed anisotropy in the M–M parameters is due mainly to crystallite shape and mode of arrangements of the molecular chains with respect to the crystallographic planes. Such anisotropy is analogous to that observed in the case of powdered metals[6]. In the samples studied a comparison of the M–M parameters derived from the (020) and (002) reflections would reveal a large anisotropy as they give structural characteristics along and perpendicular to the fibre axis. Such work is in progress and will be subsequently reported.

The crystallite sizes are found to be of the same order as derived by earlier workers in different studies[7-9]. The observations shown in *Table 4* lead one to conclude that the microparacrystallite size decreases with increase in degree of distortion. This also confirms the recent findings of Hosemann *et al.*[10]

It has thus been further established that the M–M parameters can very well differentiate the cellulose samples from the point of view of their structural differences. Exponents of the previous 'two-phase model'

did not in general use the line profile technique. For the first time the degree of crystallinity has been conveniently measured in different directions and shown to be anisotropic in contrast to the previous idea of this parameter being isotropic. The new parameter 'degree of paracrystallinity' has also been found to be anisotropic. It is thus expected that the observed anisotropy in the properties of polymers can be as a result of the anisotropy of the M–M parameters. Such a structure–property study is in progress and it is expected to lead to some useful structure–property correlations.

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