Estimation of intrinsic birefringence of poly(ethylene terephthalate) crystal

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The intrinsic birefringence of poly(ethylene terephthalate) crystal has been estimated by means of the Orito method using experimental data and using theoretical calculation. The experimental estimation was performed on the basis of the assumption of a two-phase model consisting of crystalline and amorphous phases and the additivity of birefringence contributions – that total birefringence is equal to the sum of the orientation contributions from crystalline and amorphous phases, and of form birefringence. The value experimentally extrapolated by the Orito method is approx. 0.24. On the other hand, the theoretical calculation was carried out in the usual way using the values of bond polarizabilities according to Bunn and the atomic arrangements within the crystal according to Daubeny *et al.* The calculated value is 0.251. The difference between two results is also discussed.

INTRODUCTION

It is well known that the orientation factors of crystalline and amorphous phases in semicrystalline polymers uniaxially oriented can be quantitatively and separately estimated by the combination of data from X-ray diffraction and optical measurements, provided the usual additivity of birefringences is valid. In order to determine the orientation factors in this way, however, the values of intrinsic birefringences of crystal and amorphous phases ($\Delta^\circ c$ and $\Delta^\circ a$) must be determined first. Although the estimation of intrinsic birefringence of the poly(ethylene terephthalate), PET, crystal has been reported by several researchers, most of those values are too small to be definitely ascribed to intrinsic birefringence[1,4]; (i.e. they could not be used as $\Delta^\circ c$) because the total birefringences measured on highly oriented films or fibres were greater than these values. This work, therefore, was undertaken to re-estimate a value for $\Delta^\circ c$ for the PET crystal by means of an experimental extrapolation method and theoretical calculation.

EXPERIMENTAL

Material

The original unoriented PET films used in the present study were supplied by DIA Foil Co. Ltd. The films, which were 60 μm thick, 4 mm wide and 40 mm long, were stretched at 90°C by a 5–6 elongation ratio and then heat-treated at 216°C under vacuum for 30 minutes at constant length. The uniaxial orientation of the film thus obtained was confirmed by a comparison of X-ray diffraction photographs of the film taken with the beams parallel to two mutually perpendicular directions normal to the drawing direction.

Measurements

For the highly oriented specimens thus obtained, total birefringence (Δt), density at 25.0°C (d), and the orientation factor of crystallites (f_c) were measured. The total birefringences were measured with a polarizing microscope equipped with Bereck's compensator. As the specimens used here have very high retardation, the X–Z planes of various thicknesses which are cut from a single crystal of quartz were simultaneously used as an additional compensator. The thicknesses of specimens were measured with a dial gauge with an accuracy of 1 micron. The densities of specimens were measured at 25.0°C by a flotation method using toluene–carbon tetrachloride mixtures. The orientation factors of the crystallites were determined by the X-ray diffraction method as follows. The specimens were set on a fibre-holder attached to an ordinary diffractometer, and azimuthal intensity distributions of X-ray diffraction were then measured at twice the Bragg angles (17.5°, 22.5°, and 25.7°) for the (010), ($\bar{1}$10), and (100) planes, respectively. The measured intensities were then corrected for polarization, absorption, background noise, and incoherent scattering. From the corrected intensity, further, the amorphous contribution and the overlapping component arising from the adjacent plane were subtracted to obtain the real crystalline diffraction for each plane. Then the degree of orientation of the reciprocal lattice vectors of a plane was graphically evaluated from the azimuthal intensity distribution for each crystal plane, as the average value of the squared cosine of the angle between the vectors and the stretching direction (z), $\langle\cos^2\phi_{hkl,z}\rangle$. The values obtained were substituted in the following equation which was derived by the application of the Wilchinsky method[5]:

$$\langle\cos^2\phi_{c,z}\rangle = 1 - 0.3481\,\langle\cos^2\phi_{100,z}\rangle - 0.7733\,\langle\cos^2\phi_{\bar{1}10,z}\rangle - 0.8786\,\langle\cos^2\phi_{010,z}\rangle \qquad (1)$$

Further, by substituting the value of $\langle\cos^2\phi_{c,z}\rangle$ in the following equation, f_c can be obtained;

$$f_c = 1/2\,(3\langle\cos^2\phi_{c,z}\rangle - 1) \qquad (2)$$

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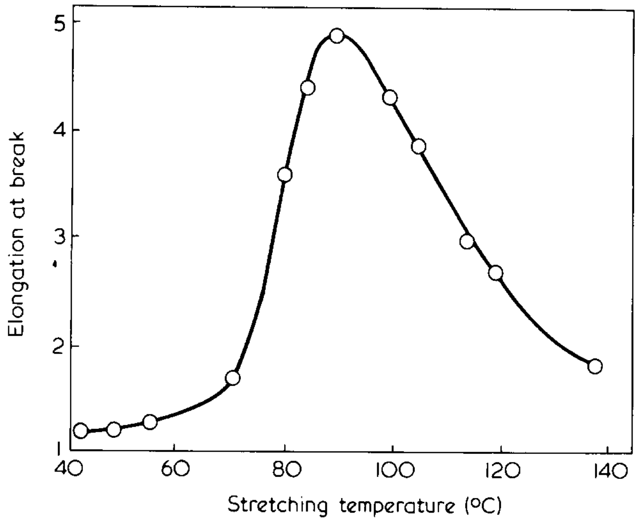

Figure 1 Relation between elongation at break and stretching temperature

RESULTS AND DISCUSSION

The estimation from experimental data was carried out by Orito's procedure[6]. This is briefly outlined below. The total birefringence of a crystalline polymer with cylindrical symmetric orientation can be represented by the additivity[7] of birefringences as in equation 3:

$$\Delta t = \Delta^\circ c f_c X + \Delta^\circ a f_a (1 - X) + \Delta f \tag{3}$$

where $\Delta^\circ c$ and $\Delta^\circ a$ are the intrinsic birefringences of the crystal and amorphous phases, respectively, X the volume fraction of the crystalline phase, f_c and f_a the orientation factors of the crystalline and amorphous phases, respectively, and Δf the form birefringence. The form birefringence results from the anisotropic shape of the crystallites or voids embeded in a matrix with a different refractive index. In general, its value is very small, compared with those of the other two terms, and so it is often[8,9] neglected.

Assuming that f_a is equal to f_c at a high degree of orientation and that the ratio of $\Delta^\circ c$ to $\Delta^\circ a$ is equal to the ratio of density of crystal (d_c) to that of amorphous region (d_a), i.e., $\Delta^\circ c/\Delta^\circ a = d_c/d_a$, the above equation may be transformed into the following equation:

$$\Delta t = \frac{\Delta^\circ c f_c d}{d_c} + \Delta f \tag{4}$$

Furthermore, if Δf is neglected,

$$\Delta t = \frac{\Delta^\circ c d f_c d}{d_c} \tag{5}$$

The equation can also be rewritten as follows;

$$\Delta^\circ c = \frac{\Delta t d_c}{f_c d} \tag{6}$$

The values of ($\Delta t d_c/f_c d$) for a number of highly oriented specimens are calculated from experimental data and then plotted as a function of f_c. Because the assumption that $f_c = f_a$ becomes more valid as the orientation increases, the most reasonable value of $\Delta^\circ c$ is estimated by extrapolating toward $f_c = 1$.

In this study, the optimum conditions for the preparation of highly oriented PET films were determined from the following preliminary experiments. First the elongation at break was examined at various stretching temperatures in an air oven, and the results shown in *Figure 1* were obtained. It is clear from *Figure 1* that, at 90°C, the specimens can be stretched by the highest elongation ratio. Next the total birefringences of specimens stretched at 90°C were measured. The results are shown in *Figure 2*. The value of birefringence increases rapidly with an increase in the elongation ratio and reaches around 0.20 or above at a high elongation ratio. *Figure 2* also shows the data for specimens heat-treated after stretching. It is clear that heat-treatment further increases the value of birefringence. Therefore, it was decided to use the highly oriented specimens which were prepared by combining the stretchings by 5–6 times at 90°C and the heat-treatment, the conditions of which have previously been described in detail.

For the highly oriented specimens prepared thus, Δt, d and f_c were experimentally obtained, and then the values of $\Delta t d_c/f_c d$ were calculated. The experimental data and the calculated values are listed in *Table 1*. The relation between f_c and $\Delta t d_c/f_c d$ is again shown in *Figure 3*. The amount of scatter in the plots is considerably small, compared with that for nylon-6 previously reported by the authors[10]. In addition, the plot of f_c against $\Delta t d_c/f_c d$ gives the predicted linear relationship which is approximated by the broken line drawn in the same Figure. Following the previously outlined procedure, when this line is extrapolated to the intercept at $f_c = 1$, a value of 0.24 is estimated for the intrinsic birefringence of the PET crystal.

On the other hand, the theoretical calculation was carried out by using the values of bond polarizabilities proposed by Bunn[11] and the arrangement of atoms within the crystal determined by Daubeny *et al.*[12]. The principal polarizability (P) in a principal direction of the molecular chain can be

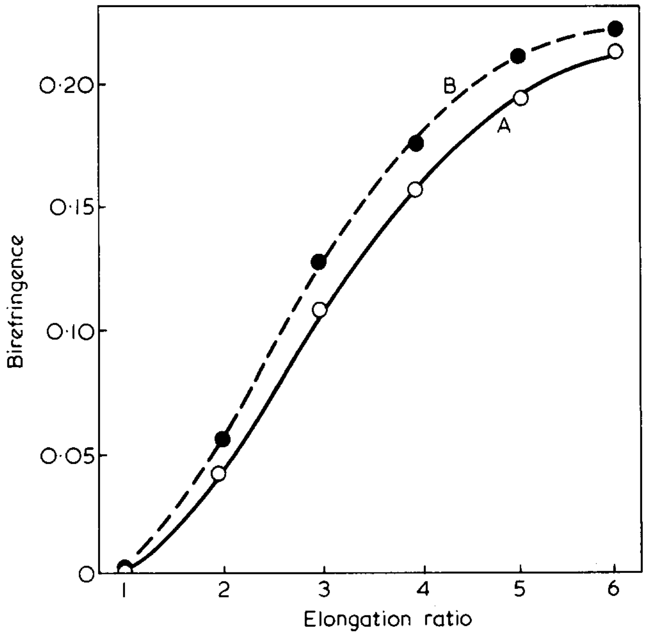

Figure 2 Relation between birefringence and elongation ratio: (A), for the specimens stretched at 90°C in an air oven; (B), for the specimens heat-treated at 216°C under vacuum at fixed length after stretching in the same way as (A)

Table 1 Values of Δt, d, f_c, and $(\Delta t d_c/f_c d)$ for highly oriented specimens

Elongation ratio	Δt_3 x 10^3	d (g/cm^3)	f_c	$\frac{\Delta t d_c}{f_c d}$ x 10^3
5.0	204.72	1.3939	0.919	232.52
5.1	204.89	1.3912	0.931	230.10
5.2	201.90	1.3930	0.928	227.33
5.3	208.18	1.3971	0.945	229.31
5.4	207.85	1.3931	0.940	230.94
5.5	212.22	1.3970	0.949	232.92
5.7	219.86	1.3983	0.954	239.75
5.8	193.50	1.3924	0.908	222.63
5.9	193.82	1.3942	0.941	214.85
6.0	201.48	1.3863	0.903	234.22

d_c = 1.455

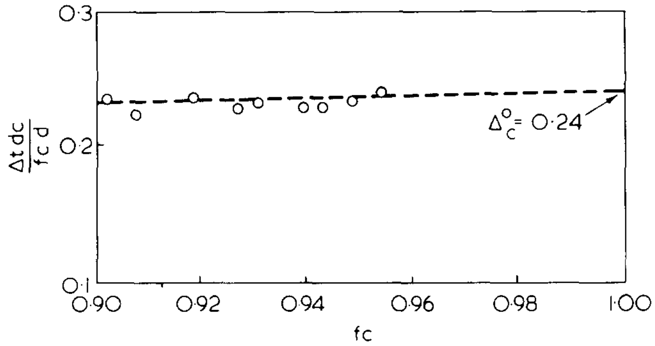

Figure 3 Estimation of the intrinsic birefringence of PET crystal from the experimental data

calculated by the following equation:

$$P = \Sigma P_L \cos^2\theta + \Sigma P_T \sin^2\theta \qquad (7)$$

where P_L and P_T are the longitudinal and transverse polarizabilities of the bond, respectively, and θ is the angle between the principal direction under consideration and the bond. The values of bond polarizabilities used for the calculation are listed in *Table 2.* In this study, three principal directions are decided as follows: the γ direction along the c axis of the unit cell, the β' direction parallel to the benzene ring and perpendicular to the c axis, and the α' direction perpendicular to the above two directions.

The principal polarizabilities in the three directions are calculated to be

$$P_{\alpha'} = 118.07 \times 10^{-25}\,(\mathrm{cm}^3)$$

$$P_{\beta'} = 215.98 \times 10^{-25}\,(\mathrm{cm}^3)$$

$$P_{\gamma'} = 227.06 \times 10^{-25}\,(\mathrm{cm}^3)$$

These values are in agreement with those calculated by Cunningham *et al.*[13] in error less than 3.4%. By substituting these values into Lorentz–Lorenz's equation, the principal refractive indices in the three directions are given as follows;

$$n_{\alpha'} = 1.3692, n_{\beta'} = 1.7621, n_\gamma = 1.8170$$

The intrinsic birefringence of the crystal is further calculated from the above values as follows, assuming a rotational distribution of the α' and β' axes around the γ axis

$$\Delta^\circ c = n_\gamma - (n_{\alpha'} + n_{\beta'})/2 = 0.251 \qquad (8)$$

Table 2 Values of bond polarizabilities presented by C. W. Bunn[11]

Bond	P_L x 10^{25} (cm^3)	P_T x 10^{25} (cm^3)
C–C	9.7	2.5
C–H	8.2	6.0
C–O	14.6	1.7
C=O	20.0	10.0
C_{aro}–C_{aro}	22.5	4.8
C_{aro}–C_{ali}	14.0	3.0

This value is greater than that calculated by Kuriyama[1], 0.217; but it is very close that calculated by Ikeda[2], 0.253 by using the atomic arrangements presented by Tomashpol'skki *et al.*[14]. Although similar calculations for the estimation of $\Delta^\circ c$ have been widely applied to various crystalline polymers, there are a few unsolved problems which must be considered:

(a) The values of bond polarizabilities themselves are still questionable, because the values presented by Bunn[11], Denbigh[15], and Vulks[16] differ markedly from each other for a certain bond.

(b) The effect of an internal field arising from neighbouring bonds within the molecule is neglected in the above calculation. The effect for polyethylene has been studied in detail by Stein[17]. For a structurally complicated polymer such as PET, however, the effect has not yet been clarified.

(c) The effect of secondary bond forces between the molecule in question and the neighbouring molecules in a crystal on the principal polarizabilities of the molecular chain is also neglected in the calculation.

Until these problems can be solved, it is generally considered[18] that the value estimated from experimental data is more reliable than the calculated one.

Okajima *et al.*[3] and Patterson[4] have reported the values obtained experimentally, 0.220 and 0.227 respectively; the former was obtained by extrapolating the relation between $\Delta t/f_c$ and crystallinity (X) to the intercept at $X = 1$; whereas, the latter is the maximum value of birefringence measured on PET filaments stretched by a high draw ratio. These values also are too small to be regarded as the $\Delta^\circ c$ value.

Although the experimental estimation procedure may involve several important problems to be discussed, it seems reasonable to conclude at the present stage that the value obtained experimentally in this study, 0.24, is most reliable and can be used as a fundamental datum for the estimation of orientation factors of PET materials.

In addition, the intrinsic birefringence of the amorphous phase can be calculated to be 0.22, if $\Delta^\circ c/\Delta^\circ a = d_c/d_a$ is valid and d_c and d_a are taken as 1.455 and 1.335, respectively[3].

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