

Optothermal Properties of Fibers. I. Relations Between Optical Properties and Change of the Density and Mechanical Loss Factor for Annealed Polyester Fibers

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SYNOPSIS

Polyester (Egyptian manufacturers) fibers were annealed in the temperature range 80–190°C for time intervals from 1 to 10 h. The density of the annealed fibers was measured by a system based on the theory of vibrating strings. The fiber diameter was also determined, using the laser forward diffraction technique. Refractive indices and birefringence for annealed fibers at different temperatures and constant time, 1 h, were measured by the polarizing interference microscope. The behavior of fiber density and the mechanical loss factor at different annealing temperatures and times were discussed at different optical parameters. The results obtained clarify the effect of annealing time and temperatures on the optical, density, and mechanical loss factor behavior of polyester fibers. Microinterferograms are given for illustration. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Birefringence is a measure of the total molecular orientation of a system; it is an excellent property to use for the study of orientation in polycrystalline polymer. The birefringence measurement is thus a rapid and powerful tool for the study of morphological characteristics of deformed polycrystalline polymers. Since birefringence is a measure of the total molecular orientation of the two-phase system, its examination in conjunction with other physical measurements (X-ray, density, mechanical loss factor, etc.) yields considerable insight into the characteristics of the bulk polymer.¹ One of the important parameters characterizing the crystalline structure of polymers is the degree of crystallinity. The relationship between the degree of crystallinity and the density of the polymer has great influence on the viscoelastic properties of crystalline polymers.² Also, it is known that annealing at different conditions leads to a change in the density and loss tangent, etc.²

Long bundles of poly(ethylene terephthalate) (PET, manufactured in Egypt) make up a crystalline

polymer that is among the most convenient ones to study.³ It can be prepared in both the amorphous and the crystallized states within a broad range of values of the degree of crystallinity.³ The dynamic mechanical loss modulus is a measure of the energy dissipated by the polymer as a consequence of molecular relaxation processes in the noncrystalline region of the polymer.¹

In this work, the density of polyester fibers, with different annealing conditions, was measured to estimate the variation due to the annealing process and, on the other hand, to describe how these variations may lead to understanding of the molecular structure response to the applied annealing process. An interferometric method and a resonance technique are used to determine the optical parameters, density, and mechanical loss factor. The relations among the density, mechanical loss factor, and optical parameters were investigated.

THEORETICAL

Refractive Indices of Fibers of Different Annealing Conditions

The Pluta^{4,5} polarizing interference microscope has been used in the following method to determine the

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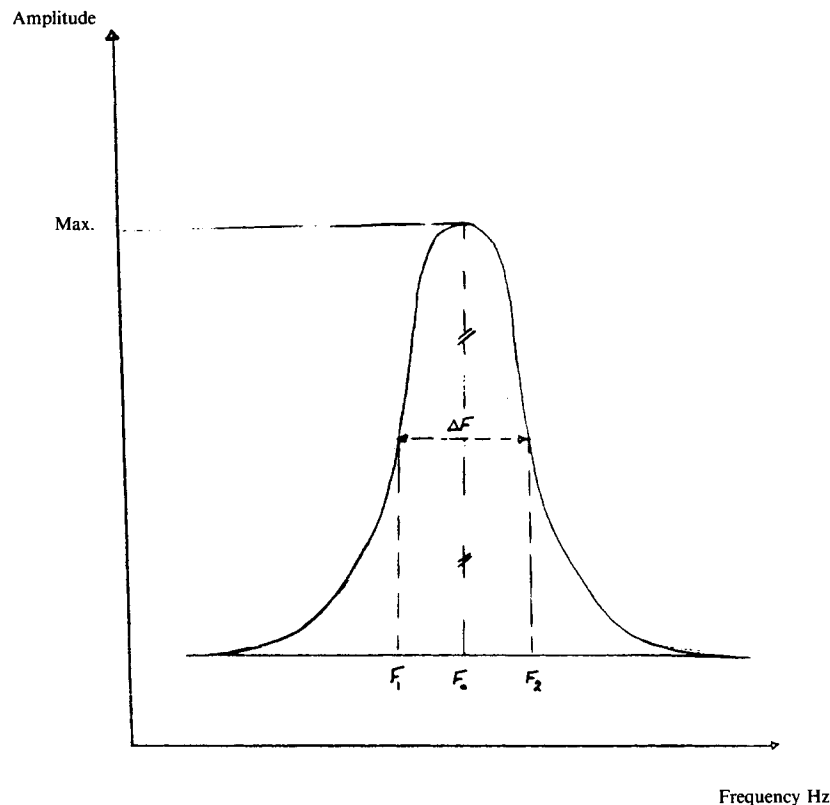


Figure 1 Resonance curve.

refractive indices of annealed and unannealed (PET) fibers: The method determines the refractive indices and the birefringence of polyester fibres at different annealing conditions. The following equations⁶ are used to determine these optical properties:

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

and

$$n_a^{\perp} = n_L + \frac{F^{\perp} \lambda}{h A} \quad (1b)$$

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

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

Determination of Mechanical Loss Factor of Polyester Fibers Using the System of Vibration

The mechanical loss factor, $\tan \delta$, of the annealed fibers was measured by the same system which is used for the density determination. The mechanical loss factor $\tan \delta$ can be determined using the following formula^{7,8}:

$$\tan \delta = \frac{f_2 - f_1}{f_0} = \frac{\Delta f}{f_0} \quad (3)$$

where f_0 is high frequency, and Δf , the half-bandwidth of the resonance curve as shown in Figure 1.

EXPERIMENTAL

Annealing of Samples

Long bundles of polyester fibers were loosely folded in a cocoon form with free ends, then left in an electric oven. The samples were heated at a constant temperature ranging from 80 to $190 \pm 1^\circ\text{C}$ for different annealing times ranging from 1 to 10 h, then left to cool at room temperature, $28 \pm 1^\circ\text{C}$. Thus, for each annealing temperature, there was a set of samples annealed at different times.

Density Measurement

When a string is stretched by a tensional force, T , and put in contact with a vibrator which vibrates at right angles to the axis of the string, a definite length, L , of the string will vibrate stationarily as the resonance condition between frequencies of the vibrator and string is achieved. Let f_0 be the resonance frequency, then⁹

$$f_0 = (P/2L)(T/m)^{1/2} \quad (4)$$

where P is the number of resonance modes within the string's length, L ($P = 1$ for the fundamental mode), and m , the mass per unit length of the string. Thus, the fiber has been clamped at one end while the other end (connected to a small-scale pan) passes over a small frictionless pulley (Fig. 2). Clamp C and pulley W are fixed to an optical bench B. An electromagnetic pulse transmitter (vibrator) T, as well as a piezo-crystal transducer R, are also fixed tightly to B. The fiber sample S is tightened by mass M and left to be in contact with T and R. The vibrator T is stimulated by sinusoidal electric pulses from the adjustable frequency pulse generator G. Pulses from G are also supplied to the frequency counter FC, to be counted and to the first channel CH1 of the double-beam cathode ray oscilloscope, to be taken as the reference wave. The frequency of the vibrator T was increased, from zero, up to the resonance frequency f_0 , at which points on the sam-

ple (from T to R) were vibrated with the same frequency f_0 . Thus, R receives pulses with a maximum amplitude. Pulses from R were magnified by the preamplifier whose output signals were supplied to the second channel CH2 of the CRO. So, the received wave on CH2 possesses maximum amplitude only at resonant modes of the fiber (odd modes were shown out of phase, while even modes were observed in the phase with the reference wave) when the vibrator's frequency was ascendingly changed. Using such a system allows determination of the fundamental resonance frequency, f_0 , of a certain length, L , of the sample (L is the distance between the vibrator and receiver) when it is loaded by a mass, $M(g)$. Then, the mass per unit length, m , of the sample under the test could be calculated from eq. (4). An accurate value of m could be obtained as an average over several modes of resonance. From the obtained value of m , the density, ρ , of the sample material can be easily calculated. If the sample is taken as a bundle of N individual fibers per bundle,

$$\rho = gM/4\pi NL^2 r^2 f_0^2 \quad (5)$$

where g is the acceleration due to gravity, and r , the radius of an individual fiber.

Measurements of the Fiber Diameter

In this work, the fiber diameter, d , was measured by the technique of laser beam forward diffraction, which was previously discussed in detail.^{7,10}

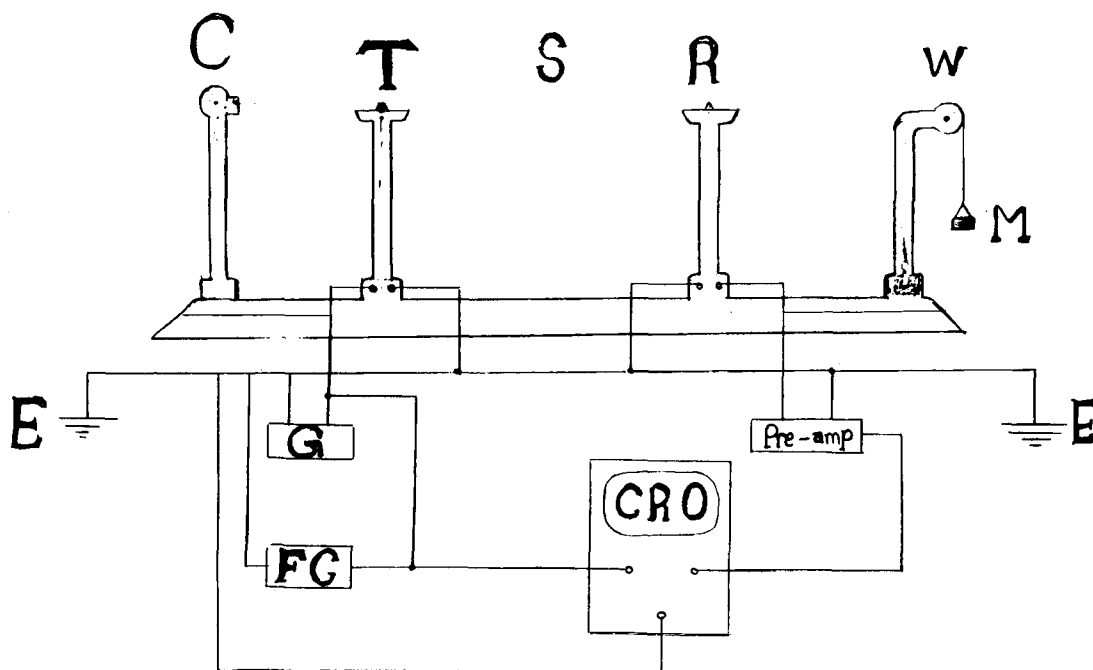


Figure 2 Schematic diagram for the constructed density measuring system.



Plate 1 Diffraction pattern for one sample of PET fiber unannealed.

In this technique, light from a He—Ne laser source falls perpendicular to the fiber axis. The shape of the cross section and the thickness of the fiber was measured from the optical diffraction pattern. The following formula was used to calculate the diameter (d) of the fiber:

$$d = \pm \lambda L/x \quad (6)$$

where $\lambda = 632.8$ nm, the wavelength of the He—Ne laser; x , the distance from the center of the obtained diffraction pattern to the first minimum; and L , the distance between the fiber and screen on which the pattern was produced. The sample was examined at several positions and the average value was considered.

RESULTS AND DISCUSSION

Annealing is performed at a temperature below the melting point of the material and above the temperature of drawing. The effects of annealing increase drastically with temperature and time intervals. Most of the effects of annealing at high temperatures occur very quickly so that extending the annealing over long periods does not make much sense. The interpretation of physical variation associated with isothermal annealing of metals was, in general, fulfilled, but the interpretation of similar variations is somewhat problematical when a polymer undergoes isothermal annealing. These difficulties are due to the anisotropic features of the polymer. Most studies, which involve variations of physical properties, considered polymers as an anisotropic polycrystalline medium, i.e., consisting of crystalline regions suspended in an amorphous medium which is partially oriented. Thus, the polymeric molecular chains were classified as suggested in Ref. 11 into crystalline (regularly and randomly distributed) and noncrystalline (oriented and unoriented; compact, loose, and random compactness).

The dynamic mechanical properties of PET were studied by many investigators. It was established that this polymer has two relaxation regions: one depends on the degree of crystallinity and the other corresponds to the glass–rubber transition.

The loss modulus maximum will be reached only when the temperature has imparted enough energy to the molecules to overcome the thermodynamic stability of the particular state represented by the orientation of the molecules in the noncrystalline region of the polymer.¹ Nevertheless, the feature of the viscoelastic behavior of polyester continues to attract great attention, especially in connection with new research on the morphology of this polymer.^{12–15} Annealing at higher temperature leads not only to an increase in degree of crystallinity, but also to a growth in the dimensions of the crystallites.^{3,16}

Plate 1 shows the diffraction pattern for one sample of PET fiber unannealed. The incident light

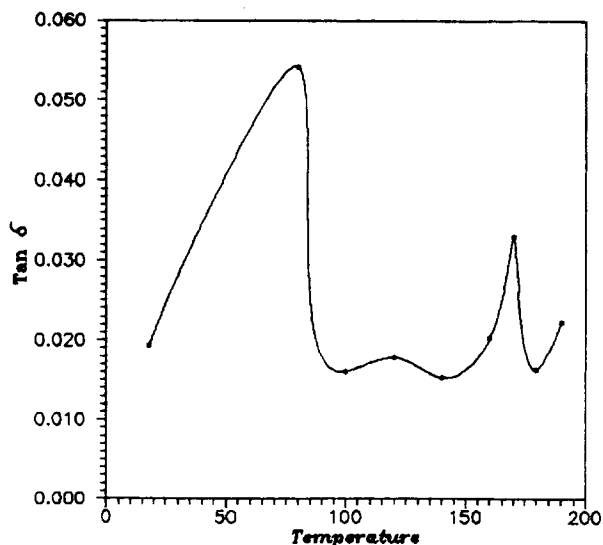


Figure 3 Relation between annealed temperature and mechanical loss factor ($\tan \delta$) for PET fibers at constant time of 1 h.

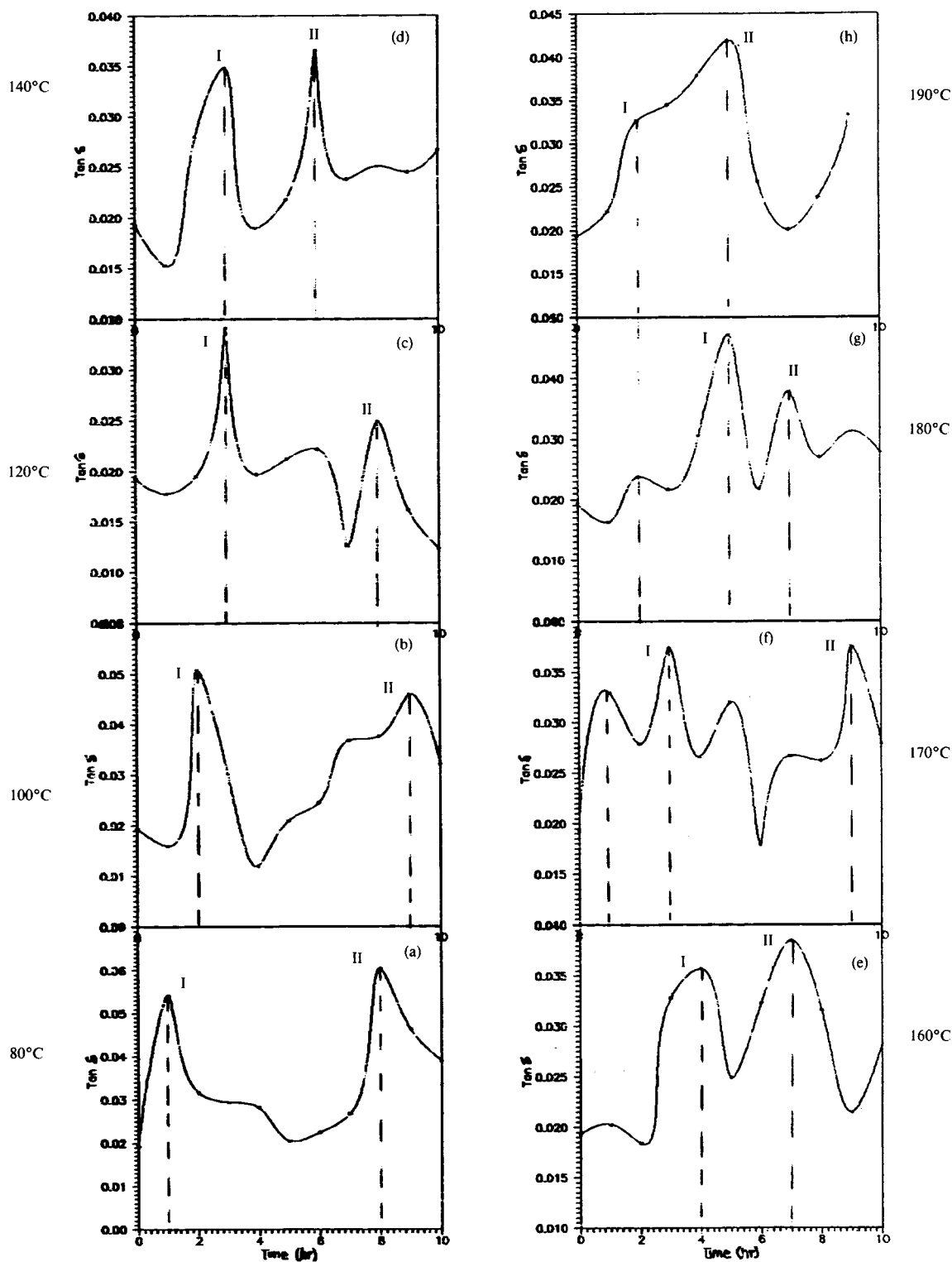


Figure 4 Mechanical loss variations of PET fibers isothermally annealed at 80, 100, 120, 140, 160, 170, 180, and 190°C [(a)–(h), respectively].

from a He—Ne laser source is normal to the fiber axis. The fiber is scanned at nine orientations separated by an angle of 40° about its axis. The posi-

tions of the minima are shown in Plate 1. Equation (6) was used to calculate the fiber diameter. It thus follows from an analysis of the experimental data

present in Figure (3) that two kinds of relaxation peaks appear in annealed PET at 80 and 170°C. Investigation of the mechanical losses in PET shows (see Fig. 4) that there are more than two peaks of the loss tangent and these depend on the ratio of the crystalline part to the amorphous part due to annealing time, annealing temperature, and the transformation processes discussed above.

Only two peaks of $\tan \delta$ are observed in PET at annealing temperatures of 80, 140, 160, and 190°C [Fig. 4(a), (d), (e) and (h)]. Three peaks of $\tan \delta$ are observed at 100 and 120°C [Fig. 4(b) and (c)].

Four peaks of $\tan \delta$ are observed at 170 and 180°C [Fig. 4(f) and (g)]. In all cases, peak (I) corresponds to the glass transition, and peak (II), to the second maximum, and the others are due to annealing transformation processes mentioned before. The increases of these peaks may be due to increase of the amorphous ratio with respect to the crystalline ratio, or that two different kinds of supermolecular organization may exist in PET depending on its previous history. Also, such behavior of $\tan \delta$ seen in Figure 4(a)–(h) may be due to the existence of two kinds of crystallites in PET. These kinds of crystallites depend on the annealing temperatures and time intervals.

From our results, in most of the structural processes associated with the isothermal annealing treatment, it is found that two processes (disorientation and crystal decomposition) cause a decrease in the density of a polymer medium, while the other three structural processes cause an increase in the density.

The density increases as a consequence of the slow partial recrystallization. Thus, the complex variations in density of polyester polymer takes place when it is isothermally annealed.

To confirm the results obtained due to the glass transition peak in Figure 4, we measured the density against the temperature changes [Fig. (5)]. Figure 5 shows that three peaks appeared at 80, 140, and 180°C. Two main peaks at 80 and 180°C, and at 140°C, a transformed peak, were observed due to several prestructural changes for the appearance of the second maximum, which is at 180°C.

Figure 6(a)–(h) can be clarified on the basis of the combination of the structural processes previously discussed. As the annealing temperature and time were increased, the fibers become more brittle; therefore, it was impossible to measure the density of the sample annealed at 190°C for periods longer than 9 h, due to the partial production of ash on the samples. So, Figure 6(a)–(h) shows the density variation of eight sets of polyester fibers with annealing times from 1 to 10 h. Each set was annealed at a

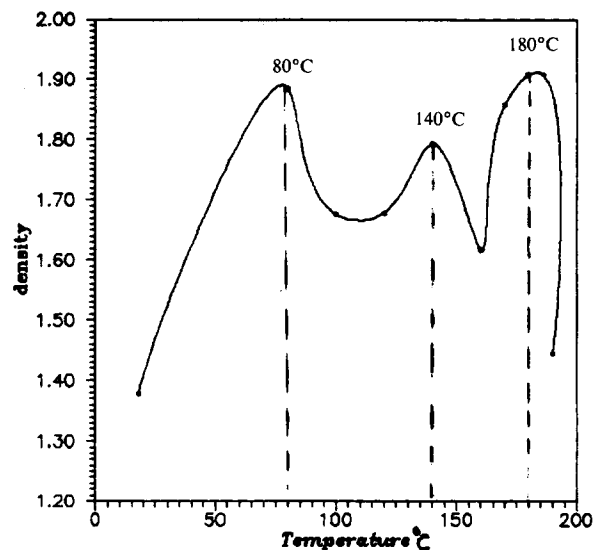


Figure 5 Relation between variation of the density ρ and annealed temperature.

selected temperature: (a) 80°C, (b) 100°C, (c) 120°C, (d) 140°C, (e) 160°C, (f) 170°C, (g) 180°C, and (h) 190°C.

To explain the widely different variations shown in Figure 6(a)–(h), it was essential to take the following assumptions into account: All thermally structural variations may be considered irreversible; at temperatures higher than the glass transition temperature when a polymer is annealed, its structural behavior is due to accumulation of several structural processes. These processes may be summarized as disorientation, recrystallization (nucleation, growth of nuclei), shrinkage, and crystal decomposition.

The optical properties of the annealed polyester samples and mechanical properties are plotted as a function of annealing temperature at a constant time of annealing (1 h). As seen in Figure 7, the birefringence increases with positive sign with annealing and shows a maximum value at $\Delta n = 0.126$ and $T_{\text{ann}} = 180^\circ\text{C}$.

These results suggest two contributions to the birefringence: (1) the result from the orientation of some structural units having positive intrinsic birefringence due to isothermal annealing ($\Delta n = 0.126$ and $T_{\text{ann}} = 180^\circ\text{C}$), and (2) the drop in the birefringence, resulting from the generation of interlamellar voids or the lowered density region upon heating and molecular weight decrease.

Figure 8 shows the variation of n_{iso} of polyester fibers due to changing annealing temperatures at a constant time of 1 h. Figure 8 shows that the isotropic refractive index of annealed polyester fibers is increased by increasing temperature and shows a

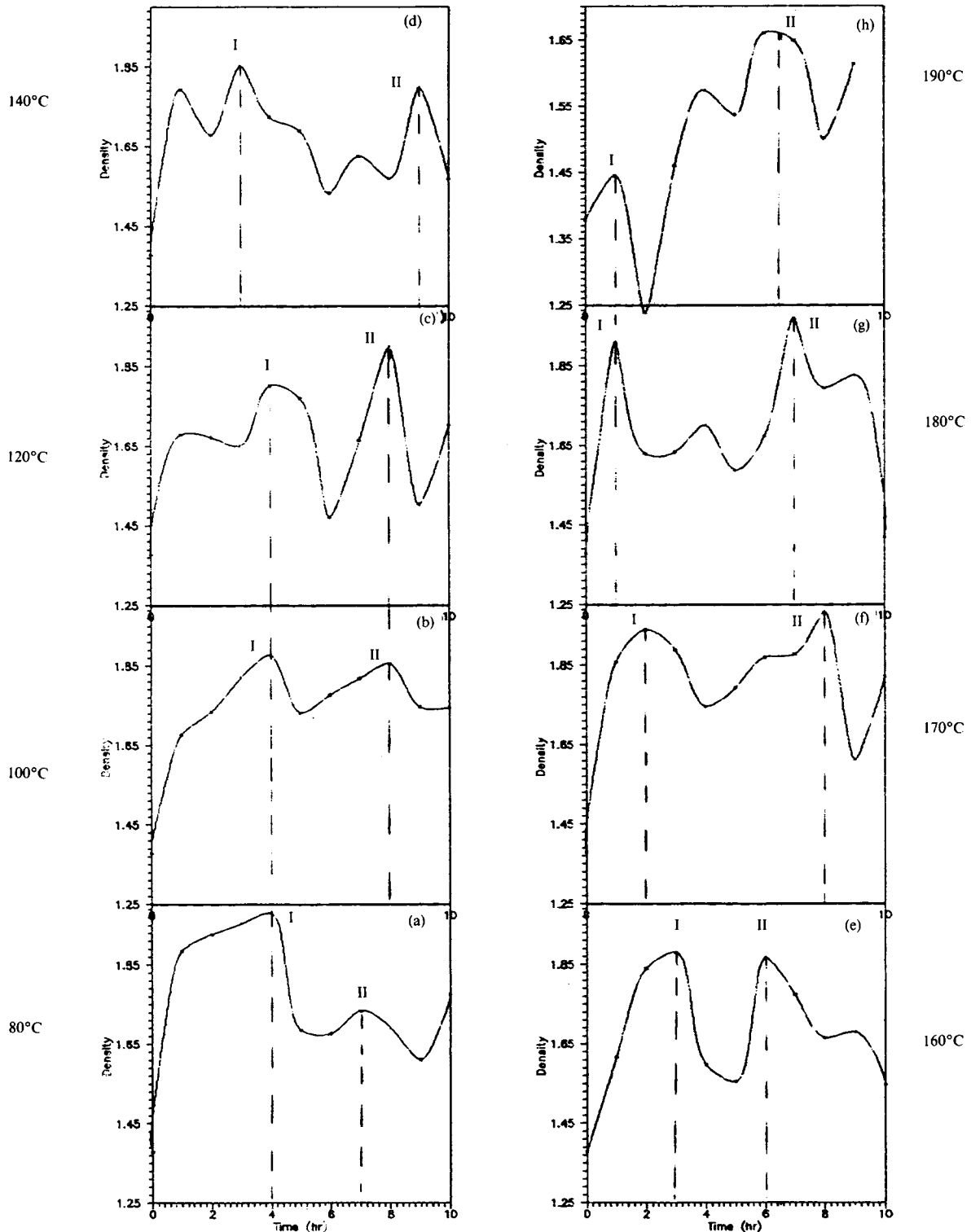


Figure 6 Density variations of PET fibers isothermally annealed at 80, 100, 120, 140, 160, 170, 180, and 190°C [(a)–(h), respectively].

maximum $n_{\text{iso}} = 1.612$ at $T_{\text{ann}} = 180^\circ\text{C}$, and then a sharp drop occurs. These behaviors are related as described due to the orientation (Δn_o) resulting from

the isothermal annealing. Figures 9 and 10 show the variation of n_o^{\parallel} and n_o^{\perp} of polyester fibers by increasing the annealing temperature (annealing time 1 h)

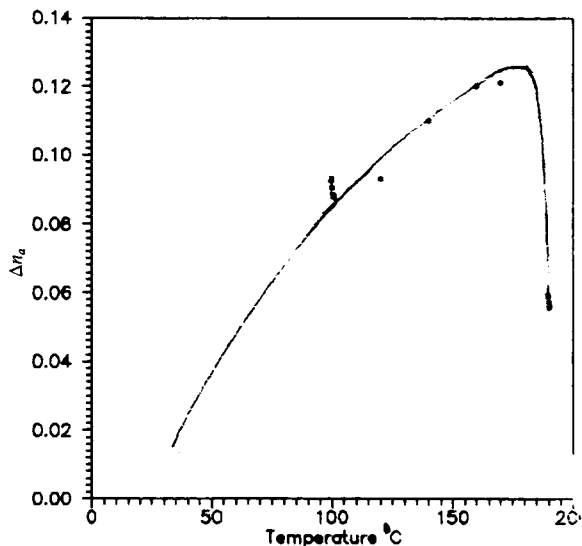


Figure 7 Relation between annealed temperature (°C) and birefringence of PET fibers at constant time of 1 h.

as obtained using the Pluta double-beam interference microscope.

From the variations shown in Figure 8 and 10, it is clear that there is a considerable change in the parallel direction compared to that in the perpendicular direction. These variations may be due to the arrangement of the molecular chains in the preferred axial orientation which constitutes the fiber.

Plate 2(a) shows a microinterferogram of totally duplicated images of unannealed polyester fibers using the Pluta microscope with mono-

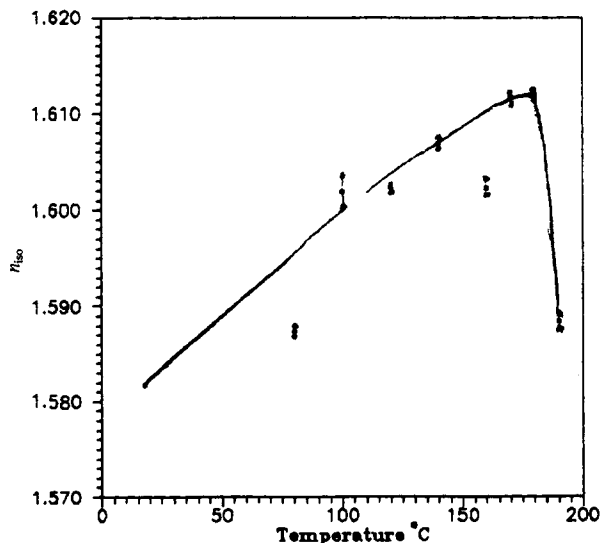


Figure 8 Relation between annealed temperature (°C) and isotropic refractive index for PET fibers at constant time of 1 h.

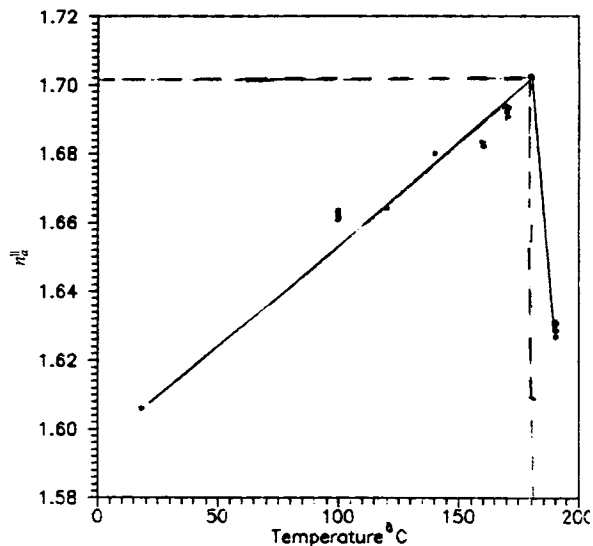


Figure 9 Relation between annealed temperature (°C) and refractive index for light vibrating parallel to the fiber axis $n_{\parallel}^{\parallel}$ of PET at constant time of 1 h.

chromatic light of wavelength 546 nm. The refractive index of the immersion liquid was 1.6035 at 18°C.

Plate 2(b)–(e) are microinterferograms of the totally duplicated images of polyester fiber samples annealed at 80, 120, 160, and 190°C for 1 h, respectively. Monochromatic light of wavelength 546 nm was used. The refractive index of the immersion liquid was 1.661 at 17°C. Using these interferograms and eq. (1a), the mean refractive index of the parallel

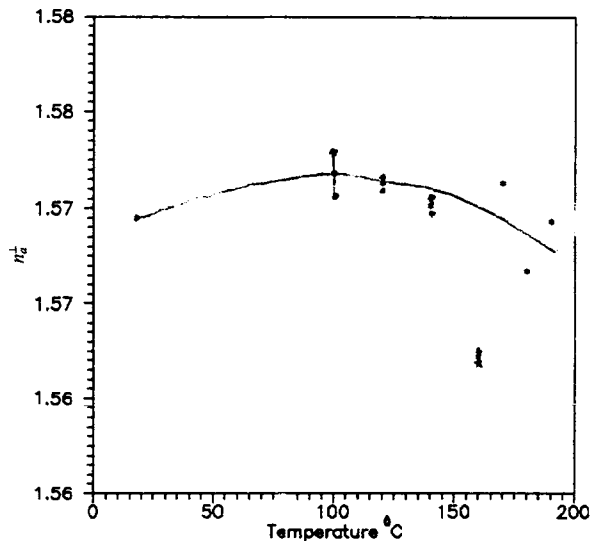
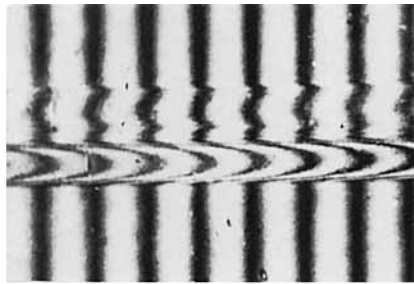
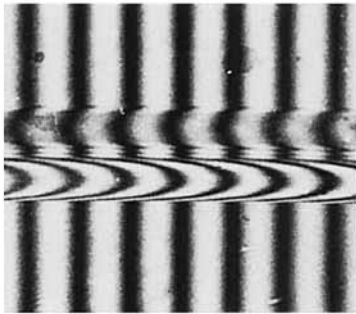


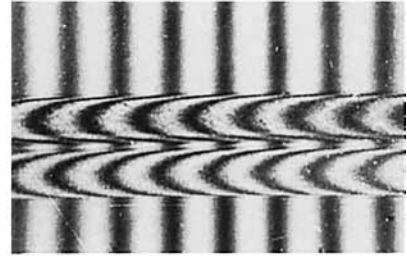
Figure 10 Relation between annealed temperature (°C) and refractive index for light vibrating parallel to the fiber axis n_{\parallel}^{\perp} of PET at constant time of 1 h.



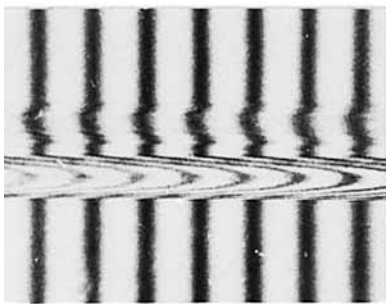
(a)



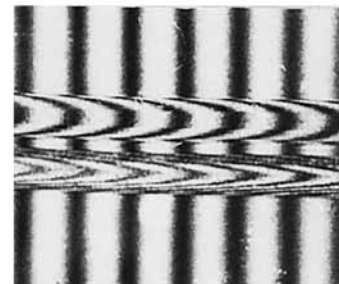
(b)



(d)



(c)



(e)

Plate 2 Two-beam interferograms of totally duplicated image of PET fibers which annealed at different temperatures. Monochromatic light of wavelength 546 nm was used parallel and perpendicular, respectively.

direction at different annealing temperatures was calculated.

Plate 3(a) shows microinterferograms of totally duplicated images of unannealed polyester fibers

using the Pluta microscope with a monochromatic light of wavelength 546 nm.

Plate 3(b)–(e) shows microinterferograms of the totally duplicated images of samples of polyester fi-

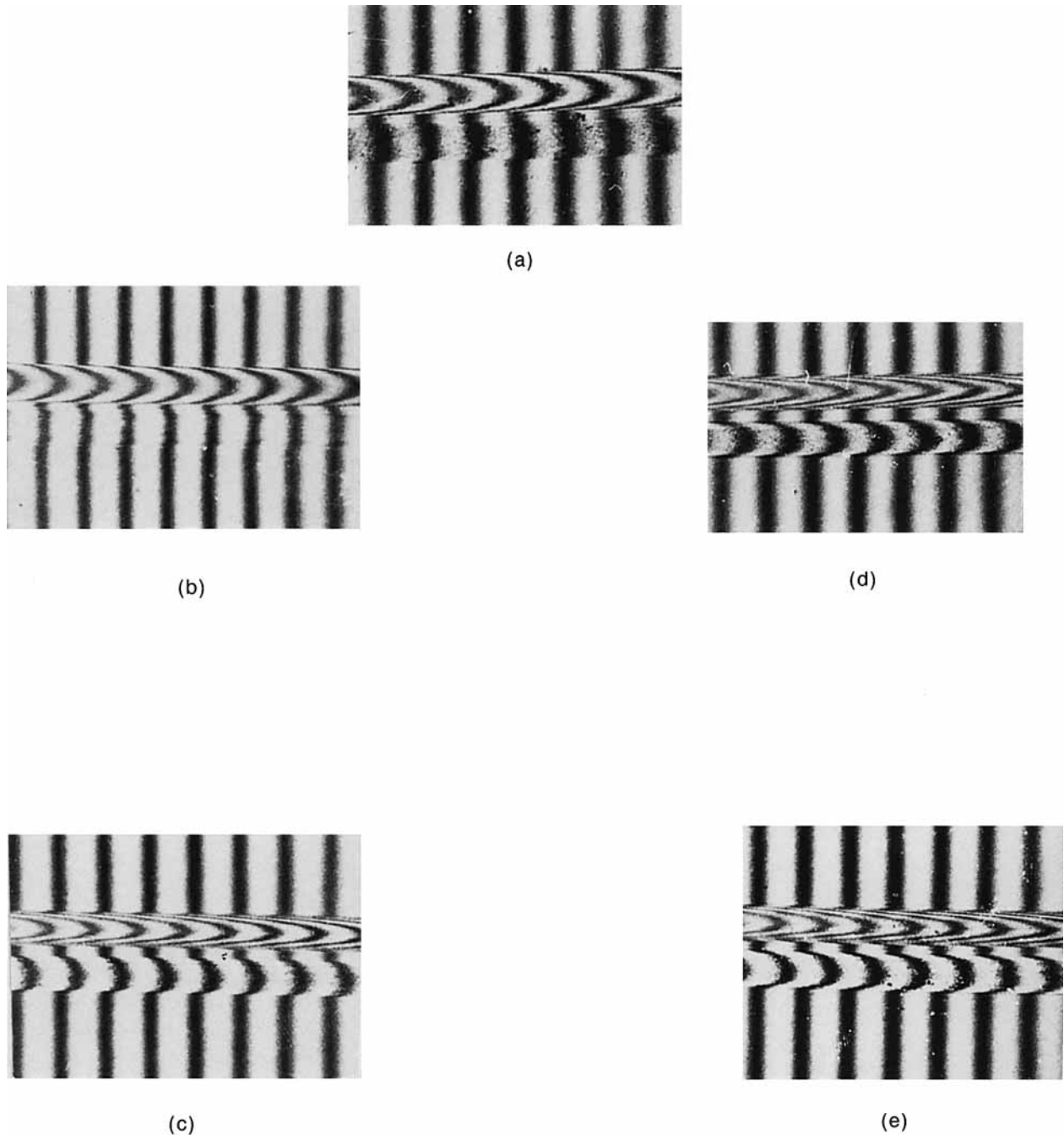


Plate 3 Two-beam interferograms of totally duplicated image of PET fibers which annealed at different temperatures. Monochromatic light of wavelength 546 nm was used parallel and perpendicular, respectively.

bers annealed at 80, 120, 160, and 190°C for 1 h, respectively. Monochromatic light of wavelength 546 nm was used. The refractive index of the immersion liquid was 1.573 at 17°C. Using these interferograms and eq. (1b), the mean refractive index of the perpendicular direction at different annealing temperatures was calculated.

Table I gives the experimental and calculated values of ρ , $\tan \delta$, n_a^{\parallel} , n_a^{\perp} , Δn_{as} , and n_{iso} . As birefringence yields information about the crystallinity and orientation of the polymer molecular chains, the isotropic refractive index of a medium also gives information about not only the molecular packing but also specifications of the unit cell of the crystalline

Table I Values of the Density, Mechanical Loss Factor, the Mean Refractive Indices (n_a , n_a), Birefringence Δn_a , and Isotropic Refractive Indices of Polyester Fibers (PET) Which Annealed at Different Temperatures

	Annealing Time (h)										
	0 (Unannealed)	1	2	3	4	5	6	7	8	9	10
n_a^{\parallel}	1.606	1.682	1.686	1.687	1.693	1.694	1.693	1.695	1.693	1.693	1.697
n_a	1.570	1.562	1.546	1.560	1.557	1.564	1.563	1.562	1.563	1.561	1.560
Δn_a	0.037	0.120	0.142	0.127	0.136	0.130	0.130	0.131	0.131	0.132	0.137
n_{iso}	1.582	1.602	1.593	1.603	1.602	1.607	1.607	1.606	1.606	1.605	1.605
ρ	1.378	1.617	1.839	1.880	1.598	1.555	1.866	1.774	1.664	1.679	1.547
Tan δ	0.0193	0.0203	0.0184	0.0328	0.0357	0.0249	0.0323	0.0385	0.0316	0.0215	0.0283

part of the medium. Hannes used the following formula¹⁷:

$$n_{iso} = \frac{1}{3}(n_a^{\parallel} + 2n_a^{\perp}) \quad (7)$$

to estimate a relationship 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. (7) to determine the isotropic refractive index values for annealed polyester fibers.

CONCLUSION

It is clear that the two-beam and vibrating string technique are useful to clarify the mechanism of the optical behavior density and mechanical loss factor of polyester fiber with different annealing conditions. From the measurement carried out for polyester (Egyptian manufacturers) fibers, the following conclusions may be drawn:

1. The macromolecular structure of polyester fibers is strongly affected by the isothermal annealing treatment.
2. The density of polyester depends, critically, on the annealing conditions.
3. The annealing process affects other physical properties (electrical, mechanical, dyeability, etc), which needs future studies.
4. The effects of the annealing process on polyester fibers depend on the time and temperature of annealing.
5. The change in n_{iso} with annealing temperatures indicates a change in the specific volume of polyester fibers on annealing.

6. As crystallinity and orientation increase, the dyeability of polyester fiber is expected to decrease.¹²
7. Increasing birefringence means increasing the crystallized volume in the polyester medium, reaching a maximum value at the annealing temperature of 170–175°C after 1 h.
8. The crystallized volume of the material is increased due to annealing. Possibly due to the nucleation process, the number of nuclei formed per unit time first increased to a maximum and then decreased.²
9. As tan δ decreases, n_{iso} increases, showing a linear relationship.
10. Measuring tan δ is indicative for the effect of structural transformation changes on the thermal properties of polyester fibers (Fig. 3).
11. As n_{iso} increases, the density increases with time (1 h). This means that the optical anisotropy of the chainlike macromolecules of the fiber is related to its mass redistribution increase due to thermal treatments.
12. The fine-density measuring system used in this work is recommended as a nondestructive technique for the determination of the linear density of individual fiber specimens.

From the above results and considerations, it could be concluded that the practical importance of these measurements provides acceptable results for the optothermal and mechanical parameters. Since Δn_a and tan δ are a consequence of the material annealed, so orientational annealing of polymer may occur not only during fabrication but also after the fabrication process. Also, the molecular mobility is characterized by the loss tangent due to a change in

the energy of intermolecular interaction which depends on the chemical structure of a polymer.

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