Effect of Physical and Chemical Modifications on Microcrystalline Parameters of Silk Fibers

H. SOMASHEKARAPPA,[1] N. SELVAKUMAR,[2] V. SUBRAMANIAM,[2,*] and R. SOMASHEKAR[3]

[1]Department of Physics, Yuvaraja's College, Mysore-570 005, India; [2]Department of Textile Technology, Anna University, Madras-600 025, India; [3]Department of Studies in Physics, University of Mysore, Mysore-570 006, India

SYNOPSIS

Wide-angle X-ray diffraction studies of physically and chemically treated silk fibers like bivoltine mulberry silk and tassar silk were carried out to evaluate their crystal size, lattice distortion, and minimum enthalpy, as these determine the properties of silk fibers. The results are also compared with tenacity measurement. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Silk, which is a fibrous protein, is one of the important textile materials and is abundantly cultivated in India. 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 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 crystal size.[2] Using Fourier analysis of the scattered X-ray reflections, we determined the crystal size and lattice distortion parameters for (201) equatorial reflections of bivoltine mulberry and tassar silk fibers. The effect of physical and chemical modifications on these parameters is reported here. 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 coefficients of the intensity profile. Somashekar et al.[8] and Hall and Somashekar[9] considered various aspects of multiple- and single-order methods. Recently, Somashekar et al.[10] extended a single-profile method to natural polymers.

Bhat and Ahirrao[11] carried out the effect of formic acid, zinc chloride, and lithium thiocyanate on silk fibers using IR and electron microscope studies. Here, the finer aspects of changes that are normally observed in terms of the microcrystalline parameters have not been investigated. Hence, we report the experimentally determined microstructural parameters and their changes due to physical and chemical treatment of bivoltine mulberry and tassar silk fibers. We also compared the results with tenacity measurements with a view to finding whether any relation exists between them.

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

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

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.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 59, 1677–1681 (1996)
 CCC 0021-8995/96/111677-05

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

$$A(n) = A_S(n) \cdot Ad(n) \tag{2}$$

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

$$A_S(n) = A(0)[1 - n/\langle N\rangle] \qquad n \le p$$
$$A_S(n) = A(0)[\exp\{-\alpha(n-p)\}/\alpha\langle N\rangle] \qquad n \ge p \tag{3}$$

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 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) the error in the background estimation. 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 the crystal size and lattice distortion.

EXPERIMENTAL AND COMPUTATION

Machine-reeled bivoltine mulberry raw silk yarn of 25.2 dtex with 15 tpcm and charka reeled tassar raw silk yarn of 40 dtex with zero twist were used in the present study. The bivoltine yarn was degummed with a sodium silicate (LR) solution having pH 10 for 1 h at boil, whereas tassar yarn was degummed with 8 gpl commercial soap and 8 gpl sodium carbonate (LR) for 3 h at boil.

Physical modification was carried out by subjecting the wet degummed yarns to stretching treatment. The yarns were stretched to 7.7 and 18.7% of their original length using a laboratory stretching device and then drying the yarns both at slack and taut conditions. Chemical modification was carried out only on bivoltine yarn by subjecting it to 5 and 20% w/v formic acid (LR) and zinc chloride (LR) for 1 h at boil. The treated yarns were thoroughly washed to remove the residual chemicals.

The breaking load of the samples was determined using an Instron tensile tester. A specimen length of 100 mm and a crosshead speed of 100 mm/min were used. Tenacity values were calculated using the linear density (denier) of the samples.

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, λ = 1.934 Å) 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 used only the (201) reflection for our study. The reflections were identified using cell parameters reported earlier.[3] 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 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 θ/λ and the Fourier coeffi-

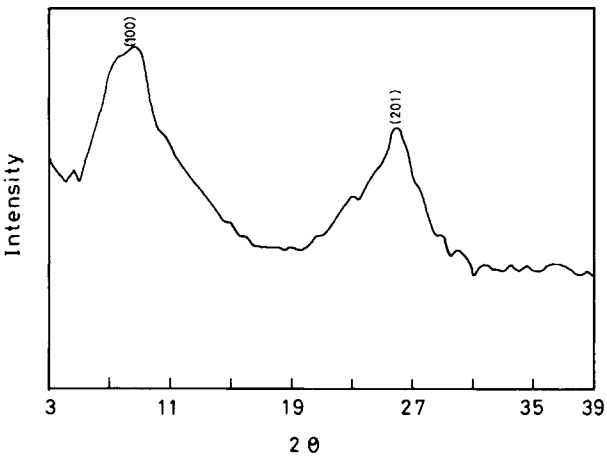

Figure 1 X-ray diffraction recording of bivoltine mulberry degummed silk fiber stretched to 18.7% and tension-dried.

Table I Microparacrystalline Parameters Obtained from (201) X-ray Reflection of Bivoltine Mulberry and Tassar Silk Fibers

No.	Samples	$\langle N \rangle$	p	α	g (%)	α^*	A_0	BG Error	$\langle D \rangle$ Å	Tenacity (g/d)
1	Bivoltine degummed (BD) —untreated	2.44 ± 0.07	0.02 ± 0.03	0.41 ± 0.01	2.39	0.04	1.39	0.00	10.69	3.13
2	BD, 7.7% stretch —slack-dried	3.01 ± 0.10	0.30 ± 0.04	0.37 ± 0.01	8.33	0.14	1.68	0.00	13.18	3.24
3	BD, 18.7% stretch —slack-dried	3.02 ± 0.11	0.24 ± 0.03	0.33 ± 0.01	1.55	0.03	1.27	0.01	12.99	4.77
4	BD, 7.7% stretch —tension-dried	2.07 ± 0.06	0.04 ± 0.01	0.48 ± 0.01	5.18	0.08	3.53	−0.01	8.91	3.66
5	BD, 18.7% stretch —tension-dried	2.67 ± 0.09	0.01 ± 0.01	0.38 ± 0.01	3.03	0.05	2.98	0.00	11.47	4.96
6	BD, 5% formic acid-treated	4.41 ± 0.11	3.12 ± 0.11	0.78 ± 0.00	6.56	0.14	1.14	0.00	19.70	3.28
7	BD, 20% formic acid-treated	8.07 ± 0.35	5.10 ± 0.28	0.34 ± 0.01	3.62	0.10	0.65	−0.01	34.01	3.09
8	BD, 5% zinc chloride-treated	3.78 ± 0.17	1.31 ± 0.11	0.41 ± 0.01	4.86	0.10	1.31	0.00	16.90	2.91
9	BD, 20% zinc chloride-treated	5.58 ± 0.22	2.77 ± 0.11	0.36 ± 0.01	2.14	0.05	1.28	−0.01	23.90	2.24
10	Tassar degummed (TD)—untreated	2.05 ± 0.34	0.03 ± 0.36	0.50 ± 0.01	8.74	0.13	1.66	−0.08	8.82	—
11	TD, 7.7% stretch —slack-dried	2.14 ± 0.06	0.01 ± 0.03	0.47 ± 0.01	7.09	0.10	1.34	0.00	9.35	—
12	TD, 18.7% stretch —slack-dried	1.76 ± 0.03	0.01 ± 0.01	0.57 ± 0.01	5.91	0.08	2.83	0.01	7.88	—
13	TD, 77% stretch —tension-dried	4.51 ± 0.14	1.90 ± 0.03	0.38 ± 0.02	3.65	0.08	1.36	0.01	19.70	—
14	TD, 18.7% stretch —tension-dried	3.56 ± 0.15	0.50 ± 0.02	0.33 ± 0.01	2.76	0.05	1.70	0.00	15.03	—

cients 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,[12] 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.

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.[13] Using these values in the above-mentioned equations gave 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

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

The value of Δ was divided by half the minimum 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.[14] Here, BG refers to the inaccuracy in background estimation.

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

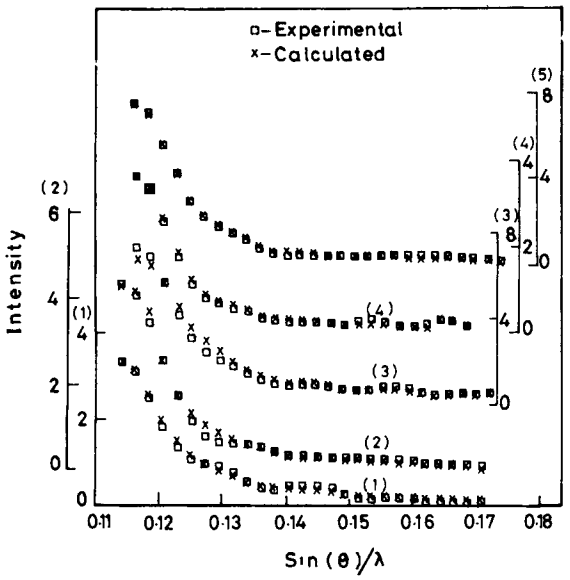

Figure 2 Experimental and calculated intensity of (201) X-ray reflection by stretched and dried bivoltine mulberry degummed silk fiber: (1) control; (2) 7.7% stretch—slack-dried; (3) 7.7% stretch—tension-dried; (4) 18.7% stretch—slack-dried; (5) 18.7% stretch—tension-dried.

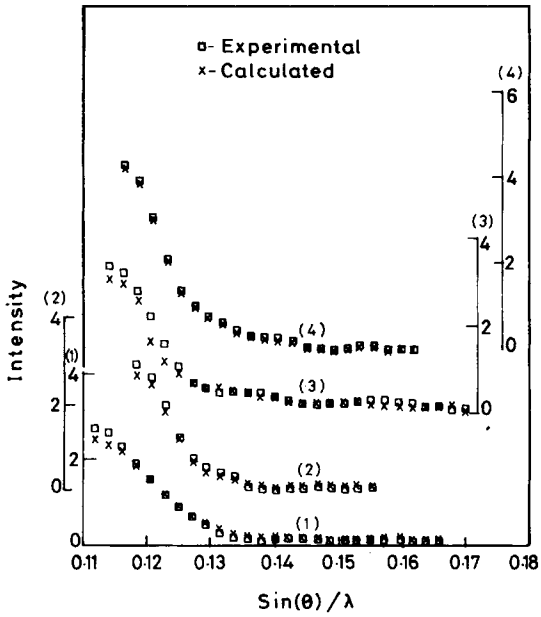

Figure 3 Experimental and calculated intensity of (201) X-ray reflection by bivoltine mulberry degummed silk fiber treated with reagents: (1) 5% formic acid; (2) 20% formic acid; (3) 5% zinc chloride; (4) 20% zinc chloride.

computer programs were written in the FIN77 language and were compiled and executed using the Cyber, Mysore University computer.

RESULTS AND DISCUSSION

Table I gives the parameters needed for recalculating the intensity using eqs. (1), (3), and (5). Figures 2–4 show good agreement between experimental and the intensity calculated on the basis of the paracrystalline model suggested for the (201) reflection of physically and chemically modified bivoltine mulberry and tassar silk fibers. 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 with the physical treatment of fibers, especially mulberry silk, there is an increase in the crystal size value, which is supported by significant improvement in tenacity values also given in Table I. Chemically treated fibers also show an increase in crystal size value. Formic acid-treated samples do not show a significant improvement in tenacity, whereas the zinc chloride-treated samples show a significant drop, which indicates that the increase in crystal size in chemically treated samples does not improve tenacity. This clearly reflects that the increase in crystal size is only a relative increase due to reduction in the amorphous content in the fibers.

In all the samples, the lattice distortion varies between 2 and 8% along the (201) direction and this estimation depends on the model used to separate

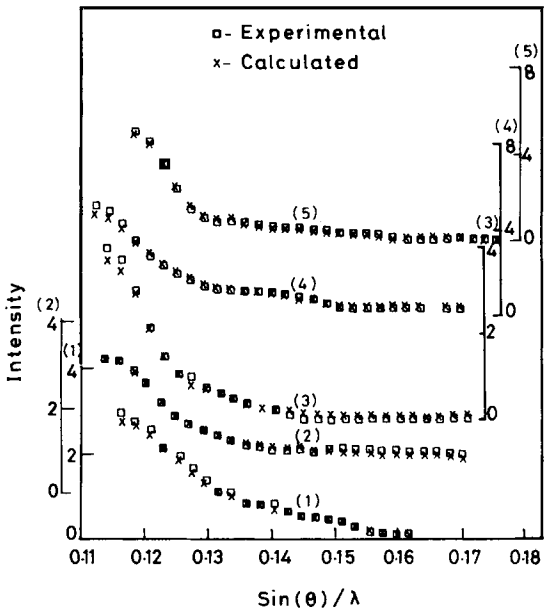

Figure 4 Experimental and calculated intensity of (201) X-ray reflection by stretched and dried tasar degummed silk fiber: (1) control; (2) 7.7% stretch—slack-dried; (3) 7.7% stretch—tension-dried; (4) 18.7% stretch—slack-dried; (5) 18.7% stretch—tension-dried.

the crystal size and distortion parameter. From these parameters, one can also estimate the minimum enthalpy that defines the equilibrium state of microparacrystals in untreated and treated silk fibers using the relation[16]

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

which is the minimum of sum of the volume enthalpy ($N^3 \Delta G_v$) and the paracrystalline tangential enthalpy $\Delta Gp = \frac{3}{2} N^4 A_0 g^2$, where A_0 is the coefficient of the atomic tangential potential.[17,18]

The value of α^* implies, physically, that the growth of paracrystal in a particular material is controlled by the level of g in the net plane structure. The minimum values of enthalpy estimated using the above relation of untreated and treated silk fibers are given in Table I. The value of α^* lies between 0.02 to 0.15 for all samples and this is true even in the case of man-made fibers.[15,19]

The same thing cannot be said about tassar silk fibers in the absence of tenacity measurement. We could not use the tenacity values determined as the variation in the results obtained is very high because the tassar yarn used is charka-reeled.

CONCLUSION

The parameters clearly indicate that the physically treated silk fibers do have higher crystal size with higher tenacity compared to chemically treated silk fibers. Significant improvements can be achieved by stretching the fiber to 18.7% and tension drying it.

REFERENCES

1. J. M. Mathews, *Textile Fibers,* Wiley-Interscience, New York, 1951.
2. H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedure,* Wiley, New York, 1954.
3. R. I. Marsh, R. B. Corey, and L. Pauling, *Biochem. Bio. Phys. Acta,* **16,** 1 (1955).
4. J. T. B. Shaw and S. G. Smith, *Biochem. Biophys. Acta,* **52,** 305 (1961).
5. J. O. Warwicker, *Biochem. Biophys. Acta,* **52,** 319 (1961).
6. N. V. Bhat, G. T. Nadigar, and A. Venkataraman, *Proc. Nucl. Phys. Solid State Phys.,* **21,** 431 (1978).
7. B. E. Warren and B. L. Averbach, *J. Appl. Phys.,* **21,** 595 (1950).
8. R. Samashekar, I. H. Hall, and P. D. Carr, *J. Appl. Phys.,* **22,** 363 (1989).
9. I. H. Hall and R. Somashekar, *J. Appl., Crystallogr.,* **24,** 1051 (1991).
10. R. Somashekar and R. Gopal Krishne Urs, *Bull. Mater. Sci.,* **14,** 87 (1991).
11. N. V. Bhat and S. M. Ahirrao, *Text. Res. J.,* 65 (1985).
12. A. R. Stokes, *Proc. Phys. Soc. Lond.,* **52**(1), 61, 382 (1948).
13. A. K. Nandi, H. R. Kuo, M. Schlosberg, B. Wissler, J. B. Chochen, and B. J. Crist, *J. Appl. Crystallogr.,* **17,** 22 (1984).
14. W. Press, B. P. Flannery, S. Tenkolsky, and W. T. Vettering, *Numer. Recipes C.U.P. Engl.,* 294 (1986).
15. R. Gopal Krishne Urs, G. Subramanya, and R. Somashekar, *Text. Res. J.,* **63**(10), 610 (1993).
16. A. M. Hindeleh and R. Hoseman, *J. Mater. Sci.,* **26,** 5127 (1991).
17. R. Hosemann, *Colloid Polym. Sci.,* **260,** 864 (1982).
18. R. Hosemann, *Progr. Colloid Polym. Sci.,* **77,** 15 (1988).
19. R. Somashekar and R. Gopal Krishne Urs, *J. Appl. Polym. Sci.,* **50,** 949 (1993).

Received March 2, 1995
Accepted September 5, 1995