Opto-Thermal Properties of Fibers XVIII—Skin-Core Structures Variations in Nylon 6 Fibers Due to Different Annealing Conditions

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ABSTRACT: Nylon 6 fibers (Amilan) were annealed at constant temperature $140 \pm 1°C$ for different time durations (1–10 h). Refractive indices have been previously measured interferometerically. Two independent techniques were used to study the optical anisotropy and density in these fibers. The first was the application of a multiple-beam to determine the skin and core "mean" refractive indices and birefringence of the samples. The technique used multiple-beam Fizeau fringes in transmission. The second technique was an acoustic method for measuring the density of the investigated fibers. The optical results were used to calculate the optical orientation factors for skin and core. The values of $(\Delta\alpha/3\alpha_0)$, which depend upon the molecular structure of the polymer, remain constant and in agreement with the previous published data. The density results were used to calculate the degree of crystallinity of nylon 6 fibers. In addition, the results were used to calculate the mean square density fluctuation, the harmonic mean polarizability of the dielectric, specific refractivity of the isotropic dielectric and the virtual refractive index. Also, the number of monomer units per unit volume, and n_1 and n_2, which are the refractive indices of fully oriented fiber, were calculated and found to be (1.606 and 1.534). Hermans optical orientation functions have been compared with the generalized Lorentz-Lorenz equation given by de Vries. Microinterferograms and curves are given for illustration. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3349–3360, 2001

Key words: skin-core structures; nylon 6

INTRODUCTION

Synthetic polymer fibers play an important role in the textile industry, where most textiles are now mixed with synthetic yarns. Thus, investigation of the characteristic properties of these fibers is important. The degree of orientation, crystallinity, and other structural parameters are corre-

lated to the final fiber use. So the degree of orientation could vary significantly from one fiber to another, depending on the fiber history during manufacture and subsequant processing operations.

The structural effects of annealing in polymers, especially in synthetic fibers, are not completely understood. Annealing close to the melting point leads to partial melting and increases in mobility. The annealing process consists of partial melting and recrystallization and its result is influenced by earlier crystallization, and furthermore by the melting point of crystalline areas already

present.[1] Several studies have been reported on the effect of annealing on the structure of synthetic and natural fibers.[2–9] Annealing may be performed with the ends of the sample free or fixed. In the former case, the sample shrinks, whereas in the latter case it retains its length but exerts measurable retroactive forces on its fixed ends. Both effects increase with increased temperature.[10]

Optical birefringence gives the average of crystalline and amorphous orientation. Frequently, orientation means orientation of ordered phases. It has to be stressed, however, that both crystalline and amorphous materials can exist in both oriented and unoriented states.

Recently, the application of double-beam and multiple-beam Fizeau fringe interferometry has stimulated interest in studying the thermal, mechanical, and chemical properties of natural and synthetic fibers.[11–15]

In the present work, the optical parameter results for samples of nylon 6, fibers having different annealing conditions and previously prepared,[15,23] are utilized to calculate some other structural parameters and orientation factors.

THEORETICAL CONSIDERATIONS

Interferometric Measurements of The Optical Parameters

Multiple beam Fizeau fringes in transmission previously used for the determination of the basic optical parameters,[15,16] and a special measuring system, were used for the measurement of fiber density[17–19] of unannealed and annealed nylon 6 fibers.

Also, for the determination of the refractive index of each layer of a cylindrical fiber having multilayers of circular cross-sections, we used the mathematical formula that was previously derived by EL-Nicklawy and Fouda.[20] Also, for the mean refractive index of a fiber having skin and core layers, we used the mathematical formula previously derived by Barakat et al.,[21] and which we have used in prior work.[13,22,23]

Determination of the Optical Orientation Factors

The optical orientation function and orientation angle can be calculated using the Hermans equations:[24]

$$F_\Delta = \frac{\Delta n}{\Delta n_{max}} = 1 - \frac{3}{2}\sin^2\theta \qquad (1)$$

where Δn_{max} is the maximum birefringence for fully oriented fiber and Δn_a is birefringence of the fiber under investigation, F_θ values are ranged between (+1, 0, and −0.5) according to the state of orientation, perfect, random, or perpendicular to the fiber axis, respectively. The value Δn_{max} has been previously determined to be 0.072.[25]

In eq. (1), θ is the angle between the chain axis and the preferred macroscopic orientation so that F_Δ varies between the limits $-\frac{1}{2} \leq F_\Delta \leq 1$.

The average Opt. Ori. Fun. $\langle P_2(\theta)\rangle$ due to Ward[26,27] is given by the following formula:

$$\langle P_2(\theta)\rangle = \frac{\Delta n}{\Delta n_{max}}; \qquad (2)$$

also, eq. (2) can be written in the form

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

where $\Delta\alpha$ is the difference between $\alpha^\parallel$ and $\alpha^\perp$, which are the electric polarizability of one molecule when using monochromatic light vibrating parallel and perpendicular to the fiber axis, respectively. The quantity $(\Delta\alpha/3\alpha_0)$ depends on the molecular structure, and is nearly constant for a given polymer,[28] where

$$\Phi^\parallel = \frac{n_\parallel^2 - n_\perp^2}{n_\parallel^2 + 2n_\perp^2}$$

and there is an analogous equation for $\Phi^\perp$.

Mean Polarizability of Monomer Unit

The polarizability of a monomer unit, like the polarizability of a simple organic molecule, usually differs in different directions. As the refractive index of a polymer depends on the total polarizability of the molecules, this leads to the Lorentz-Lorenz by the following equation:[28]

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{N_{(1)}\bar{\alpha}}{3\Psi} \qquad (4)$$

where n is the average refractive index (isotropic refractive index) and $\bar{\alpha}$ the mean polarizability of

a monomer unit and Ψ is the permttivity of free space $= 8.85 \times 10^{-12}$ Fm^{-1}.

For a bulk polymer of density ρ and monomer unit molecular weight M, the number of monomer units per unit volume, which also equals the number of carriers of the dipole moment,

$$N_{(1)} = \frac{N_A \rho}{M}$$

where N_A is Avogadro's number 6.02×10^{23} and M for nylon $6 = 113.16$.[29] Also, $N_{(1)}$ is the number of carriers of the dipole moment. The dipole moment effect was reported in considerable explanation elsewhere, with association to the well-known Lorentz-Lorenz equation for monochromatic light.

De Vries[29] gave a theory on the basis of an internal field with the aid of classical electromagnetic theory, in which he generalized the Lorentz-Lorenz equation; so for monochromatic light, the well-known Lorentz-Lorenz equation becomes eq. (4). The right-hand member of eq. (4) is proportional to the density ρ, [kg/m^3] of the medium, and may also be written

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \bar{\varepsilon}\rho \qquad (5)$$

where ε, [m^3/kg] is called the specific refractivity of the isotropic dielectric. Writing this equation for fibers in its parallel and transverse components the generalized Lorentz-Lorenz equations.

$$\frac{n_{\text{all}}^2 - 1}{n_{\text{all}}^2 + 2} = \frac{N_{(1)}\alpha^{\parallel}}{3\Psi} = \varepsilon^{\parallel}\rho \qquad (6)$$

An analogous formula is used for $n_a^{\perp}$.

Also, de Vries defined the invariant refractive index, which he call the "Virtual refractive index" n_v by

$$n_v = \sqrt{1 + \frac{3[n_{\parallel}^2 - 1][n_{\perp}^2 - 1]}{[n_{\perp}^2 - 1] + 2[n_{\parallel}^2 - 1]}} \qquad (7)$$

where the virtual refractive index n_v replaces $\bar{n}$ the isotropic refractive index $(n_{\text{iso}(1)})$, which is known as isotropic refractive index, and the above equations lead to the harmonic mean polarizability of the dielectric α_v by the following equation

$$\alpha_v = \frac{3\Psi}{N_{(1)}} \cdot \frac{n_v^2 - 1}{n_v^2 + 2} \qquad (8)$$

Likewise, for the harmonic mean specific refractivity, we have

$$\varepsilon_v = \rho^{-1} \cdot \frac{n_v^2 - 1}{n_v^2 + 2} \qquad (9)$$

In a recent approach to the continuum theory of birefringence of oriented polymer,[29] it was found that

$$F_{\theta} = \left[\frac{n_1^2 n_2^2}{n_{\parallel}^2 n_{\perp}^2}\right] \cdot \left[\frac{n_{\parallel} + n_{\perp}}{n_1 + n_2}\right] \cdot \frac{\Delta n_a}{\Delta n_{\max}} \qquad (10)$$

This is slightly different from the original simple expression of the degree of orientation and orientation angle used by Hermans.

Also, based on Hermans[30] and Platzek and Kratky,[31] we can derive the following equation:

$$F_{\theta} = (1 + a)F_{\Delta} - aF_{\Delta}^2$$

$$(1 + a) = \frac{2n_1^2 n_2^2}{n_v^3(n_1 + n_2)} \qquad (11)$$

where n_1, n_2 are the refractive indices of fully oriented fiber, where using a monochromatic light-vibrating parallel and perpendicular to the fiber axis, from eq. (11) the constant (a) was calculated and found to be (0.68), (0.68) and (0.68) for skin, core, and mean.

Also, the specific refractivity $\varepsilon_{\parallel}$ can be determined by the following equations considering the anisotropy index

$$n_{\parallel}^2 + \frac{n_{\parallel}^2 - 1}{2 + S(n_{\parallel}^2 - 1)} = \varepsilon_{\parallel}'\rho \qquad (12)$$

and an analogous formula is used for $\varepsilon_{\perp}'$ and ε_v', where ρ is the density and S the anisotropy index and equal for nylon $6 = -0.048$[29]

As we applied the multiple beam Fizeau fringes in transmission, we can obtain all the previous mentioned structural parameters for the skin and core layers of the fibers by applying analogous equations for the skin, core, and mean layers.

Crystallinity Equation

The degree of crystallinity, χ, was calculated from

$$\chi = (\rho - \rho_a)/\Delta\rho \qquad (13)$$

where $\Delta\rho = (\rho_c - \rho_a)$, ρ_c and ρ_a are the densities of the crystalline and noncrystalline regions, and ρ is the experimental measured value of density, $\rho_c = 1.23 \times 10^3$ kg/m$^{3(1)}$ and $\rho_a = 1.11 \times 10^3$ kg/m$^{3(1)}$.

Equation of the Mean Square Density Fluctuation

For two phase structure consisting of amorphous and crystalline regions with densities ρ_a and ρ_c, respectively. The mean square density fluctuation $\langle\eta^2\rangle$, can be calculated from the following equation.[32]

$$\langle\eta^2\rangle = [\rho_a - \rho_c]^2 \cdot \chi[1 - \chi] \qquad (14)$$

Calculation of the Isotropic Refractive Index

The specific volume, V, and constant K, are given by the following equations

$$(n_{iso} - 1)V = \text{constant}$$

Also, the Lorentz-Lorenz equation is used to relate polarizabilities and refractive index. We have:[33]

$$\frac{n_{iso(2)}^2 - 1}{n_{iso(2)}^2 + 2} = \frac{1}{3}\frac{\rho_i}{\rho}\left[\frac{n_\parallel^2 - 1}{n_\parallel^2 + 2} + 2\frac{n_\perp^2 - 1}{n_\perp^2 + 2}\right] \qquad (15)$$

and analogous formulae for skin and core layers.

where ρ and ρ_1 are the densities of the measured and of the isotropic nylon 6 respectively. The resulting values of $n_a^\parallel$, $n_a^\perp$ and ρ are used with equation (15) to determine the isotropic refractive index values for annealed nylon 6 fibers, where $\rho_i = \rho_a = 1.11 \times 10^3$ kg/m^3.

Evaluation of the Number of Molecules per Unit Volume

The experimental values of the mean polarizabilities per unit volume parallel $P_a^\parallel$ and perpendicular $P_a^\perp$ to the fibers axis were derived from the measured values of the refractive indices by application of Lorentz-Lorentz equations:
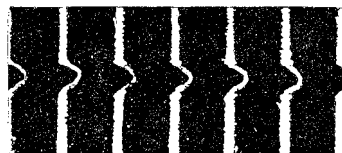

Plate (1-a)

Plate (1-b)

Plate 1(a–b)   Gives the microinterferogram of multiple-beam Fizeau fringes in transmission of an unannealed nylon 6 fiber, in parallel and perpendicular direction, respectively, of ($\lambda = 546$ nm).

The values are used in the following equation[34] to calculate the number of molecules per unit volume

$$\Delta n = \frac{2\pi N_2}{\bar{n}}\left(\frac{\bar{n}^2 + 2}{3}\right)^2 (\bar{P}_\parallel - \bar{P}_\perp) \qquad (16)$$

where N_2 is the number of molecules per unit volume, $\bar{n}$ is the mean refractive index of the sample, where $\bar{n} = n_\parallel + n_\perp/2$. $\bar{P}_\parallel$ and $\bar{P}_\perp$ are the mean polarizabilities of the macromolecules in the same direction as for the mean refractive indices.

EXPERIMENTAL PROCEDURE

The effect of annealing conditions were studied by interferometery and acoustic technique, and were the procedures outlined in previous publications.[23,35]

Annealing Process

Long bundles of nylon 6 fibers [(Amilan) Maruleni Co Osaka, Japan, nylon 6 Filament Yarn 70 Den/24 Fil on bobbin] were loosely folded in a cocoon form with both ends free. Several samples, placed in small glass bottles, were heated in an
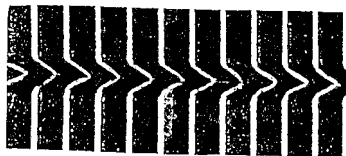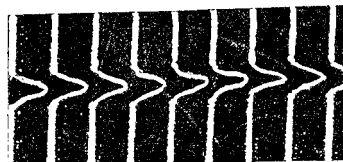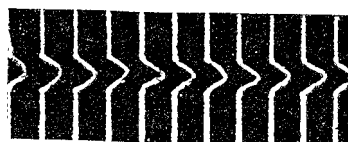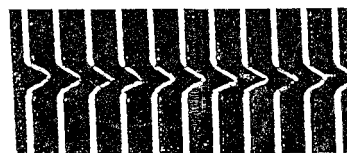
Plate (2-a)

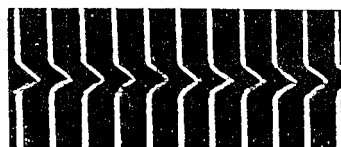Plate (3-a)

Plate (2-b)

Plate (3-b)

Plate (3-c)

Plate (2-c)

Plate 2(a–c) and Plate 3(a–c) Gives the microinterferogram of multiple-beam Fizeau fringes in transmission of nylon 6 fiber annealed for constant temperature 140 ± 1°C at different annealing times, in parallel and perpendicular direction, respectively, of (λ = 546 nm).

oven (Model WT, binder-type E53, Germany) at a constant temperature of 140°C, with an error of ±2°C for different annealing times, ranging from 1 to 10 h. The samples were then left to cool for 2 days in the oven to room temperature (27°C) with an error of ±1°C.

Multiple-Beam Interference

The multiple-beam Fizeau fringes transmission technique was described in detail elsewhere,[23,35] and was used to study the principal optical parameters of unannealed and annealed samples of nylon 6 fibers.

Density Measurement

The acoustic density technique, used for estimated the density of the investigated samples, was also discussed in detail elsewhere.[17,19]

RESULTS

Previous measurement of transverse sectional area for these nylon 6 fibers showed that the cross-section of nylon 6 fiber seen by high power optical microscope was perfectly circular in shape.[23,35]

Application of Interferometry

The multiple-beam Fizeau fringes transmission method was used for determining the optical parameters of the skin, core, and mean refractive indices, namely $n_s^{\parallel}$, $n_s^{\perp}$, $n_c^{\parallel}$, $n_c^{\perp}$, $n_a^{\parallel}$, $n_a^{\parallel}$, and $n_a^{\perp}$. The skin, core, and mean birefringence, Δn_s, Δn_c, and Δn_a, were also calculated.

The values were determined for several samples of nylon 6 fibers annealed at different annealing times and constant temperature (140 ± 1°C).

Table I(a)   Refractive Indices for Skin Layer, Isotropic Refractive Index, Virtual Refractive Index. The Ratio $F_\theta - F_\Delta/F_\theta$, Number of Molecules per Unit Volume, Density, Crystallinity, at Constant Temperature (140°C ± 1)

Annealing Time (h)	$n_a^{\parallel}$	$n_{\mathrm{iso}(1)}$	$n_{\mathrm{iso}(2)}$	n_v	$F_\theta - F_\Delta/F_\theta$	$N_{(1)} \times 10^{21}$	$N_{(2)}$	ρ	$\chi\%$	$\langle \eta^2 \rangle \times 10^{-2}\,\%$	K
Unannealed	1.5773	1.5449	1.5388	1.5439	0.0694	5.96	0.999	1.120	8.33	11.0	0.481
1	1.5782	1.5465	1.5145	1.5456	0.0668	6.21	0.999	1.167	47.5	35.9	0.441
2	1.5827	1.5485	1.5070	1.5474	0.0622	6.30	0.999	1.185	62.5	33.7	0.428
3	1.5844	1.5495	1.4956	1.5484	0.0600	6.43	0.999	1.210	83.3	20.0	0.409
4	1.5851	1.5496	1.4867	1.5485	0.0596	6.54	0.999	1.229	99.1	1.19	0.396
5	1.5855	1.5496	1.5050	1.5484	0.0594	6.33	0.999	1.191	67.5	31.6	0.424
6	1.5855	1.5501	1.5308	1.5489	0.0588	6.08	0.999	1.143	27.5	28.7	0.464
7	1.5876	1.5502	1.5309	1.5490	0.0577	6.08	0.999	1.143	27.5	28.7	0.465
8	1.5892	1.5516	1.5224	1.5503	0.0551	6.17	0.999	1.161	42.5	35.2	0.450
9	1.5902	1.5513	1.5126	1.5499	0.0551	6.27	0.999	1.179	57.5	35.2	0.435
10	1.5887	1.5509	1.5186	1.5496	0.0562	6.21	0.999	1.167	47.5	35.9	0.444

Throughout this experiment, the green wavelength of a mercury lamp of equal 546.1 nm was used.

Plate 1(a)–(b) is a microinterferogram of multiple-beam Fizeau fringes in transmission for an unannealed nylon 6 fiber in parallel and perpendicular directions, respectively.

Plate 2(a)–(c) is a microinterferogram of multiple-beam Fizeau fringes in transmission of annealed fiber for different times at constant temperature. The microinterferogram of multiple-beam Fizeau fringes in transmission of nylon 6 fiber is shown in Plate 3(a)–(c) corresponds to fiber annealed for constant temperature at different annealing times. The values of the fringe shift for the parallel component of the fiber skin $dz_s^{\parallel}$, of the fiber core $dz_c^{\parallel}$, and the interfering spacing h were measured from microinterferograms. The thickness of the skin r_s and the radius of the core r_c were also obtained from the microinterferograms. The radius of the fiber r_f was deduced from both the microinterferograms and from the obtained optical cross-section. Analogous formulae were obtained for the other direction $n_s^{\perp}$ and $n_c^{\perp}$.

With the aid of eqs. (9) and (18) the obtained values of the skin, core, and mean refractive indices using multiple-beam Fizeau fringes, were used to determine the skin, core and mean isotropic refractive indices $n_{\mathrm{iso}\text{-}s}$, $n_{\mathrm{iso}\text{-}c}$ and $n_{\mathrm{iso}\text{-}a}$ respectively, and are given in Table I(a–c).

Figure 1(a)–(c) show the relation between the birefringence Δn_s, Δn_c Δn_a and the refractive indices differences ($n_s^{\parallel} - n_{\mathrm{iso}}$, $n_c^{\parallel} - n_{\mathrm{iso}}$, $n_a^{\parallel} - n_{\mathrm{iso}}$, $n_s^{\perp} - n_v$, $n_c^{\perp} - n_v$, $n_a^{\perp} - n_v$, $n_s^{\parallel} - n_{\mathrm{iso}}$, $n_c^{\parallel} - n_{\mathrm{iso}}$, $n_a^{\parallel} - n_{\mathrm{iso}}$, $n_s^{\perp} - n_{\mathrm{iso}}$, $n_c^{\perp} - n_{\mathrm{iso}}$, $n_a^{\perp} - n_{\mathrm{iso}}$). Figure 1, n_v, and $\Delta n_{\max}$ are used to predict the values of refractive indices n_1 and n_2 for fully oriented fibers. These values are found to be 1.603 and 1.535, respectively, at 28°C.

Table I(a–c) gives some experimental results for annealed nylon 6 fiber refractive indices, the calculated values of virtual refractive index (n_v) the calculated values of the number of monomer units per unit volume (N_1) and the number of molecules per unit volume (N_2), are constant and its value was found to be 0.999.

$$\frac{F_\theta - F_\Delta}{F_\theta}$$

for skin, core layer and for the mean, results are given in Table I(a–c).

Table I(b)   Refractive Indices for Core Layer, Isotropic Refractive Index, Virtual Refractive Index. The Ratio $F_\theta - F_\Delta/F_\theta$, at Constant Temperature (140°C ± 1)

Annealing Time (h)	$n_a^{\parallel}$	$n_a^{\parallel}$	$n_{\mathrm{iso}(1)}$	$n_{\mathrm{iso}(2)}$	n_v	$F_\theta - F_\Delta/F_\theta$	$N_{(1)} \times 10^{21}$	K
Unannealed	1.5720	1.5216	1.5384	1.5324	1.5373	0.0806	5.96	0.475
1	1.5728	1.5235	1.5399	1.5084	1.5389	0.0781	6.21	0.435
2	1.5786	1.5241	1.5422	1.5013	1.5410	0.0725	6.30	0.423
3	1.5802	1.5251	1.5434	1.4902	1.5422	0.0702	6.43	0.405
4	1.5810	1.5247	1.5434	1.4813	1.5421	0.0699	6.54	0.391
5	1.5786	1.5243	1.5424	1.4985	1.5412	0.0723	6.33	0.418
6	1.5814	1.5255	1.5441	1.5251	1.5428	0.0688	6.08	0.459
7	1.5810	1.5241	1.5430	1.5240	1.5417	0.0704	6.08	0.458
8	1.5827	1.5253	1.5444	1.5157	1.5431	0.0678	6.17	0.444
9	1.5838	1.5244	1.5442	1.5061	1.5427	0.0677	6.27	0.429
10	1.5823	1.5246	1.5438	1.5119	1.5424	0.0688	6.21	0.438

These values in fair agreement with similar polymers (PP, PE, nylon 6, and cellulose) by de Vreis[19] within less than 3%.

The apparent volume fraction of crystallinity (χ) was calculated from eq. (15) using the calculated density values. Also, we consider ρ, χ, and η^2 are the same for the skin and core layers because there are difficulties in evaluation for different layers. The results are given in Table II. Also, in Table II, the orientation angle θ is calculated from eq. (1b). In Table II(a–c) the calculated values of $\alpha^{\parallel}$, $\alpha^{\perp}$ and $\bar{\alpha}$, and the specific refractivity of the isotropic dielectric for parallel, perpendicular, and its mean values are given for annealed nylon 6 fibers.

Figure 2 shows the variation between the crystallinity and the density of nylon 6 fibers due to changing annealing for different times periods.

Figure 3 shows the angle of orientation as a function of annealing times of nylon 6 fibers.

Figure 4 shows the relation between corrected values of optical orientation function $F_{\theta(s)}$, $F_{\theta(c)}$, $F_{\theta(a)}$ and the Hermans function $F_{\Delta(s)}$, $F_{\Delta(c)}$ $F_{\Delta(a)}$ for different annealing temperatures with a constant annealing time of 6 h.

Figure 5 shows the relation between the birefringence Δn_s, Δn_c, Δn_a and the optical orientation function $F_{\theta(s)}$, $F_{\theta(c)}$, $F_{\theta(a)}$ for different annealing times of nylon 6 fibers.

Figure 6 shows the relation between Hermans function, $F_{\Delta(s)}$, $F_{\Delta(c)}$, $F_{\Delta(a)}$ and $|\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\parallel}|_{(s)}$, $|\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}|_{(c)}$, $|\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}|_{(a)}$ for different annealing times, which give the linear relation and from that we find the value of $\Delta\alpha/3\alpha_0$, which equals (0.033), and is the same for the skin and core layers because these

Table I(c)   Refractive Indices for Mean, Isotropic Refractive Index, Virtual Refractive Index: The Ratio $F_\theta - F_\Delta/F_\theta$, at Constant Temperature (140°C ± 1)

| Annealing Time (h)	$n_a^{\parallel}$	$n_a^{\parallel}$	$n_{\mathrm{iso}(1)}$	$n_{\mathrm{iso}(2)}$	n_v	$F_\theta - F_\Delta/F_\theta$	$N_{(1)} \times 10^{21}$	K
Unannealed	1.5766	1.5278	1.5440	1.5380	1.5431	0.071	5.96	0.480
1	1.5775	1.5298	1.5457	1.5138	1.5447	0.068	6.21	0.440
2	1.5821	1.5304	1.5476	1.5063	1.5465	0.063	6.30	0.427
3	1.5838	1.5311	1.5486	1.4948	1.5475	0.061	6.43	0.409
4	1.5845	1.5309	1.5487	1.4859	1.5476	0.061	6.54	0.395
5	1.5846	1.5307	1.5486	1.5041	1.5475	0.061	6.33	0.423
6	1.5849	1.5315	1.5493	1.5300	1.5481	0.060	6.08	0.463
7	1.5867	1.5306	1.5493	1.5300	1.5480	0.059	6.08	0.463
8	1.5884	1.5318	1.5506	1.5215	1.5493	0.057	6.17	0.449
9	1.5894	1.5308	1.5503	1.5117	1.5489	0.057	6.27	0.434
10	1.5879	1.5311	1.5500	1.5177	1.5487	0.058	6.21	0.443
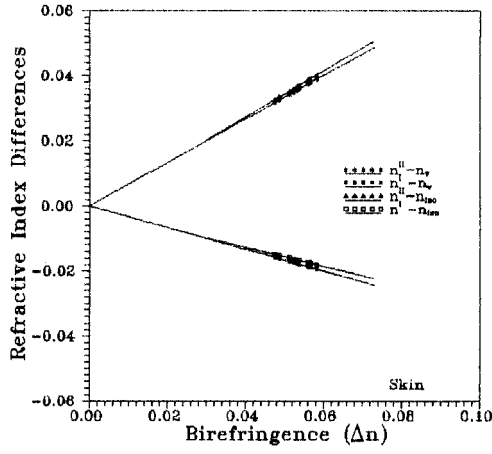
(a)
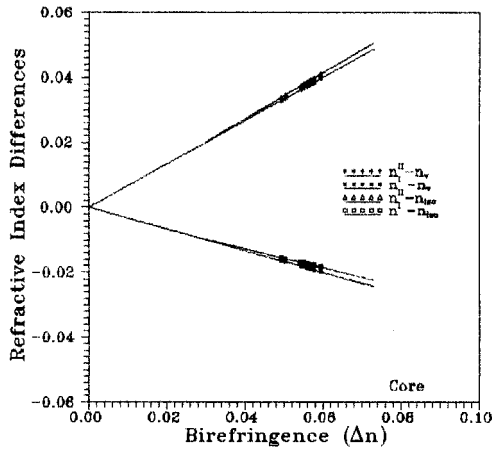
(b)
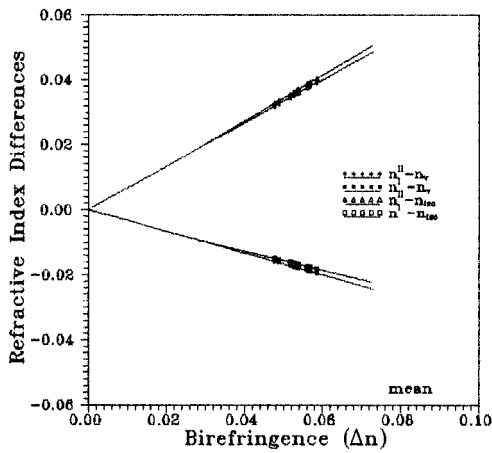
(c)

Figure 1 Show the variations of Δn_s, Δn_c, Δn_a, the refractive indices differences ($n_s^{\parallel} - n_{\text{iso}}$, $n_c^{\parallel} - n_{\text{iso}}$, $n_a^{\parallel} - n_{\text{iso}}$, $n_s^{\perp} - n_{\text{iso}}$, $n_c^{\perp} - n_{\text{iso}}$, $n_a^{\perp} - n_{\text{iso}}$, $n_s^{\parallel} - n_v$, $n_c^{\parallel} - n_v$, $n_a^{\parallel} - n_v$, of fiber at different annealing times for the constant annealing temperature ($\pm 140°$C).

Table II(a) The Polarzability of a Monomer for Skin Layer $\alpha^{\parallel}$, $\alpha^{\perp}$, and $\bar{\alpha}$, and the Specific Refractivity of the Isotropic Dielectric for Parallel, Perpendicular, and Its Mean Values at Constant Annealing Temperature (140°C ± 1)

Annealing Time (h)	$\alpha^{\parallel} \times 10^{-33}$	$\alpha^{\perp} \times 10^{-33}$	$\bar{\alpha} \times 10^{-33}$	$\alpha_v \times 10^{-33}$	$\varepsilon^{\parallel}$	$\varepsilon^{\perp}$	$\bar{\varepsilon}$	ε_v	$\varepsilon'^{\parallel}$	$\varepsilon'^{\perp}$	ε'	ε'_v
Unannealed	1.477	1.373	1.425	1.406	0.296	0.275	0.285	0.282	0.301	0.279	0.290	0.286
1	1.419	1.322	1.371	1.353	0.284	0.264	0.274	0.271	0.289	0.269	0.279	0.275
2	1.407	1.304	1.355	1.336	0.282	0.261	0.271	0.267	0.286	0.265	0.276	0.272
3	1.381	1.278	1.329	1.3110	0.276	0.255	0.266	0.262	0.281	0.260	0.270	0.266
4	1.361	1.258	1.309	1.290	0.272	0.251	0.262	0.258	0.277	0.256	0.266	0.262
5	1.405	1.298	1.351	1.331	0.281	0.259	0.270	0.267	0.286	0.264	0.275	0.271
6	1.464	1.534	1.409	1.388	0.293	0.270	0.282	0.278	0.298	0.275	0.286	0.282
7	1.468	1.352	1.410	1.389	0.294	0.270	0.282	0.278	0.299	0.275	0.287	0.282
8	1.449	1.333	1.391	1.370	0.290	0.267	0.278	0.274	0.295	0.271	0.283	0.278
9	1.429	1.311	1.370	1.348	0.286	0.262	0.274	0.270	0.291	0.266	0.279	0.274
10	1.440	1.325	1.383	1.361	0.288	0.265	0.276	0.273	0.293	0.269	0.281	0.277

Table II(b) The Polarizability of a Monomer for Core Layer $\alpha^\parallel$, $\alpha^\perp$ and $\bar{\alpha}$, and the Specific Refractivity of the Isotropic Dielectric for Parallel, Perpendicular, and Its Mean Values at Constant Annealing Temperature (140°C ± 1)

Annealing Time (h)	$\alpha^\parallel \times 10^{-33}$	$\alpha^\perp \times 10^{-33}$	$\bar{\alpha} \times 10^{-33}$	$\alpha_v \times 10^{-33}$	$\varepsilon^\parallel$	$\varepsilon^\perp$	$\bar{\varepsilon}$	ε_v	$\varepsilon'^\parallel$	$\varepsilon'^\perp$	$\bar{\varepsilon}'$	ε'_v
Unannealed	1.466	1.358	1.412	1.392	0.293	0.272	0.283	0.279	0.298	0.276	0.287	0.283
1	1.408	1.307	1.358	1.339	0.282	0.262	0.272	0.268	0.287	0.266	0.276	0.272
2	1.399	1.289	1.344	1.323	0.280	0.258	0.269	0.265	0.285	0.262	0.273	0.269
3	1.373	1.264	1.318	1.298	0.275	0.253	0.264	0.260	0.279	0.257	0.268	0.264
4	1.353	1.244	1.298	1.278	0.271	0.249	0.260	0.256	0.275	0.253	0.264	0.260
5	1.391	1.282	1.337	1.317	0.279	0.257	0.268	0.264	0.283	0.261	0.272	0.268
6	1.456	1.339	1.397	1.376	0.291	0.268	0.280	0.275	0.296	0.272	0.284	0.280
7	1.455	1.336	1.395	1.374	0.291	0.277	0.279	0.275	0.296	0.271	0.284	0.279
8	1.436	1.318	1.377	1.355	0.287	0.264	0.276	0.271	0.292	0.268	0.280	0.275
9	1.416	1.296	1.356	1.333	0.283	0.259	0.271	0.267	0.288	0.263	0.276	0.271
10	1.428	1.309	1.368	1.345	0.286	0.262	0.274	0.270	0.290	0.266	0.278	0.274

Table II(c) The Polarzability of a Monomer for Mean $\alpha^\parallel$, $\alpha^\perp$, and $\bar{\alpha}$, and the Specific Refractivity of the Isotropic Dielect for Parallel, Perpendicular, and Its Mean Values at Constant Annealing Temperature (140°C ± 1)

| Annealing Time (h)	$\alpha^\parallel \times 10^{-33}$	$\alpha^\perp \times 10^{-33}$	$\bar{\alpha} \times 10^{-33}$	$\alpha_v \times 10^{-33}$	$\varepsilon^\parallel$	$\varepsilon^\perp$	$\bar{\varepsilon}$	ε_v	$\varepsilon'^\parallel$	$\varepsilon'^\perp$	$\bar{\varepsilon}'$	ε'_v
Unannealed	1.476	1.371	1.423	1.404	0.295	0.275	0.285	0.281	0.300	0.279	0.289	0.285
1	1.418	1.320	1.369	1.351	0.284	0.264	0.274	0.271	0.288	0.268	0.278	0.275
2	1.405	1.301	1.353	1.334	0.281	0.261	0.271	0.267	0.286	0.264	0.275	0.271
3	1.380	1.276	1.328	1.309	0.276	0.255	0.266	0.262	0.281	0.259	0.270	0.266
4	1.360	1.256	1.308	1.289	0.272	0.251	0.262	0.258	0.277	0.255	0.266	0.262
5	1.403	1.296	1.349	1.330	0.281	0.259	0.270	0.266	0.286	0.263	0.274	0.270
6	1.463	1.351	1.407	1.387	0.293	0.271	0.282	0.278	0.298	0.275	0.286	0.282
7	1.466	1.350	1.408	1.387	0.294	0.270	0.282	0.278	0.298	0.274	0.286	0.282
8	1.447	1.331	1.389	1.368	0.290	0.267	0.278	0.274	0.294	0.271	0.283	0.278
9	1.427	1.309	1.368	1.346	0.286	0.262	0.274	0.269	0.290	0.266	0.278	0.274
10	1.439	1.323	1.381	1.359	0.288	0.265	0.276	0.272	0.293	0.269	0.281	0.276
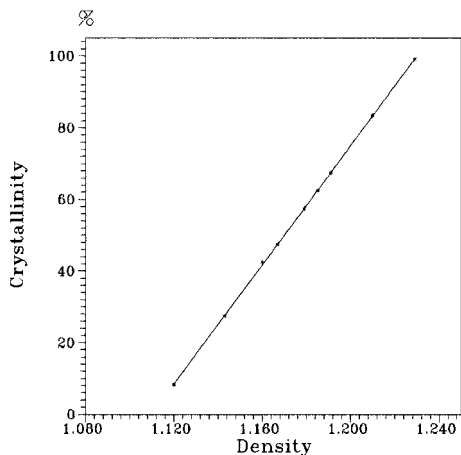
Figure 2   Shows the variation between the crystallinity and the density of fiber at different annealing times for the constant annealing temperature (140 ± 1°C).

constants are related to the structure constituents.

DISCUSSION

To elucidate the structural variations induced in fibers by any physical or chemical modification, the use of interferometric methods are very useful tools. The importance of studying various optical properties such as refractive indices and birefringence for skin and core layers are recognized in fibers as the main source of good information to correlate the structural properties of synthetic
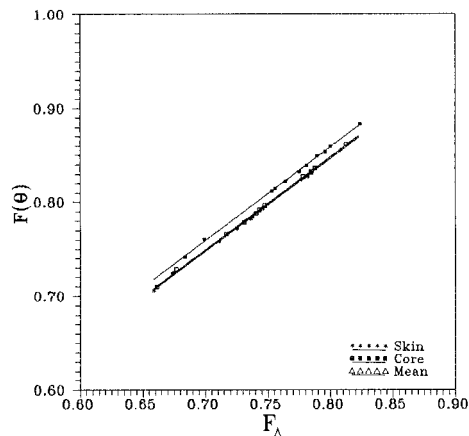

Figure 4   Relation between corrected values of optical orientation function $F_{\theta(s)}$, $F_{\theta(c)}$, $F_{\theta(a)}$, and the Hermans function $F_{\Delta(s)}$, $F_{\Delta(c)}$, $F_{\Delta(a)}$ of fiber with different annealing times for the constant annealing temperature (140 ± 1°C).

fibers with their physical, thermal, chemical, and mechanical properties.

The surface of any material is different from the interior or bulk of the material. In fibers, the skin is always different from its core layer. Differences can be chemical, or physical, or both. In polymer, due to thermal annealing in air, surface oxidation can exist. The orientation of the fiber at the surface is almost always different from the interior, the polymer (fiber) chains may be lying flat, oriented in the surface plane or, if some special group is attracted to the surface, the orientation may be normal to the plane of the surface.
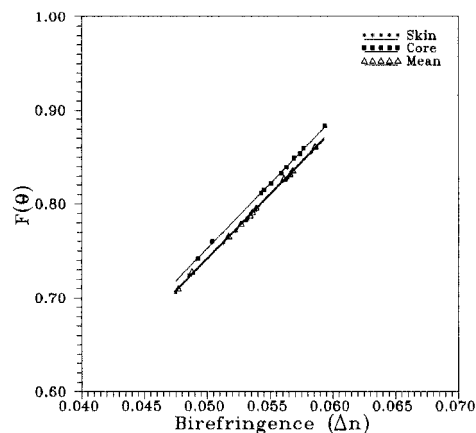

Figure 3   Shows the angle of orientation as a function of annealing fiber at different annealing times for the constant annealing temperature (140 ± 1°C).

Figure 5   Shows relation between $F_{\theta(s)}$, $F_{\theta(c)}$, $F_{\theta(a)}$, and birefringence Δn_s, Δn_c, Δn_a of fiber with different annealing times for the constant annealing temperature (140 ± 1°C).
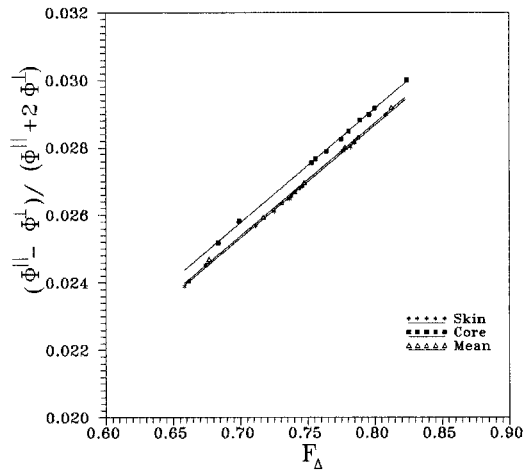
Figure 6 Shows the relation between Hermans function, $F_{\Delta(s)}$, $F_{\Delta(c)}$, $F_{\Delta(a)}$ and $|\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}|_{(s)}$, $|\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}|_{(c)}$, $|\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}|_{(a)}$ of fiber with different annealing times for the constant annealing temperature ($140 \pm 1°C$).

So in the present study using multiple beam Fizeau fringes in transmission provides acceptable results for detection of the variation of orientations in the skin and core layers due to different thermal annealing conditions. Also indicated are the variations in other structural parameters, which could establish a connection between the molecular structure and these properties that aid in producing a certain type of fiber for a specified purpose.

Also, during the production of the films and engineered parts, a polymer is exposed to varying degrees of heat and humidity. The processing conditions have significant influence on the physical properties of the product. Most studies, which involve variations of physical properties, considered polymer as an anisotopic polycrystalline medium, i.e., consisting of crystalline regions suspended in an amorphous medium, which is partially oriented.

Just as birefringence yields information about the crystallinity and orientation of polymer molecular chains, the isotropic refractive index of medium also gives information about not only the molecular package but also specification of the unit cell of the crystalline part.

So, to explain variations in our results, 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. It has been shown from our results that changes in the densities occur due to different annealing conditions, which are accompanied by significant changes in the physical and chemical properties. So the overall changes in density are important influences on the orientation, optical properties (refractive index, light reflection and absorption, luster), crystallinity, etc as seen from our results.[36–39]

CONCLUSION

It is clear that the multiple beam and the acoustic methods are useful techniques to clarify the mechanism of the optical and density parameters of nylon 6 fibers with different thermal conditions. From the measurements relating the changes of optical properties, density, and crystallinity parameters to thermal effect in nylon 6 fibers, the following conclusions may be drawn:

1. The multiple-beam Fizeau fringes method showed that the fiber surface (skin) has a different orientation from that of its core, and it is a useful technique to study multilayer fibers to give information on the interfaces between the fiber layers in the limit of the wavelengths used.
2. There are variations in the crystallinity and crystalline parameters of the fiber material with different annealing conditions, which affect other physical properties (swelling, dyeability, dielectric, etc.) which need further studies. Also, the density and crystallinity greatly depend on the thermal energy of the intermolecular interaction that affects the molecular motion, and is indicative of the effect of a structures transformation changes.
3. The present work demonstrates and realizes the applicability of methods of multiple-beam and acoustic techniques to determine the principal optical parameters and density to be used in calculations of the crystallinity with fair accuracy. Also it is of value to detect small variations in optical structural parameters at different annealing conditions and different layers.

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