Optothermal Properties of Fibers. XIII. Evaluation of the Form Birefringence and Some Other Structural Parameters Due to Thermal Annealing for Polyester (PET) Fibers

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ABSTRACT: In this work, changes in the structure of polyester [poly(ethylene-terephtalate)(PET)] fibers after annealing at constant temperature (120 and 140°C) and different times were studied interferometrically. The density of annealed PET fibers were measured by a system based on vibrating string. The Pluta polarizing interference microscope was used to determine the optical parameters of these fibers. The density and optical results were used to calculate the degree of crystallinity, the form birefringence, the number of monomeric units per unit volume, harmonic mean polarizability of the dielectric, harmonic mean specific refractivity, and the virtual refractive index. The behavior of fiber crystallinity at different annealing conditions were discussed with different optical parameters. Hermans optical orientation function have been compared with the generalized Lorentz–Loranz equation given by de Vries. Microinterferograms and curves are given for illustration. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1955–1963, 1998

Key words: polyester; annealing; crystallinity; formbirefring; orientation; thermal

INTRODUCTION

The molecular mechanism responsible for the variation in the optical properties is clarified by observation of the birefringence. Birefringence depends on molecular orientation in polymer fibers as it contains contribution to the polarizabilities of all molecular units in the sample. 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 polymers.[1]

The good thermal stability is another attractive characteristic that makes polymer fibers suitable for several applications. Therefore, the purpose of improving the thermal properties of polymer fiber by suitable treatments should be considered as a recent approach for research in the field of structural polymeric materials in order to make mate-

rials with new characteristics and expand their utilization. The most available techniques for changing the polymeric structure are annealing and quenching processes.[2–10] The effects of annealing depends on the time during which the sample is held at the annealing temperature. Therefore, thermal treatment was used to vary the degree of crystallinity in polymeric materials.

In a previous article,[11–15] the birefringence values of annealed poly(ethylene terephthalate) (PET) fibers were resolved into crystalline and amorphous contributions. The contribution of form birefringence was neglected in this work. This contribution has been determined and found to be appreciable.

In the present article, the changes in fiber structures due to annealing have been previously studied using two-beam interference and acoustic technique.[13,15] These are utilized to calculate some other structural parameters, the form birefringence (Δn_f), virtual refractive index (n_v), the harmonic mean polarizability of the dielectric

(α_v), the harmonic mean specific refractivity (ε_v), and the values of $[(1 + a) = f_\theta/f_\Delta]$, which is a measure of the nonlinearity of f_θ as a function of Δn.

THEORETICAL CONSIDERATIONS

Two different techniques were used in the present work: (1) Double-beam interferometry, the use of a Pluta interference microscope to calculate the mean refractive indices for light vibrating parallel and perpendicular to the fiber axis $(n_a^\parallel$ & $n_a^\perp)$ and the mean birefringence Δn; and (2) the density measured by a system based on acoustic method vibrating strings. The two techniques were discussed in detail elsewhere.[16–18] Also, by applying the equations used by Hermans[19] and Ward,[20,21] we can obtain the optical orientation parameters as previously discussed in extensive works.

CALCULATION OF THE FORM BIREFRINGENCE

The stress birefringence of a crystalline polymer is given by the orientation of the amorphous chains between crystallites, the orientation of these crystallites, and the form birefringence arising from the interfaces between crystalline and amorphous regions.[22–24] The total birefringence is given by

$$n_\parallel - n_\perp = \chi_c \Delta n_c + (1 - \chi_c)\Delta n_a + \Delta n_f \quad (1)$$

where the subscripts c, a, and f refer to the three contributions, χ_c the volume fraction of crystalline regions. $\Delta n_c = 0.22$,[25] and $\Delta n_a = 0.27$.[25]

The form birefringence, which results from the orientation of asymmetrical particles, not necessarily themselves, display intrinsic birefringence in a medium of different refractive index. The dimensions of such particles are large compared to atomic dimension, yet small compared to the wavelength of light.

CALCULATION OF THE ISOTROPIC REFRACTIVE INDEX

The isotropic refractive index is given by[26]

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

Also, the optical measurements of the refractive indices $n_a^\parallel$ and $n_a^\perp$ were used to calculate the refractive index of the isotropic polymer, on the basis of averaging the polarizabilities and assuming that the samples were transversely isotropic. This leads to the Lorentz–Loranz equation by the following equation[27] to relate polarizabilities and refractive index:

$$\frac{n_{\mathrm{iso}_{(2)}}^2 - 1}{n_{\mathrm{iso}_{(2)}}^2 + 2} = \left[\frac{\rho_i}{3\rho}\right]\left[\frac{n_\parallel^2 - 1}{n_\parallel^2 + 2} + 2\frac{n^2 - 1}{n^2 + 2}\right] \quad (3)$$

where ρ and ρ_i are the densities measurement and the isotropic polymer, respectively, to estimate a relation showing the crystallization inhomogenity for some types of polymers. The resulting values of $n_a^\parallel$, $n_a^\perp$, and ρ are used with eq. (3) to determine the isotropic refractive index values for annealed PET fibers, where $\rho_i = \rho_a = 1.336 \times 10^3$ kg/m^3.

MEAN POLARIZABILITY OF A 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–Loranz by the following equations.

$$\frac{n^{\parallel 2} - 1}{n^{\parallel 2} + 2} = \frac{N\alpha^\parallel}{3\psi} \quad (4)$$

An analogous formula used for $n_a^\perp$, where $n_a^\parallel$ and $n_a^\perp$ are the mean refractive indices of the fiber for light vibrating parallel and perpendicular to the fiber axis, respectively.

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{N\bar{\alpha}}{3\psi} \quad (5)$$

where $\bar{n}$ is the average refractive = isotropic refractive, $\bar{\alpha}$ is the mean polarizability of a monomer unit, and ψ is the permitivity 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 $N = N_A\rho/M$ where N_A is Avogadro's number 6.02 $\times$ 10^{23} and M for PET = 192.[28] Also, N is equal the number of the dipole moment.

De Vries[29] gave a theory on the basis of the internal filled with the aid of classical electromagnetic theory, in which he generalized the Lorentz–Loranz equation. For monochromatic light, Lorentz–Loranz becomes

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha}{3\psi} \qquad (6)$$

The right-hand member of eq. (6) is proportional to the density ρ (units Kg/m^3) of the medium and may also be written as

$$\frac{n^2 - 1}{n^2 + 2} = \varepsilon\rho \qquad (7)$$

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–Loranz equations become

$$\frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2} = \frac{N\alpha^{\parallel}}{3\psi} = \varepsilon_{\parallel}\rho \qquad (8)$$

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

Also, de Vries defined the invariant refractive index, which he calls the "virtual refractive index" n_v as

$$n_v = \sqrt{1 + \frac{3[n_{\parallel}^2 - 1][n_{\perp}^2 - 1]}{[n_{\perp}^2 - 1] + 2[n_{\parallel}^2 - 1]}} \qquad (9)$$

The virtual refractive index n_v replaces the isotropic refractive index of eq. (2); this equation leads to the harmonic mean polarizability of the dielectric α_v by the following equation:

$$\alpha_v = \frac{3\psi}{N} \cdot \frac{n_v^2 - 1}{n_v^2 + 2} \qquad (10)$$

Likewise, for the harmonic mean specific refractivity, we have

$$\varepsilon_v = \rho^{-1} \cdot \frac{n_v^2 - 1}{n_v^2 + 2} \qquad (11)$$

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

$$F_{\theta} = \left[\frac{n_1^2 n_2^2}{n_{\parallel}^2 n_{\perp}^2}\right] \cdot \left[\frac{n_{\parallel} + n_{\perp}}{n_1 + n_2}\right] \cdot \frac{\Delta n_a}{\Delta n_{max}} \qquad (12)$$

This is slightly different from the original simple expression for the degree of orientation in the following equation:

$$F_{\Delta} = \Delta n_a / \Delta n_{max} \qquad (13)$$

where Δn_{max} is the maximum birefringence for fully oriented fiber and Δn_a is the birefringence of the fiber under investigation. Values ranged between $+1$, 0, and -0.5 according to the following states of orientation: perfect, random, or perpendicular to the fiber axis, respectively. The value of Δn_{max} has been previously determined[27] to be 0.24, used by Hermans and Platzek[30] and Kratky,[31] and can be given by the following equation:

$$F_{\theta} = (1 + a)F_{\Delta} - aF_{\Delta}^2$$
$$(1 + a) = 2n_1^2 n_2^2 / n_v^2 (n_1 + n_2) \qquad (14)$$

where n_1 and n_2 are the refractive indices of fully oriented fiber, where monochromatic light vibrating parallel and perpendicular to the fiber axis are used. The constant a was calculated from eq. (14) and was found to be 0.88.

CRYSTALLINITY EQUATION

The degree of crystallinity χ was calculated from the following equation:[23]

$$\chi = (\rho - \rho_a)/\Delta\rho \qquad (15)$$

where $\Delta\rho = (\rho_c - \rho_a)$, ρ_c and ρ_a are the densities of the crystallinity and noncrystallinity regions, ρ is the experimental measured value of density, $\rho_c = 1.457 \times 10^3$ kg/m^3, and $\rho_a = 1.336 \times 10^3$ kg/m^3. The volume fraction of amorphous material was determined by the relation

$$1 - \chi = 1 - (\rho - \rho_a)/(\rho_c - \rho_a) \qquad (16)$$

where χ is the volume fraction of crystallinity material.

For a 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]:

$$\langle \eta^2 \rangle = 1 - (\rho_a - \rho_c)^2 \chi(1 - \chi) \qquad (17)$$

The values of $\langle \eta^2 \rangle$ for PET fiber are given in Tables IIa and b.

EXPERIMENTAL PROCEDURE

Sample Preparation

Annealing Process

PET fibers were provided by Kafer EL-Dawer Co., an Egyptian manufacture. Each fiber was a bundle of 30 filaments. As received, the fibers had a diameter of 20 μm, a density of 1.378 gm/cm^3, and a birefringence number 0.034.

The samples were distributed in a cocoon form on a glass rods with free ends, which were then heated in an electric oven whose temperature was adjusted to 120 and 140 $\pm$ 1°C. Hence, the samples were annealed for the 1–10 h, then left to cool in air at room temperature 28 $\pm$ 1°C.

The above annealing temperature was chosen above T_g of PET so that the degree of crystallinity and crystallite size would not be altered appreciably, but stresses in noncrystalline chains could be relieved.

### Results

Double-Beam Interferometry

The totally duplicated image of the fiber obtained with Pluta polarizing interference microscope was used to calculate the mean refractive indices $n_a^{\parallel}$ and $n_a^{\perp}$ of PET fibers.[33,34]

Plates 1(a)–(c) and 2(a)–(c) show a microinterferogram of totally duplicated images of PET fiber using the Pluta microscope with annealing time at constant temperature 120 and 140 $\pm$ 1°C at parallel and perpendicular direction, respectively. The refractive index of the immersion liquid was 1.658 and 1.569 at 18 $\pm$ 1°C in parallel and perpendicular directions, respectively. Using these interferograms, the mean refractive index of the parallel and perpendicular direction at different annealing times and constant annealing temperature were calculated. The refractive index of the immersion liquid was selected to allow the fringe shift to be small. Plates 1 and 2 also show that the fringes shift changed as the time of annealing increases and at a constant temperature.
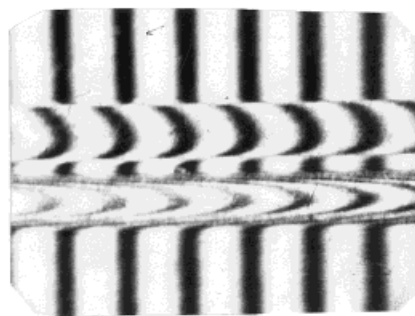
Figures 1(a) and (b) show the relation between the birefringence Δn and the refractive indices differences ($n^{\parallel} - n_v$, $n^{\perp} - n_v$, $n^{\parallel} - n_{\mathrm{iso}}$ and $n^{\perp} - n_{\mathrm{iso}}$). In Figure 1, n_v, and $\Delta n_{\max}$ are used to predict the values of the refractive indices n_1 and n_2 for fully
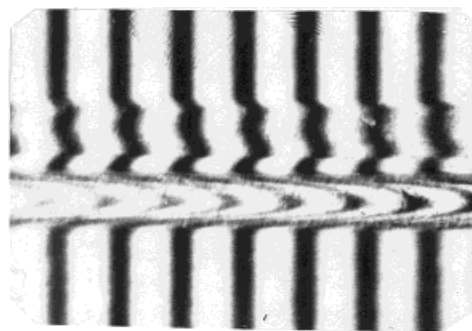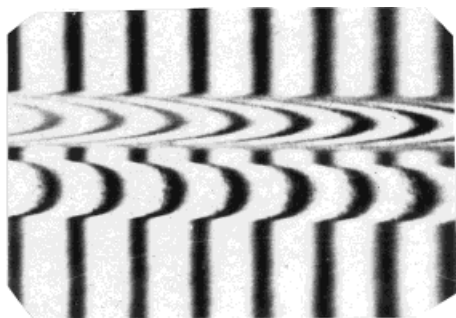

(a)
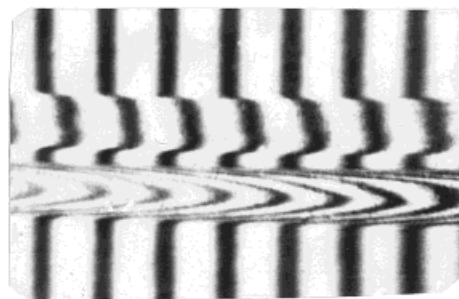
(b)

(c)

Plate 1   (a)–(c) Microinterferograms of the totally duplicated image of PET fiber annealed at 120 and 140°C (λ = 546 nm) in a parallel direction.

oriented fibers. These values are found to be 1.800 and 1.560, respectively, at 28°C, which are in agreement with the published values.[29]

Tables I(a) and (b) give some experimental results for annealed PET fibers, refractive indices, and the calculated values of virtual refractive in-

bles I(a) and (b). Also, in Tables II(a) and (b), the calculated values of $\alpha^{\parallel}$, $\alpha^{\perp}$, and α and the specific refractivity of the isotropic dielectric for parallel and perpendicular directions and its mean value ($\varepsilon^{\parallel}$, $\varepsilon^{\perp}$, and $\bar{\varepsilon}$) at different annealing times are given for annealing PET fibers.

Figure 2 show the relation between the corrected values of the optical orientation function f_{θ}
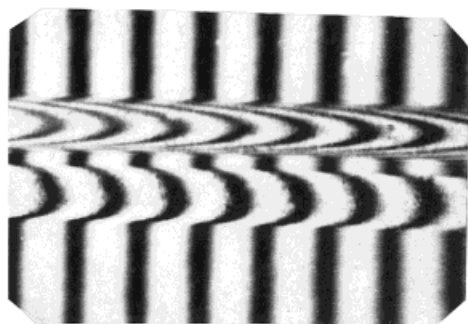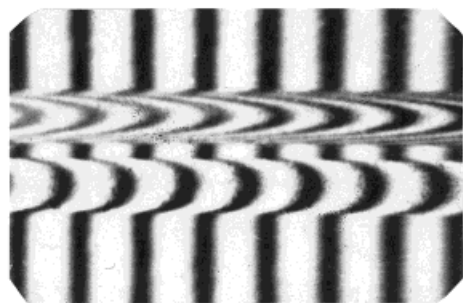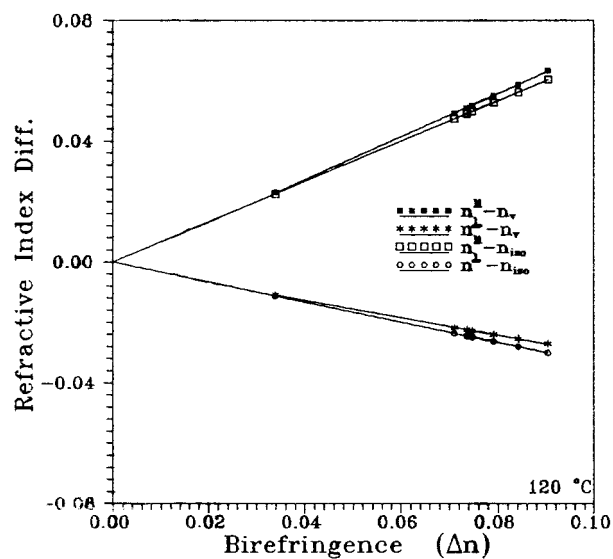

(a)

(b)

(c)

Plate 2   (a)–(c) Microinterferograms of the totally duplicated image of PET fiber annealed at 120 and 140°C of ($\lambda = 546$ nm) in a perpendicular direction.

dex (n_v); the form birefringence (Δn_f) and isotropic refractive index was calculated using eqs. (2) and (3), respectively.

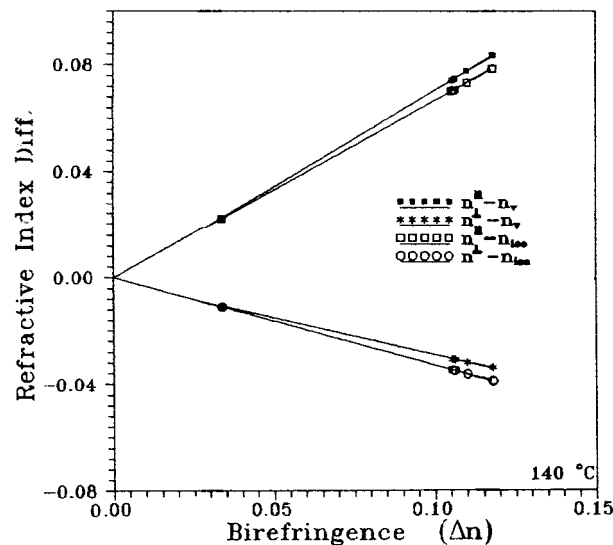The apparent volume fraction of crystallinity (χ) was calculated from eq. (15) using the calculated density values. The results are given in Ta-

(a)

(b)

Figure 1   (a) and (b) Relation between the birefringence Δn and the refractive index differences ($n^{\parallel} - n_v$, $n^{\perp} - n_v$, $n^{\parallel} - n_{\text{iso}}$, and $n^{\perp} - n_{\text{iso}}$) of fiber at 120 and 140°C.

Table I(a)   Experimental Results for Annealed PET Fibers, Refractive Indices, and the Calculated Values of the Virtual Refractive Index (n_v)

Annealing Time (h)	$n_a^{\parallel}$	$n^{\perp}$	Δn_a	χ (%)	$1 - \chi$ (%)	Δn_f	$n_{\text{iso}_{(1)}}$	$n_{\text{iso}_{(2)}}$	n_v
Unannealed	1.606	1.572	0.0339	34.71	65.29	−0.2187	1.584	1.562	1.583
1	1.662	1.572	0.0904	46.61	53.39	−0.1563	1.602	1.573	1.599
2	1.660	1.576	0.0842	56.45	43.55	−0.1576	1.604	1.575	1.601
4	1.657	1.578	0.0791	47.19	52.81	−0.1673	1.604	1.571	1.602
5	1.650	1.579	0.0710	43.97	56.03	−0.1770	1.603	1.574	1.601
7	1.657	1.582	0.0747	65.87	34.13	−0.1624	1.607	1.573	1.605
10	1.646	1.573	0.0736	32.89	67.11	−0.1799	1.597	1.573	1.595

Table I(b)   Experimental Results for Annealed PET Fibers, Refractive Indices, and the Calculated Values of the Virtual Refractive Index (n_v)

Annealing Time (h)	$n_a^{\parallel}$	$n^{\perp}$	Δn_a	χ (%)	$1 - \chi$ (%)	Δn_f	$n_{\text{iso}_{(1)}}$	$n_{\text{iso}_{(2)}}$	n_v
Unannealed	1.606	1.572	0.0339	34.71	65.29	−0.2187	1.584	1.562	1.583
1	1.680	1.570	0.1101	39.09	60.91	−0.1404	1.607	1.580	1.602
2	1.672	1.566	0.1063	59.92	40.08	−0.1337	1.601	1.563	1.597
4	1.674	1.568	0.1060	63.55	36.45	−0.1322	1.604	1.563	1.600
5	1.680	1.562	0.1180	38.10	61.90	−0.1330	1.601	1.576	1.596
7	1.677	1.571	0.1054	45.70	54.30	−0.1417	1.606	1.576	1.602
10	1.682	1.577	0.1060	46.03	53.97	−0.1414	1.612	1.581	1.608

and the Herman's function f_{Δ} for annealing fibers at two annealing temperature, from which f_{θ}/f_{Δ} is found to be 0.8095 for 120 and 140°C. The calculated values of the orientation angle θ from f_{θ} and θ' from f_{Δ} and the number of monomer units per unit volume (N) at different annealing times are given in Tables III(a) and (b).

Figures 3 show the relation between the birefringence Δn and the optical orientation function f_{θ} for annealing fibers.

DISCUSSION

Polyethylene-terephthalate (PET) finds wide commercial application in the form of fibers and films. The conversion of PET into commercial products such as fibers and films requires that the polymer be highly oriented and have a high degree of crystallinity. Amorphous or semicrystalline PET can be thermally crystallized by heating it above its glass transition temperature. However, annealing of fibers produces realignment of the crystalline regions due to thermal mobility. The structure and properties of PET due to annealing are accompanied by reorientation, which is dependent upon the conditions presented.

So the optical parameters measurements and density were used to calculate the structural parameters due different thermal stresses.

Also, to explain the isotropic refractive index result variations; it is preferable to use Lorentz–Loranz equation because it contains the density parameter that is responsible for the polymer material mass redistribution.

To explain the different variations obtained in the form birefringence, this could be explained due to the entropy driven to recoil the chains. As crystallization begins, chains are anchored in the crystals, and long-range motion and further shrinkage are hindered. So overall birefringence changes are going to change the three birefringences, which are responsible for giving the overall birefringence (Δn_c, Δn_a, and Δn_f).

Another explanation may be due to the change in the free-volume effect, which effects the interfaces between crystalline and amorphous regions.

CONCLUSION

From the previous results and discussion, the following conclusions may be drawn.

Table II(a)   Calculated Values of $\alpha^{\|}$, $\alpha^{\perp}$ and α and the Specific Refractivity of the Isotropic Dielectric for Parallel and Perpendicular Directions and Its Mean Value at Different Annealing Times for Annealing PET Fibers

Annealing Time (h)	ρ	$\langle\eta\rangle^2 \times 10^{-2}$ (%)	$\alpha^{\|} \times 10^{-36}$	$\alpha^{\perp} \times 10^{-36}$	$\bar{\alpha} \times 10^{-36}$	$\varepsilon^{\|} \times 10^{-4}$	$\varepsilon^{\perp} \times 10^{-4}$	$\bar{\varepsilon} \times 10^{-4}$
Unannealed	1.378	33.18	2.119	2.023	2.071	2.503	2.389	2.446
1	1.392	36.43	2.314	2.008	2.161	2.733	2.372	2.510
2	1.404	35.99	2.252	1.961	2.106	2.659	2.316	2.491
4	1.393	36.49	2.250	1.962	2.106	2.658	2.317	2.510
5	1.389	36.07	2.315	1.987	2.151	2.753	2.346	2.509
7	1.416	32.92	3.291	2.000	2.146	3.706	2.362	2.477
10	1.376	32.32	2.306	2.016	2.161	2.723	2.381	2.516

Table II(b)   Calculated Values of $\alpha^{\|}$, $\alpha^{\perp}$ and α and the Specific Refractivity of the Isotropic Dielectric for Parallel and Perpendicular Directions and Its Mean Value at Different Annealing Times for Annealing PET Fibers

Annealing Time (h)	ρ	$\langle\eta\rangle^2 \times 10^{-2}$ (%)	$\alpha^{\|} \times 10^{-36}$	$\alpha^{\perp} \times 10^{-36}$	$\bar{\alpha} \times 10^{-36}$	$\varepsilon^{\|} \times 10^{-4}$	$\varepsilon^{\perp} \times 10^{-4}$	$\bar{\varepsilon} \times 10^{-4}$
Unannealed	1.378	33.18	2.119	2.023	2.071	2.503	2.025	2.446
1	1.383	34.86	2.314	2.009	2.161	2.733	2.009	2.552
2	1.409	35.16	2.252	1.961	2.106	2.659	1.961	2.487
4	1.413	33.91	2.250	1.962	2.106	2.658	1.962	2.487
5	1.382	34.53	2.315	1.987	2.151	2.734	1.987	2.540
7	1.391	36.33	2.291	2.000	2.146	2.706	2.000	2.534
10	1.392	36.37	2.306	2.016	2.161	2.723	2.016	2.552

1. It is found that $a = 0.88$ is constant in the annealing processes and is not affected by the variation in the physical process that occurred.
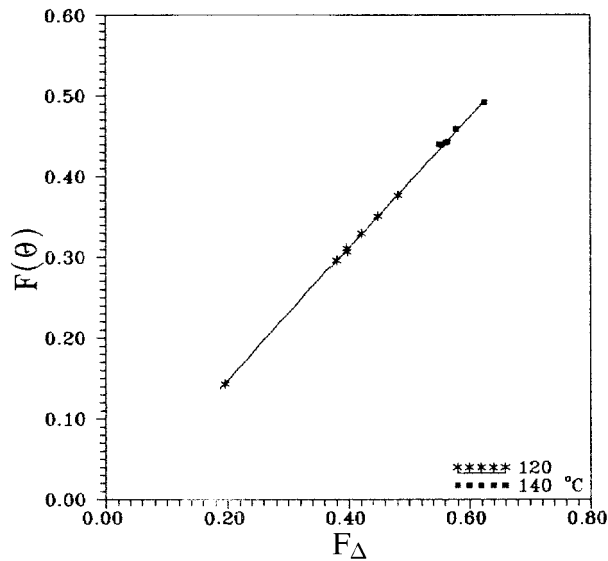
Figure 2 Relation between corrected values of optical orientation function f_θ and the Herman's function f_Δ of fiber at 120 and 140°C.

2. Comparison between $n_{iso(1)}$, $n_{iso(2)}$, and n_v show that every equation has its own merit due to its conditions of derivations and uses.
3. The form birefringence cannot be neglected and must be considered in evaluation of the total structure due to its value, which varies from -0.1322 to -0.2187.
4. The values of calculated form birefringence in Table I increase or decrease for PET according to the ratio between the crystalline and amorphous regions, which depends on the induced thermal conditions.
5. Following different structural parameters due to different annealing conditions gives new physical characteristics.
6. Observed changes in the numbers of monomer units per unit volume are accompanied by change of the density due to annealing and quenching processes, which also indicates the change in the number of the dipole moment.

In conclusion, the structural parameter changes (ε_v, α_v, $\varepsilon^{\|}$, $\varepsilon^{\perp}$, etc.) due to the annealing process

Table III(a)   Calculated Values of the Orientation Angle θ from f_θ and θ' and from f_Δ and the Number of Monomer Units per Unit Volume (v) at Different Annealing Times

Annealing Time (h)	$\varepsilon_v \times 10^{-36}$	$\alpha_v \times 10^{-4}$	$N \times 10^{24}$	f_Δ	f_θ	$\dfrac{f_\theta - f_\Delta}{f_\theta}$	θ	θ'	a
Unannealed	2.425	2.054	43.21	0.141	0.190	0.2579	32.36	49.10	0.88
1	2.453	2.078	43.66	0.377	0.482	0.2178	36.00	40.14	0.88
2	2.439	2.066	44.03	0.351	0.448	0.2165	37.34	41.14	0.88
4	2.461	2.084	43.68	0.330	0.421	0.2162	38.39	41.95	0.88
5	2.465	2.088	43.56	0.296	0.380	0.2211	40.01	43.25	0.88
7	2.432	2.059	44.39	0.311	0.396	0.2146	39.37	42.66	0.88
10	2.470	2.091	43.14	0.307	0.398	0.2286	39.32	42.83	0.88

Table III(b)   Calculated Values of the Orientation Angle θ from f_θ and θ' and from f_Δ and the Number of Monomer Units per Unit Volume (v) at Different Annealing Times

Annealing Time (h)	$\varepsilon_v \times 10^{-36}$	$\alpha_v \times 10^{-4}$	$N \times 10^{24}$	f_Δ	f_θ	$\dfrac{f_\theta - f_\Delta}{f_\theta}$	θ	θ'	a
Unannealed	2.425	2.054	43.21	0.141	0.190	0.2579	47.29	49.10	0.88
1	2.450	2.078	43.37	0.459	0.578	0.2059	32.01	36.92	0.88
2	2.439	2.066	44.16	0.443	0.565	0.2159	32.59	37.55	0.88
4	2.461	2.084	44.30	0.442	0.561	0.2121	32.76	37.60	0.88
5	2.466	2.088	43.33	0.492	0.625	0.2128	30.00	35.60	0.88
7	2.432	2.059	43.62	0.439	0.555	0.2090	33.00	37.70	0.88
10	2.470	2.091	43.64	0.440	0.550	0.2000	33.20	37.66	0.88

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

Figure 3 Relation between birefringence Δn_a and optical orientation function f_θ of fiber at 120 and 140°C.

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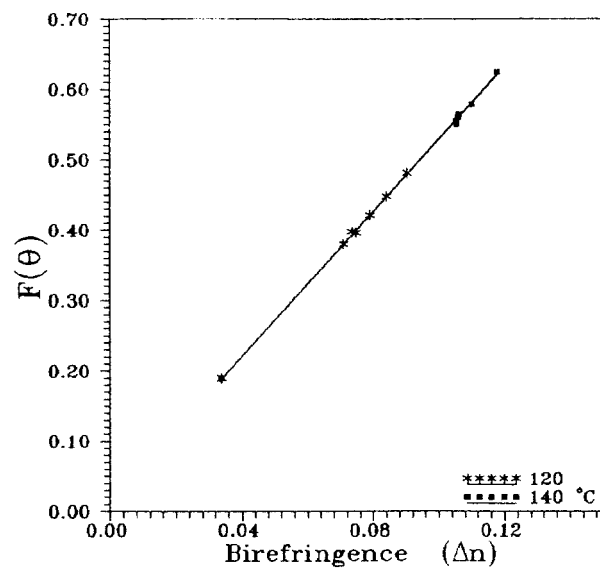
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