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WAXS studies on silk fibres treated with acid (blue) and metal complex (brown) dyes

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The changes in microstructural parameters in bivoltine and multivoltine silk fibres due to (i) degumming, (ii) bleaching, (iii) blue acid dye and (iv) brown metal complex dye processing have been studied using wide angle X-ray scattering (WAXS) method. The crystal size has been determined by Fourier analysis and also by matching the simulated intensity profile obtained from one-dimensional Hosemann's paracrystalline model using (201) reflection observed in these silk fibres. Volume weighted and surface weighted crystal sizes have been estimated and compared. The variations of tenacity and elongation results justify the results of X-ray studies reported here. © 1997 Elsevier Science Ltd.

INTRODUCTION

Silk fibres are extensively used in the textile industry. It is quite important to know microstructural changes in silk fibres due to dye processing as these parameters determine the property and strength of the fibres. Such studies have not been carried out except for the chemical effect on these fibres[1–7]. Okuyama's[8] group have reported crystal structure for silk-I and silk-II fibres. Recently, we have reported the effect of degumming and dye processing on the microstructural parameters in pure Mysore silk, nistari, NB_7 and NB_{18} silk fibres.

In this paper, we have attempted to determine surface, weighted, volume weighted crystal size and lattice distortion parameters from the intensity profile of a fairly clear (201) X-ray reflection obtained from silk fibres processed with bleaching, degumming, acid/metal complex dyeing and also untreated at room temperature. These dyes are used in the textile industry as they give good lustrous colours like blue and brown. In addition to this, we have also calculated the parameters by matching the experimental profile with that of the simulated profile using Hosemann's paracrystalline model.

THEORY

Crystal size and lattice distortion parameters can be obtained fairly accurately using the Warren–Averbach[9] method when two orders of reflections from the same set of lattice planes are available. Silk fibres are partially crystalline and we observe only a few reflections. Thereby, the existing multiple order method cannot be used to determine crystal size and lattice distortion parameters. Somashekar et al.[10], and Hall and Somashekar[11] have considered various aspects of multiple and single order methods, and have suggested a suitable single order method to obtain crystal

size and lattice distortion parameters from polymer fibres. Recently, we have extended this method to natural polymers[12].

The intensity profile of the X-ray reflection from a partially crystalline sample like natural silk fibre is a function of the distribution of crystal sizes $\langle D \rangle$ and of the lattice distortion (g), and these are related through the Fourier coefficients $A(n)$ to the profile intensity $I(s)$ and the corresponding theoretical approach has been described in an earlier paper[12].

It has been pointed out by Balzar and Ledbetter[13] that Fourier analysis of the intensity profile gives surface-weighted crystal size, whereas integral breadth method gives volume-weighted crystal size. The second derivative of the size coefficients is proportional to the surface-weighted column-length distribution function, and is given by

$$P_s(L) \alpha \frac{d^2 A_s(n)}{dL^2} \qquad (1)$$

and the volume-weighted column-length distribution function is given by

$$P_v(L) \alpha L \frac{d^2 A_s(n)}{dL^2}, \quad L = nd_{hkl} \qquad (2)$$

If the column-length distribution function is known, then the corresponding surface-weighted or volume-weighted crystal size is given by the integral

$$\langle D \rangle_{s,v} = \frac{\int_0^\infty L P_{s,v}(L) dL}{\int_0^\infty P_{s,v}(L) dL} \qquad (3)$$

This is a well-known integral and can be evaluated[14]. It has been found analytically that the ratio of $\langle D \rangle_v / \langle D \rangle_s$ is $\Gamma(3)$ and lies between 0 and 2 depending on the form of distribution function[13]. Using an exponential distribution function [equation(3)], we can determine the surface-weighted and volume-weighted crystal sizes.

The reasons for using non-normalized Fourier coefficients in all these calculations are (i) truncation of the profile and (ii) error in the background estimation, and these affect the low-order Fourier coefficients of the intensity profile, as explained in an earlier paper[12]. We have used an asymmetric exponential distribution function for the crystal size distribution, since this function gives fairly reliable results.

Using equations (1),(2),(4),(5) and (9) of ref.[12], along with experimental intensity data, it is possible to obtain surface-weighted and volume weighted crystallite size, width of the distribution function and lattice distortion parameters.

EXPERIMENTAL AND COMPUTATION

Sample

For our study, both Bivoltine (raw) and Multivoltine (raw) silk fibres which are locally popular races in this area were drawn from cocoons kept in boiling water for about 2–3 min and then processed at 45°C. These raw silk fibres were conditioned and degummed with 4 g/l soap and 1 g/l soda ash for 60 min. The treated material was given a hot wash, cold wash and then dried. These degummed silk fibres were bleached using 2 vol. of hydrogen peroxide and 1 g/l sodium silicate at 80°C for 2 h. The bleached sample was given a hot wash, cold wash and then dried. The degummed and bleached fibre was dyed with acid dye [Blue (poly acid silk blue BRR)] and metal complex dye [Brown (Luganill Brown FB2RL)] in 1% shade. The dyeing was started at 40°C using acid dye, glauber salt (10%) and acetic acid (4%) The temperature of the dyeing bath was gradually raised to 85° and dyeing was carried out at this temperature for 45 min.The dyed yarn was rinsed and dried. The breaking load of the sample was determined using a Instron tensile test.

X-ray diffraction patterns

The X-ray diffraction profile of equatorial reflections from silk fibres was recorded using an X-ray diffractometer (JEOL, Japan) target Fe, $\lambda = 1.934$ A for all the samples with and without treatment of acid dye, and has only two reflections. Of these, the (100) reflection overlaps with the (110) reflection and hence we were not able to record a clear profile of the (100) reflection. We have, therefore, used the

(201) reflection for our study. The reflections were identified using cell parameters reported earlier[15]. 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 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. X-ray patterns obtained with the same specifications from raw as well as metal oxide dyed fibres did not show any changes in the background level due to the presence of metallic ions. 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. In order to correct for instrumental line broadening using Stokes method[16], an X-ray diffraction pattern was recorded for aluminium foil under the same conditions as used for silk fibres and the Al reflection whose Bragg angle lies in the region of the present one was used for this purpose. This procedure was repeated for all the samples treated with acid dye.

The refinement procedure

The calculation of intensity profile using equations (1),(3) and (5) of ref.[12] requires four parameters, i.e. 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.[17]. 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

$$\Delta^2 = [I_{cal} - (I_{exp} + BG)]^2/\text{Number of points} \qquad (4)$$

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 multi-dimensional minimization algorithm of SIMPLEX methods was used[18]. Here, BG refers to inaccuracy in background estimation. It was observed that the variation of $\langle N \rangle$, p and α defined in equation (3) of ref.[12] with respect to g for exponential distribution function is

Table 1 Microcrystalline parameters of dye processed silk fibres obtained by both Fourier and model calculations

Sample	$\langle N \rangle$	α	g in %	α	D_s in A	D_v in A	Tenacity (g/d)	Elongation (in%)	Hosemann's paracrystalline model $\langle N \rangle$	g in %
BV	7.3 ± 0.1	0.33 ± 0.01	3.7	0.10	29.7	33.9	4.0	19.0	8.56	9.69
BV Degummed	2.6 ± 0.1	0.78: ± 0.02	5.5	0.09	11.3	14.7	3.6	11.3	5.30	11.65
BV Bleached	2.7 ± 0.1	0.81 ± 0.01	3.8	0.04	11.2	14.3	3.8	11.8	4.38	9.95
BV Acid dye (blue)	4.8 ± 0.2	0.48 ± 0.01	2.9	0.06	20.3	20.9	4.4	13.0	5.50	6.76
BV Metal complex dye (brown)	4.9 ± 0.1	0.63 ± 0.01	3.4	0.08	21.5	23.3	3.9	12.3	4.69	5.64
MV	4.5 ± 0.1	0.62 ± 0.01	3.2	0.07	18.6	21.2	3.7	19.0	5.70	11.08
MV Degummed	2.6 ± 0.1	0.68 ± 0.01	5.1	0.08	11.7	15.8	3.1	13.43	4.62	8.88
MV Bleached	2.9 ± 0.1	0.57 ± 0.01	2.8	0.11	12.9	17.7	3.4	12.34	5.40	9.76
MV Acid dye(blue)	2.8 ± 0.1	0.58 ± 0.01	2.2	0.04	12.7	17.6	3.1	1.40	5.23	10.45
MV Metal complex dye (brown)	4.4 ± 0.1	0.82 ± 0.01	2.1	0.04	18.6	20.2	3.0	11.10	4.27	7.28

BV: Bivoltine; MV: Multivoltine
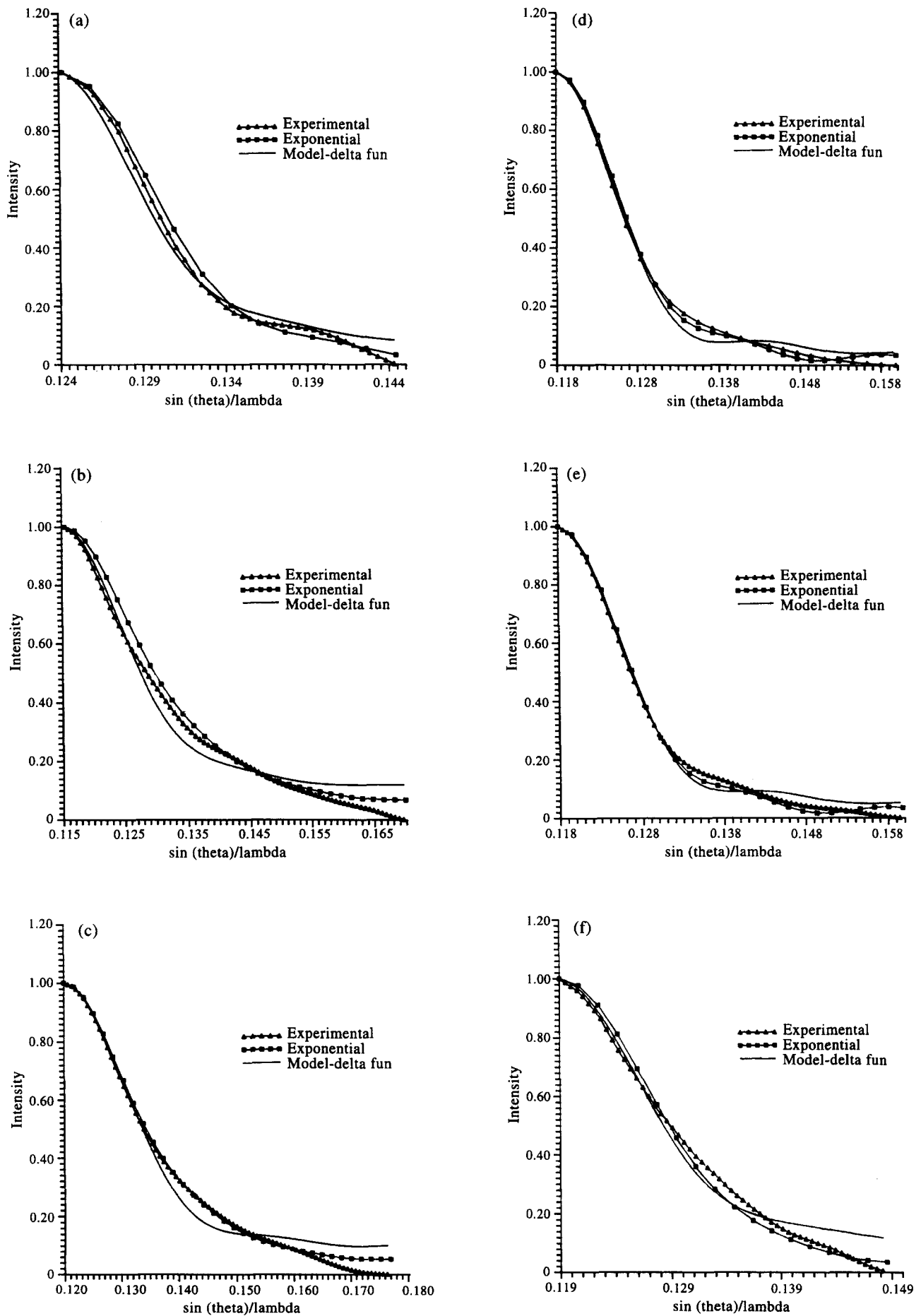
Figure 1 Experimental and calculated data from Fourier and paracrystalline model intensity profiles of (201) reflection. (a) Pure Bivoltine (BV), (b) BV degummed, (c) BV bleached, (d) BV acid dye (blue), (e) BV metal complex dye (Brown), (f) Pure multivoltine (MV), (g) MV degummed, (h) MV bleached, (i) MV acid dye (blue) and (j) MV metal complex dye (Brown)

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 1*. All the necessary computer programs were written in FTN77 language and were compiled and executed using Cyber, University Computer Centre, Mysore.

RESULTS AND DISCUSSION

Table 1 gives the parameters needed for recalculating the intensity profile, using the equations mentioned earlier in the text. The values of microstructural parameters for raw bivoltine silk fibres do not agree with the earlier reported values[12] since these fibres were obtained from two different regions wherein the feeding, rearing and environmental conditions do determine the slight changes in these values. Hence, for relative comparision we have re-determined the microstructural parameters for raw bivoltine silk fibres. *Figure 1a* and *b* shows good agreement between experimental and calculated intensity on the basis of exponential column length distribution suggested in this paper, for (201) reflection in silk fibres of various races treated with acid dye. This clearly indicates that the parameters obtained here

are quite reliable. The reliability of this procedure has been investigated[11,12] by comparing with the existing multiple order method of Warren and Averbach[9]. The surface-weighted crystal size and the volume-weighted crystal size values calculated using equation (2) are given in *Table 1*. Assuming that there is no paracrystalline disorder and also including the uncertainty in the Scherrer constant K, the D_v values obtained for the Scherrer equation broadly agree with the values obtained here. Small descrepancies can be accounted for in terms of the changes that are there in the lattice distortion g. It is evident that on treatment of fibres with acid dye, there is a decrease in these values, which indicates that there is rearrangement of β-pleated structure of protein molecules which results in a decrease of the crystalline region. It has been shown in the case of polymer fibres that the decrease in crystallite size results in a decrease in tenacity of the fibres[19]. Extending this argument, we feel that the strength of the fibres decreases when treated with acid dye and may result in poor quality of fibres. In fact, to test the reliability of these results, we have also carried out the calculation of these parameters, i.e. the crystal size (N) and distortion parameter by matching the experimental profile between s_0 and $s_0 + s_0/2$ (or s_0 and
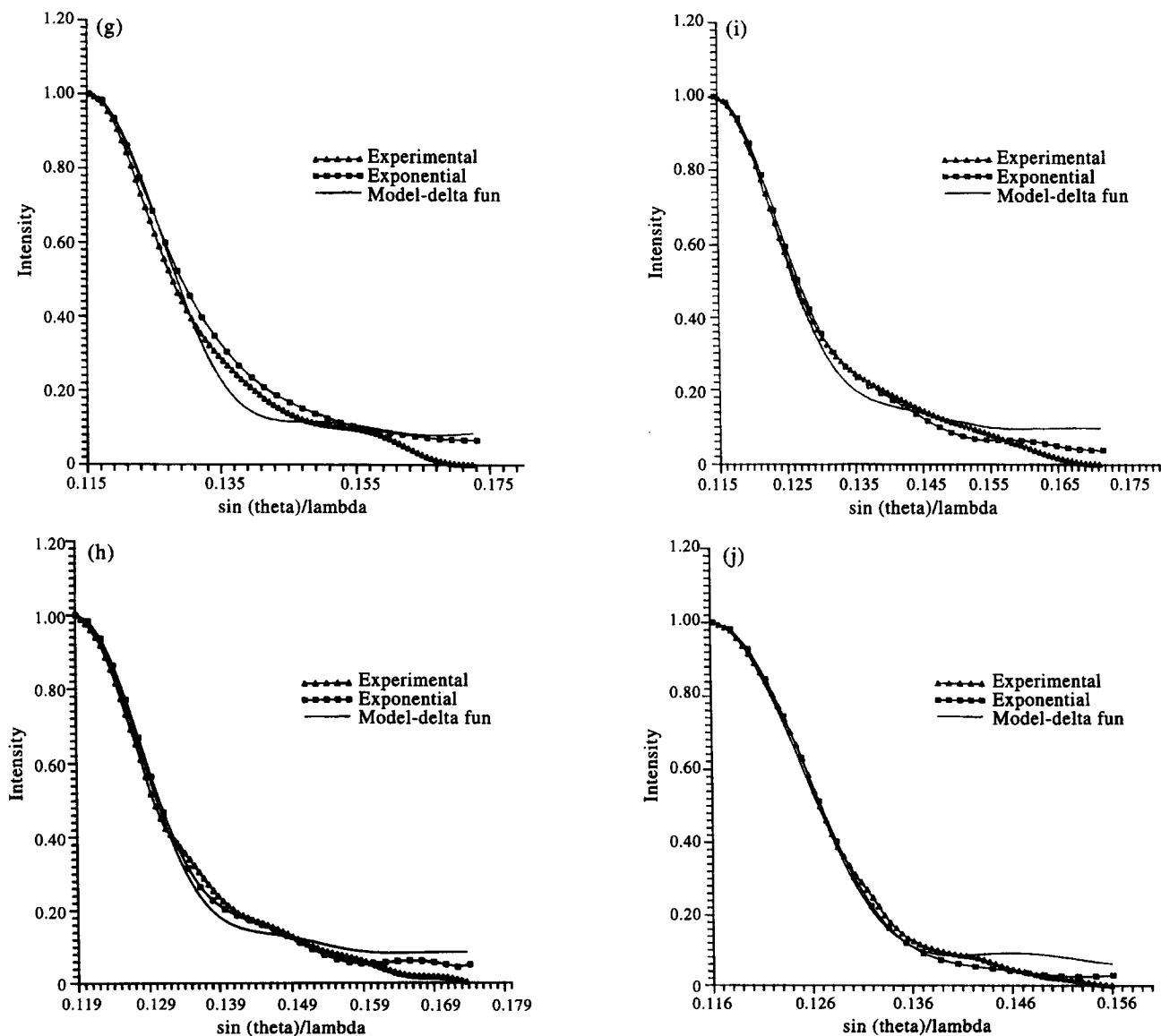

Figure 1 Continued.

$s_0 + B/2d$, if there is truncation of the profile $B < 1$) with the simulated profile by using the equation[20]

$$I(s) = I_{N-1}(s) + I'_N(s) \qquad (5)$$

where

$$I'_N(s) = \frac{2aN}{D\pi^{1/2}} \exp(idNs)[1 - a_N s\{2D(a_N s) + i(\pi)^{1/2} \exp(-a_N^2 s^2)\}] \qquad (6)$$

and

$$a_N^2 = Nw^2/2$$

and $D(a_N s)$ is Dawson's integral or the error function (for symbols refer to ref.[20]), which has been obtained on the basis of a one-dimensional paracrystalline model with a delta-type column length distribution. Here, a tri-dimensional minimization programme has been used to compute the microcrystalline parameters which give the best fit between experimental and simulated profiles. The parameters so obtained are given in *Table 1*. Here, we would like to emphasis that the distortion parameter obtained earlier with the Fourier coefficient method is a model dependent parameter, where it is not so in the case of matching of simulated profiles. We observe that the distortion parameters do not vary much with the treatments, whereas the crystal size obtained by both methods decreases with the acid dye processing. This result is in agreement with the tenacity and elongation measurements at breaking points of the same samples given in *Table 1*. It may also be noted from *Table 1*, that the ratio $\langle D \rangle_v/\langle D \rangle_s$ is <1.3, which is in agreement with earlier observations using the integral breadth method for man-made fibres, and most experiments give the ratio in the range 0 to 2. This ratio also indicates that the size broadening is not a case of pure Cauchy size broadening. The lattice distortion parameter almost remains unchanged within the experimental errors, when silk fibres are treated with acid dye. From these parameters, we can also estimate the minimum enthalphy, which defines the equilibrium state of microparacrystals in acid dye treated silk fibres, using the relation[21]

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

This α^* value implies physically that the growth of paracrystals in a particular material is appreciably controlled by the level of g in the net plane structure. This estimated minimum value of enthalphy is given in *Table 1* and we can conclude that the acid dye treated silk fibres which have a smaller crystal size, consume less energy in order to build up the crystal network compared to untreated silk fibres. Note that the value of α^* lies between 0.1 and 0.2 for both man-made and natural fibres.

CONCLUSIONS

With acid dye treatment of silk fibres of various races, it has been shown by Fourier analysis of the profile and also by one-dimensional Hosemann's paracrystalline method that the crystal size decreases and there is no significant change in lattice distortion parameter. Such a decrease in crystal size also results in decrease in tenacity or elongation at breaking of the fibres. Volume-weighted crystal size reported here is greater than the surface-weighted crystal size and the ratio is less than 2, showing that the broadening is purely Cauchy type.

ACKNOWLEDGEMENTS

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