Optothermal Properties of Fibers. IX. Study Changes of Optical Parameters by Multiple-Beam Technique Due to Thermal Annealing for Natural Silk Fibers

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ABSTRACT: Multiple-beam Fizeau fringes were used for studying the effect of the annealing process on the refractive indices and birefringence of natural silk fibers (best yellow Italian silk, Ford & Co. Ltd). Silk fibers were annealed at a constant time of 2 h with different annealing temperatures ranging from 60 to 160 ± 1°C. A scanning electron microscope was used for measuring the cross-sectional shape and a longitudinal view of the natural silk fibers. The Becke-line method was used for measuring the skin refractive indices and the birefringence of the natural silk fibers. The thermal coefficient of the refractive index, Cauchy dispersion constants, dispersive power, dielectric constant at infinity, polarizability per unit volume, isotropic polarizability, and isotropic refractive index were determined interferometrically. Microinterferograms and curves are given for illustration. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1495–1504, 1998

Key words: silk fibers; annealing; refractive index; dispersive power; anisotropy; birefringence

INTRODUCTION

For optically anisotropic fibers, the refractive index and the double refraction are parameters characterizing the structure of the material. The dependence of the refractive index on the directions were probably the first of the anisotropic properties observed in fibers and was cited by early workers as proof of the presence of crystalline elements within the fiber.[1] It is now known that double refraction arises from the inherent optical anisotropy of the chainlike macromolecules and forms the preferred axial orientation of the molecular chains which constitute the fiber.[2] Consequently, birefringence gives a measure of the orientation, which is an average of that of the amorphous and crystalline regions.[3] Multiple-beam microinterferometry is a precise tool in fiber science. It provides some structural information on each layer of a fiber at the molecular level of regular and irregular transverse sections.[4,5]

One of the most available techniques for changing the polymeric structure is the annealing process.[6–10] The effects of annealing not only increase drastically with temperature, but also depend on the time the sample is held at the annealing temperature. To understand the annealing effects, their molecular source must be known.[11,12] Several studies have been reported on the effect of annealing on the structure of natural and synthetic fibers.[13–16]

EXPERIMENTAL

Sample Preparation (Annealing)

The degummed silk fibers were distributed in seven small glass dishes, then left in an electric

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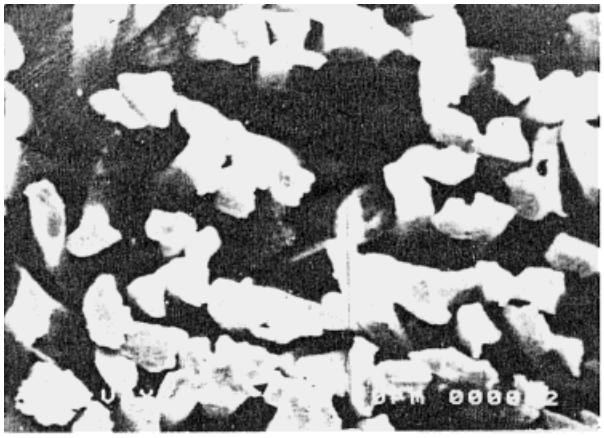

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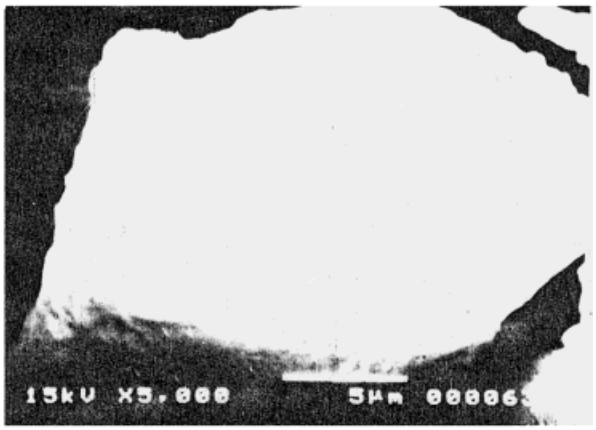

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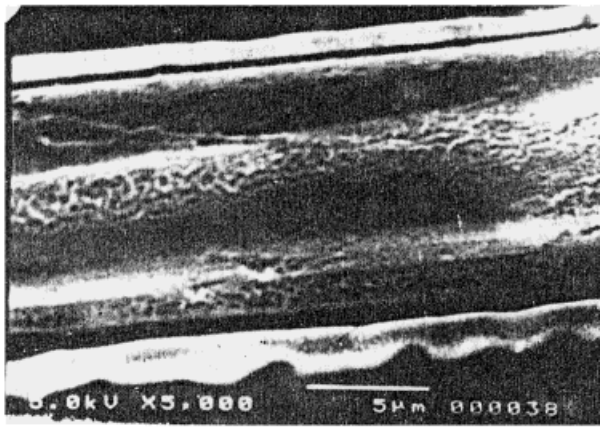

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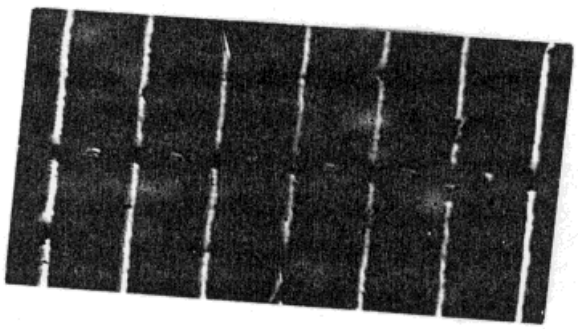
Plate 1 (a–c) Cross-sectional shape of a bundle of natural silk fiber, the cross-sectional shape of a single fiber, and the longitudinal view of natural silk fiber, respectively.



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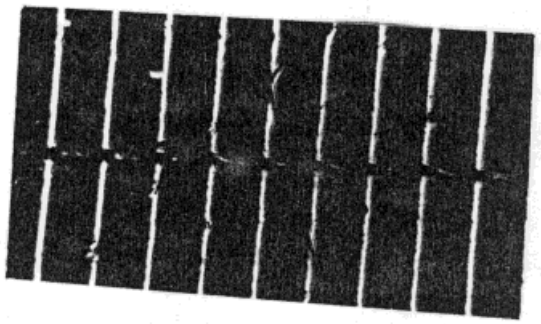


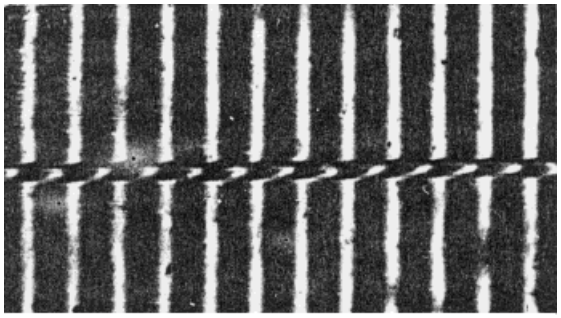
(b)

Plate 2 (a,b) Microinterferograms of multiple-beam Fizeau fringes in transmission for natural silk fibers for light vibrating parallel (a) and perpendicular (b) to the fiber axis, respectively.

oven whose temperature was adjusted to be constant to within ±1°C. The samples were heated at constant time of 2 h for different temperatures ranging from 60 to 160 ± 1°C. The samples after heating were then left to cool at the room temperature of 31 ± 3°C.

Scanning Electron Microscopy (SEM)

A high-resolution scanning electron microscope (JOEL JSM 5400-LV) was used to study the cross-sectional shape and longitudinal view of the natural silk fibers. Plate 1(a) shows the cross-sectional shape of a bundle of natural silk fibers. Plate 1(b) shows the cross-sectional shape of a single fiber under high magnification. It is clear that the cross section has more irregular shapes



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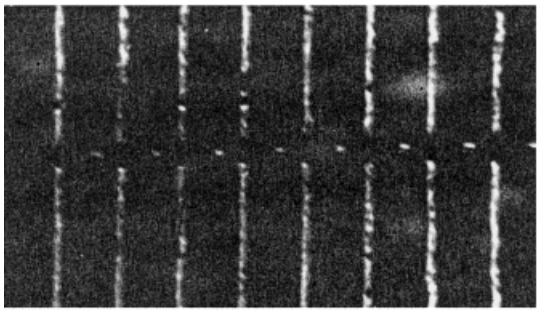

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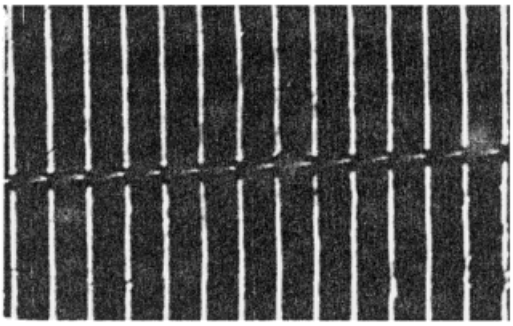
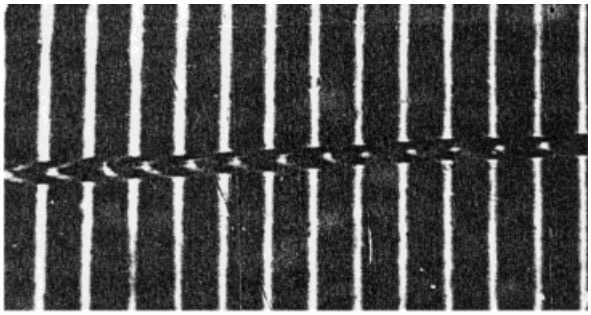


(c)

Plate 3 (a–c) Microinterferograms of multiple-beam Fizeau fringes in transmission of annealed silk fibers for light vibrating parallel to the fiber axis: 60, 100, and 160 ± 1°C, respectively.

as seen in the SEM. The mean cross-sectional area was found to be (A = 64.3 + 8.5 μm^2). Plate 1(c) shows the longitudinal view of a natural silk fiber, from which it is clear that the surface of the fiber is not smooth, but contains longitudinal grooves.



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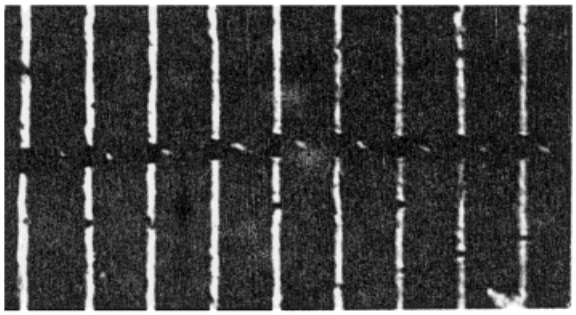

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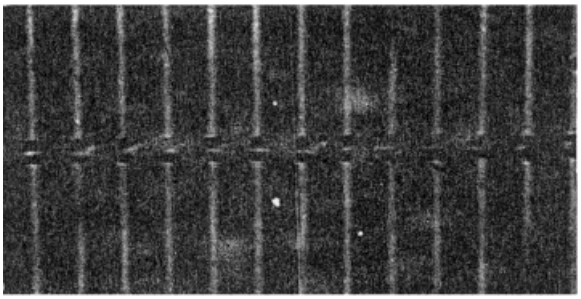


(c)

Plate 4 (a–c) Mirointerferograms of multiple-beam Fizeau fringes in transmission of annealed silk fibers for light vibrating perpendicular to the fiber axis: 60, 100, and 160 ± 1°C, respectively.

Table I Results Obtained for Natural Silk Fibers Annealed at a Constant Time of 2 h for Different Annealing Temperatures Using Multiple-beam Fizeau Fringes in Transmission

Annealing Temperature (±1°C)	$n_a^{\parallel}$		$n_a^{\perp}$		Δn_a	
	Max	Min	Max	Min	Max	Min
31	1.5968	1.5929	1.5569	1.5508	0.0399	0.0421
60	1.5957	1.5923	1.5589	1.5524	0.0368	0.0399
80	1.5961	1.5924	1.5579	1.5503	0.0382	0.0422
100	1.5933	1.5889	1.5558	1.5498	0.0375	0.0391
120	1.6004	1.5954	1.5601	1.5534	0.0403	0.0411
140	1.6032	1.5993	1.5651	1.5571	0.0381	0.0422
160	1.5964	1.5933	1.5579	1.5518	0.0385	0.0415

Values have an accuracy of $\pm 6 \times 10^{-4}$.

Becke-line Method

The Becke-line method can be used for the measurement of the refractive indices and birefringence of the outer layers of a fiber.[17] Mixtures of α-monobromonaphthalene ($n_L = 1.658$ at 20°C) and liquid paraffin oil ($n_L = 1.481$ at 20°C) were found to be suitable immersion liquids. The values of the refractive indices of the natural silk fibers for a light vibrating parallel $n_s^{\parallel}$ and perpendicular $n_s^{\perp}$ to the fiber axis were determined using this technique and were found to be $n_s^{\parallel} = 1.5925$, $n_s^{\perp} = 1.5550$, and $\Delta n_s = 0.0375$. The temperature of the experiment was 22°C. Mclean[18] used an interferometric technique to measure the refractive index across the fiber and showed that the Becke-line refractive indices are not confined to the surface but may occur at any point on the radius.

Multiple-beam Technique

Multiple-beam Fizeau is an accurate technique for measuring the refractive indices and birefringence of fibers.[19] For fibers having irregular cross sections, the area enclosed under the interference fringe shift is related to the refractive indices of the media inside the wedge interferometer, where

$$n_a^{\parallel} = n_L + \frac{F^{\parallel}}{h} \frac{\lambda}{2A}$$

where $n_a^{\parallel}$ is the mean refractive index of the fiber material for a plane polarized light vibrating parallel to the fiber 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 fiber cross-sectional area; and λ, the wavelength of the monochromatic light used. The above equation has an analogous form for light vibrating perpendicular to the fiber axis for the determination of $n_a^{\perp}$, the mean birefringence Δn_a, given by

$$\Delta n_a = n_a^{\parallel} - n_a^{\perp}$$

Table II Published Data of the Birefringence Δn_a Using the Two-beam Technique[16] with Accuracy of $\pm 2 \times 10^{-3}$ and the Obtained Data Using the Multiple-beam Technique with Accuracy of $\pm 6 \times 10^{-4}$

Annealing Temperature (±1°C)	Published $\Delta n_a = n^{\parallel} - n^{\perp}$		Published Δn_a (Directly)		Multiple-Beam ΔN_a	
	Max	Min	Max	Min	Max	Min
31	0.042	0.041	0.043	0.035	0.0399	0.0421
60	0.041	0.032	0.042	0.032	0.0368	0.0399
80	0.044	0.034	0.041	0.032	0.0382	0.0422
100	0.038	0.028	0.037	0.029	0.0372	0.0391
120	0.046	0.035	0.046	0.035	0.0403	0.0411
140	0.047	0.036	0.044	0.033	0.0381	0.0422
160	0.042	0.033	0.045	0.034	0.0385	0.0415

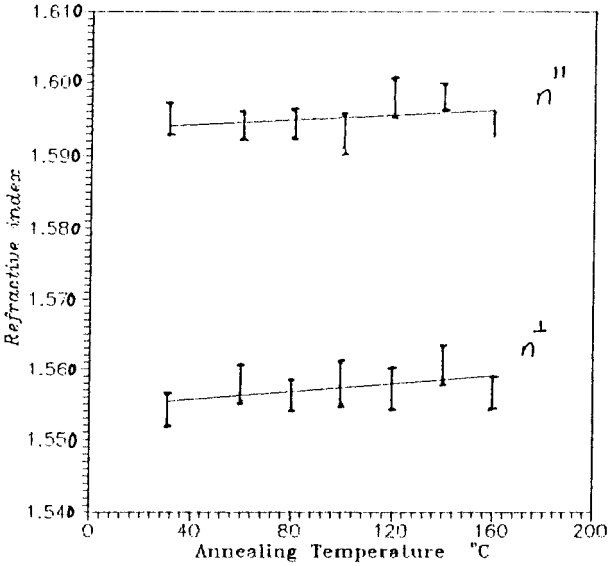


Figure 1 Relation between the refractive indices $n_a^{\parallel}$ and $n_a^{\perp}$ of natural silk fibers and the annealing temperature.

A multiple-beam interference technique in transmission was used for the determination of the optical properties of the natural silk fibers before and after annealing at a constant time of 2 h for different temperatures ranging from 60 to 160 ± 1°C.

Plate 2(a,b) shows microinterferograms of multiple-beam Fizeau fringes in transmission for natural silk fibers for light vibrating parallel and perpendicular to the fiber axis, respectively. A monochromatic light of wavelength 546.1 nm was used; the refractive index of the immersion liquid was 1.5782 at 21°C.

Plates 3(a–c) and 4(a–c) are microinterferograms of multiple-beam Fizeau fringes in transmission of the natural silk fiber annealed at a constant time of 2 h for different temperatures of 60, 100, and 160 ± 1°C, respectively, for monochromatic light of wavelength 546.1 nm vibrating parallel and perpendicular to the fiber axis, respectively. The refractive index of the immersion liquid was 1.5782 at 21°C.

The mean refractive indices $n_a^{\parallel}$ and $n_a^{\perp}$ and the mean birefringence Δn_a were determined using the above equations and the results are given in Table I. Table II gives a comparison between the published data[16] of the birefringence using a two-beam technique and a multiple-beam technique. The obtained variations of the data between the maximum values and minimum values are attributed to the great variation in the cross-sectional area of these fibers and to the greater accuracy and sensitivity of the multiple-beam than that of the two-beam technique.[20]

Figure 1 shows the variation of both $n_a^{\parallel}$ and $n_a^{\perp}$ of natural silk fibers by increasing the annealing temperature, as obtained using the multiple-beam interferometric technique. It is clear that both $n_a^{\parallel}$ and $n_a^{\perp}$ increase with increase in the annealing temperature and, hence, the birefringence Δn_a is nearly constant with increasing temperatures as given in Figure 2. Also, this indicates reorientations in both parallel and perpendicular directions at the same time.

Refractive Index Temperature Dependence of Natural Silk Fibers

By using the multiple-beam technique in transmission and measuring the change in the fringe shift due to the change of temperature within the range 22 to 18°C, we obtain dn/dT. Plate 5(a,b) shows microinterferograms of multiple-beam Fizeau fringes in transmission for light vibrating parallel to the fiber axis at the two different temperatures (18 and 22°C), respectively. The wavelength of the light used was 546.1 nm. The results of the calculations were $n_a^{\parallel} = 1.5943$ at 18°C, while at 22°C, $n_a^{\parallel} = 1.5924$. The mean value of the $dn^{\parallel}/dT$ of the natural silk fibers was found to be equal to 4.75×10^{-4}/°C for the parallel direction.

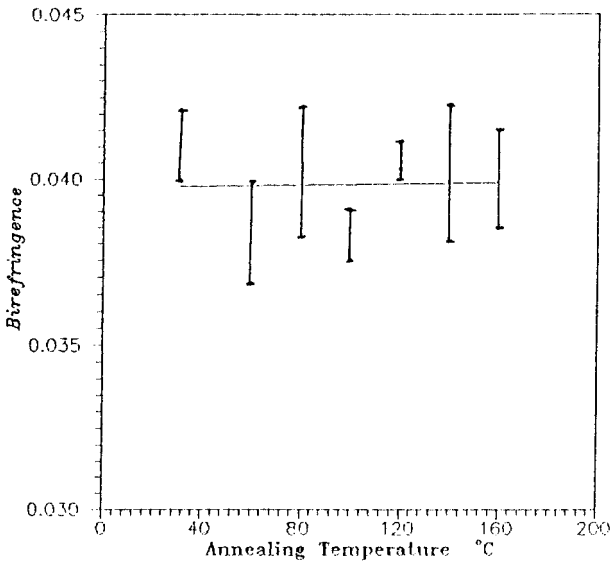
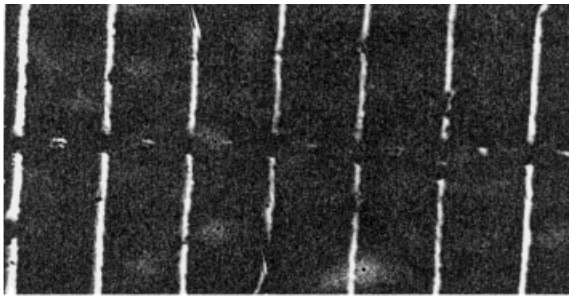


Figure 2 Relation between the birefringence Δn_a of the natural silk fibers and the annealing temperature.

Dispersion Properties and Dielectric Constant of Natural Silk Fibers

Multiple-beam Fizeau fringes in transmission were used to calculate the refractive indices of the natural silk fibers at different wavelengths. Plates 6(a–c) and 7(a–c) show microinterferograms of multiple-beam Fizeau fringes of the natural silk fibers at different wavelengths of 589.3, 546.1, and 436 nm, respectively, for light vibrating parallel and perpendicular to the fiber axis (at 21 ± 1°C). The mean refractive indices were calculated at different wavelengths and the results are given in Table III.

A relation shown in Figure 3 between the refractive indices $n_a^{\parallel}$ and $n_a^{\perp}$ and $1/\lambda^2$ was constructed to evaluate the constants A and B of the well-known Cauchy formula:



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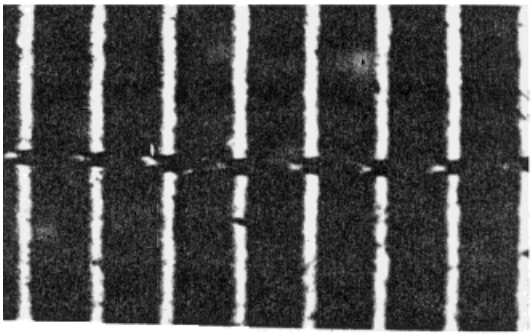

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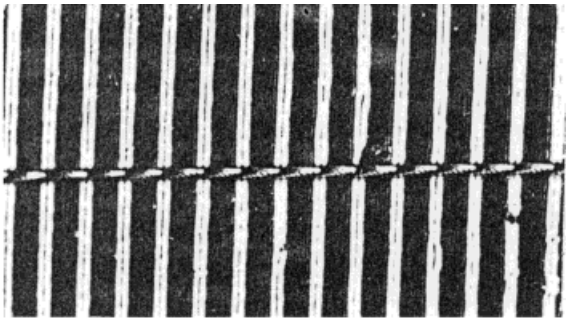
Plate 5 (a,b) Microinterferograms of multiple-beam Fizeau fringes in transmission for light vibrating parallel to the fiber axis at two different temperatures, 18 and 22°C, respectively, for natural silk fiber.



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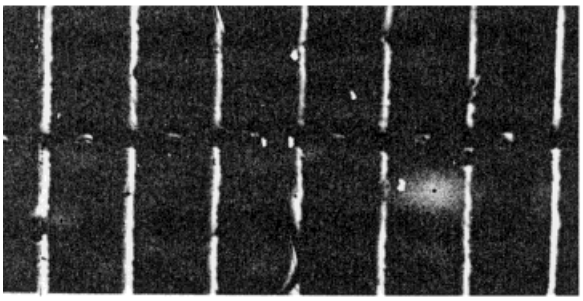

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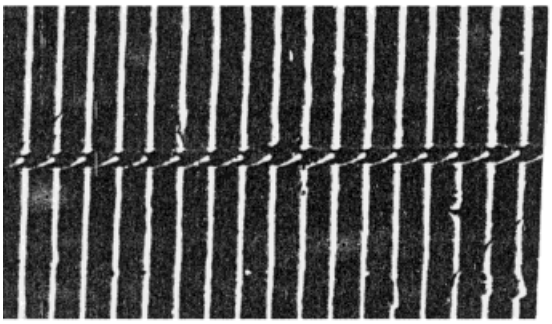
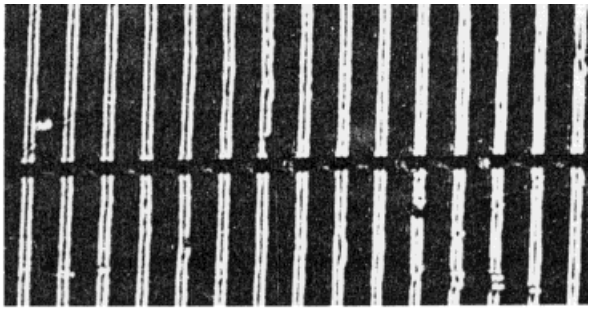


(c)

Plate 6 (a–c) Microinterferograms of multiple-beam Fizeau fringes of natural silk fibers at different wavelengths 589.3, 546.1, and 436 nm, respectively, for light vibrating parallel to the fiber axis.

$$n_\lambda^{\parallel} = A + \frac{B}{\lambda^2}$$

with an analogous form for $n_\lambda^{\perp}$, where A and B



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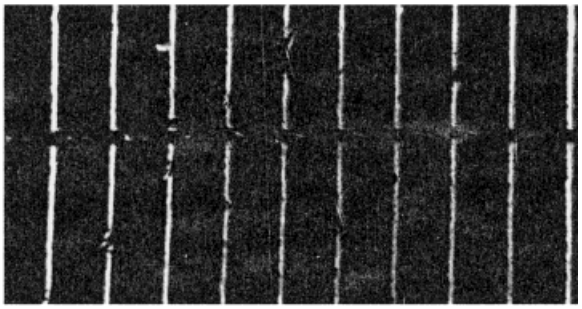

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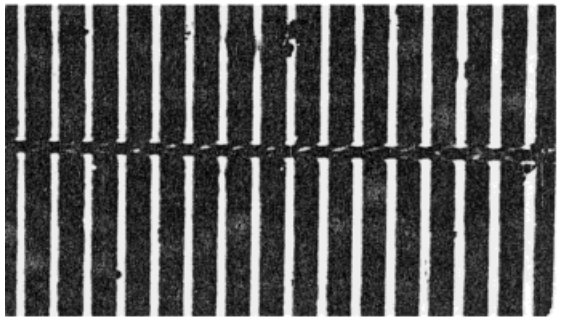

(c)

Plate 7 (a–c) Microinterferograms of multiple-beam Fizeau fringes of natural silk fibers at different wavelengths 589.3, 546.1, and 436 nm, respectively, for light vibrating perpendicular to the fiber axis.

are the Cauchy dispersion constants to characterize the dispersion activity of the material. Also, the dispersion power is given by

$$\frac{dn}{d\lambda} = -\frac{2B}{\lambda^3}$$

Table III Refractive Indices for Different Wavelengths of Light of Natural Silk Fibers

Wavelength (nm)	$n_a^{\parallel}$		$n_a^{\perp}$	
	Max	Min	Max	Min
436.0	1.6127	1.6118	1.5566	1.5557
546.1	1.5949	1.5939	1.5542	1.5533
578.0	1.5927	1.5918	1.5532	1.5522
589.3	1.5920	1.5911	1.5526	1.5517

Values have accuracy of $\pm 6 \times 10^{-4}$.

The results of the constants A and B and $dn/d\lambda$ are tabulated in Table IV.

The dielectric constant at infinity can be calculated from the following equation:

$$n = \sqrt{\varepsilon_\infty}$$

where ε_∞ is the dielctric constant of the medium at infinity and n is the index of refraction. By plotting the relation between $[1/(n^2 - 1)]$ and $1/\lambda^2$ (Fig. 4), we obtain a linear relation from which we can calculate the dielectric constant at infinity ε_∞, which equals 2.4159 for natural silk fibers.

Polarizability per Unit Volume and Isotropic Refractive Index

The experimental values of the refractive indices were utilized to calculate the polarizability per unit volume using the Lorentz–Lorenz equation:

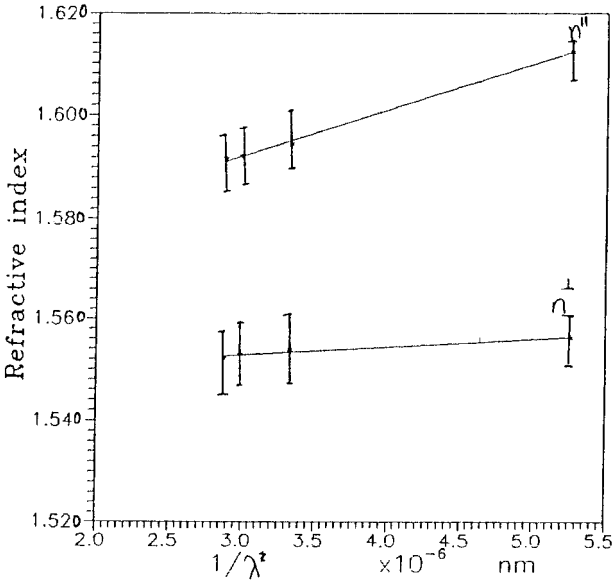

Figure 3 Relation between the refractive indices $n_a^{\parallel}$ and $n_a^{\perp}$ $(1/\lambda^2)$.

Table IV Values Obtained from the Cauchy Formula and Dispersive Power Constants of Natural Silk Fibers

Direction of Light Vibration	A	$B \times 10^3$ nm^2	$dn/d\lambda$
Parallel	1.5656	8.8476	1.626×10^{-4}
Perpendicular	1.5481	1.5678	2.179×10^{-5}

$$P^{\parallel} = \frac{3(n_{\parallel}^2 - 1)}{4\pi(n_{\parallel}^2 + 2)}$$

and with an analogous formula for the perpendicular direction, the isotropic polarizability per unit volume was calculated using the equation

$$p_{\text{iso}} = \frac{p^{\parallel} + 2p^{\perp}}{3}$$

Figures 5 and 6 give the relationships between the polarizability per unit volume $p^{\parallel}$ and $p^{\perp}$ of the natural silk fibers before and after annealing at a constant time of 2 h and different annealing temperatures ranging from 60 to 160 ± 1°C.

Figure 7 shows the variation of the isotropic polarizability per unit volume with the annealing temperature. It is clear that the isotropic polarizability per unit volume p_{iso} is nearly constant with the annealing temperature.

The isotropic refractive index n_{iso} was calculated using the following formula[21]:

$$n_{\text{iso}} = \left(\frac{n^{\parallel} + 2n^{\perp}}{3}\right)$$

Figure 8 shows the relation between the isotropic refractive index n_{iso} and the annealing temperature of natural silk fibers annealed at a constant time of 2 h at different annealing temperatures ranging from 60 to 160 ± 1°C. The variation of n_{iso} with different thermal conditions is indicative of the density and crystallinity variations due to the applied conditions.

CONCLUSIONS

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

1. The effect of the annealing process depends on the temperature and time of annealing. Also, the annealing process affects other physical properties (mechanical, color, thermal, electrical, etc.) of natural silk fibers, as well as their optical properties.
2. The use of multiple-beam Fizeau fringes verifies the Cauchy dispersion formula and

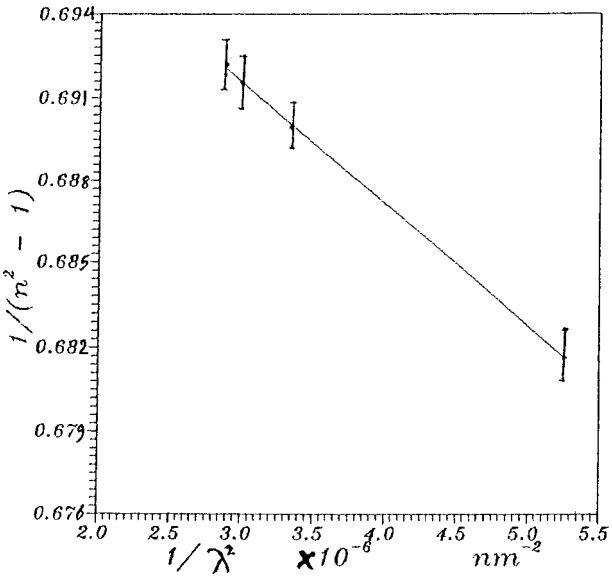

Figure 4 Relation between $[1/(n^2 - 1)]$ and $(1/\lambda^2)$.

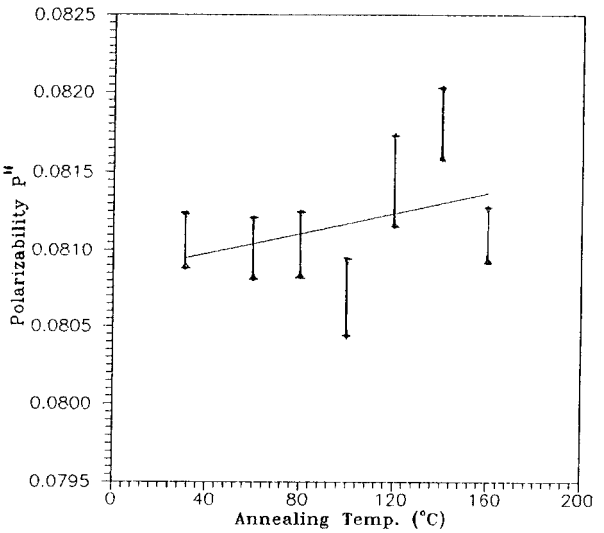

Figure 5 Relation between the polarizability $p^{\parallel}$ of the natural silk fibers and the annealing temperature.

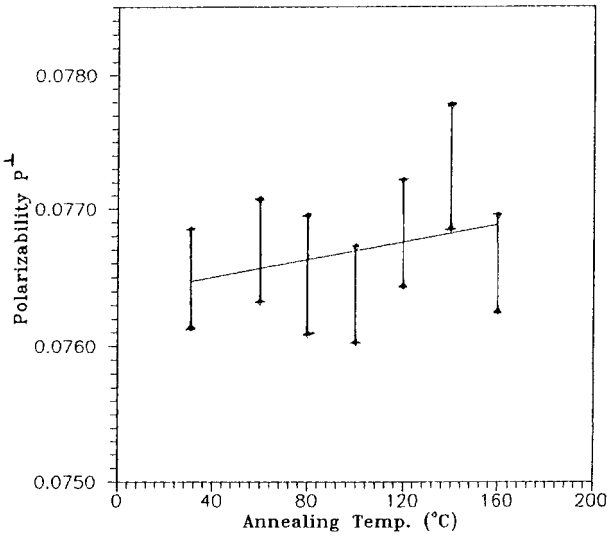

Figure 6 Relation between the polarizability $p^{\perp}$ of the natural silk fibers and the annealing temperature.

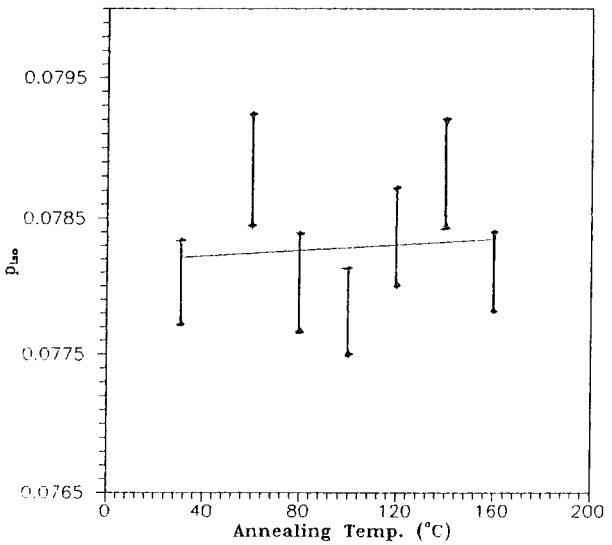

Figure 7 Relation between the isotropic polarizability p_{iso} of the natural silk fibers and the annealing temperature.

determines the constants A and B of this formula for natural silk fibers.

3. As the temperature increases, the birefringence Δn_a is nearly constant with different variations of the thermal parameters. This verifies that molecular orientation is constant at high temperature for these conditions of thermal trearments.
4. The determination of the thermal coefficients of the refractive indices for natural silk fibers emphasizes the importance of the radiative properties of the fiber media which define the fiber orientation, size distribution, and relation to the optical properties.
5. Due to the annealing process, the variation of the isotropic refractive indices is related to the changes in the specific volume, degree of order of orientation, mass redistribution of the sample, and crystallinity of the fiber as well as the density of the sample[21] $[(n_{iso} - 1)/\rho = k]$.
6. As natural silk fibers are anisotropic material, the refractive indices show unequal behavior in different directions. Clearly, this behavior is proof that the structure of the fiber is different along and across its axes.
7. The variation between the values obtained by two-beam and multiple-beam techniques is due to
   (a) The precision of the multiple-beam technique over that of the two-beam technique.
   (b) The great variation of the area of the cross section of silk fibers.

Also, the above two techniques are more precise than is the Becke-line technique.

One can conclude from the above results and considerations that new reorientation is due to the thermal treatment which promotes a new re-

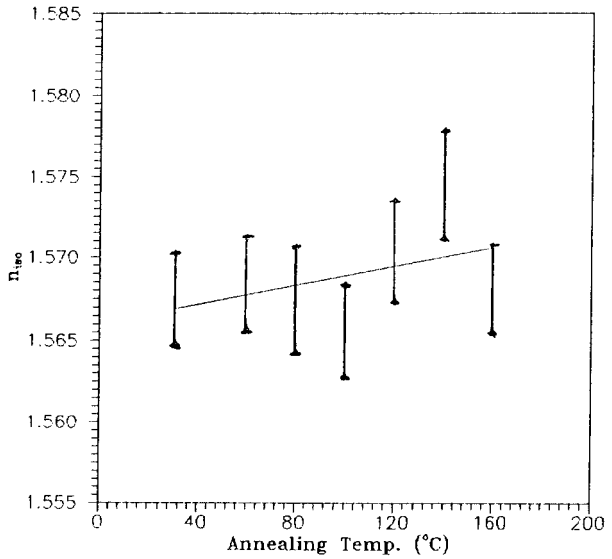

Figure 8 Relation between the isotropic refractive index n_{iso} of the natural silk fibers and the annealing temperature.

arrangement of the structure of the thermally treated fiber. Interferometric techniques are very promising for studying the optical anisotropy of the fibers.

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