Comparative Study of Orientation in Hot-Drawn Poly(ethylene Terephthalate) by Means of Refractive Index and Microhardness Measurements

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Synopsis

Refractive index and microhardness of drawn samples of poly(ethylene terephthalate) were measured by means of an Abbé refractometer and a microindentation hardness equipment. The optical and mechanical anisotropies determined from these measurements were compared with the birefringences obtained by using compensators and fitted to the affine deformation scheme, showing that microhardness anisotropy is a suitable technique for studying the overall orientation in polymers.

INTRODUCTION

The adequate characterization of the orientation of a drawn polymer may require the joint application of several complementary techniques, due to the structural complexity of polymers. Among the methods of measuring orientation, the study of anisotropy of optical, thermal, and mechanical properties of stretched polymers are well known and properly reviewed.[1-5] The birefringence measurements by means of compensators are particularly simple, but knowledge of the individual refractive indices is sometimes necessary. Because of this, in the present work measurements of birefringence as well as refractive indices of poly(ethylene terephthalate) (PET) are reported and compared. Moreover, the studies of anisotropy of the mechanical properties are mainly referred to moduli and compliances, whereas the anisotropy of microhardness indentations of drawn polymers is scarcely studied.[6] Notwithstanding this, anisotropy of microhardness is expected to be a convenient tool for measuring the orientation produced by drawing a polymer, due to its easy calculation and nondestructive character. Thus, in the following we will compare the results of two techniques of anisotropy measurements (microhardness and birefringence) using the same samples of drawn PET, fitting the latter results to the affine deformation scheme, which application to that polymer is well documented.[7,8]

EXPERIMENTAL

Materials

An isotropic film of PET of 145 μm thickness was used. The number average molecular weight of the polymer was 1.8×10^4, determined from the

viscosity of a solution in o-chlorophenol at 28°C, following the Mark–Houwink relationship[9]:

$$[\eta] = 1.7 \times 10^{-4} M_n^{0.83} \tag{1}$$

Drawing Procedures

Strip-shaped specimens were carefully cut from the PET film. The width of the samples was 4 mm and the gauge length ranged from 2 to 10 cm. The drawing of the PET strips was carried out on an Instron dynamometer at 80°C and various crosshead speeds, ranging from 0.1 to 20 cm/min. The drawing temperature was selected in order to obtain a homogeneous deformation. Draw ratios were determined from the displacement of ink marks initially spaced at 2 mm intervals.

Optical Measurements

Refractive indices of the samples were determined by using an Abbé refractometer (Carl Zeiss, Jena) and a polaroid film. The apparatus can measure indices over the range from 1.300 to 1.700 and is provided with a scale which is accurate to 0.001. A calibrated immersion liquid ($n = 1.700$) was used to ensure good optical contact between the sample and the prism of the refractometer. The measurements were carried out at room temperature and the wavelength of the illuminating light was 551 nm.

Birefringences of the samples were also measured by means of an Ehringhaus compensator attached to an Amplival Pol polarizing microscope. Due to the difficulty of identifying the zero order fringe, the compensator measurements made with white light were compared with the cross-calibrated ones of a previous work[10] and the final lecture was obtained with 551 nm light.

Microhardness Indentations

Microhardness values of the samples were measured using a Vickers indentor attached to a Leitz microhardness tester. A loading cycle of 15 s and a load of 5 g were selected for obtaining small enough indentations in order to avoid any perturbing influence of the platform of the microhardness tester. All the measurements were performed at room temperature. Microhardness values were calculated according to the expression $\text{MH} = 2 \sin 68° \ P/d^2$ (MPa), where P is the contact load (N) and d is the diagonal of the indentation base (mm).

RESULTS AND DISCUSSION

The refractive indices and the mechanical properties (elastic moduli and microhardness values) of the anisotropic samples are designated by the inferior letters x, y, and z, corresponding to three mutually perpendicular directions, normal to the plane of the drawn strip, along the width of the strip, and along the draw direction, respectively.

The compensator technique, which is very simple, measures directly the birefringence Δn_{zy}, i.e., the difference in n_z and n_y, but gives no indication

about the absolute values of these two refractive indices themselves. These values can be measured by using an interference microscope with the adequate immersion liquids and the birefringence Δn_{zy} is calculated from these data. The three refractive indices can be obtained by means of an Abbé refractometer[11] and, consequently, the two independent birefringences can be evaluated. This additional information allows to check if the orientation of the sample is perfectly uniaxial, that is, if $n_y = n_x$. Moreover, the refractometer characterization is much quicker than the interference microscope measurement and slightly slower than the compensator measurement. For these reasons, the Abbé refractometer technique was selected in order to obtain the refractive indices in this work.

Figure 1 shows the birefringence in the plane of the film, Δn_{zy}, of a series of hot-drawn PET samples against the draw ratio λ. Birefringence data, which have been obtained by using two different techniques (an Ehringhaus compensator attached to a polarizing microscope and an Abbé refractometer), are compared with those from Ref. 10, which were determined by means of an image-splitting interference microscope with calibrated immersion liquids. Two of the refractive indices of the samples measured by using the Abbé refractometer, n_y and n_z, are shown as a function of the birefringence Δn_{yz} in Figure 2 together with the previously reported values.[10] The refractive index in the drawing direction, n_z, increases linearly with Δn_{zy} (correlation coefficient = 0.999) while the refractive index in the transverse axis direction, n_y, decreases linearly when Δn_{yz} increases (correlation coefficient = 0.995). The ordinate of the point where these two straight lines intercept the vertical axis corresponds to the refractive index of the isotropic polymer. As can be seen in Figures 1 and 2, the agreement among the data obtained by using the three experimental techniques is excellent and only small deviations are observed for the highest oriented samples. Similar deviations have been reported by other authors who studied optical anisotropy for PET[10] and hydroxypropylcellulose.[12]
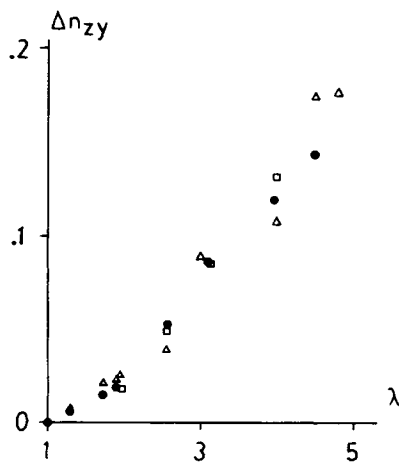

Fig. 1.   Dependence of birefringence on draw ratio: (● and △) refractometer and compensator measurements, respectively; (□) Ref. 10.
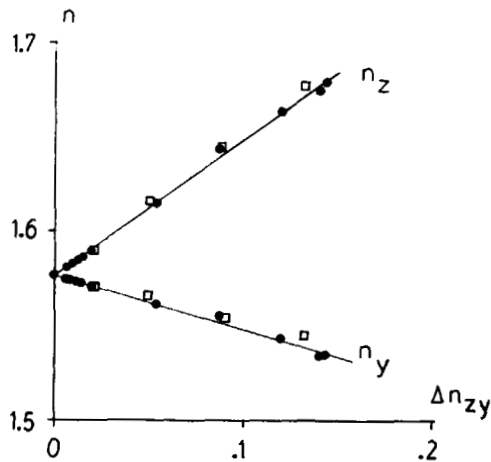
Fig. 2. Correlations between the refractive indices along the draw (z) and transverse (y) directions as a function of the birefringence: (●) refractometer measurements; (□) Ref. 10.

The values of the Hermans function $\langle P_2(\cos\theta)\rangle_{opt}$, which are related to the molecular orientation, have been determined from n_y and n_z measurements by means of the expression

$$\langle P_2(\cos\theta)\rangle_{opt}\Delta\alpha/(3\alpha_0) = \left(\phi_z^e - \phi_y^e\right)/\left(\phi_z^e + 2\phi_y^e\right) \tag{2}$$

where

$$\phi^e = \left(n^2 - 1\right)/\left(n^2 + 2\right) \tag{3}$$

The ratio $\Delta\alpha/(3\alpha_0)$ can be estimated from measurements on highly oriented samples, resulting a value of 0.105 for this parameter.[13] Figure 3 shows that $\langle P_2(\cos\theta)\rangle_{opt}$ is proportional to $\lambda^2 - \lambda^{-1}$. This behavior is consistent with the
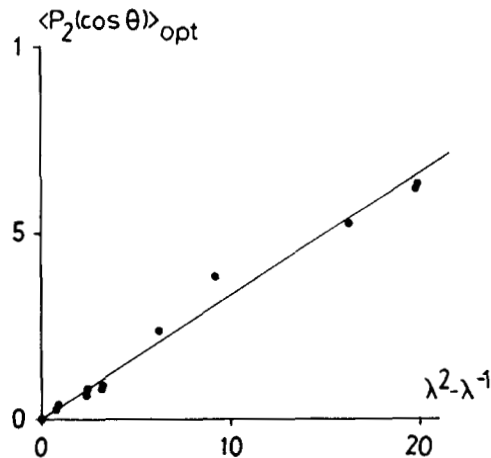

Fig. 3. Dependence of Hermans orientation function on the stretching parameter $\lambda^2 - \lambda^{-1}$ derived from the draw ratio λ.

predictions of the affine deformation scheme[7]:

$$\langle P_2(\cos\theta)\rangle_{\text{opt}} = (\lambda^2 - \lambda^{-1})/(5N) \tag{4}$$

where N is the number of random links per chain. This straight line presents a correlation coefficient of 0.990 and a value of 6.2 is obtained for N. This value is close to those obtained in previous works which range from 5 to 6.[10, 14, 15] These results confirm that the Abbé refractometer is a suitable technique for measuring refractive indices of polymers.

Anisotropy of microhardness measurements in drawn samples of polymers is expected to be an alternative procedure for providing information on the molecular orientation. The base of the Vickers indentations on these samples is not square-shaped because the resistance to plastic deformation when the load is applied and the elastic recovery after releasing the indentor are different at parallel and normal directions with respect to the OZ axis. For uniaxially drawn polymers the length of the diagonals of Vickers indentations depends on the angle ψ formed between the draw direction and the edge of the indentor. This length reaches a minimum, d_z, when $\psi = 0°$ and reaches a maximum, d_y, if $\psi = 90°$. If one of the diagonals of the base of the Vickers pyramid is parallel to the draw direction, the base of the indentation appears to be rhomb-shaped and two well-defined microhardness values can be obtained for the oriented polymer:

$$\text{MH}_i = 2\sin 68° \ P/d_i^2 \qquad (i = y, z) \tag{5}$$

The microhardness anisotropy, ΔMH_{zy}, can be derived from these extreme values by means of the expression

$$\Delta\text{MH}_{zy} = 1 - \text{MH}_y/\text{MH}_z \tag{6}$$

that is, as the ratio of the difference between longitudinal and transverse microhardness to the former.

The rhombic shape of the base of Vickers indentations in stretched polymers reflects the mechanical anisotropy of the sample that is a consequence of the structural anisotropy. As microhardness anisotropy is related to molecular orientation, a correlation between ΔMH_{zy} and the draw ratio can be expected. Figure 4 shows that ΔMH_{zy} rises when λ increases, resembling the relation of Δn_{zy} on λ. The same trend has been previously observed for the dependence of microhardness anisotropy of polyethylene (PE) and polyoxymethylene (POM) on λ.[6] This behavior suggests that Vickers microhardness anisotropy is closely related to birefringence and, consequently, to the optical molecular orientation average, $\langle P_2(\cos\theta)\rangle_{\text{opt}}$. This last dependence is illustrated by Figure 5 and it can be concluded from this result that microhardness anisotropy measurement is an adequate technique to study molecular orientation. Moreover, Figure 6 shows that the values of MH_y and MH_z against ΔMH_{zy} fit two straight lines (correlation coefficients = 0.997 and 0.989, respectively) that extrapolate at the isotropic microhardness value when $\Delta\text{MH}_{zy} = 0$ in a way that parallels the dependences of n_z and n_y on Δn_{zy} (see Fig. 2), showing again the similar behavior of these two orientation measurement techniques.
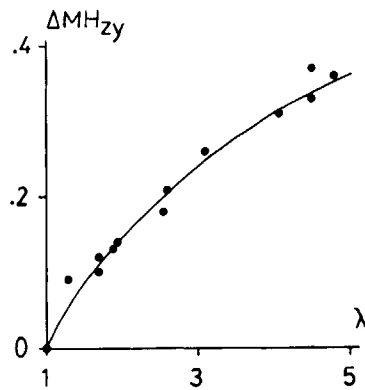
Fig. 4. Anisotropy of microhardness indentations as a function of draw ratio.

It is interesting to analyze the variations of the microhardness extreme values, MH_y and MH_z, with the draw ratio, which are illustrated by Figure 7. It can be seen that MH_z increases with λ and MH_y decreases when λ increases. This is a new example of the agreement between the microhardness anisotropy and the birefringence measurements as can be checked by comparing Figure 7 with previously reported results.[10,16] However, this behavior is different from that observed in cold-drawn polyethylene because for this polymer the indentation diagonals are at their greatest in the isotropic samples, that is, because both MH_y and MH_z increases when the molecular orientation increases.[6] This result applies for draw ratios higher than 5, due to the curvature of the neck, that hinders the measurements for the lowest draw ratios whereas microhardness anisotropy for hot-drawn PET can be measured for moderate draw ratios (lower than 5) because in this case the deformation is homogeneous throughout the gauge length.

The variations of MH_y and MH_z with λ for hot-drawn PET can be explained taking account of the relation of MH to other mechanical properties
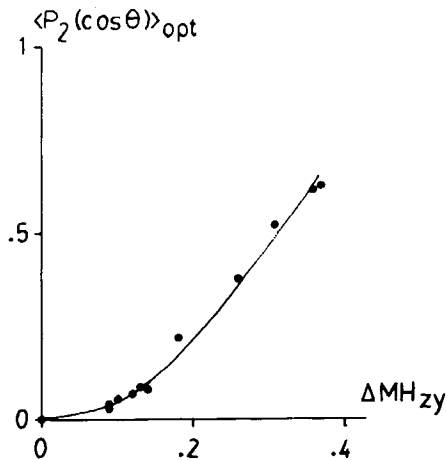

Fig. 5. Dependence of Hermans orientation function on the microhardness anisotropy.
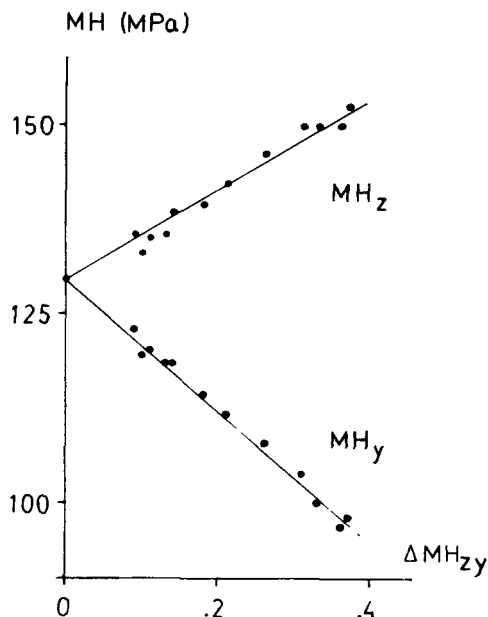
MH (MPa)

Fig. 6. Correlations between the longitudinal (z) and transverse (y) microhardness values and microhardness anisotropy.

because it has been proved that the elastic modulus and the yield stress of different polymers increase with microhardness.[6,17-19] It has been reported that compliance constants of PET, S_{11} ($= 1/E_y$) rises and S_{33} ($= 1/E_z$) falls with increasing molecular orientation.[20] According to the literature results, the modulus of isotropic PET is close to 2 GPa and the values reported for the
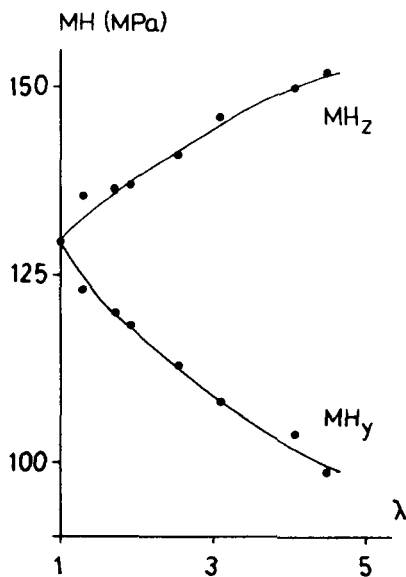
MH (MPa)

Fig. 7. Variations of the longitudinal (z) and transverse (y) microhardness values as a function of draw ratio.

longitudinal and transverse moduli of highly oriented PET samples are over the ranges 9–18 and 0.6–1 GPa, respectively.[20,21] These results show that the transverse and longitudinal moduli are increasing functions of MH_y and MH_z respectively, confirming the relationships between microhardness and elastic moduli previously found for isotropic polymers. Similar arguments can be used in order to explain the dependence of the microhardness of anisotropic PE on λ because it has been reported that E_y and E_z increase with λ for values higher than 5 and, for each value, $E_y < E_z$.[22]

Three conclusions can be drawn from the results of this work. The most important one is that the overall molecular orientation, the most significant factor governing the mechanical anisotropy in PET, is closely related to microhardness anisotropy as has been proved by studying the dependence of Hermans orientation function on ΔMH_{zy}. Moreover, the practical utility of a scarcely used but simple and rapid optical technique, the Abbé refractometer, which provides more information on the refractive indices than other usual procedures, has been again demonstrated. Finally, the correlation between elastic modulus and microhardness, previously found for isotropic polymers, has been extended to oriented samples.

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