# Opto-Thermal Properties of Fibers. XVI. Macrostructural and Optical Properties of Cold-Drawn, Quenched PET Fibers

**I. M. FOUDA, F. M. EL-SHARKAWY**

Physics Department of Science, Mansoura University, Mansoura, Egypt

**ABSTRACT:** In this article, the relation between the macrostructural changes in uniaxially stretched polyester (PET) fibers, caused by heat treatment, and quenched in coarse-grain ice were studied. The developing macrostructure was determined using double-beam interferometry. Application was carried out by two-beam interferometry to determine the optical parameters. Using a two-beam Pluta polarizing interference microscope connected to a device to dynamically study the draw ratio with birefringence changes. The relations of drawing changes with some optical parameters are given. The evaluation of density, the mean square density fluctuation, crystallinity, amorphous orientation, crystalline orientation functions, the mean square density fluctuation $\langle \eta^2 \rangle$, the number of chains per unit volume $N_c$, and the number of random links between the network junction points $N_{(1)}$ have been found. The results obtained clarify the effect of annealing time and temperature with different draw ratios on the structure of PET fibers. Also, the optical results were used to calculate an optical orientation function and an optical orientation angle of drawn, quenched PET fibers. Relations between the optical data, draw ratios, and other parameters with different quenching conditions are given for these fibers. The change of the refractive index profile of the quenched PET fibers with various conditions are given. Illustrations are given using graphs and microinterferograms. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1881–1894, 1999

**Key words:** orientation; drawing; quenched; PET; refractive indices; crystallinity; optical

## INTRODUCTION

Nowadays, there are many nondestructive testing techniques available for determining various characteristics of material. Optical properties provide parameters that characterize the structure of the polymer on the molecular level, and the birefringence produced on stretching a network of molecular chains has been considered by Kuhn and Grün.[1]

Kolsky and Shearman[2] have shown that the birefringence produced in polyethylene when it is stretched is in agreement with the molecular rearrangements deduced from chemical and X-ray evidence. The relation between the density and the average refractive indices of drawn uniaxially stretched polyethylene (PET) was given by de Vries and his coworkers.[3]

The density of the crystalline regions in a polymer is greater than that of the amorphous component; in some cases, the difference may amount to as much as 10%, so the determination of density constitutes an accurate method for determining percentage crystallinity, and density measurements can be used to follow the continuous changes during the crystallization of a sample.

Also, when optical properties are considered, crystallinity is almost invariably important be-

**Table I   Refractive Indices $n_a^{\parallel}$ and $n_a^{\perp}$, Total Birefringence $\Delta n_a$, Form Birefringence $\Delta n_f$, and Constant Value K, at a Constant Annealing Temperature at 4 h, Quenched in Ice**

| Constant Annealing Temperature (°C) | Draw Ratio | $n_a^{\parallel}$ | $n_a^{\perp}$ | $\Delta n_a$ | $\Delta n_f$ | $F_a$ | $F_c$ | K |
|---|---|---|---|---|---|---|---|---|
| 120 ± 1 | 1.00 | 1.584 | 1.575 | 0.008 | −0.259 | — | — | 0.4304 |
| 120 ± 1 | 1.40 | 1.605 | 1.582 | 0.023 | −0.235 | 0.015 | 0.368 | 0.4320 |
| 120 ± 1 | 1.56 | 1.685 | 1.607 | 0.078 | −0.147 | −0.066 | 0.482 | 0.4379 |
| 120 ± 1 | 1.72 | 1.683 | 1.611 | 0.072 | −0.151 | −2.613 | 0.577 | 0.4381 |
| 120 ± 1 | 1.88 | 1.685 | 1.609 | 0.077 | −0.148 | −2.382 | 0.653 | 0.4380 |
| 120 ± 1 | 2.04 | 1.687 | 1.606 | 0.080 | −0.144 | −1.821 | 0.714 | 0.4377 |
| 120 ± 1 | 2.20 | 1.688 | 1.603 | 0.085 | −0.141 | −1.665 | 0.763 | 0.4376 |
| 120 ± 1 | 2.36 | 1.690 | 1.600 | 0.090 | −0.137 | −1.420 | 0.802 | 0.4375 |
| 120 ± 1 | 2.52 | 1.696 | 1.596 | 0.099 | −0.128 | −1.452 | 0.833 | 0.4375 |
| 120 ± 1 | 2.68 | 1.699 | 1.595 | 0.104 | −0.123 | −1.199 | 0.859 | 0.4373 |
| 120 ± 1 | 2.84 | 1.701 | 1.592 | 0.109 | −0.119 | −1.054 | 0.880 | 0.4372 |
| 120 ± 1 | 3.00 | 1.703 | 1.590 | 0.113 | −0.116 | −0.886 | 0.897 | 0.4371 |
| 120 ± 1 | 3.16 | 1.706 | 1.588 | 0.118 | −0.111 | −0.851 | 0.911 | 0.4371 |
| 120 ± 1 | 3.32 | 1.707 | 1.587 | 0.120 | −0.110 | −0.158 | 0.922 | 0.4371 |
| 140 ± 1 | 1.00 | 1.607 | 1.579 | 0.029 | −0.231 | — | — | 0.4318 |
| 140 ± 1 | 1.40 | 1.687 | 1.609 | 0.078 | −0.146 | 0.1580 | 0.368 | 0.4382 |
| 140 ± 1 | 1.56 | 1.691 | 1.605 | 0.086 | −0.139 | −0.481 | 0.482 | 0.4380 |
| 140 ± 1 | 1.72 | 1.693 | 1.601 | 0.092 | −0.134 | −0.701 | 0.577 | 0.4378 |
| 140 ± 1 | 1.88 | 1.693 | 1.599 | 0.094 | −0.133 | −0.787 | 0.653 | 0.4375 |
| 140 ± 1 | 2.04 | 1.697 | 1.595 | 0.102 | −0.126 | −0.779 | 0.714 | 0.4375 |
| 140 ± 1 | 2.20 | 1.701 | 1.595 | 0.106 | −0.121 | −1.034 | 0.763 | 0.4376 |
| 160 ± 1 | 1.00 | 1.610 | 1.581 | 0.029 | −0.228 | — | — | 0.4321 |
| 160 ± 1 | 1.40 | 1.692 | 1.607 | 0.085 | −0.138 | 0.818 | 0.344 | 0.4382 |
| 160 ± 1 | 1.56 | 1.691 | 1.607 | 0.083 | −0.140 | −0.598 | 0.456 | 0.4382 |
| 160 ± 1 | 1.72 | 1.696 | 1.599 | 0.097 | −0.129 | −0.283 | 0.549 | 0.4377 |
| 160 ± 1 | 1.88 | 1.697 | 1.599 | 0.098 | −0.128 | −0.754 | 0.624 | 0.4378 |
| 160 ± 1 | 2.04 | 1.702 | 1.596 | 0.106 | −0.120 | −0.879 | 0.686 | 0.4378 |
| 160 ± 1 | 2.20 | 1.703 | 1.595 | 0.108 | −0.118 | −0.893 | 0.713 | 0.4377 |

cause the crystalline component is always of higher refractive index than the amorphous regions, regardless of whether the latter are glassy or rubbery. This difference in refractive index gives rise to scattering and, hence, haziness. The refractive index of a polymer depends on the total polarizability of the monomer unit, which determines the mean refractive index of the polymer. The differences in the principal refractive indices are known as the birefringence of the material.[4] The birefringence of fibers arises from the orientation of the polymer molecules along the fiber axis averaged over the crystalline and noncrystalline region of the fiber. This molecular orientation influences the physical properties of the yarn, such as density and uptake.[5]

Since the 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 bass factor), yields considerable insight into the characteristics of the bulb polymer.[6] The relationship between the density and the degree of crystallinity of the polymer has great influence on the viscoelastic properties of crystalline polymers.[7]

In this work, the density and crystallinity of PET fibers with different quenching conditions was measured and calculated to estimate the variation due to the quenching process; on the other band, to describe these variations may lead to understanding of the variation in the molecular structure. The double-beam interferometry technique is used to determine the optical parameters related to drawing process.

## THEORETICAL CONSIDERATIONS

A Pluta interference microscope, in the case of a totally duplicated image of the fiber, connected to a device to study dynamically the draw ratio,

**Table II   Density $\rho$, Mean Square Density Fluctuation $\langle\eta^2\rangle$, the Specific Refractivity of the Isotropic Dielectric $\varepsilon^{\parallel}$ and $\varepsilon^{\perp}$, the Number of Molecules Per Unit Volume $N$, and the Number of Chains Per Unit Volume $N_1$, at a Constant Annealing Temperature at 4 h, Quenched in Ice**

| Constant Annealing Temperature (°C) | Draw Ratio | $\rho$ | $\langle\eta^2\rangle \times 10^{-4}$ | $\varepsilon^{\parallel} \times 10^{-4}$ | $\varepsilon^{\perp} \times 10^{-4}$ | $N$ | $N_1$ |
|---|---|---|---|---|---|---|---|
| 120 ± 1 | 1.00 | 1.343 | 8.11 | 30.79 | 30.33 | 0.994 | — |
| 120 ± 1 | 1.40 | 1.366 | 27.0 | 21.08 | 30.20 | 0.984 | 2.642 |
| 120 ± 1 | 1.56 | 1.445 | 13.1 | 21.61 | 29.75 | 0.947 | 1.105 |
| 120 ± 1 | 1.72 | 1.449 | 9.00 | 21.52 | 29.87 | 0.951 | 1.586 |
| 120 ± 1 | 1.88 | 1.447 | 11.0 | 21.59 | 29.78 | 0.948 | 1.883 |
| 120 ± 1 | 2.04 | 1.445 | 12.7 | 21.65 | 29.71 | 0.945 | 2.191 |
| 120 ± 1 | 2.20 | 1.442 | 16.06 | 21.72 | 29.61 | 0.942 | 2.474 |
| 120 ± 1 | 2.36 | 1.440 | 17.43 | 21.79 | 29.52 | 0.939 | 2.746 |
| 120 ± 1 | 2.52 | 1.439 | 18.48 | 21.93 | 29.35 | 0.933 | 2.877 |
| 120 ± 1 | 2.68 | 1.439 | 18.26 | 21.99 | 29.28 | 0.930 | 3.140 |
| 120 ± 1 | 2.84 | 1.437 | 20.00 | 22.06 | 29.18 | 0.927 | 3.400 |
| 120 ± 1 | 3.00 | 1.436 | 21.11 | 22.12 | 29.11 | 0.924 | 3.678 |
| 120 ± 1 | 3.16 | 1.434 | 22.22 | 22.20 | 29.01 | 0.921 | 3.923 |
| 120 ± 1 | 3.32 | 1.434 | 22.71 | 22.22 | 28.98 | 0.919 | 4.293 |
| 140 ± 1 | 1.00 | 1.362 | 25.03 | 31.57 | 30.08 | 0.980 | — |
| 140 ± 1 | 1.40 | 1.448 | 9.830 | 33.58 | 29.76 | 0.947 | 0.766 |
| 140 ± 1 | 1.56 | 1.447 | 11.59 | 33.82 | 29.63 | 0.942 | 1.004 |
| 140 ± 1 | 1.72 | 1.444 | 14.42 | 34.01 | 29.51 | 0.938 | 1.242 |
| 140 ± 1 | 1.88 | 1.440 | 17.59 | 34.07 | 29.45 | 0.936 | 1.534 |
| 140 ± 1 | 2.04 | 1.439 | 18.69 | 34.32 | 29.31 | 0.931 | 1.729 |
| 140 ± 1 | 2.20 | 1.441 | 17.35 | 34.47 | 29.25 | 0.928 | 1.978 |
| 160 ± 1 | 1.00 | 1.368 | 28.22 | 31.60 | 30.11 | 0.980 | — |
| 160 ± 1 | 1.37 | 1.449 | 8.840 | 33.81 | 29.66 | 0.942 | 0.648 |
| 160 ± 1 | 1.52 | 1.449 | 8.830 | 33.76 | 29.68 | 0.943 | 0.951 |
| 160 ± 1 | 1.68 | 1.443 | 15.44 | 34.18 | 29.41 | 0.934 | 1.081 |
| 160 ± 1 | 1.82 | 1.443 | 15.07 | 34.19 | 29.41 | 0.934 | 1.359 |
| 160 ± 1 | 1.96 | 1.443 | 15.13 | 34.45 | 29.28 | 0.929 | 1.515 |
| 160 ± 1 | 2.04 | 1.442 | 15.82 | 34.53 | 29.23 | 0.927 | 1.631 |

discussed in detail elsewhere,[8–10] was used in the present work to determine the refractive indices of drawn and undrawn for annealed fibers, where

$$n_a^{\parallel} = n_L \pm \frac{E^{\parallel} \cdot \lambda}{h \cdot A} \tag{1}$$

with an analogous formula for $n_a^{\perp}$.

$n_a^{\parallel}$ and $n_a^{\perp}$ are the mean 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, $E^{\parallel}$ is the area of the fiber enclosed under the fringes shift of the fiber, $h$ is the interference fringe spacing corresponding to the monochromatic light of wavelength $\lambda$, and $A$ is the mean cross-sectional area of the fiber. Also, by applying the equations used by Hermans[11] and Ward,[12] we can obtain the optical orientation parameters, as discussed previously

in extensive works. The axial orientation is expressed by the usual birefringence $\Delta n_a = n_a^{\parallel} - n_a^{\perp}$. The value of $n_a^{\parallel}$, $n_a^{\perp}$, and $\Delta n_a$ for PET fiber are given in Table I. From this axial birefringence, the amorphous orientation $F_a$ has been calculated by combining the two-phase model of Samuels[6] and the Gaylord model for crystalline orientation $F_c$. The Gaylord model is in good agreement with experimental data on PET.[13]

$$\Delta n_a = \chi \Delta n_c^0 F_c + (1 - \chi)\Delta n_a^0 F_a \tag{2}$$

where $\chi$ is the degree of crystallinity, $\Delta n_c^0 = 0.22$, $\Delta n_a^0 = 0.27$, and $F_c = (DR^3 - 1)/(DR^3 + 2)$, where $DR$ is the draw ratio. The values of $F_a$ and $F_c$ for PET fiber are given in Table I.

## DENSITY

The densities of the samples were estimated with the average refractive index obtained by a two-

Plate (1-a)



Plate (1-d)



Plate (1-b)



Plate (1-e)



Plate (1-c)



Plate (1-f)

**Plate 1 (a-f)**

**Plate 1**   Microinterferograms of totally duplicated images of PET fiber at different draw ratios (1.56 and 2.2), annealed at 120, 140, and 160°C ($\lambda$ = 546 nm).

beam interferometric technique. For PET, de Vries and coworkers found[3] a linear relation between the density, as follows:

$$\rho = 4.047 \frac{(\bar{n}^2 - 1)}{(\bar{n}^2 + 2)} \tag{3}$$

with $\rho$ expressed in kg cm³. This relation is independent of the degree of crystallinity $\chi$ and the

level of orientation. We calculate the average refractive index as the isotropic refractive index from the following equation[14]:

$$n_{\text{iso}} = \frac{(n_a^{\parallel} + 2n_a^{\perp})}{3} \tag{4}$$

From eqs. (3) and (4), the constant K for different draw ratios at different annealing conditions by

**Figure 1**   The relations between the refractive indices $n_a^{\parallel}$, $n_a^{\perp}$, and the different draw ratios with different annealing conditions (annealing temperatures: 120, 140, and 160 $\pm$ 1°C; annealing time, 4 h).

using the well-known Glade–Ston Dala equation can be calculated as

$$K = (n_{\text{iso}} - 1)/\rho \qquad (5)$$

The results are shown in Table I, which indicates that the constant K varies with different draw ratios at different annealing conditions. Also, the specific refractivity $\varepsilon_i$ in a certain direction $i$ can

**Figure 2** The relations between ($\chi$) and the different draw ratios of PET fibers with different annealing conditions (annealing temperatures: 120, 140, and 160 ± 1°C; annealing time, 4 h).

be determined by the following equation[15] considering the anisotropy index:

$$\frac{n_\parallel^2 - 1}{n_\parallel^2 + 2 + S(n_\parallel^2 - 1)} = \varepsilon_\parallel \rho \tag{6}$$

An analogous formula is used for $\varepsilon_\perp$, where $\rho$ is the density and $S$ is the anisotropy index and is equal to $-0.57$ for PET.[15] The values of $\varepsilon^\parallel$ and $\varepsilon_\perp$ for PET fiber are given in Table II.

## DEGREE OF CRYSTALLINITY

The degree of crystallinity $\chi$ was determined by the relation

$$\chi = \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \tag{7}$$

with $\rho_c = 1.457 \times 10^{-3}$ kg cm$^3$ and $\rho_a = 1.336 \times 10^{-3}$ kg cm$^3$[13]

The volume fraction of amorphous material was determined by the following relation:

$$1 - \chi = 1 - \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \tag{8}$$

where $\chi$ is the volume fraction of crystallinity material.

## THE MEAN SQUARE DENSITY FLUCTUATION

For drawn and undrawn PET fiber, the mean square density fluctuation $\langle \eta^2 \rangle$ can be calculated from the following equation[16]:

$$\langle \eta^2 \rangle = (\rho_c - \rho_a)^2 \chi(1 - \chi) \tag{9}$$

The values of $\rho$ and $\langle \eta^2 \rangle$ for PET fiber are given in Table II.

**Figure 3**  The relations between $(1 - \chi)$ and the different draw ratios of PET fibers with different annealing conditions (annealing temperatures: 120, 140, and 160 ± 1°C; annealing time, 4 h).

The optical orientation function was defined first by Hermans[11] as

$$f_{\theta} = \frac{(n_a^{\parallel} - n_a^{\perp})}{(n_x - n_z)} = \frac{\Delta n_a}{\Delta n_{\max}} \qquad (10)$$

where $n_x$ and $n_z$ are the refractive indices parallel and perpendicular to the fiber axis, respectively, for the ideal fiber. $\Delta n_a$ is the measured birefringence, and $\Delta n_{\max}$ is the maximum birefringence for fully oriented fiber. This function takes the values of $+1$, 0, and $-\frac{1}{2}$ according to the state of orientation, whether it is perfect, random, or perpendicular to the fiber axis, respectively. A theoretical model exists for molecular reorientation developed by stretching.[17,18] This model considers that the optical anisotropic results from the orientation of anisotropic structural units, and the optical properties of these units are identical to those for the ideal fiber. Also, this model, named the aggregate model, gives the partially oriented fiber birefringence $\Delta n_a$ as

$$\Delta n_a = \tfrac{1}{2} \Delta n_{\max}(\overline{3 \cos^2 \theta} - 1) \qquad (11)$$

where $\theta$ is the angle between the axis of the unit and the fiber axis (or draw direction), and $\overline{\cos^2 \theta}$ is the average value of $\cos^2 \theta$.

An empirical formula is suggested to evaluate the relationship between orientation function, orientation angle, area of cross section, and birefringence with the draw ratio, as follows:

$$\left[ \frac{f(\theta) \Delta n}{A \theta} \right] = CR + Y \qquad (12)$$

where C and Y are constants characterizing the proportionality between $\left[ \dfrac{f(\theta) \Delta n}{A \theta} \right]$ and $R$. The values of C and Y vary with the annealing condition (temperature and time).

In evaluating the orientation function for partially oriented aggregate $[P_2(\theta)]$ is defined by Ward[12] by the following equation:

$$\langle P_2(\theta) \rangle = \frac{\Delta n_a}{\Delta n_{\max}} \qquad (13)$$

**Figure 4** The relations between the number of chains per unit volume $N_c$ and the different draw ratios of PET fibers with different annealing conditions (annealing temperatures: 120, 140, and $160 \pm 1°C$; annealing time, 4 h).

which is the same function named by Hermans.[11] So, if $\theta$ is the angle made between the principal axis of a statistical segment of such a fiber and the stretching direction, the orientation function may be defined as $f(\theta)$, and the birefringence is then given by[19]

$$\Delta n_a = (\alpha_\parallel - \alpha_\perp)f(\theta) \qquad (14)$$

where $(\alpha_\parallel - \alpha_\perp)$ is the difference between the principal polarizabilities of the statistical segment.

The Kuhn–Treloar-type theory gives for $f(\theta)$,

$$f(\theta) = (\tfrac{2}{5})N_c\left[DR^2 - \frac{1}{DR}\right] \qquad (15)$$

where $N_c$ is the number of chains per unit volume and depends on the number of crystallinities in the polymer material.

It can be shown[20] that the orientation function for the random links as observed previously is given by

$$[P_2(\theta)] = (DR^2 - DR^{-1})/5N_{(1)} \qquad (16)$$

where $N_{(1)}$ is the number of random links between the network junction points (the entanglements), and $DR$ is the extension or draw ratio. The value of $N_{(1)}$ for PET fiber is given in Table II.

Roe and Krigbaum[21] have derived an expression for the distribution of segments at an angle $\theta$ with respect to the draw ratio.

$$\omega(\cos\theta) = \tfrac{1}{2} + \frac{1}{4N_{(1)}}(3\cos^2\theta - 1)\left(DR^2 - \frac{1}{DR}\right) \quad (17)$$

From eq. (17), we found that the distribution of segments varies and ranged from 0.5 to 1.125.

Before orientation, the segments will be randomly oriented at an angle $\theta$ with respect to the draw direction. After a draw ratio $DR$, then the segments will be constrained at an angle $\beta$ given by

$$\tan\beta = DR^{-3/2}\tan\theta \qquad (18)$$

**Figure 5**    Relation between birefringence $\Delta n_a$ and $f_\theta$ of PET fiber with different draw ratios at 120, 140, and 160°C.

## DETERMINATION OF THE NUMBER OF MOLECULES PER UNIT VOLUME

The difference of the two main refractive indices $\Delta n_a$ (birefringence) of the sample for the beams polarized along the longitudinal and transverse axis is linked, with the difference in the mean polarizabilities of the macromolecule for the same directions $(\bar{P}_\parallel - \bar{P}_\perp)$ by the following relation[22]:

$$\Delta n = \frac{2\pi N}{\bar{n}} \left( \frac{\bar{n}^2 + 2}{3} \right)^2 (\bar{P}_\parallel - \bar{P}_\perp) \qquad (19)$$

where $N$ is the number of molecules per unit volume, and $\bar{n}$ is the mean refractive index of the sample $\bar{n} = \left( \dfrac{n_\parallel + n_\perp}{2} \right)$. The experimental values of the mean polarizabilities per unit volume parallel $\bar{P}_a^\parallel$ and perpendicular $\bar{P}_a^\perp$ to the fiber axis were derived from the measured values of the refractive index by application of the following Lorentz–Lorenz equations[6]:

$$\bar{P}_\parallel = \frac{3}{4\pi} \left( \frac{n_\parallel^2 - 1}{n_\parallel^2 + 2} \right) \qquad (20)$$

An analogous formula used for $\bar{P}_a^\perp$. The value of the number of molecules per unit volume $N$ for PET fiber is given in Table II.

Also, the calculation of the form birefringence could be obtained by the following equation,[23] where the total birefringence is the sum of three contributions:

$$\Delta n = \chi_c \Delta n_c + [1 - \chi_c]\Delta n_a + \Delta n_f \qquad (21)$$

where $\Delta n$ is the total birefringence, $\Delta n_c$ is the birefringence of crystalline material, $\Delta n_a$ is the birefringence of amorphous material, $\Delta n_f$ is the birefringence of form material, and $\chi$ is the volume faction of crystalline regions.

The values of $\Delta n_f$ for PET fiber are given in Table I.

## EXPERIMENTAL PROCEDURE AND RESULTS AND DISCUSSION

### Sample Preparation and Annealing

The polyester fibers were distributed in a cocoon form on a glass rods with free ends, which were

**Figure 6**  The relation between $\langle P_2(\theta) \rangle$ and $[DR^2 - DR^{-1}]$ of fiber at 120, 140, and 160°C.

then heated in an electric oven with the temperature adjusted to different temperatures (120, 140, and 160 ± 1°C). Hence, the samples were annealed for the annealing time (4 h), then quenched in ice.

### Double-Beam Interferometry

The totally duplicated image of the fiber was used to calculate the mean refractive indices $n_a^{\|}$, $n_a^{\perp}$, and the birefringence $\Delta n_a$ of polyester fibers at different draw ratios with different conditions of annealing.

In plate 1(a)–(f), microinterferograms of the totally duplicated images in parallel and perpendicular directions, respectively, are shown at different draw ratios (1.56 and 2.2) of polyester fibers samples annealed at different temperatures (120, 140, and 160 ± 1°C) with a constant time of 4 h. A monochromatic light of 546-nm wavelength was used. In plates 1(a)–(f), it is shown that as the draw ratio increases, the diameter of the fiber decreases. The refractive index of the immersion liquid were 1.655 and 1.569 at 18°C, for parallel and perpendicular directions, respectively. Using these interferograms, the mean refractive index of the parallel and perpendicular direction with

different draw ratios at different annealing conditions was calculated.

Figure 1 shows the variation of $n_a^{\|}$ and $n_a^{\perp}$ of PET fibers due to the changing draw ratio at different annealing conditions (annealing temperatures: 120, 140, and 160 ± 1°C; annealing time, 4 h).

The apparent volume fraction ($\chi$) of crystallinity was calculated from eq. (7) using the calculated density values. The results are plotted in Figure 2, which shows the variation of the crystallinity of polyester fibers due to changing draw ratio at different annealing conditions (annealing temperatures: 120, 140, and 160 ± 1°C; annealing time, 4 h). It is quite obvious that the crystallinity is lower for undrawn fibers than for drawn samples. The value of $\chi$ increases and then decreases with an increasing draw ratio.

Figure 3 shows the variation of the $(1 - \chi)$ of polyester fibers due to the changing draw ratio at different annealing conditions (annealing temperatures: 120, 140, and 160 ± 1°C; annealing time, 4 h).

Figure 4 shows the variation of the number of chains per unit volume $N_c$ of polyester fibers due

**Figure 7**    Relation between the orientation angle ($\theta$) and the different draw ratios of PET fibers with different annealing conditions (annealing temperatures: 120, 140, and 160 $\pm$ 1°C; annealing time, 4 h).

to a changing draw ratio at different annealing conditions (annealing temperatures: 120, 140, and 160 $\pm$ 1°C; annealing time, 4 h).

Figure 5 shows the relation between the birefringence $\Delta n$ and the optical orientation function $f_\theta$ for different draw ratios, at different annealing conditions (annealing temperatures: 120, 140, and 160 $\pm$ 1°C; annealing time: 4 h).

Figure 6 shows the relation between $\langle P_2(\theta) \rangle$ and $[R^2 - R^{-1}]$, which is a straight line; from it, we calculated the values of random links per chain ($N_{(1)}$), which are given in Table II.

Figure 7 shows the variation of orientation angle ($\theta$), which was calculated from eq. (11) of the PET fiber with different draw ratios (annealing at 120, 140, and 160 $\pm$ 1°C, respectively; constant annealing time: 4 h). It shows that orientation angle is decreased by increasing the draw ratio.

Figure 8 shows the relation between tan $\beta$ and draw ratios at different annealing temperatures and a constant annealing time (4 h) tan $\beta$ decreases with increasing the draw ratios.

Figure 9 shows the relationship between $[f(\theta)\Delta n/A\theta]$ and the draw ratio at different an-

nealing conditions (annealing temperature: 120, 140, and 160 $\pm$ 1°C; annealing time, 4 h).

## DISCUSSION

From the previous results obtained in this work, several remarks can be made. There is a variation in the macrostructure due to different thermal treatments and then quenched in ice. Also, a change of a different temperature of annealing leads to different changes in the mechanical properties of PET and the orientation parameters. So, it is detected from the foregoing drawing tests that the main characteristics and properties of structural PET are mainly determined from the optical mechanical and crystallinity parameters. So, the evaluation of the annealing and quenching processes are employed in the design of new structures and for checking the main new conditions for the final physical properties for these end-product materials.

The density increase is the result of denser molecular packing from drawing-induced orienta-

**Figure 8**  Relation between tan $\beta$ and different draw ratios with different annealing conditions (annealing temperatures: 120, 140, and 160 $\pm$ 1°C; annealing time, 4 h).

tion and crystallization. The higher density indicates closer packing of chains in the noncrystalline regions, whereas the $\Delta n$ small increase is associated with reduced chain alignment in the radial direction.

To explain the variations obtained in our present work, it was essential to take the following assumptions into account; when a polymer is annealed its structural behavior is altered due to the accumulation of several structural processes. These may be summarized as

1. disorientation;
2. recrystallization by nucleation;
3. recrystallization by growth;
4. shrinkage;
5. crystal decomposition.

These processes are natural responses to both annealing temperature and time.[6,7,24–26] Overall, annealing above the $T_g$ increased chain mobility and enhanced crystallization. Also, drawing increased the overall crystallinity and molecular packing density.[27] So the above results clearly indicate that both the crystalline structure and

the noncrystalline chains are affected by the condition of annealing (temperature and time) and drawing processes.

## CONCLUSION

From the measurements and calculations relating the change of optical properties to the thermal annealing process for polyester fibers, the following conclusions may be drawn.

1. An empirical formula is suggested to relate the variation of the cross-sectional area, angle of orientation, the orientation factor, and the birefringence of PET fibers with the draw ratio.
2. The microinterferograms are clear to identify differences in optical path variations due to different drawing processes at different annealing conditions.
3. The higher the orientation, the more mutually parallel the molecules and the smaller the average angle formed by them with the fiber axis.

**Figure 9**   The relationship between $[f(\theta)\Delta n/A\theta]$ and the draw ratios at different annealing conditions (annealing temperatures: 120, 140, and 160 $\pm$ 1°C; annealing time, 4 h).

4. The orientation angle decreases with an increasing draw ratio at different annealing conditions.

5. The study of change of $n_a^{\parallel}$, $n_a^{\perp}$ and $\Delta n_a$ with respect to annealing and drawing processes clarifies that the isothermal properties of the structure in perpendicular direction to the fiber axis differ from those in an axial direction, except for an anisotropy medium.

6. As $n_a^{\parallel}$ increases, the process of axial orientation increases crystallinity, both orienting the molecules.

7. Annealing the fibrous structure, however, affects the diffusion properties.

8. The effects of annealing processes on polyester fibers depends on the time and temperature of annealing.

9. Changes in the isotropic refractive indices $n_{iso}$ is related to the degree of order and crystallinity of the fiber, as well as the density of sample $\{[(n_{iso} - 1)/\rho] = K\}$.

10. The results shown in Table I indicate that the constant K varies with the draw ratio at different annealing conditions.

11. A study of the density variations due to drawing indicates the mass redistribution associated with the drawing process of polyester fibers.

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

13. Evaluation of crystallinity with the draw ratio decreased at first in all different annealing conditions, which means a regrouping due to mobilities of chain units of polyester fiber during the drawing process.

14. Thermal annealing can provide supplementary information on the structural features related to the thermal performance of materials, where the variation of specific volume is related to crystallinity, density, and mass redistribution of the sample.

In conclusion, the structural orientation changes due to the annealing and drawing processes, as observed by both two-beam techniques,

is very promising, and further study is required in areas that have not yet been explored. Since $n_a^{\parallel}$, $n_a^{\perp}$, $\Delta n_a$, and $n_{iso}$ are a consequence of the material annealed, reorientation of PET fibers may occur not only during fabrication but also after the fabrication process.

## REFERENCES

1. Kuhn, W.; Grün, F. Kolloid-Z 1942, 101, 248.
2. Kolsky, H.; Shearman, A. C. Proc Phys Soc 1943, 55, 343.
3. de Vries, A. J.; Bonnebat, C.; Beatutemps, J Polym Sci Polym Symp 1977, 5, 159.
4. Jenkins, A. D. Polymer Science: A Materials Science Handbook, Vol. 1; North Holland: Amsterdam, The Netherlands, 1972; Chaps. 4 and 7, pp. 261, 283, 491.
5. Angad Gaur, H.; de Vries, H. J Polym Sci, Phys Ed 1975, 13, 835.
6. Samuels, J. R. Structural Polymer Properties, Vol. 20; John Wiley & Son: New York, 1974; pp. 63, 219.
7. Polukhin, P.; Gorelik, S.; Vortontsov, V. Physical Principals of Plastic Deformation; Mir: Moscow, USSR, 1983; p. 275.
8. Pluta, M. J Opt Acta 1971, 18, 661.
9. Pluta, M. J Microsc 1972, 96, 309.
10. Hamza, A. A.; Fouda, I. M.; El-Tonsy, M. M.; El-Sharkawy, F. M. J Appl Polym Sci 1995, 56, 1355.
11. Hermans, P. H. Contributions to the Physics of Cellulose Fibers; North Holland: Amsterdam, The Netherlands, 1946.
12. Ward, I. M. J Polym Sci, Polym Symp 1977, 58, 1.
13. Bourvelles, G. L.; Beautemps, J. J Appl Polym Sci 1990, 39, 329.
14. Ward, I. M. Structure and Properties of Oriented Polymers; Applied Science: London, UK, 1975; p. 57.
15. de Vries, H. Z Colloid, Polym Sci 1979, 257, 226.
16. Fischer, E. W.; Fakirov, S. J Mater Sci 1976, 11, 1041.
17. Foot, J. S.; Ward, I. M. J Mater Sci 1975, 10, 955.
18. Ward, I. M. Proc Phys Soc London 1977, 80, 1176.
19. Stein, R. S. J Polym Sci, Symp 1959, 34, 709.
20. Perena, J. M.; Duckett, R. A.; Ward, I. M. J Appl Polym Sci 1980, 25, 1381.
21. Roe, R. J.; Krigbaum, W. R. J Appl Phys 1964, 35, 2215.
22. Sarkisyan, V. A.; Asratyan, M. G.; Mkhitoryan, A. A.; Katrdzhyan, K. KH.; Dadivanyan, A. K. Vysokomal Sayed 1985, A27, 1494.
23. Happy, F. Applied Fiber Science, Vol. 1; Academic Press: London, UK, 1983; p. 130.
24. Fouda, I. M.; El-Tonsy, M. M.; Shaban, M. M. J Mater Sci 1990, 26, 5085.
25. Porter, E. A.; Porter, S. R. The Strength and Stiffness of Polymer; Marcel Dekker: New York, 1983, p. 121.
26. Bassett, D. C. Principles of Polymer Morphology; Cambridge University Press: Cambridge, UK, 1981; p. 124.
27. Debra, T. A.; You-Lo, H. J Polym Sci, Part B: Polym Phys 1993, 31, 1873.