Optothermal Properties of Fibers: 12-Interferometric Investigation for Thermally Treated Viscose Fibers

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ABSTRACT: The present article studies the structure of annealed viscose fibers interferometrically at a constant temperature of $100 \pm 1°C$ at different times. The Pluta polarizing interference microscope has been used for determining the mean refractive indices and mean birefringence. The results were used to calculate the optical orientation function and the angle of orientation. The value $(\Delta\alpha/3\alpha_0)$, which depends on the molecular structure of the polymer, remains constant. Relationships between the mean refractive indices, birefringence, isotopic refractive index, and polarizabilities per unit volume with different times were given for these fibers. The samples were subjected to X-ray diffraction to clarify the variation of crystallinity with the annealing conditions. Differential thermal analysis measurements were used to determine the glass transition temperature of viscose fiber. Measurements of the volume swelling parameter of the viscose fibers with different liquids were given. Also, determinations of Cauchy's constants, dispersive power, and dielectric constant at infinity were carried out. Illustrations are given using graphs and microinterferograms. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 361–369, 1999

Key words: interferometric; birefringence; thermally; viscose; swelling; crystallinity

INTRODUCTION

The development of structure reorientation in viscose fiber is a continuing area of technological and scientific study. Drawing and heat treatment operations are important commercial processing steps. These steps produce the structure required for good dyeability, appearance, and mechanical properties.[1] One of the most available techniques for changing the viscose structure is the heat treatment process.[2–8] The effects of annealing increase drastically with time but also depend on the temperature at which the sample is held. The study of optical anisotropy in viscose fibers plays an important role in the knowledge of the molecular arrangement within these fibers.

Double refraction depends on molecular orientation in fibers as it contains contributions from the polarizabilities of all molecular units in the sample. The structure of these fibers can be characterized on the molecular level by determining their refractive indices and birefringence.

Birefringence is a measure of the total molecular orientation of a system, and it is excellent property to use for the study of orientation in polycrystalline polymer. Since birefringence is a measure of the total molecular orientation of the two-phase system, its examination in conjunction with other physical measurements (X-ray, density, and mechanical loss factor, for example) yields considerable insight into the characteristics of the relationship between the degree of crystallinity and the density of the polymer and it has great influence on the viscoelastic properties of crystalline polymers.[9–11]

Determination of degree of swelling is used in practice for testing finished articles intended for

service in liquid and gaseous media. Such determinations serve as a method of assessing the degree of crosslinking of polymer chains.[12]

THEORETICAL CONSIDERATION

The Pluta polarizing interference microscope[13,14] was used in the present work to determine the refractive indices and birefringences of annealed fibers. The following equations are used for determination of the optical parameters for $n_a^{\parallel}$, $n_a^{\perp}$, and Δn_a, as follows:

$$n_a^{\parallel} = n_L \pm \frac{F^{\parallel}}{A} \cdot \frac{\lambda}{h}$$

$$\Delta n_a = n_a^{\parallel} - n_a^{\perp} \qquad (1)$$

$$\Delta n_a = \frac{\Delta F \cdot \lambda}{h \cdot A} \qquad (2)$$

where $n_a^{\parallel}$ and $n_a^{\perp}$ are the refractive indices of the fiber for light vibrating parallel and perpendicular to the fiber axis, respectively; n_L is the refractive index of the immersion liquid; $F^{\parallel}$ and $F^{\perp}$ are the area of the fiber enclosed under the fringe shift as it crosses the fiber; h is the interference fringe spacing corresponding to the wavelength λ; and A is the mean cross-sectional area of the fiber. Also, Δn_a is the birefringence of the fiber, and ΔF is the area enclosed under the fringe shift using the nonduplicated image of the fiber.

The optical results for $n_a^{\parallel}$ and $n_a^{\perp}$ are used to calculate the following parameters:

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

isotropic polarizability, $P_{iso} = \dfrac{(P^{\parallel} + 2P^{\perp})}{3}$ (4)

isotropic refractive index, $n_{iso} = \dfrac{(n_a^{\parallel} + 2n_a^{\perp})}{3}$ (5)

where P is the polarizability per unit volume, P_{iso} is the isotropic polarizability, and n_{iso} is the isotropic refractive index.

The constants A and B of Cauchy's formula can be evaluated using the following equation by plotting the relation between the refractive index and $(1/\lambda^2)$, as follows:

$$n_{\lambda}^{\parallel} = A^{\parallel} + B^{\parallel}/\lambda^2 \qquad (6)$$

with an analogous formula for $n_{\lambda}^{\perp}$, $A^{\perp}$, and $B^{\perp}$ were obtained by differentiation of Cauchy's formula. The dispersive power could be obtained, such as in the following:

$$dn/d\lambda = -2B/\lambda^2 \qquad (7)$$

The index of refraction is given by the square root of the dielectric constant ε by[15]

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

that is,

$$\varepsilon_{\infty} = n^2 \qquad (8)$$

and by plotting the relation between $\{1/(n_{iso}^2 - 1)\}$ and $(1/\lambda^2)$, a linear relation, from which we can calculate ε_{∞}, the dielectric constant at infinity.

The results for the constant $A^{\parallel}$, $B^{\parallel}$, $A^{\perp}$, $B^{\perp}$, $(dn^{\parallel}/d\lambda)$, and $(dn^{\perp}/d\lambda)$ are given in Table I.

Also, the optical orientation and orientation angle can be calculated using Hermans' equation,[16] as follows:

$$(\text{Opt. Ori. Fun.}) \quad F_{\theta} = \Delta n_a/\Delta n_{max} \qquad (9)$$

$$F_{\theta} = 1 - (3/2)\sin^2\theta \qquad (10)$$

where θ is the angle between the axis of polymer unit and the fiber axis. The value of Δn_{max} has been previously determined to be 0.055[17] of the fiber under investigation for perfectly (or fully) oriented fiber, and Δn_a is the measured mean birefringence.

The average value of Opt. Ori. Fun. $\langle P_2(\theta) \rangle$ due to Ward[18,19]

$$\langle P_2(\theta) \rangle = \Delta n_a/\Delta n_{max} \qquad (11)$$

which is the same function named by Hermans'[20] $\langle P_2(\theta) \rangle$ is related to the polarizability as follows:

$$\frac{(\Phi^{\parallel} - \Phi^{\perp})}{(\Phi^{\parallel} + 2\Phi^{\perp})} = P_2(\theta_m)\langle P_2(\theta) \rangle \qquad (12)$$

where $\Phi^{\parallel}$ and $\Phi^{\perp}$ are the polarizabilities parallel and perpendicular directions to the fiber axis, respectively.

$$\langle P_2(\theta) \rangle = \tfrac{1}{2}(3 \cos^2\theta_m - 1) = \text{Constant}$$

Table I

Annealing Time (min)	A^{II}	$A^{\perp}$	$B^{\text{II}} \times 10^{-3}$ nm²	$B^{\perp} \times 10^{-3}$ nm²	$dn^{\text{II}}/d\lambda \times 10^{-5}$ nm⁻¹	$dn^{\perp}/d\lambda \times 10^{-5}$ nm⁻¹
Unannealed	1.504	1.467	8.83	15.96	−10.2	−18.1
15	1.549	1.427	−2.742	29.87	−3.11	−33.9
45	1.547	1.511	−2.359	1.968	−2.68	2.23
60	1.548	1.511	−3.193	2.108	−3.62	2.39
75	1.551	1.524	4.148	−1.751	−4.71	1.99

depends only on the molecular structure of the polymer and determined by the angle θ_m, which is the angle between the dipole moment and the chain axis. Also, eq. (12) can be written in the following form:

$$\frac{(\Phi^{\parallel} - \Phi^{\perp})}{(\Phi^{\parallel} + 2\Phi^{\perp})} = \left[\frac{\Delta\alpha}{3\alpha_0}\right]\langle P_2(\theta)\rangle \qquad (13)$$

where $\Delta\alpha$ is the difference between $\alpha^{\parallel}$ and $\alpha^{\perp}$, which are the electric polarizability of 1 molecule when using monochromatic light vibrating parallel and perpendicular to the fiber axis, respectively, and $\alpha_0 = \frac{1}{3}(\alpha^{\parallel} + 2\alpha^{\perp})$ is the isotropic polarizability. The quantity $(\Delta\alpha/3\alpha_0)$ depends on the molecular structure and is nearly constant for a given polymer,[21] where

$$\frac{(n_{\parallel}^2 - 1)}{(n_{\parallel}^2 + 2)} = \Phi^{\parallel}$$

and analogous equation for $\Phi^{\perp}$.

The results of $\dfrac{(\Phi^{\parallel} - \Phi^{\perp})}{(\Phi^{\parallel} + 2\Phi^{\perp})}$

and $\left[\dfrac{\Delta\alpha}{3\alpha_0}\right]$ are given in Table II.

MEASUREMENT OF THE VOLUME SWELLING PARAMETER OF THE ANNEALED VISCOSE FIBERS IN DIFFERENT LIQUIDS

For the determination of the volume swelling parameter[22] of the fibers, the law of Hermans[20] and Gladstone Dale has been used by the following equations:

$$S_v = \frac{(\Delta n)_0 - (\Delta n)_s}{(\Delta n)_s \alpha_0}$$

where $(\Delta n)_0$ is the dry birefringence, $(\Delta n)_s$ is the swellen birefringence, and S_v is the volume swelling parameter, where the volume swelling parameter is an indicator of the degree of crystalline and amorphous areas in the structure of the studied fiber.

EXPERIMENTAL RESULTS AND DISCUSSION

Annealing of Samples

The viscose fibers (manufactured in Egypt by the Misr Rayon Co.) distributed in a cocoon form on a glass rods with free ends, which were then heated in an electric oven and heated at constant temperature $100 \pm 1°C$ for different annealing times, ranging from 15 to 90 min, and then left in air to be cooled. The constant temperature $100°C$ was selected above T_g and less than T_m.

X-Ray Diffraction

The X-ray diffraction (XRD) technique was used in this work to examine the crystallinity and the crystalline structure of crystalline phase in the annealed samples. XRD examinations were done with an X-ray diffractogram PW 1730 with conventional Cu-Kα-Ni-filtered radiation at 40 KV and 25 mA. The scan speed was adjusted at 4° min.⁻¹

The samples were scanned over a range of 2θ equal to 4 to 35°. The lateral order, which denotes the crystallinity parameter, was measured by the method suggested by Manjunath et al.[23] and applied by different authors.[24,25] According to this method for viscose fiber, the resolution of the peak R is given by the following formula:

Table II

Annealing Time (min)	n^{II}	$n^{\perp}$	Δn	$\dfrac{\Phi^{II} - \Phi^{\perp}}{\Phi^{II} + 2\Phi^{\perp}} \times 10^{-3}$	$\langle P_2(\theta) \rangle \times 10^{-2}$	$\Delta\alpha/3\alpha_0 \times 10^{-2}$
Unannealed	1.531	1.518	0.013	6.86	23.3	0.0293
15	1.539	1.517	0.022	11.63	39.7	0.0293
30	1.538	1.517	0.021	11.16	38.2	0.0293
45	1.537	1.518	0.020	10.44	35.7	0.0293
60	1.537	1.518	0.019	10.00	34.2	0.0293
75	1.536	1.518	0.018	9.38	32.1	0.0293

$$R = \frac{2m_1}{h_1 + h_2}$$

For viscose, a baseline is drawn from 2θ equal to 4 to 72°; and the peak heights h_1 and h_2, respectively, and height m_1 of the minimum between these 2 peaks are measured. When the resolution is completely lost, R tends to be 1, and, conversely, R tends to e zero when the resolution is maximum. Thus, R is inversely related to the lateral order, and $(1 - R)$ gives the crystallinity index.

Table III shows the values of order factor obtained using the XRD technique and the values of $F(\theta)$ and θ for viscose fibers at different annealing conditions.

Figure 1 shows the XRD intensity of viscose fibers and transformation of the samples for fibers after thermal annealing for different times at a constant temperature of 100°C. It is clear that increasing the annealing time causes crystal decomposition, which is associated with a decrease in the density of the medium, where the density of the crystalline portion was considered to be the highest density in the viscose fiber.

Differential Thermal Analysis Measurements

The greatest number of applications of differential thermal analysis (DTA) in recent years has been in the area of polymeric materials. This technique is routinely used to measure glass transition temperatures T_g, melting points T_m, and other numerous parameters. Several DTA instruments were developed mainly for use in polymer measurements. In the present work, a Shimadzo thermal analyzer, model DTA-50 Shimadzu, was used. The DTA measurement of unannealed viscose fibers showed that the glass temperature (T_g) of viscose fibers is 46°C. Therefore, the annealing constant temperature was selected 100°C at different times in order to avoid any phase transition during the isothermal annealing process.

Plate 1 shows the cross-sectional of viscose fibers, from which it is clear that viscose fibers have irregular cross-section. Plate 2 shows a microinterferogram of nonduplicated images of annealed viscose fibers at a constant temperature of 100 $\pm$ 1°C, at different annealing times (15, 30, 45, 60, 75, and 90 min) with different wavelengths of 550, 546, and 590 nm.

Figure 2(a)–(c) gives the general behaviour of birefringence of annealed viscose fibers at various annealing times (15, 30, 45, 60, 75, and 90 min) using the wavelengths of 550, 546, and 590 nm, which are available in our laboratory in the present time.

Plate 3(a)–(f) are microinterferograms of the totally duplicated images of annealed viscose fi-

Table III

Annealing Time (min)	n_{iso}	$F(\theta)$	θ	R	$1 - R$	T_g
Unannealed	1.522	0.251	45.0	0.780	0.220	45.92
15	1.524	0.425	66.8	0.773	0.227	38.58
30	1.524	0.408	67.9	0.842	0.158	53.40
45	1.524	0.382	69.7	0.803	0.197	49.22
60	1.524	0.366	70.8	0.776	0.224	49.27
75	1.524	0.343	72.3	0.820	0.181	55.79

Figure 1 XRD of viscose fibers after thermal annealing condition (a constant temperature of 100°C and different times).

Plate 1 Cross-sectional view of viscose fibers.

using the birefringence measurement by a Pluta microscope for viscose fibers.

Figure 3 shows the relationship between $[1/\{n_{iso}^2 - 1\}]$ and $(1/\lambda^2)$; it gives straight line. From the slope of this straight line, we calculated ε_∞ for annealed viscose, which was found to be equal to 2.3.

Figure 4 shows the relationship between the optical orientation function $\langle P_2(\theta)\rangle$ and the value $\{\Phi^\| - \Phi^\perp/\Phi^\| + 2\Phi^\perp\}$; it gives a straight line. The slope of this straight line gives the constant $(\Delta\alpha/3\alpha_0)$ for annealed viscose fibers, which was found to be 0.0293.

Figure 5 shows the relationship between the optical orientation function and annealing time. The following empirical formula is assumed for the relation between the optical orientation function $\langle P_2(\theta)\rangle$ and annealing time T of viscose fiber,

$$\langle P_2(\theta)\rangle = A - MT$$

where A and M are constants that characterize the annealed viscose fiber, and it is found to be as follows: $A = 0.4178$; $M = 0.00129$.

This suggested empirical formula is likely to be a different empirical formula to be obtained at

Plate 2 Microinterferogram of a nonduplicated image of viscose fiber at different times and a constant temperature of 100°C with different wavelengths (550, 546, and 590 nm).

bers at a constant temperature of 100 ± 1°C at a different annealing times (15, 30, 45, 60, 75, and 90 min) with different wavelengths of 550, 546, and 590 nm.

Table IV shows the volume swelling parameter

Figure (2-a)

Figure (2-b)

Figure (2-c)

Plate 3 The microinterferogram of a totally dupli-cated image of viscose fiber at different times and a constant temperature of 100°C with different wave-lengths (550, 546, and 590 nm).

different tension levels used in heat treatment, or with a different material history or with different heat treatments temperatures.

Figure 6 shows the angel of orientation as func-tion of annealing times.

DISCUSSION

It is known that viscose rayon fiber is composed of crystalline and amorphous cellulose chains at variable ratios. When a fiber is oriented, a number of the amorphous cellulose chains are shifted to-wards the more rigid crystalline state, where they are bound more strongly by polar forces and hy-drogen bonds.[26] In the poorly oriented fibers, the attractive forces between molecules have to oper-ate over great distances, so they are weak and ineffective. But when they are brought into line and packed close together, the distances are re-duced considerably, and strong attractive forces are set up.[27] Hydrogen bonding has a considerable influence on fibers because when fibers are ori-ented, adjacent molecular chains are lined up and packed closer together. The packing is so close that hydrogen bonds can be formed. When this happens, they prevent molecular slip. The result of this is that elongation of the fiber is reduced and strength is imparted to the molecular structure.[28]

In wetting the fiber, its tenacity decreased while its elongation increased considerably. Freud

Figure 2 The relationship between direct birefrin-gence and different annealing times with different wavelengths (550, 546, and 590 nm) at a constant tem-perature of 100°C.

Table IV

Annealing Time (min)	S_v Water 0.1 Conc	S_v Paraffin 0.1 Conc	S_v Acetic Acid 0.1 Conc
15	0.500	0.4300	0.412
30	0.350	0.0380	0.389
45	0.038	0.1815	0.088
60	0.025	0.0360	0.088

and Merk pointed out that diffusion of the water into the fiber causes its swelling and leads to an increase in the mobility of the cellulose chains and to a new arrangement of the molecular chains.[26]

So, it has been known that thermal, mechanical, and chemical treatments may change the crystalline and amorphous parts in a rayon fiber. Also, the crystallized areas give to rayon high modules of elasticity, rigidity, and ultimate tensile strength, while the amorphous parts are responsible for its flexibility, recovery, elongation, and swelling. If the internal mobility of the cellulose chains is increased by appropriate measures, such as swelling or a temperature increase, a certain amount of rearrangement will take place, and the viscose rayon will undergo a change in internal structure, its external shape, and its physical properties. Hence, viscose rayon is a very complicated system of certain intrinsic metastability, which makes it very sensitive to any change of

the external conditions, such as humidity, temperature, and the presence of swelling agents. The complex structure of the interface between the crystallized and amorphous portions effects their swelling and setting properties.

Most regenerated cellulose, under the influence of heat as well as light, show a rapid loss in strength. Degradation of cellulose fibrous materials is slower in the absence of oxygen. Continued heating, however, in the absence of oxygen leads to deterioration.

In order to explain different variations shown in Figure 1, it was essential to take the following assumptions into account.

1. All thermally structural variations may be considered irreversible at temperatures higher than the glass transition temperature.
2. The most compact noncrystalline structure is not essentially the ordered structure, or, in other words, the oriented macromolecular structure may not be the most compact noncrystalline structure.

When a polymeric fiber is annealed, its structural behaviour is changed due to accumulation of several structural processes. These processes may be summarized as disorientation, recrystallization by nucleation, recrystallization by growth, shrinkage, and crystal decomposition. They are natural responses for both annealing temperature and time.[9,11,29–31] To give an acceptable explanation for all variations in the figures, we have to estimate, individually, the weight of each structural process during an isothermal annealing treatment at different temperatures.

Therefore, additional thermal treatment caused a variation in birefringence and orientation and resulted in different swelling factors, which is a fundamental parameter in dyeing conditions.

Figure 3 The relationships between $(1/\lambda^2)$ and $[1/(1 - n^2_{iso})]$ for viscose fiber at a constant temperature of 100°C.

Figure 4 The relation between the optical orientation function $\langle P_2(\theta) \rangle$ and the value $\{\Phi\| - \Phi\perp/\Phi\| + 2\Phi\perp\}$ at a constant temperature of 100°C.

CONCLUSIONS

From these measurements and calculations relating the change of optical properties to thermal effects in viscose fibers, the following conclusions may be drawn.

1. It was found that an increase in the annealing time gives a decrease in the optical orientation (Fig. 4), and the value $\Delta\alpha/3\alpha_0$, which depends upon the molecular structure, remains constant. Also, the annealing time increases, and the orientation angle increases (Fig. 6).
2. Thermal annealing can provide supplementary information on the structural features related to the thermal performance of materials, in which the variation of specific volume is related to crystallinity, density, and mass redistribution of the sample, and these need further studies.
3. The crystallinity of viscose fibers depends critically on the annealing conditions, as shown from Figure 1. From the XRD, it is seen that the type of crystal in viscose was not affected by the annealing conditions used.
4. It is clear that the orientation due to annealing leads to new and different regions of ordered and disordered structure, which give new physical properties for every state of annealing.
5. The annealing process affects other physical

properties (swelling, dyeability, electrical, mechanical, and color). These need further studies to detect which properties can be improved.
6. A study of the changes in $n\|$, $n\perp$, and Δn with respect to annealing shows that the isothermal properties of the structure perpendicular to the fiber axis differ from those in an axial direction. This is to be expected for an anisotropic medium Table II.
7. The thermal treatment process affects the color of fibrous materials due to the presence of oxygen and leads to thermooxidative degradation.
8. An empirical formula has been applied to relate the variation of optical orientation function with annealing temperature, and the constants of this formula have been determined.
9. The swelling data for different liquids show different behaviors. These may be explained due to their different molecular weights of absorbent and liquids and on their chemical concentrations.

One can conclude from the above results and considerations that the modification of viscose fiber by annealing and using the two-beam technique to clarify the mechanism of structural variation provides useful results.

Figure 5 The relation between the optical orientation function $\langle P_2(\theta) \rangle$ and the annealing time at a constant temperature of 100°C.

Figure 6 The relation between the orientation angle θ and the annealing time at a constant temperature of 100°C.

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