X-ray diffraction study of fibrous polymers. I. Degree of paracrystallinity–a new parameter for characterizing fibrous polymers*

G. B. Mitra and P. S. Mukherjee
School of Research in X-rays and Structure of Matter, Department of Physics & Meteorology, Indian Institute of Technology, Kharagpur, India
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It has been recognized that paracrystallinity dominates a considerable portion of the fibrous polymers. In the general case, the folding of long chains in fibrous polymers result in several domains, some being crystalline, some amorphous, while the remainder are paracrystalline. Based on this model a new parameter–degree of paracrystallinity–has been proposed. This paper reports a method of determining this parameter. Native cellulose fibres of ramie, hemp and jute have been studied. It is found that degree of paracrystallinity in hemp and degree of crystallinity in ramie are greater than in the other fibres. Crystallinity index has been found to be less than that generally reported in the literature. This has been attributed to the intensity peaks previously considered in calculating the degree of crystallinity having components of paracrystallinity which have been evaluated and separated.

INTRODUCTION

Fibrous polymers consist of long chains of threadlike molecules which, owing to various factors, assume random configuration. The actual conformation of the molecule is dependent on several factors like internal rotation within the molecule, geometrical shape of the domains interaction between molecular chains, thermal agitations etc. The present idea is that these fibrous polymers are chain molecules which, when arranged approximately parallel to each other, give rise to what can be called crystalline domains. However, when there is a considerable folding and twisting of the molecular chains the domain is essentially amorphous. These considerations led to the two phase model of fibrous polymers — a crystalline phase with given domain boundaries lying immersed in a matrix of amorphous materials.

In between the two phases an intermediate phase exists which is called the paracrystalline phase. While forming crystalline phases when the molecular chains are parallel, and amorphous phases when the chains are all jumbled together, it is likely that the long chains of fibrous polymers will also arrange themselves in the paracrystalline phase. In this case the unit cell parameters are all statistical quantities both in magnitude and in direction. As summarized by Alexander[1] the two basic descriptions of the molecular arrangements of fibrous polymers are (1) the two phase model; (2) the crystal defect model. The two phase model has been in use for some time and has given rise to the 'degree of crystallinity' of a polymer. Therefore, the degree of crystallinity signifies the fraction of the crystalline domains with respect to the total substance studied. It is found that degree of crystallinity differs for different methods used e.g. X-ray, n.m.r., infra-red etc., and terms such as 'X-ray crystallinity', and 'n.m.r. crystallinity' have been adopted.

In this work we shall be concerned only with X-ray studies. The degree of crystallinity measured previously has been defined as the ratio of the areas under the peak regions of X-ray diffraction pattern and the total area. The different methods for determining this parameter are discussed in the next section. It is likely that peak regions of the intensity distribution curve also contain contributions from the paracrystalline regions, other contributions from such regions being submerged in the overall background.

We propose to introduce paracrystallinity as an essential part of the molecular arrangement of fibrous polymers in addition to the crystalline and amorphous parts. This leads to the new concept of 'degree of paracrystallinity' which is used as a parameter to characterize these polymers.

Review of earlier work

The micellar theory was first advanced by Nageli[2]. The idea was that polymer fibres were built of submicroscopic, anisotropic crystalline particles called micelles. Later, when X-ray studies showed both crystalline and amorphous types of scattering, Mayer and Mark[3] adopted the micellar theory and emphasized the fact that many of the properties of cellulose fibres are not due to the cellulose molecule but to molecular aggregates or micelles made up of parallel cellulose molecules. Herzog[4] explained the amorphous part of the X-ray diffraction pattern of cellulose as being the cementing material between the micelles. However around 1930, ultracentrifuge and viscosity methods indicated that the length of the cellulose molecules was in the order of ten times greater than the estimated length of the micelles, and subsequently the micellar theory was abandoned. At this stage Pierce[5], Neale[6], Sponsler[7] and Astbury[8] proposed the continuous structure theory and allowed the presence of extremely long molecules as part of the continuous structure. Later, Freywyssling[9] and Kratky[10] postulated that a single

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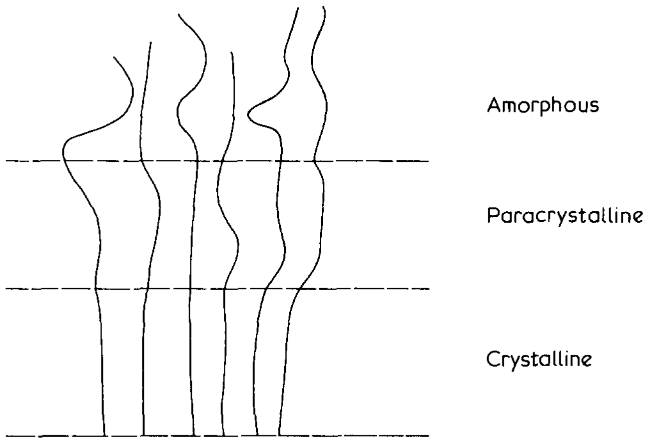

Figure 1 Arrangements of the macromolecular chains in a polymer

cellulose molecule would take part in more than one crystalline region. This theory is known as the fringe micellar theory and according to this theory the micelles are considered as statistically distributed regions of order in a matrix of approximately parallel chain molecules. The ordered region can be considered as 'crystalline', the less ordered as 'amorphous' and there was no correlation between the size of the ordered crystalline domain and chain length. Instead of the sharply defined grain boundaries in polycrystalline metals, the model was one of gradual transition from regions of high lattice order to regions of low lattice order. The complete structure will be reticular in nature with primary valence chains anchored at various points by the high cohesive forces in the ordered regions holding the structure together in a coherent three dimensional network.

Attempts at characterization of fringe micellar network have been described in detail in a review article by Howsmon and Sisson[11]. As early as 1933 Sisson and Clark[12] developed a method for determining average crystallite orientations and distribution of this orientation in respect to the fibre axis. The concept of degree of crystallinity arose out of chemical studies because of the differential behaviour of the crystalline and amorphous regions to chemical action of acids and alkalis. Phillipp, Nelson and Ziifle[13] determined degree of crystallinity in a number of cellulose samples by acid hydrolysis. The first quantitative method for determination of the degree of crystallinity or relative proportion of crystalline domains in the crystal amorphous complex were proposed in 1947 by Hermans[14] and Kast and Flaschner[15]. Both methods defined crystalline domains as those which contribute maxima in its X-ray diffraction diagram and arrived at a crystalline proportion by comparison of the integrated intentisty of maxima considered to be contributed by the crystalline part of the substance and the intensity of the background scattering supposed to be due to the amorphous region. Hermans and Weidenger[16] studied a large number of fibres by this method. Hermans[17] also proposed the use of the density of cellulose as a measure of crystallinity and obtained good agreement with X-ray diffraction results. It was recognized as early as 1954 by Howsmon and Sisson[11] that the existing methods were not capable of characterizing complex order–disorder structure of polymers and a simple subdivision into crystalline and amorphous domains was an oversimplification. Marchessault and Howsmon[18] studied the intermediate states of lateral order in cellulose fibres. The determination of degree of crystallinity in isotactic polystyrene by Challa, Hermans and Weidinger[19] is worth mentioning. Wakelin, Virgin and Crystal[20] improved upon these methods by using an amorphous standard. Kilian and Ruland[21,22] developed a method to determine the degree of crystallinity from X-ray diffraction data more rigorously and also introduced a defect parameter including paracrystallinity. However the defect parameter has been defined to be the lumped up effect of thermal vibration and lattice distortion of the first and second kind.

Present model The exponents of the two phase theory of polymers were not satisfied with their model and considered it to be a first approximation. In the mean time the concept of paracrystallinity developed. Paracrystalline substances have quasiperiodic structures. Paracrystalline states have been designated by Friedel[23] as mesomorphic structures in contrast with the suggestion of F. Rine[24] who characterized the phases originally known as nematic and smectic, as α-paracrystalline and β-paracrystalline respectively. Hosemann[25] introduced the concept of paracrystals in terms of statistical distribution function of the lattice sites. A paracrystalline substance, according to this definition, is one in which atoms are neither regularly arranged, as in crystals, nor randomly organized as in amorphous materials. The lattice of such substances consists of unit cells which are all dissimilar with respect to one another. The non-coplanar vectors defining the unit cells vary in magnitude as well as direction.

As pointed out in section I the complex arrangement of approximately parallel long chains with their folds and twists make it likely that, in addition to the usually accepted crystalline and amorphous phases, a part will also be paracrystalline. This concept is implied in the defect parameter introduced by Ruland *et al.*[21,22]. Joint existence of crystalline, amorphous and paracrystalline phases truly represent the model of a fibrous polymer. Kulshreshtha and other workers[26–30] considered cellulose samples to be fully and wholly paracrystalline. The present concept envisages a simulatneous coexistance of crystalline amorphous and paracrystalline domains. These phases are not sharply bounded but gradually develop into each other. Most probably the crystalline domains converge into the amorphous domains through an intermediate paracrystalline region. The entire substance will then be a random distribution of crystalline, paracrystalline and amorphous domains — the domains being mutually linked up by the same cluster of macromolecular chains.

Figure 1 shows the probable arrangements of the macromolecular chains and *Figure* 2 shows an idealized distribution of the three types of domains (crystalline, amorphous and paracrystalline) in the fibrous polymer. *Figure* 1 shows that the long range order tends to disappear with increase in distance. This is not explicit in *Figure* 2. *Figure* 2 merely shows that the crystalline, amorphous and paracrystalline domains are randomly distributed as has been assumed in our calculations. This is a mere representation of the mathematical model used rather than that of the physical model actually envisaged and illustrated in *Figure* 1.

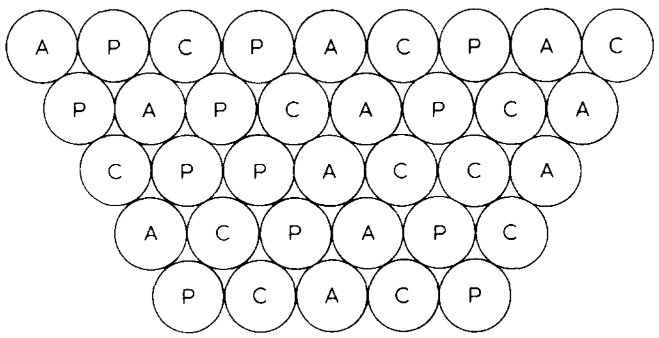

Figure 2 Model of a polymer showing idealized distribution of crystalline, amorphous and paracrystalline domains

THEORY

As explained above a fibrous polymer can be represented very well by considering it to be continuous clusters of three different types of organizations namely crystalline, paracrystalline and amorphous as shown in *Figures* 1 and 2.

The amplitude of X-rays scattering coherently in such a system is the sum of scattering amplitudes from the three different regions. Therefore the amplitude of X-rays scattered in the direction $\bar{S}$ by a polymer can be written as

$$A(\bar{S})=A_c(\bar{S})+A_p(\bar{S})+A_a(\bar{S})$$

where $A_c(\bar{S})$, $A_p(\bar{S})$ and $A_a(\bar{S})$ are the amplitudes of X-rays scattered by the atoms in the crystalline, paracrystalline and amorphous regions of the polymer respectively.

The intensity of X-rays scattered in the direction $\bar{S}$ can be written as:

$$I(\bar{S})=\sum_l\sum_m A_l(S)A_m^*(S) \qquad (1)$$

where l and m correspond to atoms in a particular type of domain namely crystalline, paracrystalline and amorphous.

According to our model depicted in *Figure* 2 the crystalline, paracrystalline and amorphous regions are interconnected but occur randomly in space. Therefore the interregion inerference should be negligible because of the virtual incoherence between the regions. Atoms in each region or domain, however, will scatter coherently. The scattering from pairs of atoms will be negligible when one lies in one domain, and one in an adjacent domain because of the incoherence of their space arrangement. These considerations indicate that the total intensity scattered in a given direction will be the sum of the total scattering from crystalline domains, the total scattering from paracrystalline domains and the total scattering from amorphous domains respectively. Thus collecting the terms from equation (1) which are purely crystalline, purely amorphous and purely paracrystalline we can write:

$$\begin{aligned}I(S)&=\sum_c\sum_i A_c^i A_c^{i*}+\sum_p\sum_j A_p^j A_p^{j*}+\sum_a\sum_l A_a^l A_a^{l*}\\&=I_c+I_p+I_a\end{aligned} \qquad (2)$$

where c, p and a represents the crystalline paracrystalline and amorphous domains respectively and $\sum_i\sum_j\sum_l$ represent summations over amplitudes scattered from atoms in a given domain–crystalline, paracrystalline and amorphous respectively. The observed scattering can be considered as a simple addition of the scattering from the three types of domains in our model. It must be mentioned that equation (2) will be valid only for wide angles of scattering. For small angles of scattering the interdomain interference can not be ruled out. This will be taken up in a forthcoming paper.

From equation (2) we write $I=x_cI+x_aI+x_pI$ where

$$x_c=I_c/I,\ x_a=I_a/I \text{ and } x_p=I_p/I \qquad (3)$$

We define the parameters x_c, x_a and x_p to be the degree of crystallinity, degree of amorphity and degree of paracrystallinity. The parameter 'degree of paracrystallinity' along with degree of crystallinity will give a better picture of a polymer.

The expressions of intensity scattered from crystalline and amorphous regions[1,31] are:

$$I_{cryst}=|F|^2\int_{\bar{M}}(M-|t|)\exp 2\pi \text{ is } t\,\mathrm{d}t \qquad (4)$$

where $|F|\rightarrow$ Absolute value of the structure factor.
$M-|t|\rightarrow$volume common to the crystallite M and its ghost obtained by a translation 't' in a direction normal to reflecting plane.

$$I_{amorph}=N\langle f^2\rangle 1-\int_0^{\infty}4\pi r^2\{\rho(r)-\rho(0)\}\frac{\sin\mu r}{\mu r}\mathrm{d}r \qquad (5)$$

where N is the total number of atoms in the irradiated volume of mean squared atomic scattering factor $\langle f^2\rangle$ and $\mu=\frac{4\pi}{\lambda}$ Sin θ, λ the wavelength and θ the angle of scattering while $\rho(r)$ is the density of atoms at a distance 'r' from any representation point and $\rho(0)$ is the average density of atoms.

We will now derive a workable expression for intensity scattered by paracrystalline regions. The ideal paracrystalline model considered here has been discussed at length by various authors[25,26,30]. We consider the model of Vainstein[30] which describes the lattice subjected to distortions of the second kind.

These paracrystalline substances can be described by distribution function of the interatomic distances which can be written as[30]

$$W(x)=N\delta(x-0)+\sum_{m=1}^{N-1}(N-|m|)H_m(x)$$

where x is the distance of the given atom from the reference atom which is considered to be situated at the origin i.e. $x=0$. $H_m(x)$ is the distribution function of the distance of the 'm'th neighbour from the reference atom.

$$H_m(x)=\frac{m-1}{H_1}\rightarrow\text{'}m-1\text{' times convolution of } H_1 \text{ — the neighbour distribution function.}$$

If we now consider the position of the sites to be ideally perfect crystals, then the distribution function $H_m(x)$ becomes delta function and the intensity diffracted in the direction $\bar{S}$ is given by

$$I(\bar{S})=|F|^2\sum_{m=-N}^{N}(N-|m|)\exp i\,2\pi\bar{S}.\bar{r}_m \qquad (6)$$

where $\bar{r}_m=m\bar{a}$. $\bar{a}$ being the repeat distance in the direction considered. In a paracrystalline lattice

$$\bar{r}_m=m\bar{a}+\Delta_m \qquad (7)$$

$\Delta_m\rightarrow$ being the deviation of the 'm'th atom from the ideal crystalline lattice site.

Combining equation (6) and (7) and averaging over fluctuation terms Δ's we have

$$I(S)=|F|^2\Sigma(N-|m|)\exp\mathrm{i}2\pi m\bar{a}.\bar{s}\int_{-\infty}^{\infty}H_m(\Delta)\exp\mathrm{i}2\pi\ s.\Delta_m d\Delta$$

or,

$$I(s)=|F|^2\Sigma(N-|m|)\exp\mathrm{i}2\pi m\bar{a}.\bar{s}\ \mathscr{F}(H_m) \qquad (8)$$

where $\mathscr{F}(H_m)$ is the fourier transform of H_m.

Assuming H_1 to be Gaussian function[30] we can write

$$H_1(x)=\frac{1}{\sqrt{2\pi\delta}}e^{-\frac{1}{2}(x^2/\delta^2)} \qquad (9)$$

The fourier transform of which is given by

$$FT(H_1)=e^{-2\pi^2s^2\delta^2}$$

Since fourier transform of convolution of unrelated functions is the product of fourier transforms of the functions we have

$$FT(H_m)=e^{-2\pi^2s^2\delta^2.m} \qquad (10)$$

Substituting equation (10) in equation (8) we get

$$I(\bar{s})=|F|^2\sum_{m=-N}^{N}(N-|m|)\exp\ -2\pi^2s^2\delta^2m.\ \exp\ i2\pi\bar{s}.m\bar{a}.$$

We substitute $g=\delta/a$, $t=ma$, $M=Na$

$$I(\bar{s})=|F|^2\tfrac{1}{a}\sum_{t=-M}^{M}(M-|t|)\exp\ -2\pi^2ag^2s^2t.\ \exp\ i2\pi\bar{s}.\bar{t} \qquad (11)$$

Now we define $D=2\pi^2ag^2s^2$ and replace the summation by integration

$$|F|^2I(\dot{s})=\int_0^M(M-|t|)\exp-Dt.\ \exp\ i2\pi s.t\ \mathrm{d}t$$

$$=|F|^2\int_0^M V(t)Y(t)\exp\ i2\pi s.t\ \mathrm{d}t \qquad (12)$$

where $V(t)$ — Paracrystalline domain size term

$$=M-|t|$$

$Y(t)$ — Distortion or strain term in paracrystalline region

$$=e^{-Dt}$$

Since the sizes of the domains are different, experimental observations yield only an averaged value. We average the domain size term by using a frequency distribution function $g(M)\mathrm{d}M$. Thus

$$V(t)=\int(M-|t|)\ g(M)\mathrm{d}M$$

$$=\bar{M}-|t| \qquad (13)$$

$\bar{M}=\int Mg(M)\mathrm{d}M$ — is the average domain size.

Thus expression of $I(s)$ in equation (12) is a combination of two functions whose 't'th order fourier transforms are $(\bar{M}-t)$ and exp-Dt respectively. Kulshrestha *et al.*[27] had also derived an identical expression for the intensity profile due to paracrystalline substances. However, they made the approximation in the intensity expression to the effect that $\bar{M}-t$ in equation (11) has been taken to be $\bar{M}$ exp $-(t/\bar{M})$. They concluded, therefore, that variance, along with fourth moment technique, is necessary to find out the fine textures in a polymer which is incapable of producing higher order reflections. We have been able to separate the domain size and defect terms from single line only. In our method the approximation made by Kulshrestha *et al.*[27] has not been made. Wilson[32] also showed that the approximation leads to untenable conclusions.

METHOD OF SEPARATING THE THREE TYPES OF SCATTERING

The intensity corresponding to the amorphous parts can be calculated from the known or partially known structural parameters determined from the fibre diagram of the polymer and model calculations. Then using equation (5) the theoretical amorphous scattering of the polymer can be determined[33]. Substances which are also available in complete amorphous form can be taken as amorphous standard. The observed intensity has to be converted to absolute scale using the standard[31] method. Thus $I_a(s)$ was separated. Unless unit cell parameters of crystalline and paracrystalline domains are distinctly different, apparent unit cell parameters are average nearest neighbour distances in paracrystalline domains as given by

$$\int_{-\infty}^{\infty}xH_n(x)\mathrm{d}x=n\ \bar{a}$$

where x — The distance of the 'n'th neighbour from an atom. $H_n(x)\mathrm{d}x$ — The probability of 'n'th neighbour lying between

x and $x+\mathrm{d}x$.

$\bar{a}$ — The average unit cell parameter in the 'x' direction.

To separate I_c and I_p, we define p_1 and p_2 as the fractional proportions of diffracted intensities from crystalline and paracrystalline components respectively.

From equations (4) and (12) we can write

$$I_c(s)=p_1|F_M|^2\int_M(\bar{M}-|t|)\exp 2\pi\ s.t\mathrm{d}t \qquad (14)$$

$$I_p(s)=p_2|F_M|^2\int_M(\bar{M}-|t|)\exp-Dt.\exp\ i2\pi s.t\ \mathrm{d}t \qquad (15)$$

In equations (14) and (15), the average domain size for both crystalline and paracrystalline phases have been taken to be the same, however, they need not be the same. On average the difference between these two parameters will be negligible, considering the large width of their distribution curves, the average value of the two parameters can be taken to be the same. The distortion factor 'D' characterizes the mean deviation of atoms in the paracrystalline state from the lattice sites in the corresponding crystalline state. Thus

$$I_c(s)+I_p(s)=|F|^2\int_M(\bar{M}-|t|)(p_1+p_2\exp-Dt)\exp\ i2\pi s.t\ \mathrm{d}t \qquad (16)$$

The above expression gives the major contributions to the broadened peaks of the distribution curves.

We use the techniques of variance and integral breadth to determine the fine texture parameters $\bar{M}$, D and p_1 and p_2.

From equation (16) the intensity diffracted from the crystalline and paracrystalline component can be written as:

$$I_{p+c}=|F_M|^2\int(\bar{M}-|t|)(p_1+p_2\exp-Dt)\cos 2\pi\bar{s}.t\ \mathrm{d}t$$

$$=K\int A(t)\cos 2\pi\bar{s}.t\ \mathrm{d}t$$

where K is a constant.

$A(t)$ – tth order Fourier coefficients $=(\bar{M}-|t|)(p_1+p_2\exp-Dt)$

The expression for variance is given by[34]:

$$W(\bar{s})=-\frac{1}{4\pi^2}\left[2\sigma\frac{A'(0)}{A(0)}+\frac{A''(0)}{A(0)}\right] \qquad (17)$$

Now $A(t)=(\bar{M}-|t|)(p_1+p_2\exp-Dt)$

$$\frac{A(t)}{A(0)}=[1-|t|/\bar{M}][p_1+p_2\exp-Dt]$$

$$\frac{A'(t)}{A(0)}=p_2\exp-Dt\left[-\frac{1}{M}-D\left(1-\frac{|t|}{\bar{M}}\right)-\frac{p_1}{M}\right]$$

$$\frac{A'(0)}{A(0)}=-\frac{1}{\bar{M}}(p_1+p_2)-Dp_2=-(1/\bar{M}+dp_2) \qquad (18)$$

Similarly

$$\frac{A''(0)}{A(0)}=p_2D(2/\bar{M}+D) \qquad (19)$$

Thus, putting the values from equation (18) and (19) in equation (17) we get:

$$W(\sigma)=-\frac{1}{4\pi^2}[-2\sigma(1/\bar{M}+Dp_2)+p_2D(2/\bar{M}+D)]$$

or

$$W(\sigma)=\frac{\sigma}{2\pi^2}(1/\bar{M}+p_2D)-\frac{1}{4\pi^2}p_2D\left(\frac{2}{\bar{M}}+D\right) \qquad (20)$$

The expression for integral breadth can be written as

$$\beta(t)=\frac{A(0)}{\int_0^{\bar{M}}A(t)\,\mathrm{d}t}$$

Now

$$A(t)=(\bar{M}-|t|)(p_1+p_2\exp-Dt)$$

$$=1/\bar{M}[p_1\exp-|t|/\bar{M}+p_2\exp-|t|(1/\bar{M}+D)]$$

Thus

$$\beta(t)=\frac{(p_1+p_2)\bar{M}}{1/\bar{M}[p_1\int_0^{\bar{M}}\exp-\frac{|t|}{\bar{M}}\mathrm{d}t+p_2\int_0^{\bar{M}}\exp-|t|(1/\bar{M}+D)\mathrm{d}t]}$$

$$\beta(t)=\frac{1}{(1-\mathrm{e}^{-1})p_1\bar{M}+p_2/(D+1/\bar{M})} \qquad (21)$$

From equation (20) a plot of $W(\sigma)$ against a σ gives a straight line whose intercept with $W(\sigma)$ axis gives $p_2D(2/\bar{M}+D)$ and slope gives the value of $(1/\bar{M}+p_2D)$. Hence along with the value of integral width given in equation (21) and the relation $p_1+p_2=1$, we have four equations with four unknowns — $\bar{M}$, D, p_1 and p_2. Hence solving these four equations the values of the above quantities can be determined. From the values of p_1 and p_2, I_c and i_p can be separated.

Thus knowing the values of I_c, I_p and I_a quantitatively we can find the parameters — degree of crystallinity, degree of paracrystallinity and degree of amorphity from equation (3) These along with the texture parameters $\bar{M}$ and D completely characterize the polymer.

EXPERIMENTAL

The cellulose fibres selected for study were ramie, hemp and jute. These fibres were cleaned and delignified. The samples were then finely powdered to remove the orientation and were rotated while the intensity distribution was recorded. A powder photograph was taken to make sure the randomization of the sample. Intensity distribution was then recorded using symmetrical reflection technique using a Philips diffractometer. CuKα radiation at 35 kV, 10 mA along with balanced filter of Ni–Al were used. Intensity measurements were taken using G.M.

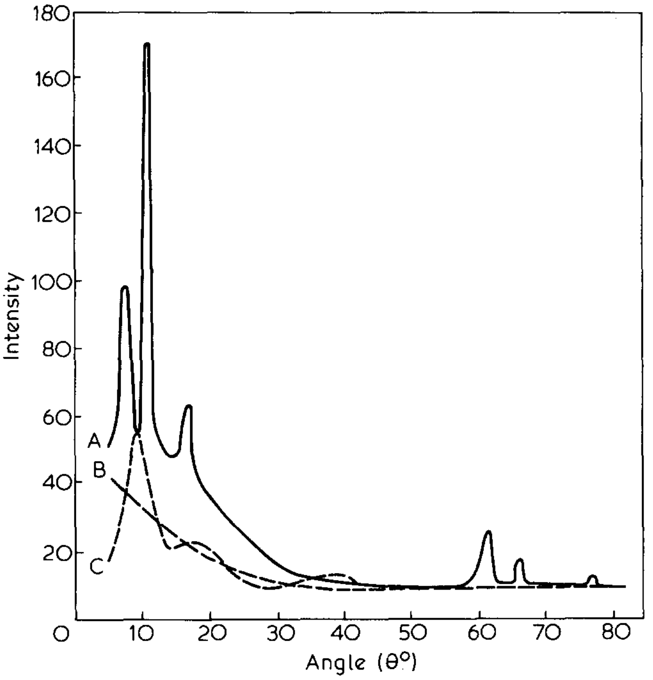

Figure 3 Normalized observed scattered intensity distribution of Ramie (A); total independent scattering (B); normalized amorphous scattering of cellulose (C)

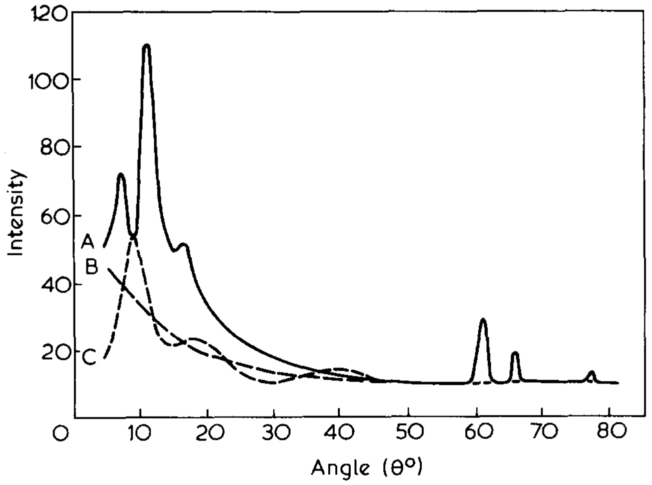

Figure 4 Normalized observed scattered intensity distribution of Hemp (A); total independent scattering (B); normalized amorphous scattering of cellulose (C)

counter employing fixed count step scanning. Quartz powder was used as instrumental standard.

The observed intensity was corrected for Lorentz factor, polarization factor and absorption factor.

Fibre diffraction pattern was taken to determine and refine the cell parameters. For this a specially designed fibre camera[35] was used and with CuKα radiation the fibre photgraphs were taken. [002] profiles were taken to determine the variance and integral breadth. Overlapped reflections were separated by the method of Mitra and Bhattacherjee[36].

A programme was written for computing variance with range and was run in Rayard-1030 computer.

As background determination plays an important part in line profile analysis a proper method must be followed while determining the proper background. It is also found[27,37] that the background in polymeric profiles has a curved shape especially at low Bragg angles. Since there is no simple way of separating background, a few trials with different backgrounds were taken and the linearity for moderately large ranges of the variance range functions so obtained are chosen to be the criteria for accurate backgrounds.

Figures 3, 4 and 5 show the normalized observed intensity distribution of ramie, hemp and jute respectively. In each figure scattering from amorphous cellulose as well as independent scattering from cellulose are also shown. *Figure* 6 represents the observed, corrected and separated profiles of ramie. The variance–range function for the [002] profile is shown in *Figure* 7.

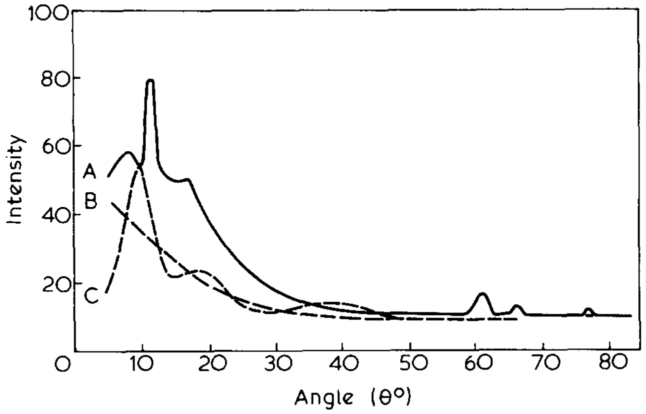

Figure 5 Normalized observed scattered intensity distribution of Jute (A); total independent scattering (B); normalized amorphous scattering of cellulose (C)

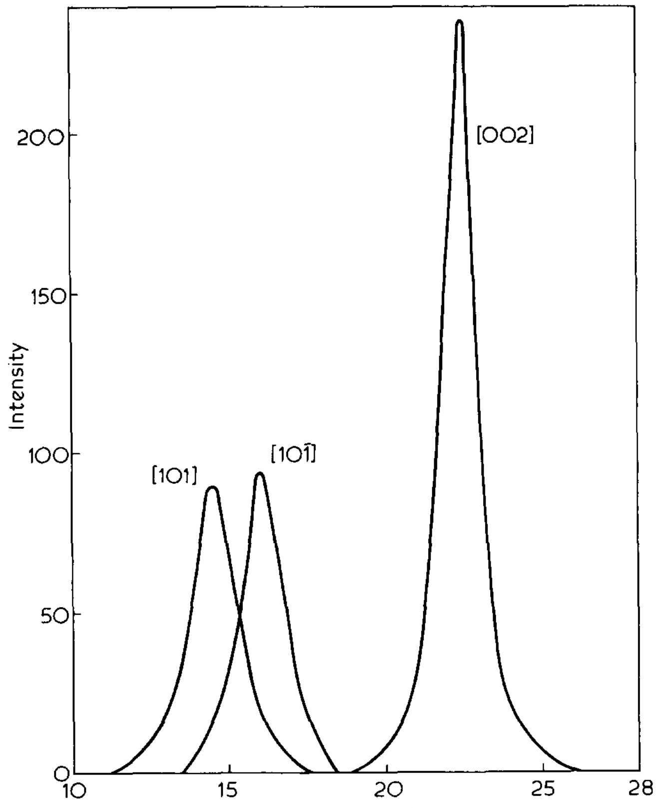

Figure 6 Corrected and separated overlapped profiles of Ramie

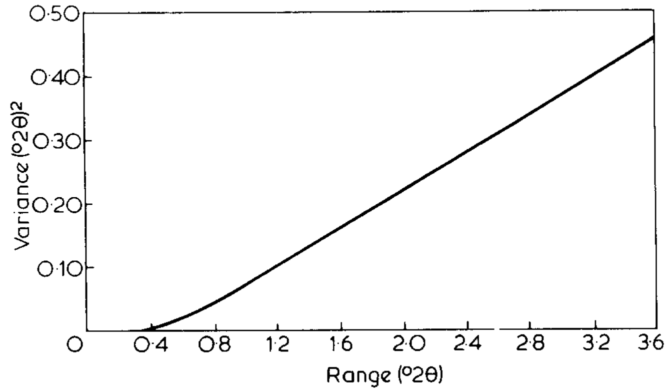

Figure 7 Variance-range function of the [002] profile of Ramie

Table 1

Sample	Ramie	Hemp	Jute
Degree of paracrystallinity (%)	31	35	30
Degree of crystallinity (%)	14	8	8
Degree of amorphity (%)	55	57	62
Distortion parameter (*D*) x 10^{-20} $Å^{-1}$	0.95	1.4	0.96
Crystallite size (Å)	46	28	22

RESULTS AND DISCUSSION

From the results the degree of crystallinity in ramie is more than in the other two fibres while the degree of paracrystallinity is more, in the case of hemp.

As reported in the literature the degree of crystallinity of these fibres were found to be much higher. This is because of the limitations placed in their range of measurement as well as lumping the crystalline and paracrystalline contribution together.

The amorphous contribution has been chosen arbitrarily by previous workers. They did not utilize the intensity distribution in the entire observed reciprocal space but confined themselves to a rather narrow range. They have terminated their calculations at points where the main crystalline peaks merge into a high variable background which has been attributed to the amorphous contribution to the intensity distribution. The intensity distribution, however, extends to a much higher angle of scattering. Thus the amorphous contribution has always been underestimated, which increases the apparent crystalline contribution. In our method a suitable quantitative method has been put forward to estimate the amorphous contribution up to the maximum angle which can be obtained experimentally.

According to the two phase concept it was assumed that when the amorphous intensity is subtracted from the total intensity we get the intensity from the purely crystalline region. But this is not so and the paracrystallinity factor dominates in fibrous polymers. In this work we separated the contributions from paracrystalline and purely crystalline regions. We found that paracrystallinity, not crystallinity, dominates a considerable region in these polymers. These paracrystalline regions are characterized further by the distortion parameter '*D*'. For purely crystalline regions the distortion parameter '*D*' is zero.

In the light of this work it can be concluded that polymer properties can be described in a better way in terms of the new parameter, namely 'degree of paracrystallinity'.

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REFERENCES

1 Alexander, L. 'X-ray Diffraction Methods in Polymer Science', John Wiley & Sons Inc., 1969, New York
2 Nageli, C. and Schwendener, S. 'Das Mikroskop', 2nd ed., W. Engelmann, Leipzig, 1877
3 Meyer, K. H. and Mark, H. *Z. Physik Chem.* 1929, **B2**, 115
4 Herzog, R. O. *Kolloid Z.* 1926, **39**, 98
5 Pierce, F. T. *Trans. Faraday Soc.* 1933, **29**, 50
6 Neale, S. M. *Trans. Faraday Soc.* 1933, **29**, 228
7 Sponsler, O. L. *Quart. Rev. Biol.* 1933, **8**, 1
8 Astbury, W. T. *Trans Faraday. Soc.* 1933, **29**, 193
9 Frey–Wyssling, A. 'Submicroscopic morphology of protplasm and its derivatives'. Elsevier New York, 1948, pp. 45–90
10 Kratky, O. *Kolloid Z.* 1935, **70**, 14
11 Howsmon, J. A. and Sisson, W. A. 'High Polymers Vol. V. Cellulose and Cellulose Derivatives' Interscience Publishers Inc., New York, p 231
12 Sisson, W. A. and Clark, G. L. *Ind. Eng. Chem. Anal.* 1933, **5**, 296
13 Phillipp, H. J., Nelson, M. L. and Zifle, H. M. *Textile Research Journal*, 1947, **17**, 585
14 Hermans, P. H. *J. Appl. Phys.* 1948, **19**, 491
15 Kast, W. and Flaschner, L. *Kolloid Z.* 1948, **111**, 6
16 Hermans, P. H. and Weidinger, A. *J. Polym. Sci.* 1951, **6**, 533
17 Hermans, P. H. 'Contributions to the Physics of Cellulose Fibres.'
18 Marchessault, R. H. and Howsmon, J. A. *Textile Research Journal* 1957, **27**, 30
19 Challa, G., Hermans, P. H. and Weidinger, A. *Makromol. Chem.* 1962, **56**, 1969
20 Wakelin, J. H., Virgin, H. S. and Crystal, E. J. *Appl. Phys.* 1959, **30**, 1654
21 Kilian, H. G. *Kolloid Z. Z. Polymere*, 1962, **185**, 13
22 Ruland, W. *Polymer*, 1964, **5**, 89
23 Friedel, G. and E. *Z. Cryst.* 1931, **79**, 1
24 Rinne, F. *Z. Cryst.* 1932, **82**, 379
25 Hosemann, R. and Bagchi, S. N. 'Direct Analysis of Diffraction by Matter', North Holland, Amsterdam 1962
26 Kulshrestha, A. K., Patil, N. B., Dweltz, N. E. and Radhakrishnan, T. *Text. Res. Journ.* 1969, **39**, 1158
27 Kulshreshtha, A. K., Dweltz, N. E. and Radhakrishnan, T. *J. Appl. Cryst.* 1971, **4**, 116
28 Bonart, R., Hosemann, R. and McCullough, R. L. *Polymer*, 1963, **4**, 199
29 Hosemann, R. J. *Polym. Sci.* (*C*) 1967, **20**, 1
30 Vainslein, B. K. 'Diffraction of X-rays by Chain Molecules'.
31 Kaeble, E. F. 'Handbook of X-rays', McGraw–Hill Book Company, New York, 1967
32 Wilson, A. J. C. *J. Appl. Cryst.* 1972, **5**, 301
33 Ruland, W. *Acta Cryst.* 1961, **14**, 1180
34 Wilson, A. J. C. 'Mathematical theory of X-ray Powder Diffracometry', Philips Technical Library, 1963
35 Mukherjee, P. S. and Bhattacherjee, S. *The Indian Mineralogist* 1976, **17**, 49
36 Mitra, G. B. and Bhattacherjee, S. *Acta. Cryst.* 1970, **B26**, 2124
37 Hindeleh, A. M. and Johnson, D. J. *Polymer*, 1974, **15**, 697