# Crystal Size and Minimum Enthalpy of Crossbreed Silk Fibers Annealed at Various Temperatures

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SYNOPSIS

Wide-angle X-ray diffraction studies of crossbreed silk fibers and fibers annealed at various temperatures for different periods of time were carried out to evaluate the crystal size and lattice distortion parameters, as these determine the properties of silk fibers. Also, minimum enthalpy for the formation of these fibers has been estimated and compared. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Silk, which is a fibrous protein, is one of the industrially important fibers. Wide-angle X-ray scattering studies (WAXS) by earlier investigators of silk fibers have shown that they are partially crystalline.[1] For a perfect crystal, the diffraction pattern would comprise of an array of very small spots. For silk fibers, the spots are made into arcs that are caused by two types of defects present in the silk fibers: first, the lattice distortion, and, second, the effect of the crystal size.[2] Using Fourier analysis of the scattered X-ray reflections, we determined the crystal size and lattice distortion parameters for (210) equatorial reflections of crossbreed silk fiber and the effect of annealing on these parameters has been studied. Also, we determined the minimum enthalpy for the formation of these fibers. Such studies have not been reported earlier except for determining the cell parameters[3-5] and percentage of crystallinity[6] for natural silk fibers.

Both multiple- and single-order methods used to separate crystal size and distortion parameters are derived from the theory of Warren–Averbach[7] utilizing the Fourier cosine coefficients of the intensity profile. Somashekar et al.[8] and Hall and Somashekar[9] considered various aspects of multiple- and single-order methods. Recently, we extended a single-profile method to natural polymers.[10]

## THEORY

The intensity profile of the X-ray reflection from a partially crystalline sample like natural silk fibers 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

$$I(S) = \sum_{n=-\infty}^{\infty} A(n)\cos\{2\pi nd(S - S_0)\} \quad (1)$$

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 $A_d(n)$:

$$A(n) = A_S(n) \cdot A_d(n) \quad (2)$$

These are not normalized. By taking the exponential distribution function for crystal sizes, which gives fairly reliable results,[10] we have the following relations for $A_S(n)$:

$$A_S(n) = A(0)[1 - n/\langle N\rangle] \quad n \le p$$

$$A_S(n) = A(0)[\exp\{-\alpha(n-p)\}/\langle N\rangle] \quad n \ge p \quad (3)$$

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Journal of Applied Polymer Science, Vol. 50, 949–952 (1993)
 CCC 0021-8995/93/060949-04

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 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 paracrystal with the separation of neighboring lattice planes having a Gaussian distribution of standard deviation given by

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

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

The reasons for using nonnormalized Fourier coefficients are (i) the truncation of the profiles and (ii) error in the background estimation, and these affect the low-order Fourier coefficients of the intensity profile as explained in detail by Somashekar et al.[8] Using eqs. (1), (3), (4), and (5) along with experimental intensity data, it is possible to determine crystal size and lattice distortion.

## EXPERIMENTAL AND COMPUTATION

Indigenous crossbreed cocoons of multivoltine with Bivoltine race were used in the present study. The cocoons were kept in boiling water for 3–4 min and the fiber reeling was processed at 45°C. Samples of crossbreed fibers were annealed at 100, 140, and 200°C for various lengths of time without stretching the fiber. At 200°C, there is a slight change in color of the fibers, but without losing the characteristic fiber properties.

### X-ray Diffraction Pattern

The X-ray diffraction profile of equatorial reflections from silk fibers, recorded using an X-ray diffractometer (JOEL, Japan, Target Fe, $\lambda$ = 1.934 A) is given in Figure 1 and has only two reflections. Of these, the (100) reflection has too much background and overlapping with inner reflection and, hence, we could not record a clear profile of the (100) reflection using the X-ray diffractometer. We have used only the (210) reflection for our study. The reflections were identified using cell parameters reported earlier.[3] The profile of the (210) reflection used to obtain the crystal size and lattice distortion was assumed to be symmetric, and the half where

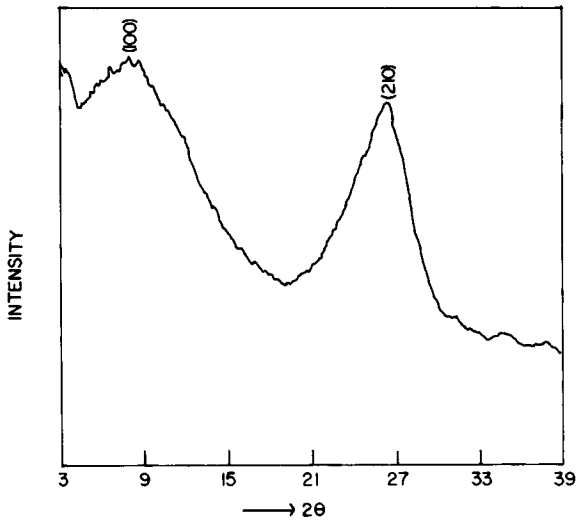


**Figure 1** X-ray diffraction recording of native crossbreed silk fiber along equatorial direction.

the overlap with the neighboring reflection is minimum was used to determine the cosine Fourier 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 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.

To correct for instrumental line broadening using the Stokes method,[11] the X-ray diffraction pattern was recorded for powdered KCl under the same conditions as used for silk fibers. This procedure was repeated for all the samples of various crossbreed silk fibers.

### The Refinement Procedure

The calculation of the intensity profile using eqs. (1), (3), (4), and (5) requires four parameters, namely, lattice distortion $g$, crystal size ($\langle N \rangle$ or $\langle D \rangle = \langle N \rangle d_{hkl}$), error in the background, and a parameter defining the width of the exponential distribution function of column lengths. Initial values of $g$ and $\langle N \rangle$ were obtained using the method of Nandi et al.[12] Using these values in the above-mentioned equations gave the corresponding values for the distribution width. These are only rough estimates, but the refinement procedure must be sufficiently robust to start with such inaccurate values.

Here we compute

$$\Delta^2 = [I_{cal} - (I_{exp} + BG)]^2/\text{number of points} \tag{6}$$

The value of $\Delta$ 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 the SIMPLEX method was used.[13] Here, *BG* refers to inaccuracy in background estimation.

It was observed that the variation of $\langle N \rangle$, $p$, and $\alpha$ defined in eq. (3) with respect to $g$ for the exponential function is almost constant, and under these circumstances, the average values of parameters $\langle N \rangle$, $p$, and $\alpha$ were used to determine the $g$ value and these are given in Table I.

All the necessary computer programs were written in FTN77 language and were compiled and executed using Archimedes 310M, Acorn (U.K. make).

## RESULTS AND DISCUSSION

Table I gives the parameters needed for recalculating the intensity profile using eqs. (1), (3), and (5). Figure 2 shows good agreement between experimental and the intensity calculated on the basis of the paracrystalline model suggested for the (210) reflection of crossbreed silk fibers annealed at various temperatures. This clearly indicates that the parameters obtained here are quite reliable. The crystal size $\langle D \rangle$ values shown in Table I for various samples indicates that the native crossbreed fiber has a higher value compared to all other annealed fibers, and from this, one can infer that the native crossbreed (without annealing) has a higher strength compared to other annealed crossbreed silk fibers. The lattice distortion in all cases is about 2–7% along the [210] direction and this estimation of lattice distortion to some extent depends on the model used to separate the crystal size and distortion parameters from Fourier coefficients. From these parameters, one can also estimate the minimum enthalpy that defines the equilibrium state of microparacrystals in pure and annealed crossbreed silk fibers using the relation[14]

$$\alpha^* = \langle N \rangle^{1/2} g \tag{7}$$

which is the minimum of sum of the volume enthalpy ($N^3 \Delta G_v$) and the paracrystalline tangential enthalpy $\Delta G_p = 3/2N^4 A_0 g^2$, where $A_0$ is the coefficient of the atomic tangential potential.[15,16]

The value of $\alpha^*$ implies, physically, that the

**Table I Microparacrystalline Parameters Obtained from (210) X-ray Reflection of Crossbreed Silk Fibers**

| Fiber | $\langle N \rangle$ | $P$ | $\alpha$ | $g$ | $\alpha^*$ | $A_0$ | *BG* Error | *D* (Å) |
|---|---|---|---|---|---|---|---|---|
| Crossbreed (CB) native | 5.74 ± 0.19 | 3.53 ± 0.12 | 0.45 ± 0.02 | 7.4% | 0.18 | 45 | −1.83 | 24.23 |
| CB, 100°C for 7 h | 5.23 ± 0.14 | 3.04 ± 0.10 | 0.46 ± 0.01 | 2.0% | 0.05 | 48 | −2.30 | 22.09 |
| CB, 100°C for 14 h | 4.22 ± 0.11 | 1.94 ± 0.06 | 0.44 ± 0.01 | 5.5% | 0.11 | 38 | −1.75 | 17.83 |
| CB, 140°C for 7 h | 5.63 ± 0.17 | 3.09 ± 0.10 | 0.40 ± 0.01 | 2.6% | 0.06 | 48 | −2.13 | 23.76 |
| CB, 140°C for 14 h | 4.98 ± 0.13 | 2.73 ± 0.07 | 0.45 ± 0.01 | 6.6% | 0.14 | 68 | −3.39 | 21.02 |
| CB, 200°C for 7 h | 5.43 ± 0.16 | 2.85 ± 0.08 | 0.39 ± 0.01 | 5.6% | 0.13 | 58 | −2.54 | 22.93 |
| LDPE (200) and (400) reflections | 10.1 | — | — | 1.9% | 0.06 | — | — | — |
| LDPE (110) and (220) reflections | 14.9 | — | — | 5.6% | 0.21 | — | — | — |

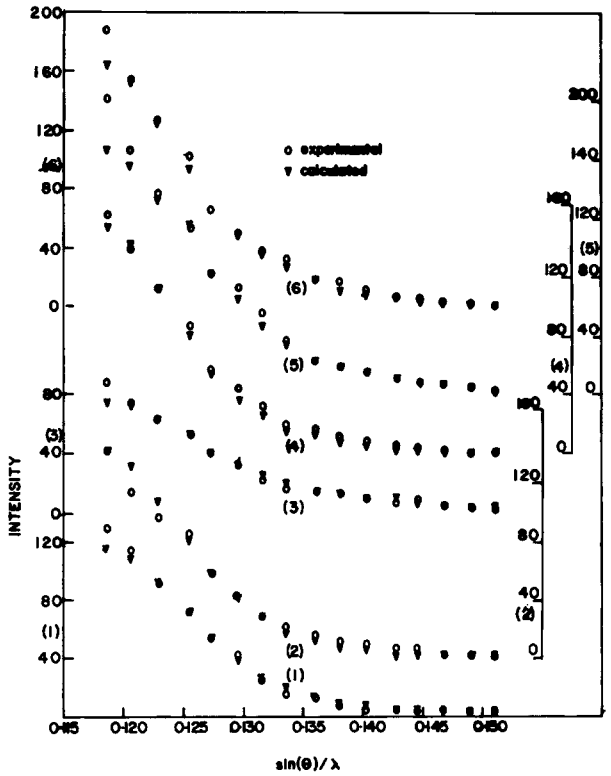


**Figure 2** Experimental and calculated intensity of (210) X-ray reflection by crossbreed (CB) silk fibers annealed at various temperatures for various lengths of time: (1) CB native; (2) 100°C 7 h; (3) 100°C 14 h; (4) 140°C 7 h; (5) 140°C 14 h; (6) 200°C 7 h.

growth of paracrystal in a particular material is controlled appreciably by the level of $g$ in the net plane structure. The minimum value of enthalpy estimated using the above relation for silk fibers of pure and annealed crossbreed race is given in Table I and one can conclude that the native crossbreed silk fiber with a higher value of crystal size consumes more energy in order to build up the crystal network compared to all other annealed fibers. Also, the value of $\alpha^*$ lies between 0.05 to 0.2 for both natural and man-made fibers. We also compared in Table I the crystal size and lattice distortion parameters of man-made fibers like low-density polyethylene (LDPE). From this comparison, it is evident that the crystal size in silk fibers is much less compared to that of man-made fibers.

## CONCLUSION

The parameters clearly indicate that the pure crossbreed silk fiber do have higher crystalline regions compared to annealed fibers and pure Mysore silk fiber (native). This implies that heat treatment of these crossbreed fibers does not improve the crystal size value, but significant improvement in the crystal size value in the case of pure Mysore silk fiber has been noticed in our earlier paper.[10]

The authors thank the Director, Central Sericulture Research and Training Institute, Mysore, for providing the samples and Dr. I. H. Hall, UMIST Manchester, England, for updating the information with regard to the single-order method.

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*Received August 9, 1992*
*Accepted January 9, 1993*