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Birefringence behaviour of annealed silk fibres

I. M. FOUDA, M. M. EL-TONSY
Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Silk fibres were annealed at 140° C for different annealing times ranging from 2 to 10 h. Refractive indices and birefringence of annealed fibres were measured by two different interferometric methods. An interference polarizing microscope and multiple-beam Fizeau fringes in transmission techniques were used. The scanning electron microscope was used to estimate the geometrical parameters of silk fibres. The behaviour of birefringence for annealed silk fibres showed that the birefringence reach a maximum value when silk was annealed for 5 to 6 h at 140° C. The isotropic refractive index of annealed silk is also slightly increased with increasing annealing time. The results obtained clarify the effect of annealing time on the optical behaviour of natural silk fibres. Microinterferograms are given for illustration.

1. Introduction

In recent years, interferometric methods have been used to determine the refractive indices and birefringence of both natural and man-made fibres [1–5]. The importance of studying various optical properties, such as refractive index and birefringence, is recognized in fibres as the main source of accurate information for correlating the structural properties of fibres with the conditions of production or growth mechanism of natural fibres.

For optically anisotropic fibres, the refractive index and the double refraction are parameters characterizing the structure of the material. The dependence of the refractive index on direction was probably the first of the anisotropic properties observed in fibres, and was cited by early workers as proof of the presence of crystalline elements within the fibre. It is now known that the double refraction arises from the inherent optical anisotropy of the chain-like macromolecules and from the preferred axial orientation of the molecular chains which constitute the fibre [6]. Consequently, birefringence gives a measure of the orientation which is an average of that of the amorphous and crystalline regions [7].

More recently, application of double-beam and multiple-beam Fizeau fringe interferometry has stimulated interest in studying the effect of different types of thermal and mechanical properties of natural and man-made fibres [8, 9].

Natural silk fibres have a double refraction of positive value, because their refractive index is greater for light vibrating parallel to the fibre axis. The cross-sectional shape of the majority of the individual fibres is triangular with rounded corners. This shape is one of the most characteristic features of cultivated silk.

Recently, mathematical expressions have been developed for the shape of multiple-beam Fizeau fringes crossing fibres of irregular cross-sections [10, 11]. The application and validity of these recent mathematical formulae [10] for multiple-beam Fizeau fringes crossing preheated natural silk fibres of irregular cross-sections have been investigated in this work.

2. Theory

Two different interferometric techniques were used in the present work.

2.1. Multiple-beam Fizeau fringes in transmission

For fibres having irregular cross-sections, the area enclosed under the interference fringe shift was related to the refractive indices of media inside the wedge interferometer where

$$n_a^{\parallel} = n_L + \frac{F^{\parallel}}{h}\frac{\lambda}{2MA} \quad (1)$$

with $n_a^{\parallel}$ the mean refractive index of the fibre material for plane polarized light vibrating parallel to the fibre axis, n_L the refractive index of the immersion liquid, $F^{\parallel}$ the total area enclosed under the fringe shift, h the interfringe spacing in the liquid region, A the fibre cross-sectional area, M the magnification of the optical system, and λ the wavelength of the monochromatic light used.

Equation 1 has an analogous form for light vibrating perpendicular to the fibre axis for the determination of $n_a^{\perp}$.

2.2. Double-beam interferometry

For the determination of the mean refractive indices and birefringence, the Pluta polarizing interference microscope is used to produce a duplicated image for the samples. Equation 1 and its analogous form are employed by using the quantity λ/A instead of $\lambda/2A$ [11].

The Pluta microscope can be used to determine, directly, the mean birefringence, Δn_a, by producing a non-duplicated image for the sample where

$$\Delta n_a = (F/h)(\lambda/MA) \quad (2)$$

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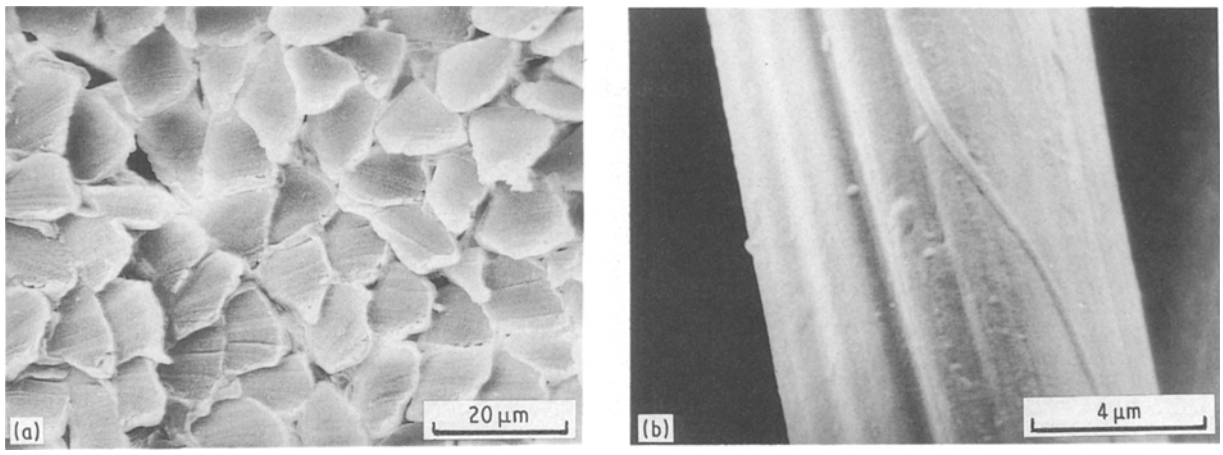


Figure 1 Scanning electron micrographs of (a) cross-section and (b) surface of natural silk fibres.

where F is the total area enclosed under the fringe shift in the non-duplicated image.

3. Experimental procedure and results

3.1. Sample preparation

3.1.1. Scouring

In order to make the raw silk fibre soft and glossy, it is necessary to remove the sericin or gum by a special treatment known as stripping, discharging or degumming. It is really a scouring operation and for the preparation of samples for this work, silk bundles were boiled in water containing 1% soap for 45 min. Then samples were boiled again in another bath containing 0.5% soap for 30 min, then washed thoroughly with distilled water and dried.

3.1.2. Annealing

The scoured silk fibres were distributed in seven small glass bottles which were then heated in an electric oven whose temperature was adjusted to be constant to within $\pm 1°$ C.

Silk can be heated, for instance, to 140° C without danger of decomposition, at 170° C, however, it is rapidly disintegrated [12]. Hence, the samples were annealed at 140° C for the annealing times 2, 3.5, 5, 6, 7, 8 and 10 h.

3.2. Measurement of cross-sectional area

3.2.1. Scanning electron microscopy

The high-resolution scanning electron microscope (Cambridge Stereoscan 150 MK) was used for studying the cross-sectional and longitudinal view of silk fibres. Fig. 1a shows the cross-section of natural silk fibres as seen in the SEM. The figure shows the nearly triangular shape of the silk. Fig. 1b is a longitudinal view of a silk fibre; it is clear that the surface of the fibre is not smooth, but contains longitudinal grooves.

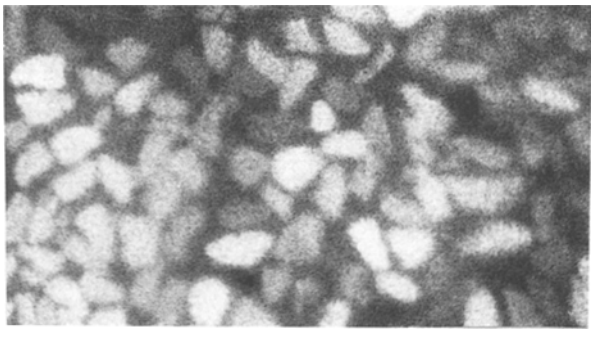


Figure 2 The optical micrograph of a cross-section of natural silk fibres.

3.2.2. Optical microscopy

Fig. 2 shows the cross-section of silk fibres seen by high-power optical microscopy. It is clear that silk fibres have not only an irregular cross-section, but also a wide range of cross-sectional area.

A statistical determination for the average cross-sectional area, A, of silk fibres, using Figs 1a and 2, shows that $A = 84.75 \pm 9.0\,\mu m^2$, i.e. the expected error is about $\pm 10.6\%$, thus the maximum and minimum values of A are separated by more than 20% from the average value. Therefore, it is difficult to determine a definite value for the refractive indices of fibres having major irregularities in both cross-sectional area and shape, such as silk fibres.

3.3. Interferometric determination of silk refractive indices

3.3.1. Multiple-beam interferometry

The optical apparatus for producing multiple-beam Fizeau fringes in transmission was described in detail previously [1, 3].

Figs 3a and b are microinterferograms for multiple-beam Fizeau fringes crossing silk fibre, before the thermal treatment, using plane polarized monochromatic light of wavelength 546.1 nm, vibrating (a) parallel and (b) perpendicular to the fibre axis. The values of refractive indices and birefringence obtained for natural silk fibres are found in agreement with those previously published and measured by the Becke line method. Table I clarifies a comparison between

TABLE I Refractive indices and birefringence of natural silk fibres

$n_a^{\parallel}$	$n_a^{\perp}$	Δn_a	Remarks	Reference
1.591	1.538	0.053	20° C, D line of Na	[13, 14]
1.591–1.595	1.538–1.543	0.048–0.057		[15]
1.587–1.589	1.543–1.549	0.039–0.047	At 24° C $\lambda = 546.1$ nm	Recent values

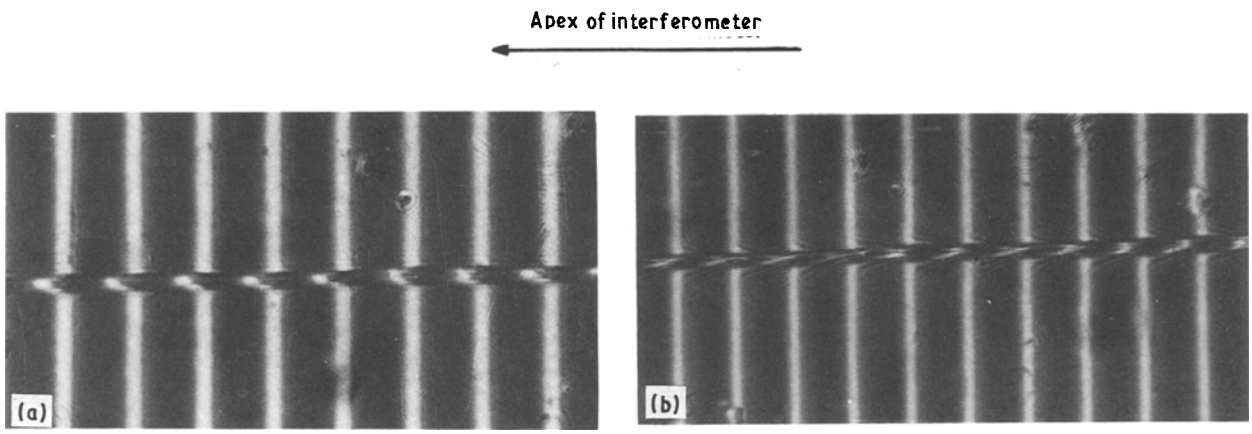


Figure 3 Multiple-beam Fizeau fringes in transmission, crossing untreated silk fibres. Monochromatic light of wavelength 546.1 nm vibrating (a) parallel and (b) perpendicular to the fibre axis, at 24° C, was used.

the interferometric values obtained recently and the previously obtained values for the refractive indices and birefringence of natural silk fibres [13–15].

Figs 4a to c are microinterferograms for multiple-beam Fizeau fringes in transmission crossing silk fibres annealed at 140° C for (a) 3.5 h, (b) 5 h and (c) 10 h. Plane polarized monochromatic light of wavelength 546.1 nm, vibrating parallel to the fibre axis was used.

It is worth noting that in spite of the increase in the annealing time, the length of fringe shift did not change, due to the irregularity of the fibre cross-sections. The area enclosed under the fringe shift is considered, in this case, to be the main parameter which indicates the variation of the fibre refractive indices.

Fig. 5 shows the variation of both $n_a^{\parallel}$ and $n_a^{\perp}$ of silk fibres by increasing the annealing time (annealing temperature 140° C) as obtained using multiple-beam Fizeau fringes in transmission. It is clear that the refractive indices of silk fibres are slightly changed with respect to values of the untreated sample, and values of $n_a^{\parallel}$ and $n_a^{\perp}$ reach a nearly stable level as the annealing time exceeds 5 h.

3.3.2. Double-beam interferometry

The totally duplicated image of the fibre obtained with the Pluta polarizing interference microscope [2], was used to calculate the mean refractive indices $n_a^{\parallel}$ and $n_a^{\perp}$ of silk fibres. Figs 6a to c are microinterferograms showing the totally duplicated images of samples of silk fibres annealed at 140° C for 0, 3.5 and 6 h, respectively. White light of average wavelength 550 nm was used.

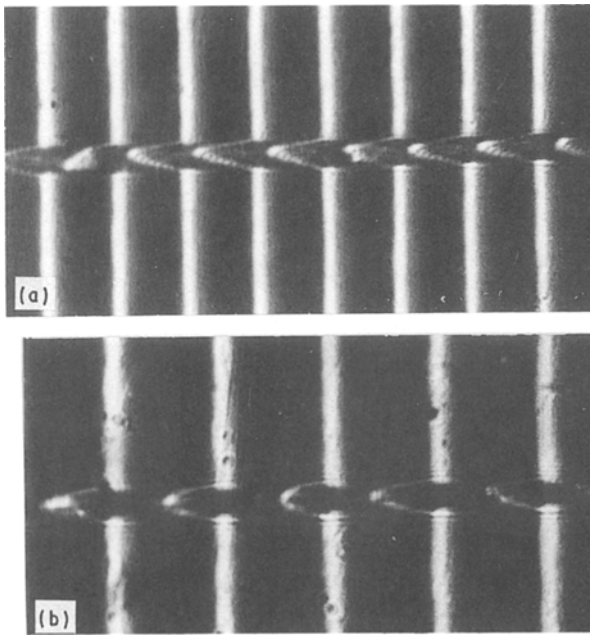
Figure 7 shows the variation of both $n_a^{\parallel}$ and $n_a^{\perp}$ of silk as measured using the Pluta double-beam interference microscope, and gives the same information as given in Fig. 5. The small numerical discrepances in values of $n_a^{\parallel}$ and $n_a^{\perp}$ given in Figs 5 and 7 are due to differences in the room temperature, wavelength and accuracy of the interferometric techniques used.

The mean birefringence, Δn_a, can be determined either from the values of $n_a^{\parallel}$ and $n_a^{\perp}$ or directly from the non-duplicated image of the fibre using the Pluta microscope.

Figs 8a to c are microinterfergrams showing the non-duplicated images of silk fibres annealed at 140° C for 0, 3.5 and 6 h, respectively. White light of average wavelength 550 nm was used.

Table II gives the maximum and minimum values of Δn_a obtained by three different methods.

Figs 9a and b give the general behaviour of birefringence of annealed silk fibres at different annealing times as detected using (a) multiple-beam interferometry and (b) double-beam interferometry. It is



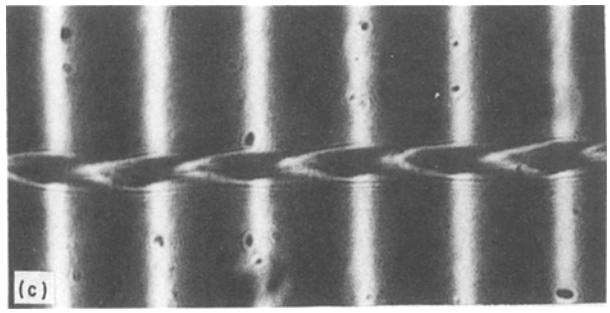


Figure 4 Multiple-beam Fizeau fringes in transmission, crossing annealed silk fibres at 140° C for (a) 3.5, (b) 5 and (c) 10 h. Monochromatic light of wavelength 546.1 nm vibrating parallel to the fibre axis was used.

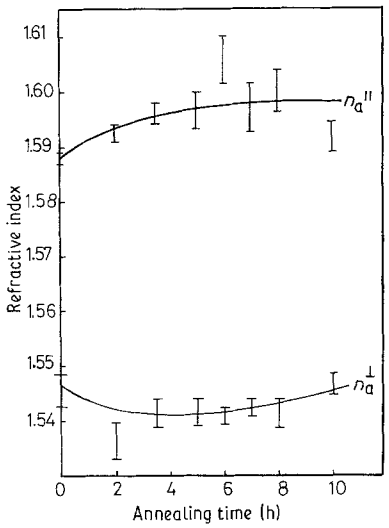


Figure 5 The variation of $n_a^{\parallel}$ and $n_a^{\perp}$ of annealed silk with annealing time. Annealing temperature = 140° C. Results were obtained using multiple-beam interferometric technique (λ = 546.1 nm at 24° C).

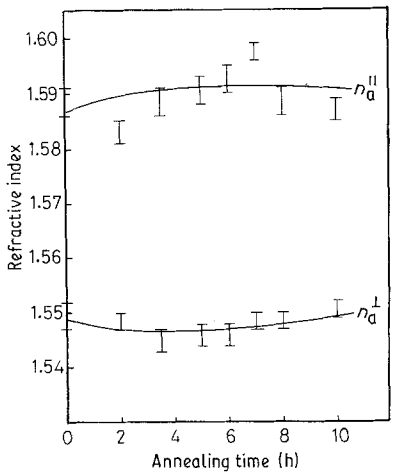


Figure 7 The variation of $n_a^{\parallel}$ and $n_a^{\perp}$ of annealed silk fibres with annealing time. Annealing temperature = 140° C. Results are obtained using a Pluta microscope (λ = 550 nm, T = 28° C).

clear that birefringence of the silk fibres reaches a maximum value when silk is annealed at 140° C for 5 to 6 h. This result is observed from the data obtained by both interferometric techniques.

Just as birefringence yields information about the crystallinity and orientation of the polymer molecular chains, the isotropic refractive index of a medium also gives information about not only the molecular backage but also specifications of the unit cell of the crystalline part of the medium [16]. Hannes [16] used the following formula

$$n_{iso} = \tfrac{1}{3}(n^{\parallel} + 2n^{\perp}) \quad (3)$$

to estimate a relationship showing the crystallization inhomogeneity for some types of polymers. Obtained values of $n_a^{\parallel}$ and $n_a^{\perp}$ from the interferometric techniques are used with Equation 3 to determine the isotropic refractive index values for annealed silk fibres.

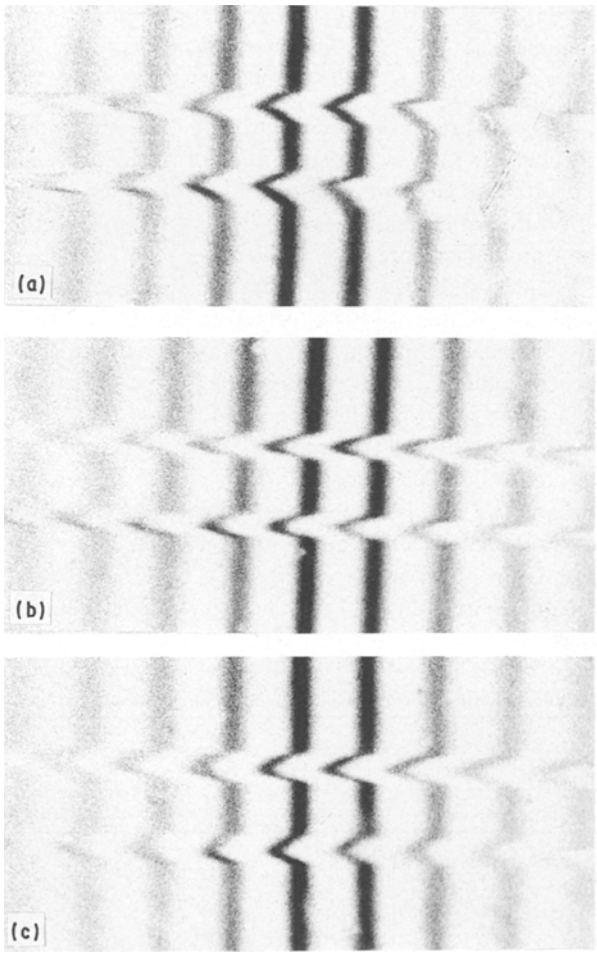


Figure 6 Totally duplicated images of annealed silk fibres at 140° C for annealing times of (a) 0, (b) 3.5 and (c) 6 h, using the Pluta microscope. White light of average wavelength 550 nm was used at 28° C.

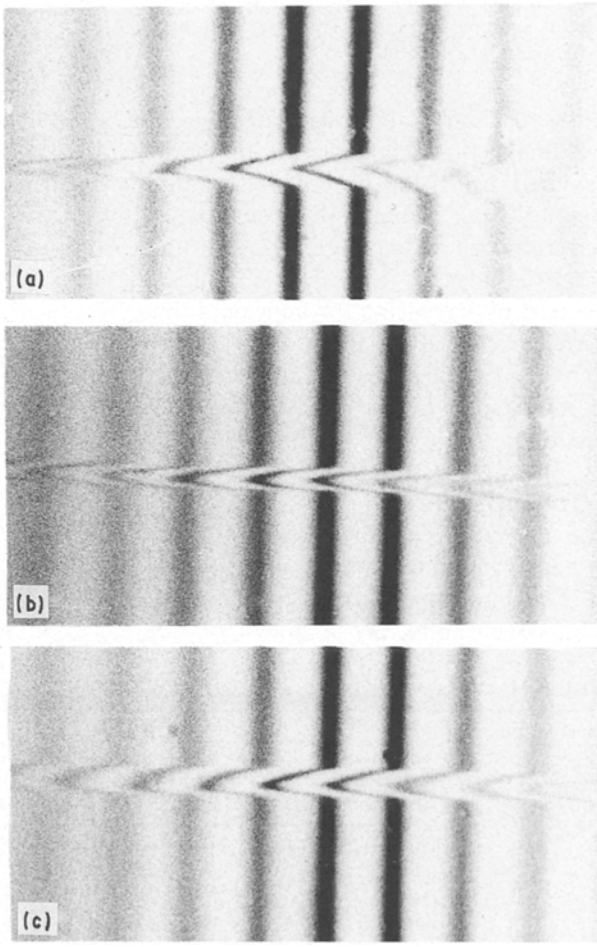


Figure 8 Microinterferograms of differentially sheared (non-duplicated) images of annealed silk fibres at 140° C for annealing times of (a) 0, (b) 3.5 and (c) 6 h using the Pluta microscope (λ = 550 nm, T = 28° C).

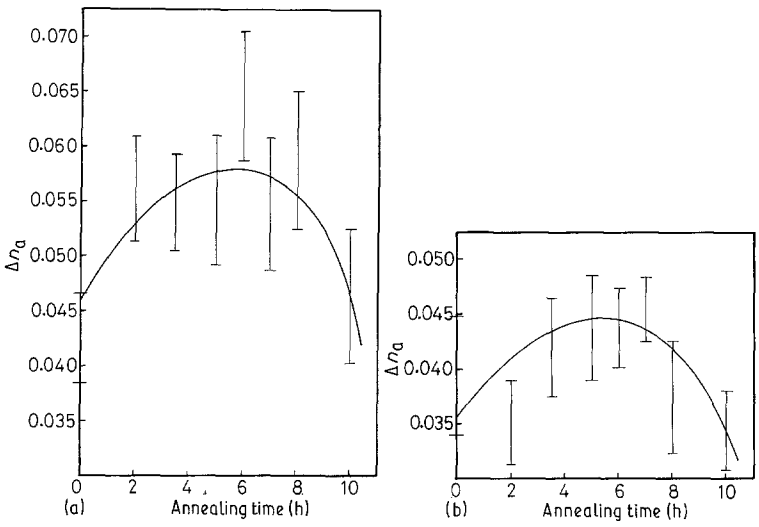


Figure 9 The variation of birefringence of annealed silk fibres with annealing time. Results are obtained using (a) multiple-beam and (b) double-beam interferometric techniques.

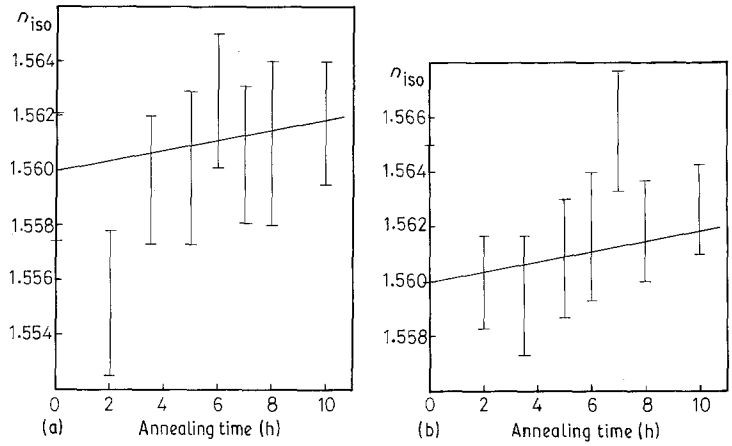


Figure 10 The variation of n_{iso} of annealed silk fibres with annealing time. Results are obtained using (a) multiple-beam and (b) double-beam interferometric techniques.

Figs 10a and b show the variation of n_{iso} of silk fibres due to changing annealing time, where (a) n_{iso} is calculated using the multiple-beam interferometric data and (b) n_{iso} is calculated using the double-beam interferometric data. Fig. 10 show that isotropic refractive index of annealed silk fibres is slightly increased by increasing the annealing time.

Data given in Figs 5 and 7 can be used to calculate the polarizabilities per unit volume when they are introduced in the well-known Lorentz–Lornz equation.

4. Conclusion

From the measurements carried out in the present work to investigate the change in optical properties due to the annealing process for natural silk, the following conclusions may be drawn.

1. The direction dependence of the refractive index was cited by early workers as a proof of the presence of crystalline elements within a fibre. As $n_a^{\parallel}$ increases with different annealing times, the crystallinity of the fibre must also increase.

2. As crystallinity and orientation increase, so the dyeability of silk fibre is expected to decrease [17].

3. Increasing birefringence means increasing crystallized volume in silk medium reaching a maximum value after 5 to 6 h annealing at 140° C.

4. The crystallized volume of the material is increased due to annealing. Possibly due to the nucleation process, the number of nuclei formed per unit time first increased to a maximum and then decreased [18]. Thus from observation of Fig. 9, it may be inferred that due to annealing of silk, new crystallized regions are formed.

TABLE II Values of birefringence obtained by two different techniques for annealed silk fibres at 140° C

Annealing time (h)	Two-beam technique						Multiple-beam technique	
	$\Delta n_a = n_a^{\parallel} - n_a^{\perp}$		Δn_a (directly)		Δn_a (average)		$\Delta n_a = n_a^{\parallel} - n_a^{\perp}$	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
0.0	0.044	0.034	0.046	0.034	0.045	0.034	0.047	0.039
2.0	0.039	0.031	0.039	0.031	0.039	0.031	0.061	0.051
3.5	0.048	0.039	0.045	0.037	0.047	0.038	0.059	0.050
5.0	0.049	0.040	0.048	0.039	0.049	0.039	0.061	0.049
6.0	0.047	0.042	0.049	0.039	0.047	0.040	0.071	0.059
7.0	0.049	0.046	0.049	0.039	0.048	0.043	0.061	0.049
8.0	0.044	0.036	0.041	0.033	0.043	0.034	0.065	0.053
10.0	0.040	0.032	0.036	0.029	0.038	0.031	0.050	0.040

5. The effects of the annealing process on natural silk fibres depend on the time and temperature of annealing.

6. Changes in n_{iso} with annealing time indicate a change in the specific volume of silk fibres on annealing.

7. A comparative study of Figs 4 and 6 shows that multiple-beam interferometry is more sensitive than the double-beam technique and gives valuable information about the skin–core structure of the fibre, as observed from Fig. 4c, which requires further study.

8. The annealing process affects other physical properties (mechanical, colour, thermal, electrical, etc.) of natural silk as well as its optical properties. Further studies should be carried out in order to detect which properties are improved by annealing.

In conclusion, the structural orientation changes due to the annealing process as observed by both two-beam and multiple-beam Fizeau fringes is very promising, and further study is required in areas which have not yet been explored.

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