

Optothermal Properties of Fibers. II. Annealing Effect on the Birefringence Variations of Polyester Fibers

A. A. HAMZA, I. M. FOU DA,* M. M. EL-TONSY, and F. M. EL-SHARKAWY

Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

SYNOPSIS

The variation of refractive indices and birefringences of Egyptian-manufactured polyester fibers with different annealing times at constant temperature 160°C are studied by interferometry. The polarizing interference microscope is used for determining the mean refractive indices and mean birefringence of these fibers. The results are used to calculate optical orientation function and the angle of orientation. Also, the acoustic method has been used for measuring the density and the mechanical loss factor of these fibers. Relations between the mean refractive indices, birefringence, polarizabilities, mechanical loss factors, and densities with annealing time are given for these fibers. Illustrations are given using graphs and microinterferograms. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years there has been a great effort to evaluate the optical parameters of fibers with a high degree of precision. Application of double-beam and multiple-beam interferometry has stimulated interest in studying the effects of different types of thermal and mechanical properties of natural and man-made fibers.¹⁻³ Polyester fibers have a double refraction of positive value because their refractive indices are greater for light vibrating parallel to the fiber axis.^{4,6} Part of the modern trend in fiber research is to alter fiber properties, one property modification method involves the annealing process under different conditions. Several studies have reported the effects of annealing on the structure of synthetic and natural fibers.^{2,5,7-9}

Annealing implies heating a solid to temperatures approaching its melting point. This activates internal mobility and promotes greater stability by, for example, the elimination of stresses or defects in general movement towards the thermodynamic equilibrium condition.¹⁰ The effects of annealing increase drastically with temperature, but also depend on the amount of time that the sample is held at

the annealing temperature. The sample may be annealed with its ends free or fixed; the difference between the two cases is the ratio of shrinkage.

In the present work the changes in density, optical properties, and the mechanical loss factor due to the annealing process are studied for polyester fibers. These studies are performed before and after annealing at constant temperature 160°C and with different times.

THEORY

Two different techniques were used in the present work.

Double-beam Interferometry

The Pluta polarizing interference microscope was used for the determination of the mean refractive indices and birefringence.^{11,12} The following equations are used to determine these optical properties¹³:

$$n_a^{\parallel} = n_L + (\lambda/h)(F^{\parallel}/A) \quad (1)$$

and

* To whom correspondence should be addressed.

$$\Delta n_a = \frac{\Delta F \lambda}{hA} \quad (2)$$

where n_a^{\parallel} is the refractive index of fiber for light vibrating parallel (an analogous equation, using n_a^{\perp} , applies for light vibrating perpendicular) to the fiber axis, n_L is the refractive index of the immersion liquid, F^{\parallel} is 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.

Density Measurements

The measuring system for the measurement of fiber density was discussed in detail elsewhere.^{14,15} From the following equation¹⁶:

$$F_0 = (P/2l)(T/m)^{(1/2)} \quad (3)$$

the mass per unit length m can be calculated, where F_0 is the resonance frequency, P is the number of resonance modes within the string's length, and T is the tensional force.

From the obtained value of the mass per unit length m , one can easily calculate the density ρ of the fiber material from the relation

$$\rho = m/(\pi r^2) \quad (4)$$

where r is the radius of the cylindrical fiber.

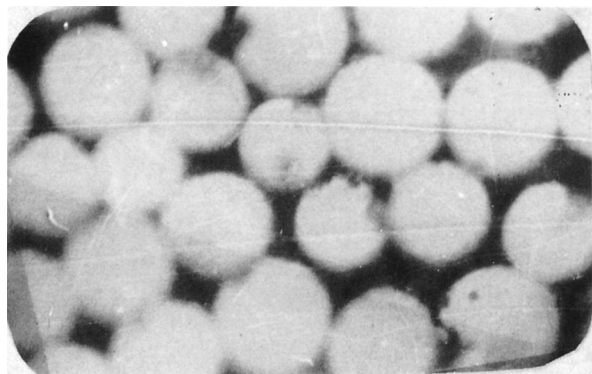


Plate 1 The cross-sectional area of the unannealed PET fiber.

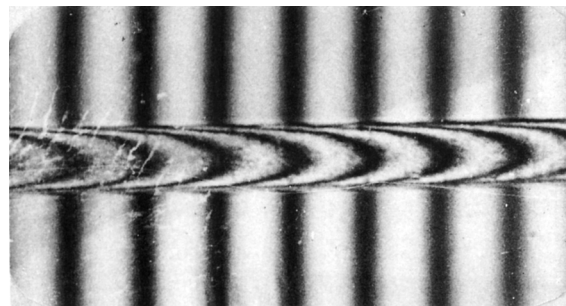


Plate 2 The microinterferogram of nonduplicated image of unannealed PET fiber. Monochromatic light of $\lambda = 546$ nm was used.

EXPERIMENTAL PROCEDURE AND RESULTS

Sample Preparation

Annealing

The polyester fibers were distributed in a cocoon form on glass rods with free ends, which were then heated in an electric oven whose temperature was adjusted to a constant $160 \pm 1^\circ\text{C}$. The samples were annealed for times of 1 to 10 h.

Optical Microscopy

Plate 1 shows the cross section of polyester fibers seen by high-power optical microscopy. It is clear that polyester fibers have regular, circular cross-sections.

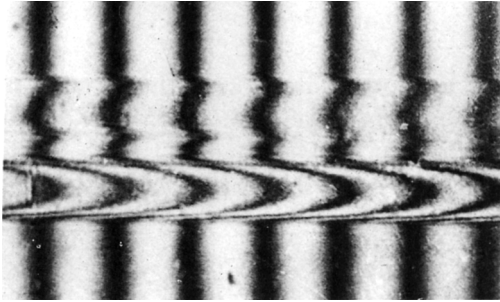
Double-beam Interferometry

The totally duplicated image of the fiber obtained with a Pluta polarizing interference microscope^{11,12} was used to calculate the mean refractive indices n_a^{\parallel} and n_a^{\perp} of polyester fibers.

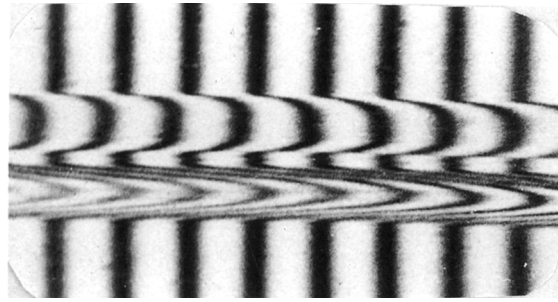
Plate 2 shows a microinterferogram of nonduplicated image of polyester fiber without annealing. Monochromatic light of wavelength 546 nm was used. The refractive index of the immersion liquid was 1.568 at 18°C . Using these interferograms and eq. (2), the mean birefringence of unannealed polyester fiber was calculated.

Plate 3 (a) shows a microinterferogram of the totally duplicated images of unannealed polyester fiber seen with the Pluta microscope and monochromatic light of wavelength 546 nm. The refractive index of the immersion liquid was 1.6035 at 18°C .

Plate 3 (b-d) are microinterferograms of the totally duplicated images of polyester fiber samples annealed at constant temperature 160°C and different time intervals between 1 and 10 h. Mono-



a)



b)

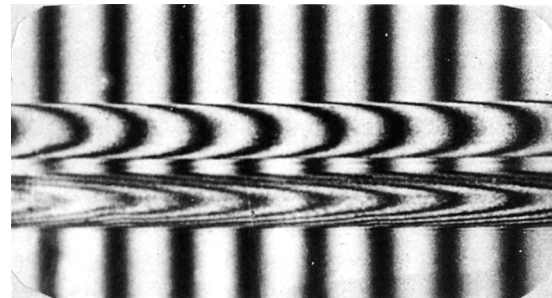
Plate 3 (a) Microinterferograms of totally duplicated image of polyester fiber which unannealed in parallel. Monochromatic light of $\lambda = 546$ nm was used. (b-d) Two-beam interferograms of totally duplicated image of polyester fiber which annealed at constant temperature 160°C at different times (1-10 h) in parallel. Monochromatic light of $\lambda = 546$ nm was used.

chromatic light of wavelength 546 nm was used. The refractive index of the immersion liquid was 1.658 at 18°C . Using these interferograms and eq. (1), the mean refractive index of the parallel direction at different annealing intervals and constant annealing temperature was calculated.

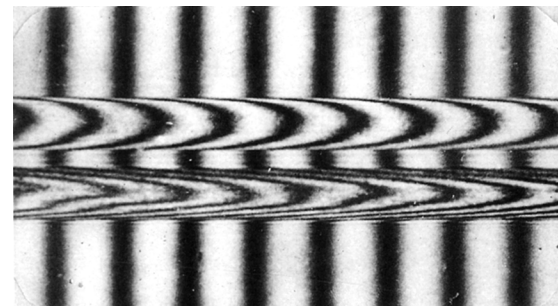
Plate 4(a) shows a microinterferogram of totally duplicated images of unannealed polyester fiber under the Pluta microscope with monochromatic light of wavelength 546 nm.

Plate 4(b-d) are microinterferograms of the totally duplicated images of polyester fiber samples annealed at constant temperature 160°C and different time intervals between 1 and 10 h. Monochromatic light of wavelength 546 nm was used. The refractive index of the immersion liquid was 1.569 at 18°C . Using these interferograms and the analog of eq. (1), the mean refractive index of the perpendicular direction at different annealing time intervals was calculated.

Figure 1 shows the n_{\parallel}^{\prime} variation of annealed polyester fibers when the annealing time is increased (annealing temperature, 160°C), as obtained using a Pluta double-beam interference microscope. It is clear that increased annealing time increases the orientation of the molecules in the parallel direction and then levels off. The process of axial orientation increases crystallinity by both orienting the molecules and bringing them closer together, enabling

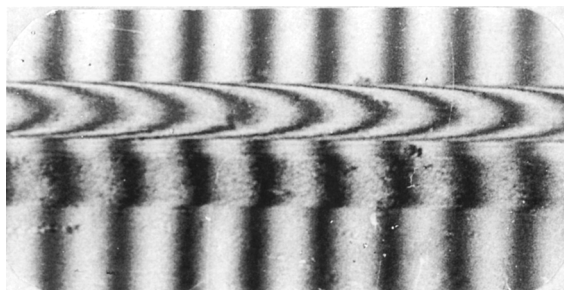


c)



d)

Plate 3 (Continued)



a)

Plate 4 (a) Microinterferograms of totally duplicated image of polyester fiber which unannealed in perpendicular. Monochromatic light of $\lambda = 546$ nm was used. (b–d) Two-beam interferograms of totally duplicated image of polyester fiber which annealed at constant temperature 160°C at different times (1–10 h) in perpendicular. Monochromatic light of $\lambda = 546$ nm was used.

crystallites to form from formerly amorphous regions.

Figure 2 shows the variation of n_a^\perp of annealed polyester fibers by increasing the annealing time similar to n_a^\parallel . It is clear that n_a^\perp decreases with increased annealing time, then increases slowly, then levels off. This behavior is attributed to disorientation of the mobility of molecules in the perpendicular direction.

Figure 3 shows the variation of Δn_a with annealing time (annealing temperature, $160 \pm 1^\circ\text{C}$). It is clear that Δn_a increases due to annealing and this means an increase in orientation due to treatment. Orientation attributed that molecular arrangement in both crystalline and amorphous regions have been occurred.

The present data for determination of the n_a^\parallel and n_a^\perp are utilized to calculate polarizability by the well-known Lorentz–Lorenz equations:

$$(n_a^\parallel - 1)/(n_a^\parallel + 1) = (4/3)\pi P^\parallel \quad (5)$$

and a similar equation for the perpendicular direction.

It is also expected that the change of P^\parallel and P^\perp with annealing time gives behavior as n_a^\parallel and n_a^\perp .

Just as birefringence yields information about the crystallinity and orientation of the polymer molecular chains, the isotropic refractive index of a medium gives information about not only the molecular backbone but also specifications of the unit cell of the crystalline part of the medium.¹⁷ Hannes¹⁷ used the following formula:

$$n_{\text{iso}} = (1/3)(n_a^\parallel + 2n_a^\perp) \quad (6)$$

to estimate a relation showing the crystallization inhomogeneity for some types of polymers. Obtained values of n_a^\parallel and n_a^\perp from the interferometric techniques are used with eq. (6) to determine the isotropic refractive index values for annealed polyester fibers.

Figure 4 shows the variation of n_{iso} of polyester fiber due to changing annealing time (at constant temperature 160°C). Figure 4 shows that n_{iso} of polyester is increased and then levels off by increasing the annealing time.

Figure 5 shows the variation of the density of polyester fibers due to changing annealing ρ , measured by the vibrating string technique and calculated from eqs. (3) and (4). It is clear that on annealing polyester fibers for different periods (at constant temperature 160°C), an increase in density occurs at annealing time 3 h and 6 h. These two relaxations may be due to an increase in the heat content of the interlamellar tie molecules or the chain folded molecules aggregated into ordered states.

Figure 6 shows the variation in the mechanical loss factor ($\tan \delta$) of polyester fibers due to the changing annealing for different periods (at 160°C). Two rapid relaxations occur at annealing times 4 h and 7 h; these peaks are indicative of the isothermal effects accompanied by considerable changes for these internal energy transformations.

As a measure of orientation, the use of n_a^\parallel is sometimes analogous given that the refractive index is a tensor. A better measure of orientation for fibers is the Hermans orientation function¹⁸:

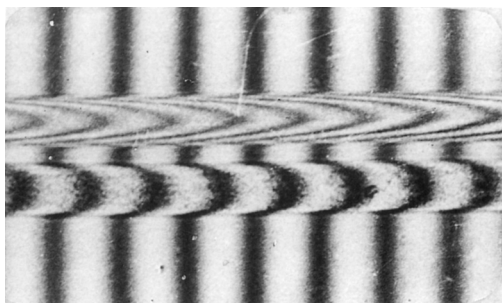
$$(\text{Opt. Ori. Fun.}) F_\theta = \Delta n_a / \Delta n_{\text{max}} \quad (7)$$

where Δn_{max} is the maximum birefringence for fully oriented fiber and Δn_a is the birefringence of the fiber under investigation. F_θ values ranged between +1, 0, and $-\frac{1}{2}$ according to the state of orientation: perfect, random, or perpendicular to the fiber axis, respectively. The value of Δn_{max} has been previously determined to be 0.24.¹⁹

Also, the optical orientation angle can be found by using the following equation:

$$F_\theta = 1 - (3/2)\sin^2\theta \quad (8)$$

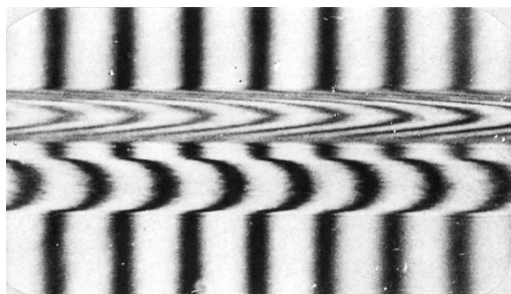
where θ is the angle between the polymer unit axis and the fiber axis. In evaluating the optical orientation with Ward's equation^{20,21}:



b)



c)



d)

Plate 4 (Continued from the previous page)

$$\langle P_2(\theta) \rangle = \Delta n_a / \Delta n_{\max} \quad (9)$$

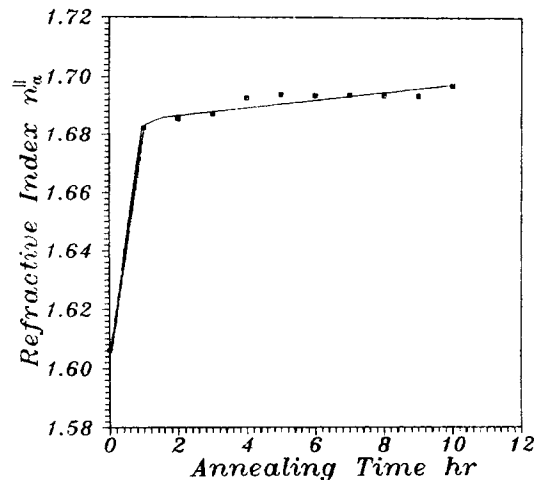


Figure 1 Relation between annealed time (h) and refractive index for light vibrating parallel to the fiber axis n_a^{\parallel} of polyester fiber at constant temperature 160°C.

which is the same function named by Hermans,¹⁸ $\langle P_2(\theta) \rangle$ is related to the polarizability per unit volume²² as follows:

$$\{ \Phi^{\parallel} - \Phi^{\perp} / \Phi^{\parallel} + 2\Phi^{\perp} \} = P_2(\theta_m) \langle P_2(\theta) \rangle \quad (10)$$

where Φ^{\parallel} and Φ^{\perp} are the polarizability per unit volume parallel and perpendicular to the fiber axis, respectively.

Then

$$P_2(\theta_m) = \frac{1}{2}(3 \cos^2 \theta_m - 1) = \text{Const. Quant.}$$

Equation (10) can also be written in the form

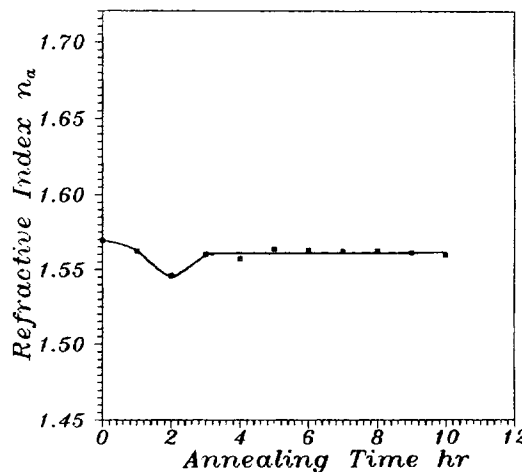


Figure 2 Relation between annealed time (h) and refractive index for light vibrating perpendicular to the fiber axis n_a^{\perp} of polyester fiber at constant temperature 160°C.

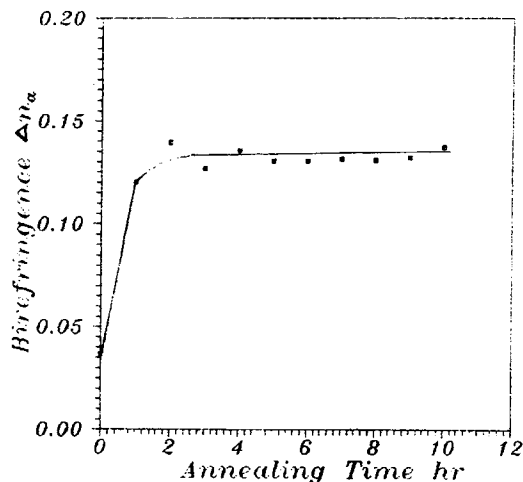


Figure 3 Relation between annealed time (h) and birefringence of polyester fiber at constant temperature 160°C.

$$\{\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}\} = [\Delta\alpha/3\alpha_0]\langle P_2(\theta) \rangle \quad (11)$$

where $\Delta\alpha$ is the difference between α^{\parallel} and α^{\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.²³ The value of Φ^{\parallel} and Φ^{\perp} can be determined from eq. (5):

$$[n_{\parallel}^2 - 1/n_{\parallel}^2 + 2] = \Phi^{\parallel} \quad (12)$$

In a recent approach to the continuum theory of birefringence of oriented polymer,¹⁹ it was found that

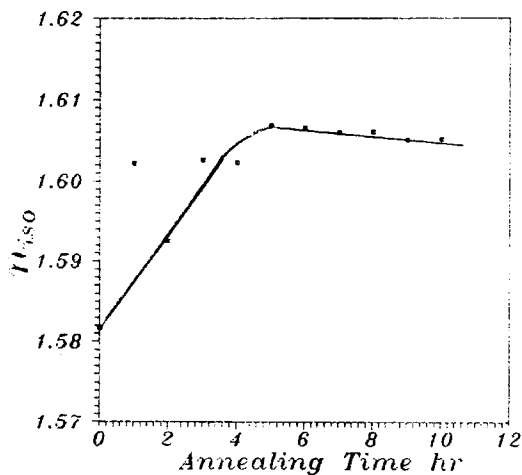


Figure 4 Relation between annealed time (h) and isotropic refractive index n_{iso} constant temperature 160°C.

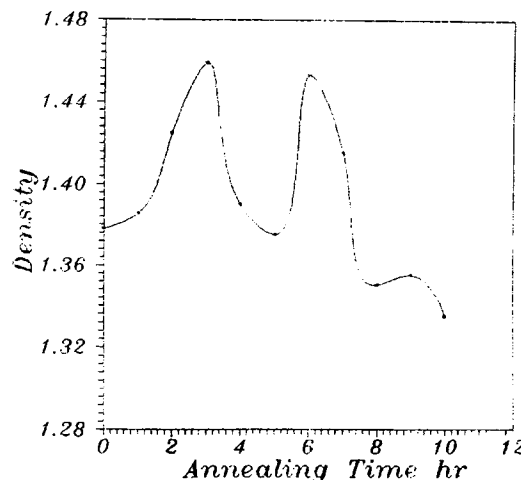


Figure 5 Relation between annealed time (h) and variation of the density ρ at constant temperature 160°C.

$$F_{\theta} = [n_1^2 n_2^2 / n_{\parallel}^2 n_{\perp}^2] \times [n_{\parallel} + n_{\perp} / n_1 + n_2] \cdot \Delta n_{\alpha} / \Delta n_{max} \quad (13)$$

This is slightly different from the original simple expression of the degree of orientation in eq. (7) used by Hermans and Platzek²⁴ and Kratky²⁵ can be given by the following equation:

$$F_{\theta} = (1 + a)F_{\Delta} - aF_{\Delta} \quad (14)$$

$$(1 + a) = 2n_1^2 n_2^2 / n_v^2 (n_1 + n_2) \quad (15)$$

where n_1 , n_2 , and n_v are given from Hermans¹⁸ and $n_v = n_{iso}$. From eq. (15), the constant a was calculated and found to be 0.880.

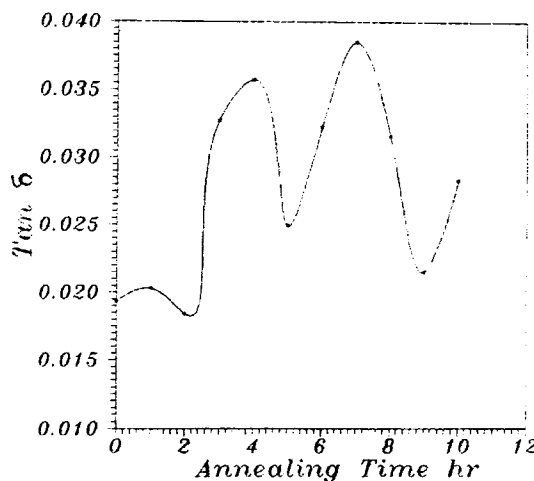


Figure 6 Relation between annealed time (h) and the mechanical loss factor $\tan(\delta)$ at constant temperature 160°C.

Table I Refractive Indices, Birefringence, and Optical Orientation Function for Annealed PET Fibers

Annealing Time (h)	n_a^{\parallel}	n_a^{\perp}	Δn_a	$\frac{\phi^{\parallel} - \phi^{\perp}}{\phi^{\parallel} + 2\phi^{\perp}} \times 10^{-2}$	$\langle P_2(\theta) \rangle \times 10^{-2}$	$(\Delta\alpha/3\alpha_0) \times 10^{-2}$
Unannealed	1.606	1.569	0.0366	17.048	15.250	10.35
1	1.682	1.562	0.1201	53.035	50.042	10.35
2	1.686	1.546	0.1395	62.769	58.125	10.35
3	1.687	1.560	0.1268	55.917	52.833	10.35
4	1.693	1.557	0.1355	59.741	56.458	10.35
5	1.694	1.564	0.1303	56.910	54.292	10.35
6	1.694	1.563	0.1304	56.998	54.333	10.35
7	1.694	1.562	0.1314	57.498	54.750	10.35
8	1.693	1.563	0.1308	57.215	54.500	10.35
9	1.693	1.561	0.1321	57.907	55.042	10.35
10	1.697	1.556	0.1372	60.101	57.167	10.35

Using deVries' value of $\Delta n_{\max} = 0.24$ for PET fibers,¹⁹ the values of $\langle P_2(\theta) \rangle$, $(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})$, and $(\Delta\alpha/3\alpha_0)$ for PET can be calculated and are given in Table I.

Figure 7 shows the relationship between the optical orientation function $\langle P_2(\theta) \rangle$ and the value $(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})$ gives a straight line. The slope of this straight line gives the constant $(\Delta\alpha/3\alpha_0)$ for PET fibers, which was found to be 0.103496.

Figure 8 shows the relationship between the optical orientation function and annealing times: the optical orientation function increases as the annealing time increases. These results indicate that annealing of PET fibers causes changes in the alignment of polymeric chains.

Figure 9 shows the angle of orientation as a function of annealing times.

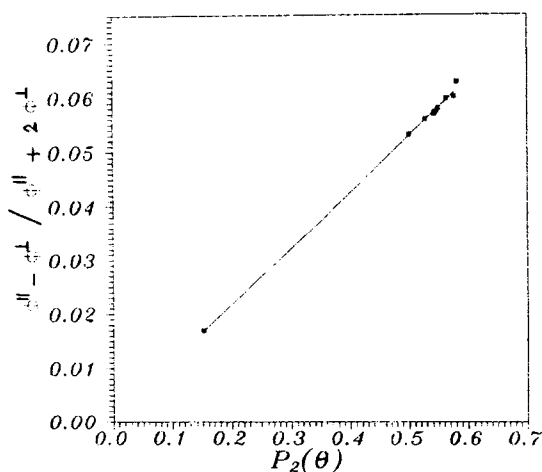


Figure 7 Relation between the optical orientation function $\langle P_2(\theta) \rangle$ and the value $\{\Phi^{\parallel} - \Phi^{\perp}/\Phi^{\parallel} + 2\Phi^{\perp}\}$ of annealed PET fibers.

CONCLUSION

From the measurements carried out in the present work investigating the change in optical properties, density, and mechanical loss factor due to the annealing process for polyester fibers, the following conclusions may be drawn:

1. The microinterferograms clearly identify differences in optical path variations due to different annealing times.
2. As n_a^{\parallel} increases, the process of axial orientation increases crystallinity by both orienting the molecules and bringing them closer together, enabling crystallites to form from formerly amorphous regions.
3. Annealing the fibrous structure, however, affects the diffusion properties.

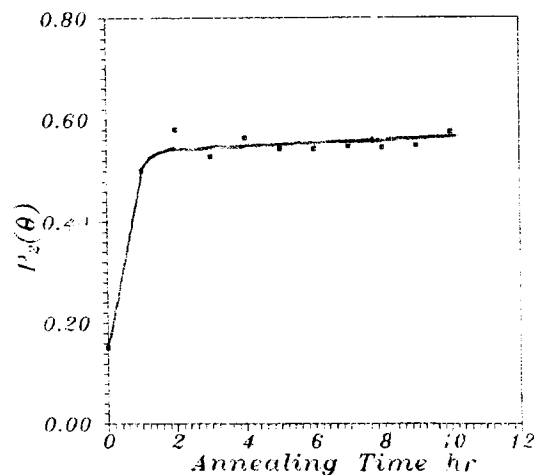


Figure 8 Relation between the optical orientation function $\langle P_2(\theta) \rangle$ and annealed times (h).

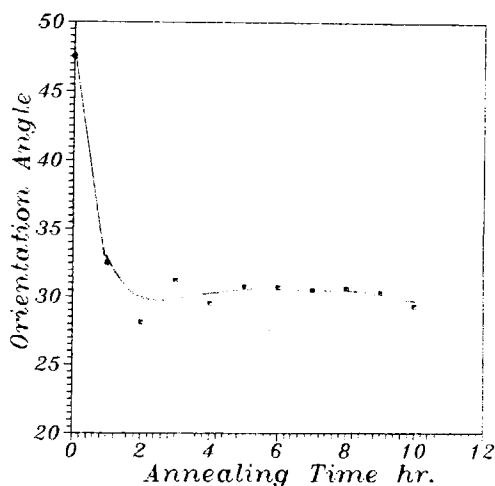


Figure 9 Angle of orientation as a function of annealed times (h).

4. The effects of the annealing process on polyester fibers depends on the time and temperature of annealing.
5. Changes in n_{iso} with annealing time indicate a change in the specific volume of polyester fibers on annealing.
6. The annealing process affects other physical properties (mechanical, 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.
7. Evaluation of $\tan(\delta)$ with the annealing time shows two relaxation times, which means a regrouping due to mobilities of the polyester fiber chain units during the annealing process.
8. Study of the density variations due to annealing indicates the mass redistribution associated with the annealing process of polyester fibers.
9. As the annealing time increases, the orientation angle decreases (Fig. 9).
10. We found that increasing the annealing time increases the optical orientation function and the levels shown in (Figure 7), while the value $(\Delta\alpha/3\alpha_0)$, which depends upon the molecular structure, remains constant.

In conclusion, the structural orientation changes due to the annealing process, as observed by both

two-beam and acoustic techniques, are very promising and further study is required in areas which have not yet been explored.

REFERENCES

1. N. Barakat and A. A. Hamza, *Interferometry of Fibrous Materials*, Adam Hilger, Bristol, 1990.
2. I. M. Fouda and M. M. El-Tonsy, *J. Mater. Sci.*, **25**, 4752 (1990).
3. A. A. Hamza, I. M. Fouda, T. Z. N. Sokkar, M. M. Shahin, and E. A. Seisa, *Polym. and Polym. Composites*, **1**(5), 367 (1993).
4. A. A. Hamza, I. M. Fouda, T. Z. N. Sokkar, M. M. Shahin, and E. A. Seisa, *Polym. Testing*, **11**, 233 (1992).
5. D. Hofman, R. Leonhardt, and P. Weigel, *J. Appl. Polym. Sci.*, **46**, 1025 (1992).
6. I. M. Fouda and M. M. El-Tonsy, *J. Mater. Sci.*, **25**, 212 (1990).
7. W. H. Wyckoff, *J. Polym. Sci.*, **62**, 83 (1962).
8. S. N. Murthy, H. Minor, and A. J. Latif, *Macromol Sci. Phys. B*, **26**(4), 427 (1987).
9. E. A. Zachariades and S. R. Pater, *The Strength and Stiffness of Polymers*, Marcel Dekker Inc., New York, 1983, p. 121.
10. D. C. Bassett, *Principal of Polymer Morphology*, Cambridge University Press, Cambridge, 1981, pp. 124, 233.
11. M. Pluta, *J. Optica Acta*, **18**, 661 (1971).
12. M. Pluta, *J. Microsc.*, **96**, 309 (1972).
13. A. A. Hamza, T. Z. N. Sokkar, and M. A. Kabeel, *J. Phys. D: Appl.*, **18**, 1773 (1985).
14. I. M. Fouda, M. M. El-Tonsy, and A. M. Shaban, *J. Mater. Sci.*, **26**, 5085 (1990).
15. M. M. El-Tonsy, A. M. Shaban, and I. M. Fouda, *Polym. Bull.*, **25**, 507 (1991).
16. N. Subrahmanyam and Brijilal, *A Textbook of Sound*, Second ed., Vikas, New Delhi, 1979, p. 143.
17. H. Hannes, *Z. Kolloidz Polym.*, **250**, 765 (1972).
18. P. H. Hermans, *Contribution to the Physics of Cellulose Fibers*, North Holland, Publ., Amsterdam, 1946.
19. H. de Vries, *Colloid. Z. Polym. Sci.*, **257**, 226 (1979).
20. I. M. Ward, *Proc. Phys. Soc. Lond.*, **80**, 1176 (1962).
21. I. M. Ward, *J. Polym. Sci., Polym. Sym.*, **53**, 9 (1977).
22. A. Cunningham, G. R. Davies, and I. M. Ward, *Polymer*, **15**, 743 (1974).
23. J. H. Nobbs, D. I. Bower, and I. M. Ward, *Polymer*, **17**, 25 (1976).
24. P. H. Hermans and P. Platzek, *Kolloid-Z.*, **88**, 68 (1939).
25. O. Kratky, *Kolloid-Z.*, **64**, 213 (1933).

Received April 4, 1995

Accepted October 20, 1995