Variation in crystallite shape ellipsoid in non-mulberry silk fibres

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Wide angle X-ray scattering data recorded from the coarse and fine fibres of mulberry and non-mulberry silk, like muga, tassar and eri, have been used along with exponential, Reinhold and Lognormal functions for crystal size distributions to determine the microstructural parameters and hence to compute the shape of the crystallite ellipsoid. The estimated microstructural parameters have been correlated with the reported physical parameters like tenacity and toughness of silk fibres. It is observed that the tenacity decreases with the increase in crystal size for both mulberry and non-mulberry silk fibres, which essentially reflects the fact that ordering in the lattice may not be a favoured factor in the textile industry.

Keywords: Crystallite shape, Silk fibre, Tensile strength, Wide angle X-ray scattering

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1 Introduction

Silk is a fibrous protein secreted by insects for building structures external to the body known as cocoons. Silk fibre is a semicrystalline polymer. It is one of the most important materials extensively used in Indian textile industry, especially in Karnataka, Tamil Nadu, Andra Pradesh and Uttar Pradesh. Mulberry, muga, tassar and eri are all the commercial varieties of silk fibres produced in India. Therefore, it is very important to know the microstructural changes in these fibres as these parameters determine the strength and property of the fibres. Extensive research work has been carried out on the structure and property of mulberry silk fibres but to a lesser extent on non-mulberry silk fibres. Some of these studies report mechanical properties, particularly the load elongation behaviour, of raw mulberry silk fibres and to some extent of tassar and muga silk fibres. Rajkowha et al. have reported the tensile strain and recovery behaviour of these silk fibres and their structural dependence. However, the variation in crystallite shape ellipsoid in these silk fibres has not been studied so far. Therefore, in this paper, the wide angle X-ray scattering (WAXS) data reported by Rajkowha et al. have been used to determine the exact behaviour of crystal size distribution in polymers like silk by employing three asymmetric functions and hence to find out a function which gives a better fit with the experimental profile and also the consistent microstructural parameters values in silk fibres. These parameters are further used to compute the crystallite shape ellipsoid. Also, the obtained microstructural parameters are correlated with the reported physical parameters, like tenacity and toughness, in these silk fibres.

2 Materials and Methods

2.1 Theory

Microstructural parameters, like crystal size $<N>$ and lattice strain ($\sigma$ in %), are usually determined by employing Fourier method of Warren. The following equation was employed to compute the microstructural parameters:

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

where coefficients of harmonics $A(n)$ are the functions of size crystallite and disorder of the lattice; $S$, the $\sin(\theta)/2\lambda$; $S_0$, the value of $S$ at the peak of the profile; $\theta$, the Bragg angle at the peak of the profile; $\lambda$, the wavelength of the X-ray; $n$, the harmonic number; and $d$, the lattice spacing. Three asymmetric...
column length distribution functions (exponential, Reinhold and Lognormal) were used for the computation of microstructural parameters.

**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 decays exponentially. Thus,

\[
P(i) = \alpha \exp(-\alpha(i-p)), \quad i \geq p
\]

where \( \alpha = \frac{1}{(N-p)} \)

This gives

\[
A_s(n) = A(0)(1 - n/N)\); \quad n \leq p
\]

and

\[
A_s(n) = A(0)[\exp(-\alpha(n-p))] / \alpha N; \quad n \geq p
\]

**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

\[
P(i) = \beta^2(i-p)\exp(-\beta(i-p)), \quad i \leq p
\]

where \( \beta = \frac{2}{(N-p)} \)

Hence,

\[
A_s(n) = A(0)(1 - n/N)\); \quad n \leq p
\]

and

\[
A_s(n) = A(0)(n - p + 2/\beta)N]\exp(-\beta(n-p)); \quad n \geq p
\]

where \( \alpha, \beta \) are the widths of the distribution which has been varied to fit the experimental results; \( p \), the smallest number of unit cells in a column; \( N \), the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane; \( d \), the spacing of the (hkl) planes; \( \lambda \), the wavelength of X-rays used; \( i \), the number of unit cell in a column; \( n \), the harmonic number; and \( D_s \), the surface weighted crystal size [\( <N> \) dsek].

**Lognormal Distribution**

The Lognormal size distribution density function is given by the following equation:

\[
P(i) = \frac{1}{(2\pi)^{1/2} \sigma i} \exp\left(-\frac{[\log(i/m)]^2}{2\sigma^2}\right)
\]

where \( \sigma \) is the variance; and \( m \), the median of the distribution. Using the above equation, the equation for size coefficients is obtained as given below:

\[
A_s(n) = \frac{m^3 \exp[(9/4)(2^{1/2} \sigma)^2]}{3} \exp\left[\frac{\log(n/m)}{2^{1/2} \sigma} - \frac{3}{2^{1/2} \sigma}\right] - \frac{m^2 \exp(2^{1/2} \sigma)^2}{2} \exp\left[\frac{\log(n/m)}{2^{1/2} \sigma} - 2^{1/2} \sigma\right] + \frac{|n^3|}{6} \exp\left[\frac{\log(n/m)}{2^{1/2} \sigma}\right]
\]

The surface weighted mean column length \( <N>_{surf} \) is given by

\[
<N>_{surf} = \frac{2m \exp[(5/4)(2^{1/2} \sigma)^2]}{3}
\]

The volume weighted mean column length \( <N>_{vol} \) is given by

\[
<N>_{vol} = \frac{3m \exp[(7/4)(2^{1/2} \sigma)^2]}{4}
\]

**2.2 X-ray Profile Analysis**

These equations [Eqs (2)-(15)] were used in Eq (1) to simulate the intensity profile by varying the necessary parameters till one gets a good fit with the experimental profile. For this purpose, a multidimensional algorithm (Simplex) was used for minimization. WAXS data of mulberry and non-mulberry silk fibres of coarse (c) and fine (f) varieties have been used for the X-ray profile analysis. Here, coarse fibre refers to filaments collected from the outer layer of the cocoons and fine fibre is the degummed filament. The computed crystal imperfection parameters along with the reported physical parameters are given in Tables 1 and 2 for
3 Results and Discussion

Using various distribution functions, [100] and [201] X-ray reflections of non-mulberry silk fibres were simulated. Figs 1(a-f) show the experimental and simulated X-ray intensity profiles obtained on the basis of different column length distribution functions for [201] reflection in mulberry fine and non-mulberry (tassar) coarse silk fibres. Such investigations have also been carried out for mulberry silk fibre to bring out the distinction between the two types of silk fibres. From Tables 1 and 2, it is observed that there is a relatively better fit between experimental and simulated profile in the case of exponential distribution function for the distribution of crystal sizes in polymers. Here, it is emphasized that the standard deviations in all the cases for the microstructural parameters are given in Tables 1 and 2 as 'delta'. Since exponential distribution function gives a better fit than others, the corresponding results given in Tables 1 and 2 have been used to infer some important conclusions. From Tables 1 and 2, following three important features are observed:

(i) Surface weighted crystal size ($D_s$) is more for non-mulberry silk fibres when compared to mulberry silk fibre,
(ii) Crystal size decreases with degumming treatment, and
(iii) Crystal size is more for coarse fibres.

The variation in lattice strain ($g$) lies between 1% and 4.5% in the case of exponential distribution for both coarse and fine fibres. From the obtained microcrystalline parameters, one can estimate the minimum enthalpy ($\Delta H$), which defines the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lognormal</th>
<th>Exponential</th>
<th>Reinhold</th>
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<tr>
<td></td>
<td>$D_s$, Å</td>
<td>$D_s$, Å</td>
<td>$D_s$, Å</td>
</tr>
<tr>
<td>Muga(c)</td>
<td>51.61±4.1</td>
<td>56.37±4.5</td>
<td>5.96±3.9</td>
</tr>
<tr>
<td>Muga(f)</td>
<td>38.38±3.5</td>
<td>43.48±1.3</td>
<td>43.53±1.3</td>
</tr>
<tr>
<td>Tassar(c)</td>
<td>54.54±4.4</td>
<td>61.29±1.2</td>
<td>61.52±1.2</td>
</tr>
<tr>
<td>Tassar(f)</td>
<td>41.74±3.3</td>
<td>47.54±1.4</td>
<td>47.63±1.4</td>
</tr>
<tr>
<td>Eri(c)</td>
<td>50.43±3.0</td>
<td>57.19±4.0</td>
<td>53.61±0.7</td>
</tr>
<tr>
<td>Eri(f)</td>
<td>43.11±3.5</td>
<td>48.31±1.9</td>
<td>48.21±1.9</td>
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$g$ — Lattice strain, $D_s$ — Crystal size, c—Course, and f—Fine

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<td></td>
<td>$D_s$, Å</td>
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<tr>
<td>Mulberry(c)</td>
<td>36.62±2.5</td>
<td>40.53±1.6</td>
<td>40.51±1.6</td>
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<tr>
<td>Mulberry(f)</td>
<td>32.13±1.6</td>
<td>3.57±1.1</td>
<td>3.52±1.1</td>
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<tr>
<td>Muga(c)</td>
<td>50.58±4.1</td>
<td>3.04±2.7</td>
<td>52.81±3.2</td>
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<tr>
<td>Muga(f)</td>
<td>36.46±2.6</td>
<td>40.94±1.2</td>
<td>41.08±1.2</td>
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<tr>
<td>Tassar(c)</td>
<td>45.57±2.7</td>
<td>50.25±2.0</td>
<td>48.87±2.0</td>
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<tr>
<td>Tassar(f)</td>
<td>45.03±3.6</td>
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<tr>
<td>Eri(c)</td>
<td>46.11±2.8</td>
<td>49.00±2.0</td>
<td>48.75±2.0</td>
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<td>Eri(f)</td>
<td>3.51±2.7</td>
<td>36.85±1.8</td>
<td>36.93±2.2</td>
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</table>

$g$ — Lattice strain, $D_s$ — Crystal size, c—Course, and f—Fine

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<td></td>
<td>$D_s$, Å</td>
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<tr>
<td>Eri(c)</td>
<td>4.18±0.2</td>
<td>36.85±1.8</td>
<td>4.52±0.3</td>
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<tr>
<td>Eri(f)</td>
<td>5.09±0.4</td>
<td>36.85±1.8</td>
<td>4.52±0.3</td>
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The relationship is $\alpha^2 = \langle N \rangle^{1/2} g$, as given by Hosemann$^{16}$. This value of $\alpha^2$ implies physically that the growth of paracrystals in a particular material is appreciably controlled by the level of lattice strain in the net plane structure. The estimated minimum value of enthalpy obtained on the basis of exponential distribution function lies between 0 and 0.12 for the coarse and fine non-mulberry silk fibres. Normally, for polymers, this value lies between 0.0 and 0.2, which is the case in silk fibres. The variation in crystal size distribution along [20\text{I}] direction obtained on the basis of various column length distribution function for eri fine fibres is shown in Fig. 2. It is to be noted here that the decrease in crystal size value for the fine fibres as compared to coarse fibres is also supported by tensile properties like tensile strain and toughness$^6$. The computed microstructural parameters have been used for computing the shape of coherent domains in terms of the shape of ellipsoid by taking the surface weighted crystal size value corresponding to [20\text{I}] direction along X-axis and [100] direction along Y-axis for non-mulberry coarse silk fibres$^{17}$. It is evident from Fig. 3 that there are significant changes only in the periphery of the crystallite shape ellipsoid. The shape could not be estimated in
mulberry silk because of the lack of X-ray data. The variation in tenacity with crystallite size for coarse and fine fibres of mulberry and non-mulberry silk is shown in Figs 4(a and b). The tenacity value for coarse and fine fibres of non-mulberry does not show significant change, the reason being the corresponding changes in the estimated microstructural parameters.

The differences between mulberry and non-mulberry silk fibres arise due to the significant changes in the amino acid compositions, which, in turn, lead to a different molecular packing and crystalline morphology\(\text{\textsuperscript{18,19}}\). Also, it has been reported\(\text{\textsuperscript{20}}\) that in mulberry, 29% of alanine, 45% glycine and 12% of serine are present, whereas in non-mulberry silk fibres, 41% of Alanine, 27% glycine and 11% of serine are present. Mulberry silk fibre has a crystal structure whose space group is \(P2_1\) with \(\beta\) pleated structure and fibre axis along \(b\)-axis, whereas non-mulberry silk fibre belongs to \(P2_12_12_1\) with a difference in \(\beta\) structure and a fibre axis along \(c\)-axis. These structural differences might lead to different crystalline regions and hence the wide angle X-ray patterns. It has been established\(\text{\textsuperscript{20}}\) that alanine is the material which concentrates in helical regions and also designated as helix-making, whereas glycine is found to be concentrated in non-local helical regions and referred as helix-indifferent. These aspects have been quantified here in terms of microstructural parameters obtained by Fourier method, which has been appreciated by the round robin test conducted by IUCr.

4 Conclusions

The WAXS study of coarse and fine fibres of mulberry and non-mulberry silk shows that even though there is not much change in the positions of X-ray reflections, there is a significant change in the shape of crystallite domains of non-mulberry silk fibres. This is due to a different composition and arrangement of alanine-glycine-serine residues in non-mulberry silk fibres. The tenacity decreases with the increase in crystal size for both mulberry and non-mulberry silk fibres, which essentially reflects the fact that ordering in the lattice may not be a favoured factor in the textile industry.
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