Crystal Size and Distortion Parameter of Natural Pure Mysore Silk Fibers (*Bombyx Mori*)

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SYNOPSIS

Crystal size and lattice distortion parameters were determined experimentally by recording X-ray diffraction patterns of natural silk fiber (pure Mysore silk, *Bombyx Mori*) using Fourier cosine coefficients of the intensity profile of an X-ray (210) reflection. Also, the crystal size distribution along [210] direction is given.

INTRODUCTION

Of all the fibrous proteins, silk fibroin is one of the most industrially important fibers. It is well known that silk fibers diffract X-rays and are at least partially crystalline.[1] The X-ray scattering at wide angles ($\simeq 20°$) is due to the crystal lattice planes. For a large perfect crystal, the diffraction pattern would comprise an array of very small spots. For the silk fiber, these spots are smeared into arcs, which are caused by imperfect orientation. The broadening of the X-ray diffraction spots is caused by both lattice distortion and small crystal size.[2] Presently, we have made an attempt for the first time to obtain crystal size and lattice distortion parameter from the intensity profile of a (210) reflection of a natural silk fiber. This type of work has not been reported for silk fibers by earlier investigators except for determining the cell parameters[3–5] and percentage of crystallinity.[6]

Earlier methods proposed to obtain crystallite size and lattice distortion parameters in polymer fibers utilize two or more orders of the reflection from a given set of lattice planes. Unfortunately, in all fibers, whether manmade or natural silk, it is unusual to observe more than one order and this has led to a search for methods that can be used with the profile of a single-order reflection. Both multiple- and single-order methods derive from a theory of Warren–

Averbach[7] utilizing the Fourier cosine coefficients of the intensity profile. Recently, Somashekar et al.[8] and Hall and Somashekar[9] considered various aspects of multiple- and single-order methods and suggested a suitable single-order method to obtain crystallite size and lattice distortion parameter fairly accurately.

In this article, we summarise the theory of Warren and Averbach[7] as applied to the single-order method by Hall et al.[9] Also, we describe both the experimental procedure used to record the intensity profile and the determination corresponding Fourier coefficients.

THEORY

The intensity profile of the X-ray reflection from a partially crystalline sample like natural silk fiber is a function of the distribution of crystal sizes in the sample and of the lattice disorder. Warren[10,11] has shown that quantities like crystal size (D) and lattice distortion (g) are related through the Fourier cosine coefficients $A(n)$ of the profile $I(s)$ by the equation:

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

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

Also, the Fourier coefficients can be factorized into size $(A_S(n))$ and disorder coefficients $[A_d(n)]$:

$$A(n) = A_S(n)A_d(n) \qquad (2)$$

and these are not normalized. $A_S(n)$ is related to the distribution of crystal sizes by:

$$A_S(n) = 1 - n/\langle N \rangle$$
$$- \left\{ \int_0^n [iP(i) - nP(I)]di \right\} / \langle N \rangle, \qquad (3)$$

where $\langle N \rangle$ is the average number of unit cells in a column through the crystal in a direction normal to the lattice planes causing the reflection, $P(i)$ is the normalized distribution function for all columns in a crystal and all crystals in the sample, and the crystal size is given as

$$D = \langle N \rangle d_{hkl}. \qquad (4)$$

$A_d(n)$ is the disorder coefficient for a paracrystal with separation of neighboring lattice planes having a Gaussian distribution of standard deviation (this model of disorder will be assumed in this work) given by:

$$A_d(n) = \exp(-2\pi^2 m^2 n g^2), \qquad (5)$$

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

It was found by Hall et al. that asymmetric distributions gave fairly accurate results. Under these circumstances, we have used asymmetric distributions, namely, the exponential and Reinhold. In this section, eq. (3) is used to obtain an expression for $A_S(n)$ for each distribution.

Exponential Distribution

It is assumed that there are no columns containing fewer than p unit cells, but that the number of those longer than this decay exponentially. Thus,

$$\text{if } i \leq p \quad P(i) = 0$$
$$\text{if } i \geq p \quad P(i) = \alpha \exp[-\alpha(i - p)],$$

where $\alpha = 1/(\langle N \rangle - p)$. It follows from eq. (3) that:

$$A_S(n) = A(0)(1 - n/\langle N \rangle) \quad n \leq p$$
$$A_S(n) = A(0)\{\exp[-\alpha(n - p)]\}/\langle N \rangle \quad n \geq p.$$

Reinhold Distribution

With the exponential distribution, $P(i)$ rises discontinuously at p from 0 to its maximum value. The Reinhold function allows a continuous change by putting:

$$P(i) = 0 \quad \text{if } i \leq p$$
$$P(i) = \beta^2(i - p) \exp[-\beta(i - p)] \quad \text{if } i \geq p,$$

where $\beta = 2/(\langle N \rangle - p)$. From eq. (3), it follows that:

$$A_S(n) = A(0)(1 - n/\langle N \rangle) \quad n \leq p$$
$$A_S(n) = A(0)\frac{(n - p + 2/\beta)}{\langle N \rangle} \exp[-\beta(n - p)].$$

EXPERIMENTAL AND COMPUTATION

Pure Mysore silk is the indegenous multivoltine races of South India of mulberry silk worm (*Bombyx Mori*). The cocoons are kept in boiling water for about 2–3 min and the fiber reeling is processed at 45°C.

Recording of X-Ray Diffraction Pattern

The X-ray diffraction pattern from silk fibers was recorded (Fig. 1) using a flat film with nickel-filtered CuKα radiation. The observed reflections and corresponding d spacings are given in Table I along with calculated d spacing using reported cell para-
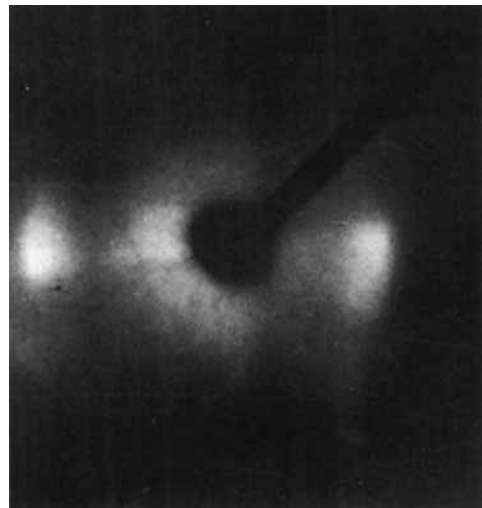

Figure 1 X-ray diffraction pattern of pure Mysore silk fiber.

Table I   *d* Spacings Observed and Calculated using Reported Cell Parameters for a Pure Mysore Silk Fiber (*Bombyx Mori*)
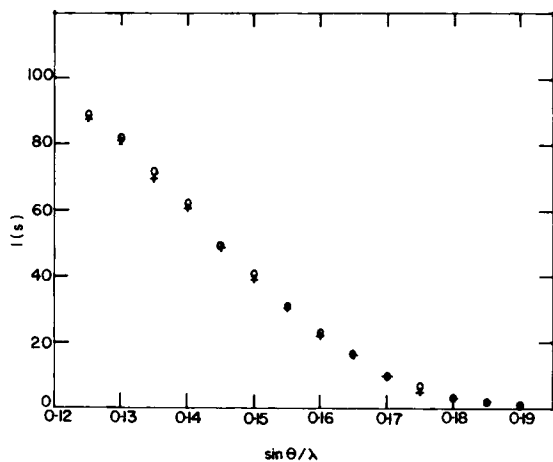
Reflections	d_{exp} (Å)	d_{cal} with a = 9.4 Å, b = 6.97 Å, c = 9.20 Å (Å)
(100)	9.70	9.40
(210)	4.00	4.19
(220)	3.32	3.28
(400)	2.45	2.35

meters.[3] Then, the intensity profile for the (210) reflection was obtained using Jarrell-Ash microdensitometer.

The profile of (210) reflection was assumed to be symmetric and the half where the overlap with the neighboring reflection is minimum was used (see Fig. 2) to determine the cosine Fourier coefficients $A(n)$. The background level was taken as that at which intensity became uniform. This was subtracted from all the points and for this particular reflection the value of B is unity as required by the theory.

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 and also nonlinearity of film response. As a check on the calculation, the profile was resynthesized and compared with the original data.

To correct for instrumental line broadening using Stokes method,[12] the X-ray diffraction pattern was recorded for aluminium foil under the same condition as used for silk fibers. The small effect of instrumental broadening is shown in Figure 2, where the intensity data is given before and after corrections.
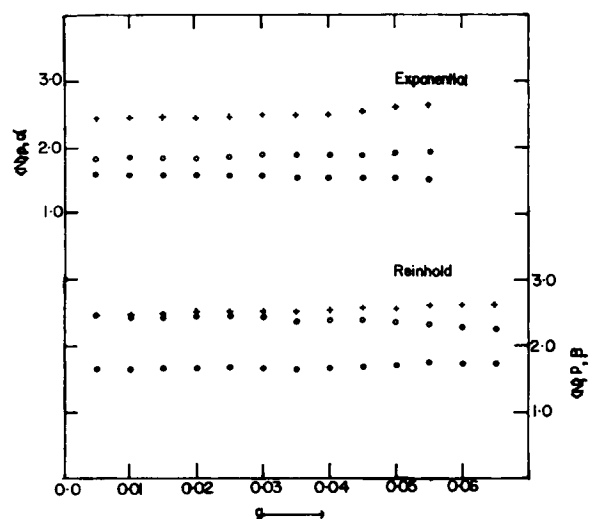
Refinement Procedure

The calculation of the intensity profile using eqs. (1), (2), (3), and (5) and various distribution functions for crystal size requires four parameters; namely, lattice distortion parameter (g), crystal size ($\langle N \rangle$ or D), error in background, and a parameter defining the width of the distribution function of column lengths. 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 gave the corresponding values for the width of the distributions. These are only rough estimates, but refinement procedures must be sufficiently robust to start with such inaccurate values.

Along with these initial values, the mean square residual was also used in the refinement. Here, we compute:

$$\Delta^2 = \sum [I_{cal} - (I_{exp} + C)]^2 /$$

$$\text{number of points,} \quad (6)$$

where this value of Δ was divided by half the maximum value of intensity so that it is expressed relative to the mean value of the intensities and this function is minimized.

For refinement, the multidimensional minimization algorithm due to Powell and Simplex methods

Figure 2   Intensity profile of (210) reflection. O and + represent without and with instrumental broadening correction, respectively.

Figure 3   Variation of $\langle N \rangle$, p, α, or β with g obtained with Exponential and Reinhold distribution functions. +, $\langle N \rangle$; O, p; ●, α or β.
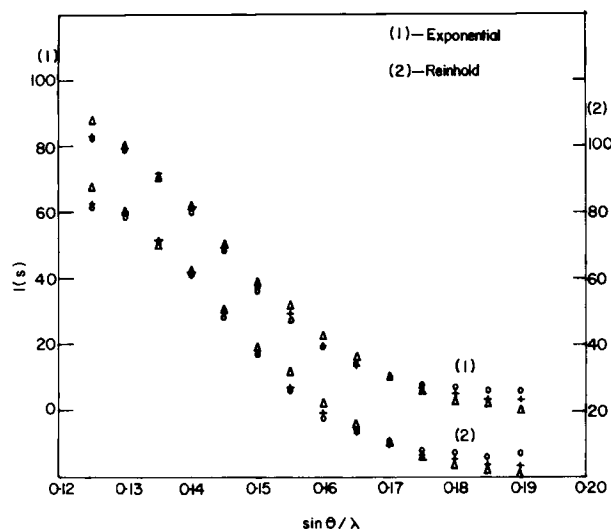
Figure 4 Resynthesized intensity profile using the parameters $\langle N \rangle$ and p corresponding to the values of g = 0.035 (+) and g = 0.045 (O) for both Exponential and Reinhold crystal size distribution. $\triangle$ are experimental intensity values.

were used.[14] Both procedures gave similar results. Since the Simplex method is a simpler and shorter program, we chose it, but the choice between the two is a matter of individual preference.

All computer programmes were written in FTN77 language and were compiled and executed using Archimedes 310M, Acorn, UK make.

RESULTS AND DISCUSSIONS

It is observed that the change in $\langle N \rangle$, p, and α for various g values is almost a constant to within ±5% (see Fig. 3) and hence there is absolutely no ambi-

guity in deciding the reliable values for $\langle N \rangle$ and p. On the other hand, there is a range of g values, and to decide the allowed range for g the following procedure was used. Using eqs. (1), (2), (3), and (5) and distribution function for crystal size and also parameters $\langle N \rangle$, p, and α/β for g = 0.035–0.045 obtained by minimization procedure, the intensity data was resynthesized and compared with experimental data in Figure 4. There is good agreement between experimental intensity and intensity calculated with the parameters obtained for g values lying below the value 0.035. This worsens for parameters corresponding to g values equal and above 0.045 in both the cases of Reinhold and Exponential distributions. Hence, the allowed values of g are 0.035 ± 0.015. The parameters obtained by this method corresponding to the reflection (210) of a silk fiber are given in Table II and compared with the data obtained for manmade fibers like Kevlar-49™ and polyethylene[8] (LDPE). Here, Kevlar-49 Aramid was a multifilament yarn. LDPE specimen was a single filament of about 0.5 mm diameter produced by extrusion from the melt at 448 K followed by drawing at 294.8 K to a ratio of 5.48 and annealing at 363 K. The results reproduced in Table II for these fibers are obtained using reliable multiple-order method. Here, p denotes the smallest number of unit cells in the column. The probability distribution function for crystal size is given in Figure 5 as obtained for both Reinhold and Exponential functions.

CONCLUSION

From Table II we can conclude that the crystallite size in natural fibers is less and distortion of the

Table II Average Number of Unit Cell ($\langle N \rangle$), Crystal Size (D), Lattice distortion (g), and Smallest Unit Cell Number (p) Obtained for (210) Reflection in Natural Pure Mysore Silk Fiber

	Exponential Function				Reinhold Function			
Specimen	$\langle N \rangle$	D (Å)	g	p	$\langle N \rangle$	D (Å)	g	p
Pure Mysore silk fiber	2.48 ± .07	9.94 ± .31	0.035 ± .015	1.86 ± .06	2.50 ± .12	10.0 ± 0.5	0.035 ± .015	1.68 ± .05
LDPE (200) & (400) reflections[a]	10.1	39.5	0.019	—	—	—	—	—
LDPE (110) & (220) reflections[a]	14.9	61.39	0.056	—	—	—	—	—
Kevlar (200) & (400) reflections[a]	9.5	36.48	0.046	—	—	—	—	—

[a] Obtained with multiple-order method.
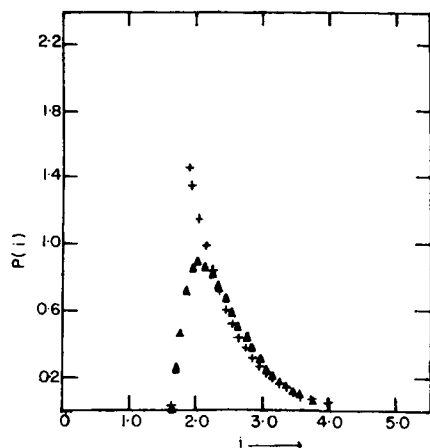
Figure 5 Crystal size distribution along [210] direction. ▲, Reinhold; +, Exponential.

lattice is comparatively more when compared with manmade fibers. To understand the reasons for the silk fibers to have less tensile strength when compared to manmade fibers, we need information on the longitudinal crystal dimension and on chain conformation of the β-pleated structure and to some extent on the lateral crystal size of the silk fibers, which has been reported in this article.

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