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Microcrystalline parameters in annealed Bivoltine silk fibres using wide-angle X-ray scattering

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Wide-angle X-ray scattering studies of Bivoltine silk fibres have been carried out to obtain the crystal size distribution along the [201] direction. The minimum enthalpy for the formation of fibres has been estimated. The crystal size varies with annealing temperature, the values of g and α^* remaining almost constant, which is a unique feature of Bivoltine silk fibre. Using paracrystalline statistics, the Laue pattern has been simulated employing the microstructural parameters reported in this paper.

(Keywords: silk fibre; lattice distortion; crystal size)

INTRODUCTION

It is interesting to study the effect of annealing of silk fibres on crystal size and disorder parameters as they determine the properties of silk fibres. In fact there is a continued interest in the study of structural characteristics of silk fibres with various treatments[1–5]. Silk fibres can be heated up to 140°C without affecting the lustre of fibres. Beyond 170°C silk fibres show decoloration, but retain the fibre characteristics up to 200°C[2,4]. It has been found that the strength of the fibre improves with annealing, which also results in increase of crystal size parameter[2]. Here, investigations have been carried out on Bivoltine silk fibres to determine the effect of annealing on crystal size and disorder parameters. Using paracrystalline statistics, we have also simulated three-dimensional X-ray Laue patterns for Bivoltine silk fibres corresponding to microstructure parameters reported in this work.

X-ray scattering at wide angle ($\simeq 20°$) is due to the crystal lattice planes, and silk fibres are partially crystalline[6,7]. The microparacrystalline parameters are determined by utilizing the Fourier cosine coefficients of the intensity profile. Somashekar *et al.*[8] and Hall and Somashekar[9] have considered various aspects of multiple- and single-order methods. Recently we have extended the single-profile method to natural polymers[10,11].

THEORY

The intensity profile of the X-ray reflection from a partially crystalline sample like natural silk fibres is a function of the distribution of crystal sizes and of the lattice distortion g and these are related through the Fourier coefficients $A(n)$ to the profile intensity $I(s)$ by the equation:

$$I(s)=\sum_{n=-\infty}^{\infty} A(n)\cos[2\pi nd(s-s_0)] \tag{1}$$

Here s_0 is the value of s ($=\sin\theta/\lambda$) at the peak of the profile, d the mean d-spacing of the lattice planes causing the reflection and n the harmonic number.

The Fourier coefficients can be factorized into size $A_s(n)$ and disorder coefficients $A_d(n)$:

$$A(n)=A_s(n)A_d(n) \tag{2}$$

These are not normalized. By taking the exponential distribution function for crystal sizes, which gives fairly reliable results[11], we have the following relations for $A_s(n)$:

$$\begin{aligned} A_s(n)&=A(0)(1-n/\langle N\rangle) && n\leqslant p \\ A_s(n)&=A(0)\exp[-\alpha(n-p)]/\langle N\rangle && n\geqslant p \end{aligned} \tag{3}$$

where $\langle N\rangle$ is the average number of unit cells in a column through the crystal direction normal to the lattice planes causing reflection. Here p is the smallest possible number of unit cells in a column.

The crystal size is given by

$$\langle D\rangle=\langle N\rangle d_{hkl} \tag{4}$$

and $A_d(n)$ is the disorder coefficient for the paracrystal with separation of neighbouring lattice planes having Gaussian distribution given by:

$$A_d(n)=\exp(-2\pi^2m^2ng^2) \tag{5}$$

where m is the order of reflection and g is the lattice distortion parameter.

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EXPERIMENTAL AND COMPUTATION

Indigenous Bivoltine-race silk fibres were used in the present study. The cocoons were kept in boiling water for 3–4 min and the fibre reeling was processed at 45°C. The fibres were annealed at 100, 140 and 200°C in air for various lengths of time without stretching the fibre (i.e. at constant length). At 200°C, there was a slight change in colour of fibre, but without losing the characteristic fibre properties.

X-ray diffraction pattern

The X-ray diffraction profile of equatorial reflections from silk fibres, recorded using an X-ray diffractometer (JEOL, Japan; target Fe, $\lambda = 1.934$ Å) and filtered with Mn, is given in *Figure 1* and has only two reflections. X-ray reflections wre identified using the data given by Marsh *et al.*[6]. Taking the *b* axis as the fibre axis, the observed equatorial reflections are (100) and (201). Of these, the (100) reflection has too much background and overlapping with the (110) reflection and hence we could not record a clear profile of the (100) reflection using the X-ray diffractometer. We have used only the (201) reflection for our study. The profile of the (201) reflection used to obtain the crystal size and lattice distortion was assumed to be symmetric, and the half where the overlap with the neighbouring reflection is minimum was used to determine the Fourier cosine coefficients $A(n)$. The background level was taken as that at which the intensity became uniform and this was subtracted from all the points. The effect of background subtraction on the Fourier coefficients has been discussed earlier in detail[8]. The scattering angle was transformed to $\sin\theta/\lambda$ and the Fourier coefficients were calculated from these intensity data after they were corrected for Lorentz and polarization factors.

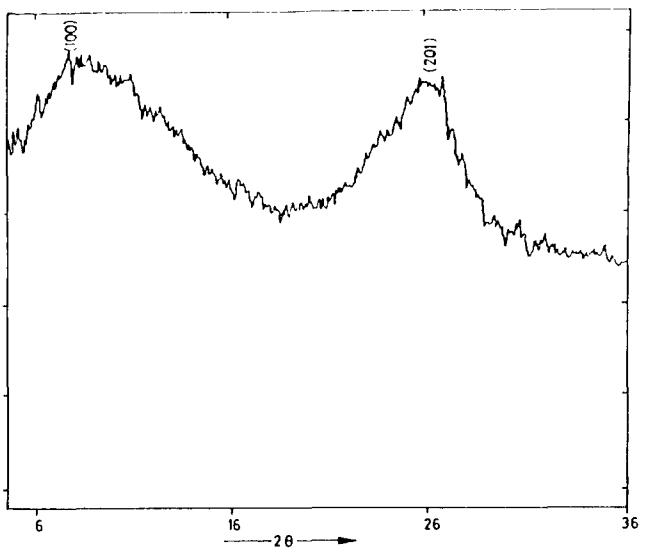

Figure 1 X-ray diffraction recording of raw Bivoltine silk fibre

In order to correct for instrumental line broadening using Stokes' method[12], the X-ray diffraction pattern was recorded for powdered KCl under the same conditions as used for silk fibres. This procedure was repeated for all the samples of various annealed Bivoltine silk fibres.

The refinement procedure

The calculation of the intensity profile using equations (1), (3), (4) and (5) requires four parameters, namely lattice disorder g, crystal size ($\langle N\rangle$ or $\langle D\rangle = \langle N\rangle d_{hkl}$), error in the background BG and a parameter α defining the width of the exponential distribution function of column lengths ($\alpha = 1/\langle N\rangle - p$). Initial values of g and $\langle N\rangle$ were obtained using the method of Nandi *et al.*[13]. Using these values in the above-mentioned equations gives the corresponding values for the distribution width. These are only rough estimates, so the refinement procedure must be sufficiently robust to start with such inaccurate values.

Here we compute:

$$\Delta^2 = [I_{calc} - (I_{expt} + BG)^2]/(\text{number of points}) \quad (6)$$

The value of Δ was divided by half the maximum value of intensity, so that it is expressed relative to the mean value of intensities and this function is minimized. For refinement, the multidimensional minimization algorithm of Simplex method was used[14].

The parameters $\langle N\rangle$, p and α are almost constant for various values of g and hence the average values of parameters $\langle N\rangle$, p and α were used to determine the g value and these are given in *Table 1*.

All the necessary computer programs were written in FTN 77 language and were compiled and executed using Archimedes 310M computer.

RESULTS AND DISCUSSION

Table 1 gives the parameters needed for recalculating the intensity profile, using equations mentioned earlier in the

Table 1 Microparacrystalline parameters obtained from (201) X-ray reflection of Bivoltine silk fibre (NB_7)

Fibre	$\langle N\rangle$	p	α	g(%)	α^*	A_0	BG	$\langle D\rangle$(Å)
Raw fibre	5.52 ±0.21	2.72 ±0.10	0.35 ±0.01	5.0	0.11	30.0	−1.0	24.0
Annealed at 100°C for 7 h	5.80 ±0.12	4.76 ±0.13	0.97 ±0.01	2.7	0.07	45.0	−4.32	25.0
Annealed at 100°C for 14 h	5.16 ±0.11	4.08 ±0.13	0.92 ±0.01	2.6	0.06	62.0	−4.33	22.2
Annealed at 140°C for 7 h	4.46 ±0.10	2.68 ±0.10	0.56 ±0.01	3.4	0.07	44.0	−2.66	19.8
Annealed at 140°C for 14 h	5.50 ±0.13	3.75 ±0.10	0.56 ±0.01	2.8	0.07	79.0	−4.42	23.8
Annealed at 200°C for 7 h	5.70 ±0.24	3.85 ±0.12	0.52 ±0.01	2.5	0.06	61.0	−3.50	24.5

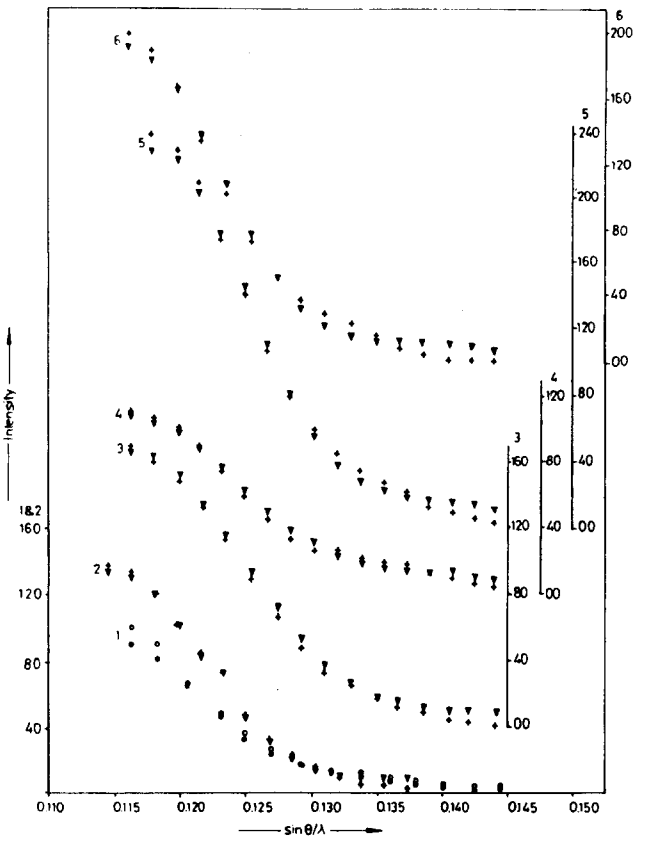

Figure 2 Experimental and calculated intensities of (201) X-ray reflection by Bivoltine silk fibres (NB_7) annealed at various temperatures for various lengths of time: (1) raw fibre, (○) experimental, (●) calculated; (2) 100°C/7 h, (3) 100°C/14 h, (4) 140°C/7 h, (5) 140°C/14 h, (6) 200°C/7 h, (+) experimental, (▼) calculated

text. *Figure 2* shows good agreement between experiment and the intensity calculated on the basis of paracrystalline model suggested in this paper for (201) reflection in Bivoltine silk fibre annealed at different temperatures.

In order to verify that we have estimated the actual crystal size, we have compared our results with Vainshtein's equation[15]:

$$g = 0.4(1/\langle N \rangle)^{1/2} \tag{7}$$

It can be noticed from *Figure 3* that, if a correlation effect is present, it will be characterized by points that lie along the straight line passing through the origin with a slope of 0.4. The fact that the points are far away from the line indicates that there is no correlation effect.

The crystal size $\langle D \rangle$ values shown in *Table 1* indicate that the crystal size differs with annealing temperature. It has a maximum value along the (201) direction when the Bivoltine silk fibre is annealed at 100°C for 7 h. At 200°C annealing temperature we have noticed external changes like decoloration. The g value at all annealing temperature is about 3%, indicating an almost constant g for all annealed Bivoltine silk fibres. *Figure 4* also gives the changes observed in crystal size distributions corresponding to different annealing temperatures of Bivoltine silk fibres.

From these parameters we have also estimated the minimum enthalpy α^*, which defines the equilibrium state of microparacrystals in Bivoltine silk fibres, using the equation[16]:

$$\alpha^* = N^{1/2} g \tag{8}$$

It is observed from *Table 1* that the value of α^* for all annealed Bivoltine silk fibres is almost a constant with a value of about 0.07. However, for raw fibre the value

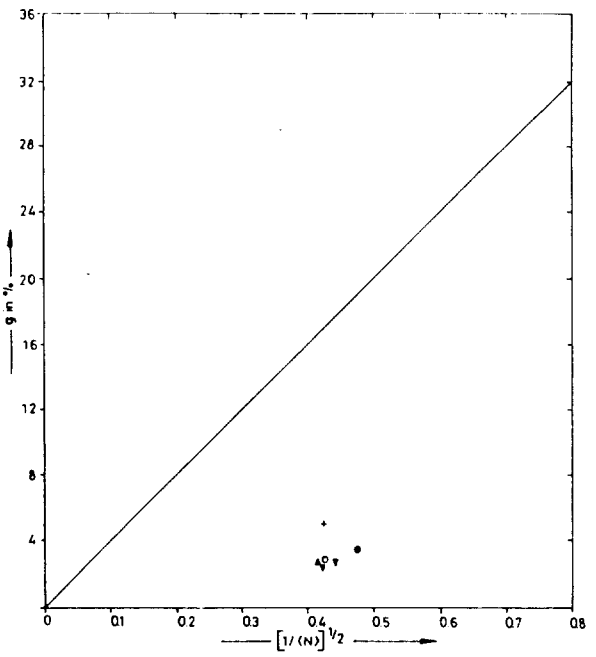

Figure 3 Variation of g with $(1/\langle N \rangle)^{1/2}$ for Bivoltine silk fibre (NB_7): (+)raw fibre: (▲) 100°C/7 h; (▼) 100°C/14 h; (●) 140°C/7 h; (○) 140°C/14 h; (▽) 200°C/7 h

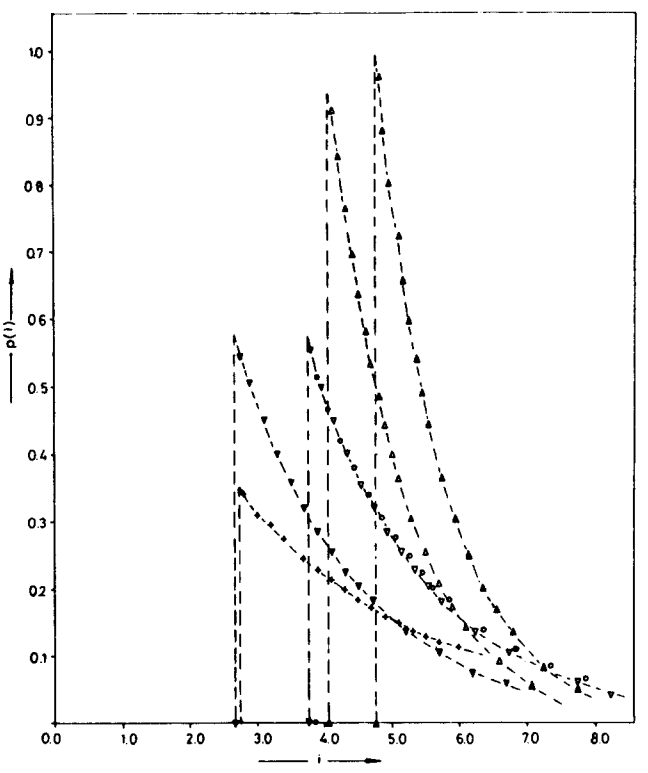

Figure 4 Crystal size distribution along the [201] direction for Bivoltine silk fibre: (+) raw fibre; (▲) 100°C/7 h; (△) 100°C/14 h; (▼) 140°C/7 h; (▽) 140°C/14 h; (○) 200°C/7 h

of α^* is 0.11. These results show that, even though the $\langle N \rangle$ value varies with annealing temperature, the values of g and α^* remain almost constant. This is a unique feature of Bivoltine silk fibre, whereas for all other races, the values of α^* and g differ with annealing temperature[17].

MODEL CALCULATIONS

The traditional model of polymer structure consists of two phases of high (crystalline) and low (amorphous) electron density. This two-phase model incorporates a statistical variation in size of crystalline and amorphous regions as well as distortion effects within crystallites. The two regions are considered to contribute separately to the X-ray scattering pattern and are unrealistically discontinuous at their boundaries. The concept of a paracrystal, introduced by Hosemann and Bagchi[18], which contains disorder of the second kind, shows much promise in calculation of computed scattering. It is hoped therefore that the X-ray diffraction pattern from such a model will not require a separate contribution from an amorphous phase.

Here we look at the theoretical construction of silk fibre model by computing the X-ray scattering from a three-dimensional finite paracrystal containing disorder of the second kind[19]. The entire probability distribution function is built up from the statistical separation of nearest neighbours in the lattice. At this point no attempt has been made to include other scattering effects.

For an ideal paracrystal, the lattice vectors form the edges of a parallelepiped and the three-dimensional distance probability distribution can be expressed in the following way:

$$I_{hkl}(\boldsymbol{r}) = [\overbrace{P_{100}(\boldsymbol{r}) * P_{100}(\boldsymbol{r})}^{h\text{ times}}] * [\overbrace{P_{010}(\boldsymbol{r}) * P_{010}(\boldsymbol{r})}^{k\text{ times}}] * [\overbrace{P_{001}(\boldsymbol{r}) * P_{001}(\boldsymbol{r})}^{l\text{ times}}] \quad (9)$$

where $\boldsymbol{r}$ is the position vector in real space and represents a convolution process. Note that the equation does not include extra terms that allow lattice edges to be non-parallels. In this paper calculations are made for an orthogonal set of axes and we hope in future that this can be extended to more general cases.

The 3D autocorrelation function is then obtained from the probability statistics and the intensity by Fourier transformation using an approach similar to the one used in 1D paracrystal[20]. The expression for intensity can be written using the convolution theorem as:

$$I(\boldsymbol{s}) = \mathrm{Re}\{F[P_{100}(\boldsymbol{r})]\}^h \{F[P_{010}(\boldsymbol{r})]\}^k \{F[P_{011}(\boldsymbol{r})]\}^l \quad (10)$$

where $\boldsymbol{s}$ is the reciprocal space position vector.

In three dimensions we have:

$$\{F[(1 - X/d_x)(1 - Y/d_y)(1 - Z/d_z)\gamma(x, y, z)]\}^{hkl} = [1 + (\mathrm{i}/d_x)\partial/\partial s]^h [1 + (\mathrm{i}/d_y)\partial/\partial t]^k \times [1 + (\mathrm{i}/d_z)\partial/\partial v]^l I_{hkl}(s, t, v) \quad (11)$$

where $(1 - X/d_x)$, $(1 - Y/d_y)$ and $(1 - Z/d_z)$ are the shape functions along x, y, z directions. For 3D statistics we have:

$$I_{hkl}(s, t, v) = \exp(-q_x^2 s^2) \exp(-q_y^2 t^2) \exp(-q_z^2 v^2) \times \exp(\mathrm{i}m_x hs) \exp(\mathrm{i}m_y kt) \exp(\mathrm{i}m_z lv) \quad (12)$$

where

$$q_x^2 = a_{11}^2 h + a_{12}^2 k + a_{13}^2 l$$
$$q_y^2 = a_{21}^2 h + a_{22}^2 k + a_{23}^2 l$$
$$q_z^2 = a_{31}^2 h + a_{32}^2 k + a_{33}^2 l$$

and

$$a_{ij}^2 = (1/2)\sigma_{ij}^2$$

Expanding and simplifying we get:

$$I(s, t, v) = \sum_l (1 - ml/d_z, -2iq_z^2 v/d_z) \exp(-q_z^2 v^2) \times \exp(\mathrm{i}m_z lv) \sum_{hk} (1 - m_x h/d_x, -2iq_x^2 s/d_x) \times (1 - m_y k/d_y, -2iq_y^2 t/d_y) \exp(-q_x^2 s^2) \times \exp(\mathrm{i}m_x hs) \exp(-q_y^2 t^2) \exp(\mathrm{i}m_y kt) \quad (13)$$

Here m_x, m_y, m_z are lattice spacings and d_x, d_y, d_z are crystal sizes (Å), a_{ij} the width by the Gaussian statistics, and distortion is given by:

$$g_{ij} = (a_{ij}/m_i)^{1/2} \quad (14)$$

Bivoltine silk fibre has orthogonal structure with unit-cell parameters $a = 9.4$ Å, $b = 6.97$ Å and $c = 9.20$ Å. Using the values for number of unit cells and lattice distortion along the [201] direction reported in this paper, we have simulated X-ray Laue type of diffraction (only one quadrant) for a 3D lattice employing equation (13), and the iso-projection of this is shown in *Figure 5b*. This pattern is nearer to the Laue pattern that is normally obtained with silk fibres. For the sake of completeness, we have also simulated the X-ray Laue pattern (*Figures 5a*) for $n = 5$ and $g = 1\%$, using paracrystalline statistics.

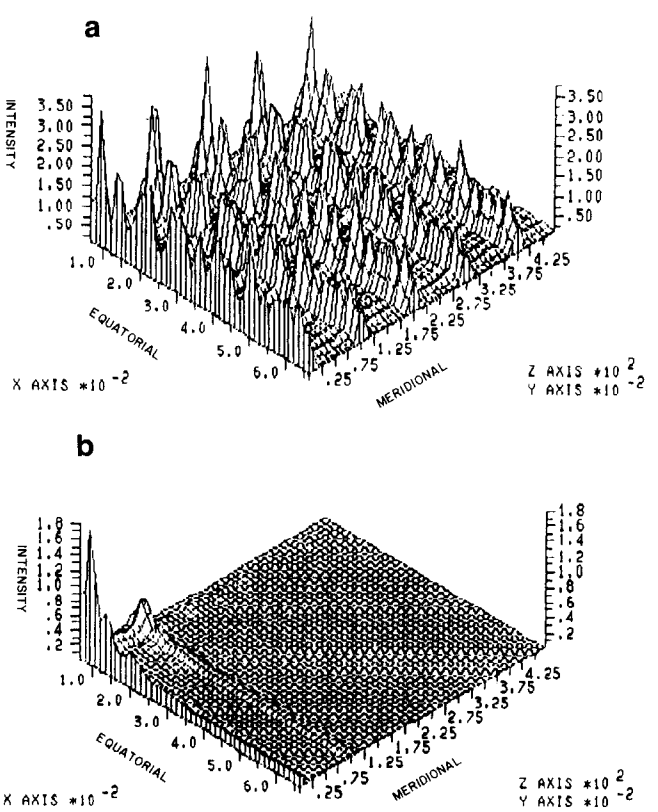

Figure 5 Iso-projections of X-ray diffraction patterns from a 3D paracrystal: (a) $g = 1\%$ and $N = 5$ units; (b) $g = 10\%$ and $N = 5$ units

Our programs were all written using FTN 77 language and executed using Cyber, University Computer Center, and the computation time was 7 h in order to simulate an X-ray Laue diffraction pattern.

CONCLUSION

The parameters in *Table 1* indicate that the Bivoltine races show significant improvement in crystal size with annealing. In analogy with man-made fibres, it can be suggested here that annealing of fibres at 100°C for 7 h improves the quality of fibres without affecting the lustre of silk fibres. We have simulated the X-ray diffraction pattern from a silk fibre using probability statistics assuming point scatterers to show the effect of crystal size and lattice distortions in broadening of the X-ray diffraction spots.

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