

Layer structure formation in oriented poly(ethylene terephthalate) relating to micromechanical properties

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Abstract

Glassy poly(ethylene terephthalate), uniaxially drawn at 25 °C (cold drawing) and at 90 °C (hot drawing), was crystallized in a taut state without shrinkage at 100 °C, 150 °C, 200 °C and 250 °C. The nanostructure and the mechanical properties were surveyed by X-ray diffraction and microhardness. Small-angle X-ray diffraction diagrams reveal typical 4-point patterns characteristic of the cold-drawn samples, whereas 2-point patterns are observed for the hot-drawn ones. Comparison of the molecular and the nanolayer inclinations in both drawings suggests that a mutual supplementary relationship holds between the *c*-axis tilting and the lamellar inclination. The layer structure formation is discussed in the light of these results. In addition, a correlation between the nanostructure formation and the micromechanical properties is offered, highlighting the differences found between the hot- and the cold-drawn materials.

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1. Introduction

Glassy poly(ethylene terephthalate) (PET) can be drawn through neck formation at room temperature. The drawn material is highly oriented, however, it does not exhibit any crystalline order [1]. A gradual increase in the degree of order can be achieved by means of annealing [2]. Bonart was the first researcher to observe the structural transformation taking place upon mechanical drawing of PET, from a totally amorphous into a nematic- and, finally, to a smectic-like states [3]. Yeh and Geil demonstrated using electron microscopy that glassy PET is composed of spherical-like structures in which the molecules exhibit a “paracrystalline” order [4]. The mechanism of transformation from the glassy nematic-like state to the smectic-like phase, and finally to the triclinic structure

has been the subject of a number of investigations and is still a matter of debate [5–9].

Morphological studies on the primary crystallization of drawn PET have been performed by several authors [10–14]. Triclinic PET sometimes reveals a unique tilted-orientation (the –230 orientation), which was first reported by Daubeny et al. [15]. Asano and Seto later studied in detail the dependence of the tilted orientation on the annealing temperature [2]. In addition, cold-drawn PET may also exhibit a lamellar inclination that seems to diminish as the annealing temperature increases [5].

For cold-drawn PET, we discussed the role of the molecular axis tilting and the lamellar inclination on the mechanism of the smectic¹ to triclinic transformation [5]. Starting from the smectic state, molecular and layer inclinations are necessary

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¹ In the following, for the sake of clarity, “smectic-like” and “nematic-like” structures of cold-drawn PET, is referred as “smectic” and “nematic”.

to produce the required density difference between the amorphous and crystalline layers. In addition, microindentation hardness was used to distinguish between the oriented glassy samples, the smectic phase and the crystalline nanofibrils. These microhardness studies provided valuable information on the mechanical behaviour of the semicrystalline fibrils, with special reference to the amorphous intercrystalline layers. It is well known that microindentation hardness is a powerful technique capable of detecting a variety of morphological and nanostructural changes in polymers [16], especially PET [17–22].

In the present work, we wish to examine the crystallization mechanism taking place in glassy PET, hot-drawn above the glass transition temperature ($T_g = 69\text{ }^\circ\text{C}$) without neck formation, as compared to the cold-drawn material. The morphological changes occurring after annealing at temperatures, T_a , above T_g and up to $250\text{ }^\circ\text{C}$ have been followed by X-ray diffraction and microindentation hardness measurements. The mechanism of nanolayer structure formation upon crystallization is discussed, with special emphasis to the process of molecular and layer inclinations. Finally, the nanostructure–micromechanical properties correlation is highlighted.

2. Experimental

2.1. Materials

Amorphous PET ($M_n = 18\,000\text{ g/mol}$) from Toray Co. Ltd., Japan was used in this study. Isotropic films having a thickness of 0.72 mm were uniaxially drawn using a Tensilon UTM 4-100, Toyo Baldwin Co. Ltd. The cold-drawing process was carried out at room temperature ($25\text{ }^\circ\text{C}$) using a drawing speed of 4.0 mm/min . On the other hand, hot drawing was performed at $90\text{ }^\circ\text{C}$ with a drawing speed of 35.2 mm/min . The draw ratio was approximately four in both hot- and cold-drawing processes. The films slightly whitened after the uniaxial drawing, the final thickness being of $\sim 0.30\text{--}0.33\text{ mm}$.

Fig. 1 illustrates the coordinates of the drawn sample, where the Z-axis is parallel to the drawing direction. X- and Y-axis is perpendicular and parallel to the film surface, respectively. Portions of the drawn samples (40 mm in length and 3 mm in width) were annealed in an oven at $100\text{ }^\circ\text{C}$, $150\text{ }^\circ\text{C}$, $200\text{ }^\circ\text{C}$ and $250\text{ }^\circ\text{C}$ for 10^4 s . The sample ends were clamped during the annealing process to fix the sample length.

2.2. Density measurements

The density values of the annealed PET samples are summarized in Table 1 and were measured by the floating method described in Ref. [5]. The volume degree of crystallinity, α , was derived from the density ρ following:

$$\alpha = (\rho - \rho_a) / (\rho_c - \rho_a) \quad (1)$$

where ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively. The amorphous density of the drawn PET material is taken to be 1.37 g/cm^3 , which is the measured density of the cold-drawn amorphous sample [5].

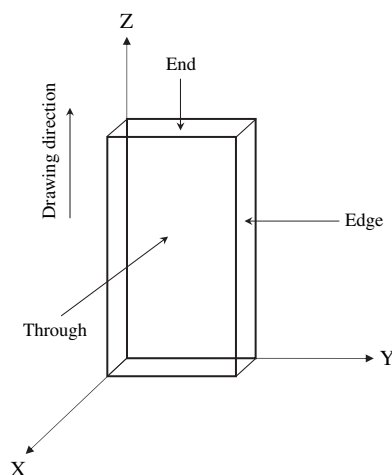


Fig. 1. Coordinates of the drawn PET sample. Schematics of the “through”, “edge” and “end” arrangements.

The density of the triclinic crystal is assumed to be $\rho_c = 1.455\text{ g/cm}^3$ [15].

2.3. X-ray diffraction

The 2D wide-angle (WAXS) and small-angle X-ray diffraction (SAXS) patterns were recorded using a high-intensity X-ray generator (Rigaku RU300). The imaging plate of Fuji Photo Film Co. Ltd. was placed at a distance of 54 mm and 434 mm from the sample for WAXS and SAXS measurements, respectively. The incident X-ray beam was monochromatized using a graphite single crystal ($\lambda = 1.54\text{ \AA}$). A point slit of $100\text{ }\mu\text{m}$ in diameter was used for collimation purposes.

The X-ray diffraction patterns were recorded with three different incident directions as shown in Fig. 1; (i) parallel to the X-axis (“through” patterns), (ii) parallel to the Y-axis (“edge” patterns) and (iii) parallel to the Z-axis (end patterns).

2.4. Microindentation hardness

Microhardness experiments were carried out at room temperature using a Leica Microsystems indentation equipment.

Table 1

Lamellar spacing along the drawing direction, L_Z ; lamellar inclination angle with respect to the ‘through’, θ_t , and ‘edge’ directions, θ_e ; volume degree of crystallinity, α ; crystal lamellar thickness in the “through”, $L_Z\alpha \cos \theta_t$, and “edge” directions, $L_Z\alpha \cos \theta_e$; for cold- and hot-drawn PET annealed at various temperatures T_a for 10^4 s

T_a ($^\circ\text{C}$)	L_Z (nm)	θ_t ($^\circ$)	θ_e ($^\circ$)	α	$L_Z\alpha \cos \theta_t$ (nm)	$L_Z\alpha \cos \theta_e$ (nm)
<i>Cold-drawn PET</i>						
100	10.7	52	53	0.22	(1.5)	(1.4)
150	11.2	41	49	0.39	3.3	2.9
200	12.6	34	39	0.55	5.8	5.4
250	16.4	18	26	0.80	12.5	11.8
<i>Hot-drawn PET</i>						
100	11.2	0	0	0.40	4.5	4.5
150	10.5	7	9	0.51	5.3	5.3
200	11.2	14	12	0.67	7.3	7.3
250	13.7	0	0	0.91	12.5	12.5

A Vickers square-based diamond pyramid was used. Microhardness values, H , are calculated following:

$$H = kP/d^2 \quad (2)$$

where P is the load applied, d is the measured diagonal of the residual impression and k is a geometric constant. A value of $k = 1.854$ is used when P is in N and d in mm to give H in MPa. A load of 0.98 N was applied for 6 s to minimize the creep of the sample under the indenter [16]. The P/d^2 ratio was observed to be constant for different loads.

The sample was positioned with the drawing axis parallel to one of the indentation diagonals. Owing to sample orientation, the residual impression shows anisometric diagonal lengths. We define H_{\parallel} and H_{\perp} as the hardness values derived from the diagonal lengths parallel and perpendicular to the drawing direction, respectively. The indentation anisotropy, ΔH , is defined as [16]:

$$\Delta H = 1 - (H_{\perp}/H_{\parallel}) \quad (3)$$

H_{\perp} is related to the plastic deformation mode of the lamellar stacks. On the other hand, the larger H_{\parallel} values arise from the instant elastic recovery of the material in the drawing direction after load release [5]. The indentation anisotropy is a consequence of the orientation of the molecular axis, giving rise to a larger elastic recovery of the material in the chain direction. It has been shown that ΔH is a suitable parameter for measuring the preferred chain axis orientation [16]. Indeed, a linear empirical correlation has been found between ΔH and the optical birefringence Δn for injection-moulded oriented polyethylene [16].

In addition, the hardness of a polymeric material is well described by a parallel model of alternating amorphous and crystalline regions, with hardness values H_a and H_c , respectively [16]:

$$H = H_c\alpha + H_a(1 - \alpha) \quad (4)$$

where α is the volume degree of crystallinity. Moreover, H_c is related to the crystalline lamellar thickness, l_c , through [16],

$$H_c = \frac{H_c^{\infty}}{1 + \frac{b}{l_c}} \quad (5)$$

where H_c^{∞} is the hardness of an infinitely thick crystal and b is a parameter defined as:

$$b = 2\sigma_e/\Delta h \quad (6)$$

σ_e being the surface free energy of the crystals and Δh the energy required for plastic deformation of the crystalline lamellae.

3. Results and discussion

3.1. Layer structure formation studied by X-ray diffraction

3.1.1. WAXS measurements at room temperature: hot- versus cold-drawing

Fig. 2a illustrates the WAXS pattern of the cold- (left-hand side) and hot- (right-hand side) drawn PET sample before annealing. Fig. 2b shows the plot of the intensity distribution at $2\theta = 20 \pm 2^\circ$ as a function of the azimuthal angle (the Z-axis is the origin of the azimuthal angle values), for both hot- and cold-drawing. For cold-drawn PET, two strong equatorial maxima can be clearly distinguished in Fig. 2a, together with several layer lines on the meridian and no trace of crystalline reflections. The meridional maxima can be associated to the highly oriented nematic-like molecule [23]. In contrast, the WAXS pattern of hot-drawn PET displays a diffuse broad ring with a slightly higher intensity around the equator. No significant crystallinity is observed, however, initiation of crystallization cannot be discarded as the drawing process was carried out above T_g . Fig. 2b shows two maxima in the intensity distribution at 90° and 270° for both drawing processes, however, the peaks are broader and the maximum intensity is substantially smaller for the hot-drawn sample. The above results suggest that cold-drawn PET exhibits a nematic structure where the molecules are preferentially arranged parallel to the drawing direction. In contrast, molecules in the hot-drawn sample are poorly oriented along the drawing axis, i.e., the chain direction exhibits a wide distribution with respect to the Z-axis.

3.1.2. Nanostructure development in cold-drawn PET: comparison of “through” versus “edge” directions

The WAXS patterns of cold-drawn PET annealed at various T_a are shown in Fig. 3, both in the “through” (left-hand side) and “edge” (right-hand side) arrangements. It is noteworthy that the reflection maxima become more intense and sharper as the annealing temperature is raised. This suggests that not only the degree of crystallinity increases with increasing annealing temperature (see Table 1) but also, in addition, improves the degree of perfection of the triclinic crystals. WAXS results also reveal that there is a tilted orientation of the molecular c -axis with respect to the Z-axis of a few degrees (less than 10°), as discussed by Asano and Seto [2].

Fig. 4 illustrates the “through” (left-hand side) and the “edge” (right-hand side) SAXS patterns recorded for the annealed cold-drawn PET samples. The 4-point diagrams shown in Fig. 4 suggest the occurrence of an inclined nanolayer packing, in agreement with the previous published work [5]. It is noteworthy the increase in scattered intensity with increasing annealing temperature, in a similar manner as that observed for WAXS (see Fig. 3). In addition, the inclination angle, θ , defined as the angle between the normal to the lamellae and the Z-axis, is larger in the edge pattern. Table 1 summarizes the θ values obtained in the through-, θ_t , and in the edge-surface, θ_e , together with the layer spacing values along the

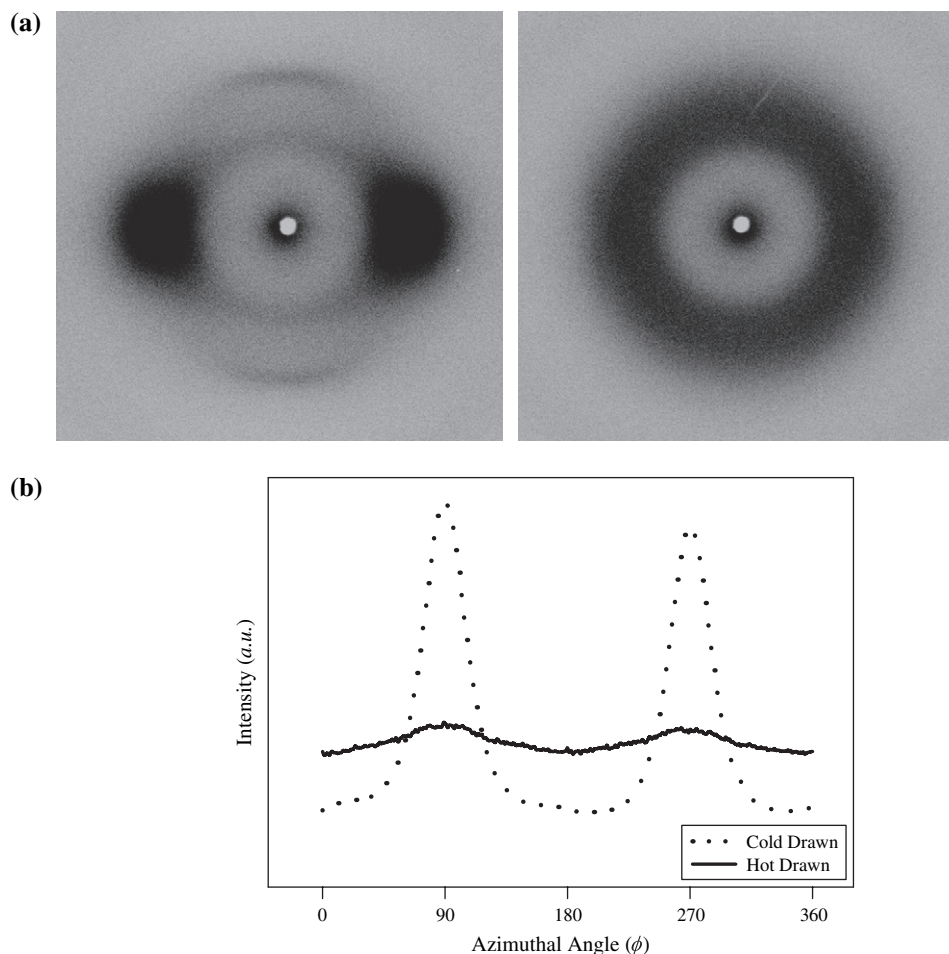


Fig. 2. (a) WAXS pattern of the un-annealed cold- (left-hand side) and hot- (right-hand side) drawn PET samples. (b) Azimuthal scan of the intensity distribution at $2\theta = 20 \pm 2^\circ$, for the un-annealed cold- (dotted line) and hot- (solid line) drawn PET samples.

Z-axis, L_Z . Table 1 also includes the average values of the crystalline layer thickness, l_c , calculated according to:

$$l_c = L_Z \alpha \cos \theta \quad (7)$$

Eq. (7) has been assumed to be valid for $\alpha \geq 0.40$. For $\alpha < 0.40$, the amount of amorphous material outside the lamellar stacks is significant and hence Eq. (7) yields l_c values that should be taken as a lower limit to the average crystal thickness of the material (see l_c values given in brackets in Table 1).

In summary, crystalline layers of annealed cold-drawn PET samples are characterized by a large inclination angle, whereas the crystalline molecules remain nearly parallel to the Z-axis. The mechanism of layer formation is discussed below, as compared to that of hot-drawn PET.

3.1.3. Crystallization of hot-drawn PET upon annealing: comparison with cold-drawn studies

Crystallization of the hot-drawn samples takes place upon annealing at $T_a \geq 100^\circ\text{C}$ (see Fig. 5), leading to a gradual development of order with increasing T_a in a similar manner as that observed for cold-drawn PET (see Fig. 3). However, the following main differences can be distinguished between

the WAXS patterns of the crystallized hot- and cold-drawn samples: (i) the intensity of each reflection for hot-drawn PET is distributed along an arc, in contrast to the distinct (hkl) reflections in the case of cold drawing. This is a consequence of an average lower degree of molecular orientation within the crystals in the hot-drawn sample with respect to the Z-axis in contrast to the cold-drawn one. (ii) The c -axis tilting with respect to the Z-axis is substantially larger for the hot-drawn material ($\approx 30^\circ$), as compared to that found for the cold-drawn one ($< 10^\circ$). For hot-drawn PET at low T_a ($100\text{--}150^\circ\text{C}$), the inclination of the (010) plane is about $10\text{--}15^\circ$, whereas that of the (100) plane is $\sim 30\text{--}40^\circ$. Hence, the average molecular inclination of the triclinic crystal is $\sim 30^\circ$. At $T_a = 200^\circ\text{C}$, the (010) and (100) reflections are displaced up and down from the equator by $20\text{--}25^\circ$, yielding an inclination of the triclinic c -axis of about 30° . Finally, the WAXS patterns at 250°C exhibit a sharp meridional (001) reflection, indicating that the normal to the triclinic (001) planes is parallel to the Z-axis, and hence the molecular c -axis is tilted about 30° .

Fig. 6 illustrates the SAXS patterns of various annealed hot-drawn PET samples. Two-point patterns are clearly displayed for $T_a = 100^\circ\text{C}$ and 250°C , indicating that the normal to the layer surface is parallel to the Z-direction. For

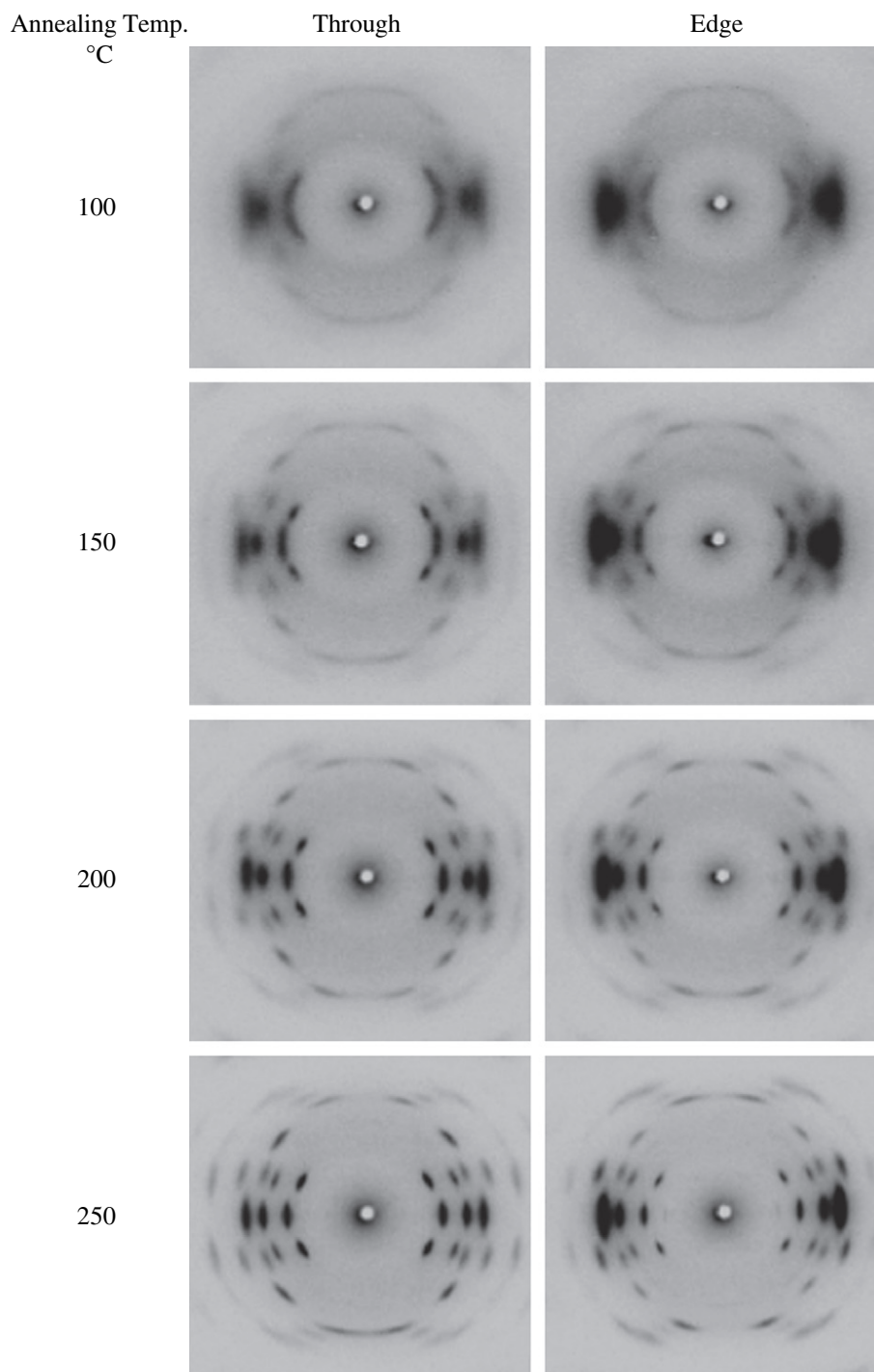


Fig. 3. WAXS patterns of cold-drawn PET annealed at various T_a for 10^4 s, taken in the “through” (left-hand side) and “edge” (right-hand side) arrangements.

$T_a = 150$ °C and 200 °C, a small θ value is observed. Table 1 summarizes the L_Z , θ_t , θ_e , and l_c values (“through” and “edge”, calculated using Eq. (7)) obtained from the analysis of the SAXS patterns of Fig. 6.

Fig. 7 (bottom) illustrates the L_Z and l_c (“edge” and “through”) variation with T_a for the hot-drawn PET. Data for cold-drawn PET, for both the through- and edge-surface, have been included in Fig. 7 (top) for comparison. It is noteworthy that the l_c increases with increasing T_a for both hot- and

cold-drawing. For hot drawing, the l_c values in the “edge” and “through” directions lie within the experimental error, while slightly larger values are found for l_c “through” in the case of the cold-drawn material.

The above WAXS and SAXS results for cold- and hot-drawn PETs are schematically summarized in Fig. 8. For cold drawing, molecules within the crystalline layers remain nearly parallel to the Z-axis while the lamellae exhibit a large inclination angle ($18^\circ \leq \theta \leq 53^\circ$). A gradual increase of T_a leads to larger

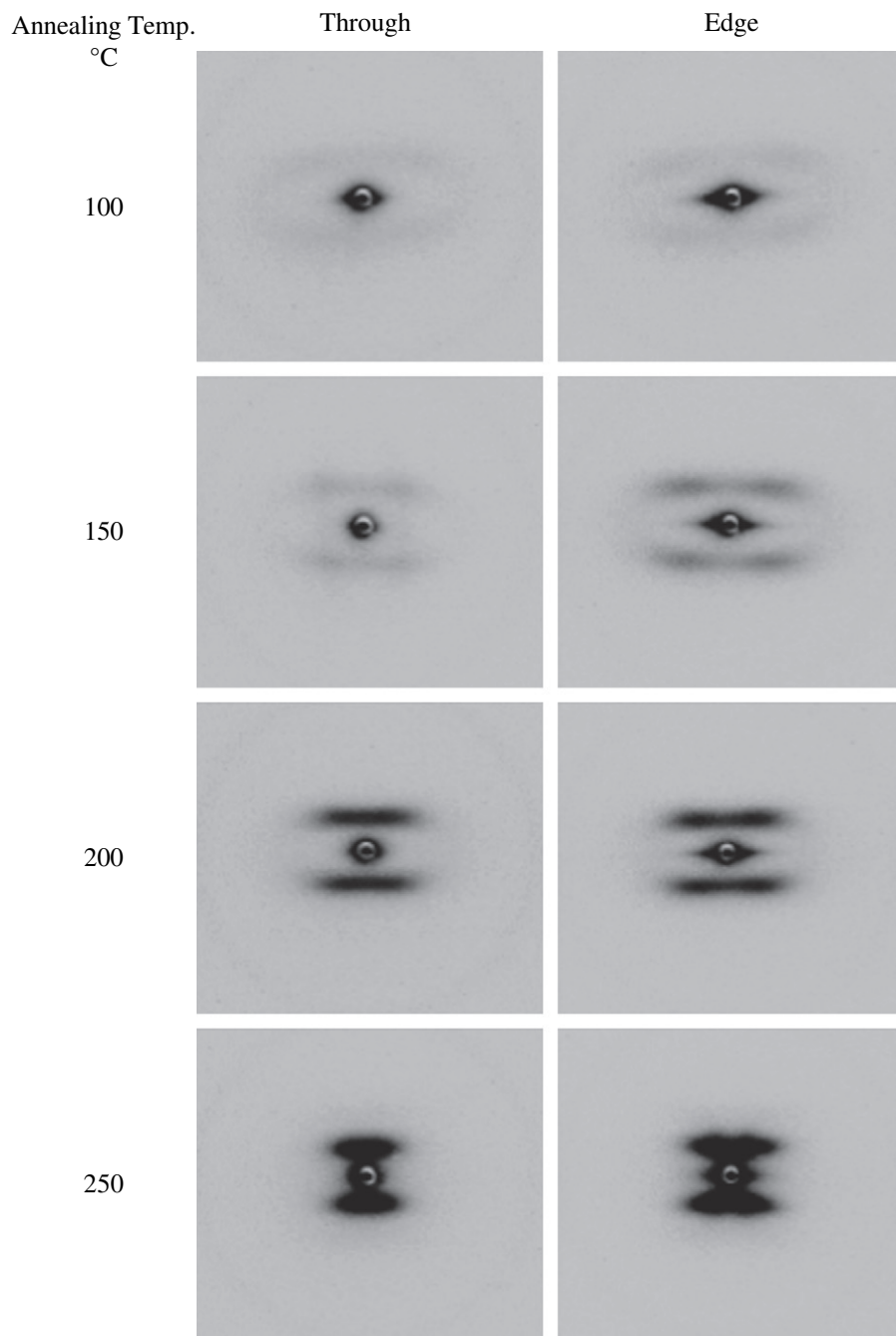


Fig. 4. SAXS patterns, in the “through” (left-hand side) and “edge” (right-hand side) directions, of cold-drawn PET annealed at various T_a for 10^4 s.

l_c values and at the same time the layer inclination angle decreases. In addition, slightly larger l_c and smaller θ values are found in the “through” direction. In the case of hot drawing, molecules within the crystalline layers are largely inclined with respect to the drawing axis ($\sim 30^\circ$), while the lamellar inclination angle remains nearly parallel to the Z-direction ($\theta < 15^\circ$). Similar l_c values are found in the “through” and “edge” directions, both increasing as T_a is raised.

In Fig. 9, the WAXS end patterns of both the cold- and hot-drawn samples annealed at 250°C are compared. The intensity distribution along the diffraction rings of Fig. 9a suggests that

PET crystals exhibit a biaxial orientation in the cold-drawn sample, where the crystalline c -axis is nearly parallel to the Z-axis and the crystallographic b -axis is contained in the ZY film surface. The degree of biaxial orientation increases with increasing annealing temperature (results not shown here), up to the extent shown in Fig. 9a, for the range of T_a considered.

The biaxial orientation in the case of cold drawing is a consequence of the cross-section of the PET molecule: the flat-shaped benzene rings of highly oriented molecules are apt to align with the film surface. Upon crystallization at increasingly high temperatures, the (100) plane moves towards the

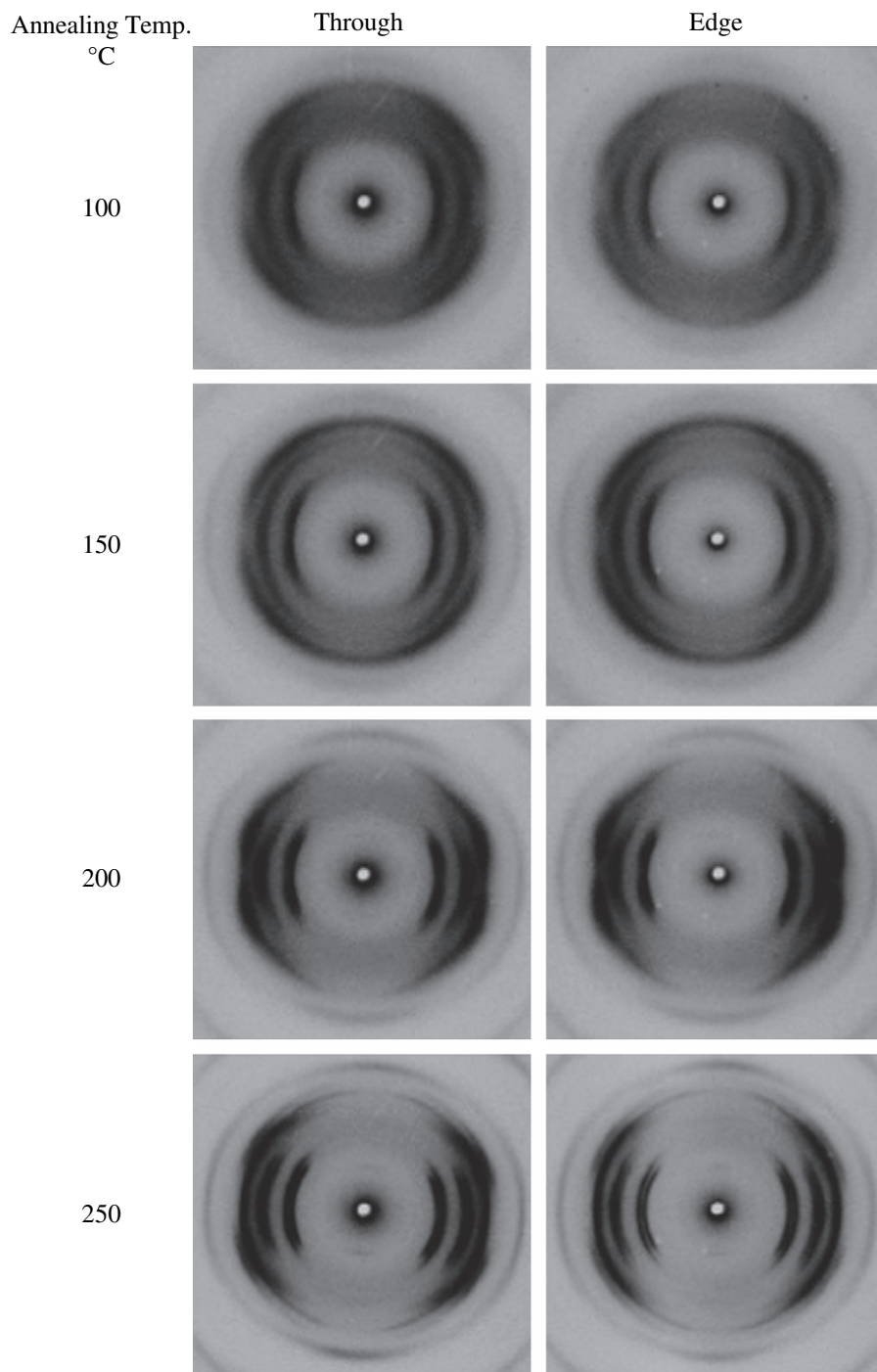


Fig. 5. WAXS patterns of hot-drawn PET annealed at various T_a for 10^4 s, taken in the “through” (left-hand side) and “edge” (right-hand side) arrangements.

Y -axis. The occurrence of biaxial orientation could clarify the differences found between the inclination of the layers in the “through” and “edge” arrangements (see Table 1). Assuming that the layer surface coincides with the (001) plane, then, the fact that the c -axis is not perpendicular to this plane ($\alpha = 98.5^\circ$ and $\beta = 118^\circ$ for the triclinic crystal structure of PET), would explain the $\theta_t - \theta_e$ values approaching $\beta - \alpha = 10^\circ$.

In the case of hot-drawn sample, the end pattern in Fig. 9b has a uniform distribution of intensity along the diffraction

rings in the XY plane. This fact indicates that the material exhibits a uniaxial orientation. As a result, no difference is found between the lamellar inclination angles for the ‘through’ and ‘edge’ X-ray patterns.

3.1.4. Layer formation mechanism

In our preceding studies, the crystallization mechanism for cold-drawn PET was explained via a tilting mechanism, giving rise to inclined surface layers [2,5]. Starting from the highly

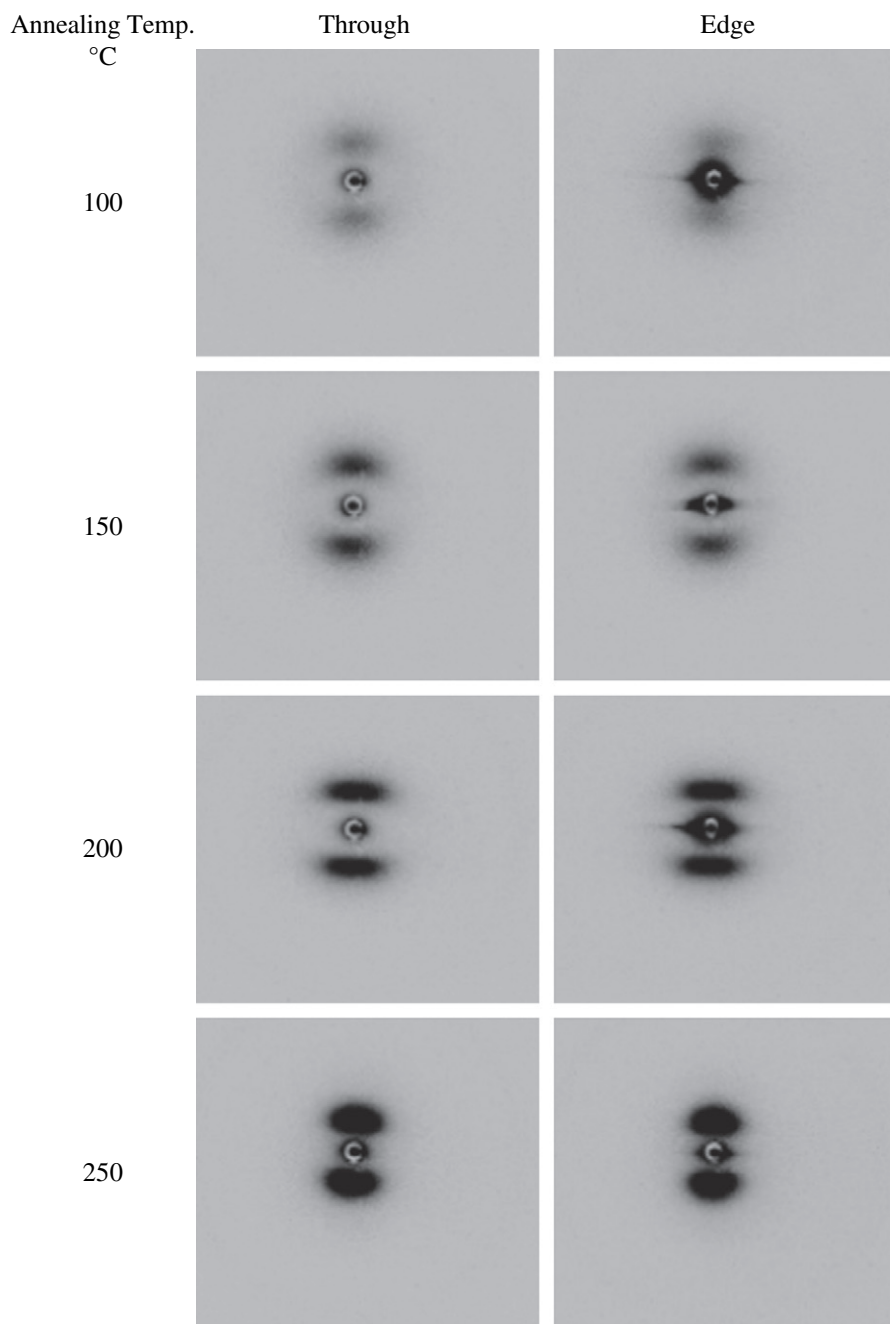


Fig. 6. SAXS patterns of hot-drawn PET, in the “through” (left-hand side) and “edge” (right-hand side) directions, annealed at various T_a for 10^4 s.

oriented paracrystalline (nematic or smectic) state, the phase separation into crystalline and amorphous layers is promoted by a slight inclination, δ , of the molecular axis. Fig. 10a (left-hand side) schematically illustrates the different average molecular distance in the crystalline and in the nematic layers, d_c and d_a , respectively, arising from a small inclination of the molecules with respect to the Z -direction, δ . In our preceding studies, we already highlighted the fact that a small δ -value ($\delta = 1^\circ$) would already yield a significant density difference between the crystalline and the amorphous layers [5]. The average density difference between the crystalline and the amorphous layers can be calculated following [5]:

$$\rho_c/\rho_a = d_a/d_c = d \sin \delta_a/d \sin \delta_c = \sin \delta_a/\sin \delta_c \quad (8)$$

where d is the molecular distance along the layer surface (see Fig. 10a), and δ_a and δ_c are defined as the angles between molecules in the amorphous and crystalline layers and the inclined layer surface, respectively (see Fig. 10a). Using $\rho_c = 1.455$ g/cm³ and $\rho_a = 1.37$ g/cm³, $\sin \delta_a/\sin \delta_c = 1.062$ [5]. It should be noted that the density value that has been taken as that of the amorphous layers could be slightly underestimated, due to the fact that microvoids could be present in the amorphous starting material that was employed to determine ρ_a . However, we believe that $\rho_a \approx 1.37$ g/cm³ is a good approximation to the

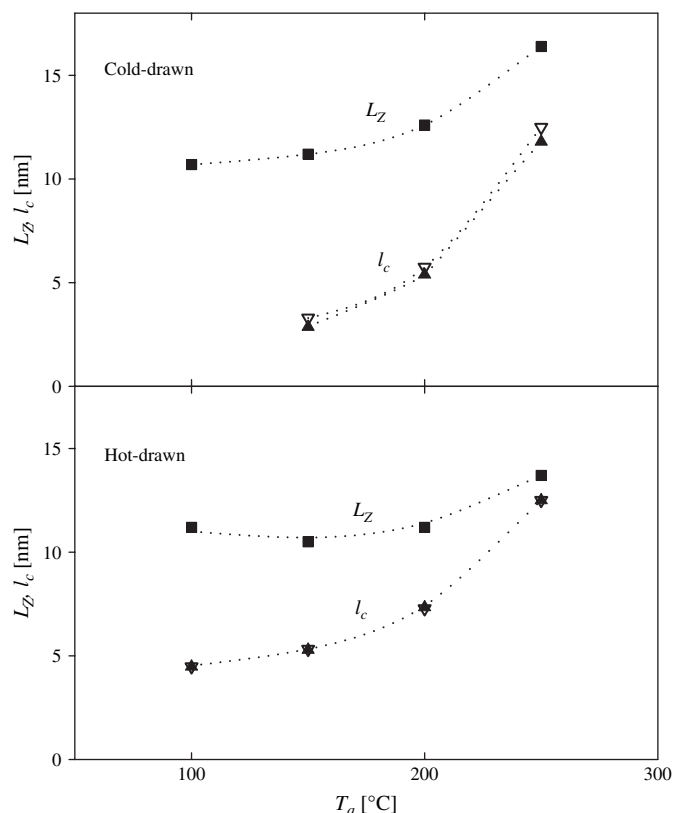


Fig. 7. Lamellar spacing along the drawing direction (■), and crystal layer thickness values in the “through” (▽) and “edge” (▲) directions, for cold- (top) and hot-drawn (bottom) PETs, as a function of T_a .

density of the amorphous regions. On the one hand, this value is larger than the density of amorphous isotropic systems [17]. On the other hand, $\rho_a \approx 1.37 \text{ g/cm}^3$ yields a satisfactory agreement between the experimentally measured δ values and those predicted using Eq. (10), as explained below.

On the other hand, the layer inclination angle θ and the average inclination of the crystalline and amorphous layers δ are directly related through (see Fig. 10a):

$$\begin{aligned} (90^\circ - \theta) + \delta + \delta_a &= 180^\circ \\ (90^\circ + \theta) + \delta + \delta_c &= 180^\circ \end{aligned} \quad (9)$$

Combination of Eq. (9) with $\sin \delta_a / \sin \delta_c = 1.062$ yields:

$$\delta = \arctan \left[\frac{0.0301}{\tan \theta} \right] \quad (10)$$

Eq. (10) permits the calculation of the c -axis tilting values based on the values of the lamellar inclination. Table 2 summarizes the δ values obtained using Eq. (10), assuming a series of θ values close to the ones reported for cold-drawn PET at different T_a (see Table 1). In all cases, a small value of δ is found, in the range of those measured experimentally ($<10^\circ$).

Eq. (10) is of great significance because it highlights the intimate interrelationship between δ and θ : the larger is the layer inclination, the smaller is the molecular inclination necessary to induce the required density difference between the

crystalline and the amorphous phases. Eq. (10) can be extended for hot-drawn PET. In Table 2, the θ values $\leq 10^\circ$ give rise to $\delta \geq 10^\circ$, in agreement with the experimental results for hot drawing. Hence, we conclude that the layer structure formation involves a supplementary relationship between δ and θ .

In view of the above considerations we envisage the mechanism of layer formation in cold-drawn PET as promoted by a slight inclination of the molecules in the nematic state, giving rise to an inclined layer surface. At low annealing temperatures, the molecular inclination is the lowest ($\delta < 2^\circ$ for $T_a = 100^\circ\text{C}$) and the lamellar inclination is the largest ($\theta = 53^\circ$ for $T_a = 100^\circ\text{C}$). Increasing the annealing temperature leads to thicker crystalline layers with slightly larger c -axis tilting as a consequence of the relaxation of the oriented molecules ($\theta = 20^\circ$ for $T_a = 250^\circ\text{C}$; $\delta \approx 5^\circ$), as schematically depicted in Fig. 10a (right-hand side).

In contrast to cold-drawn PET, the hot-drawn material exhibits a low degree of molecular orientation, as mentioned above. During crystallization, the disordered segments should be rejected from the developing crystalline layers. For hot drawing, due to the lower degree of molecular orientation, molecules are allowed to adopt a larger number of molecular conformations than those in the highly oriented sample. This would facilitate, not only the occurrence of molecular foldings at the crystal surface and within the amorphous layers, but also the matching of neighbouring chains with a certain tilting angle with respect to the drawing direction. Molecular foldings would enhance the density difference between the crystalline and the amorphous regions, hence, reducing the extent of the molecular inclination angle necessary for crystallization. The molecular c -axis tilting found in the hot-drawn crystal emerges as a consequence of the need to reduce the average molecular distance within the crystalline layers with respect to the non-crystalline ones. As a result, crystallization of hot-drawn PET gives rise to surface nanolayers perpendicular to the drawing direction (see Fig. 10b). The local molecular orientation within the amorphous layers should be randomly distributed, with an average chain direction parallel to the Z -axis (straight dotted line in Fig. 10b).

3.2. Microhardness measurements

3.2.1. Comparison of cold- and hot-drawing

Fig. 11 (top) illustrates the microhardness values measured perpendicular to the drawing direction (top), H_\perp , and the corresponding indentation anisotropy values (bottom) for the cold- and hot-drawn samples. The H_\perp values of the cold-drawn sample fit very well with the previously published data [5]. Results show that H_\perp is larger for the hot-drawn than for the cold-drawn samples. However, this difference gradually diminishes with increasing T_a , and both H_\perp values coincide for $T_a = 250^\circ\text{C}$.

Most interesting is the fact that, while the indentation anisotropy in the case of the cold-drawn material decreases with T_a , above T_g , in the case of hot drawing, ΔH is practically zero for all the samples (see Fig. 11 bottom). The cold-drawn

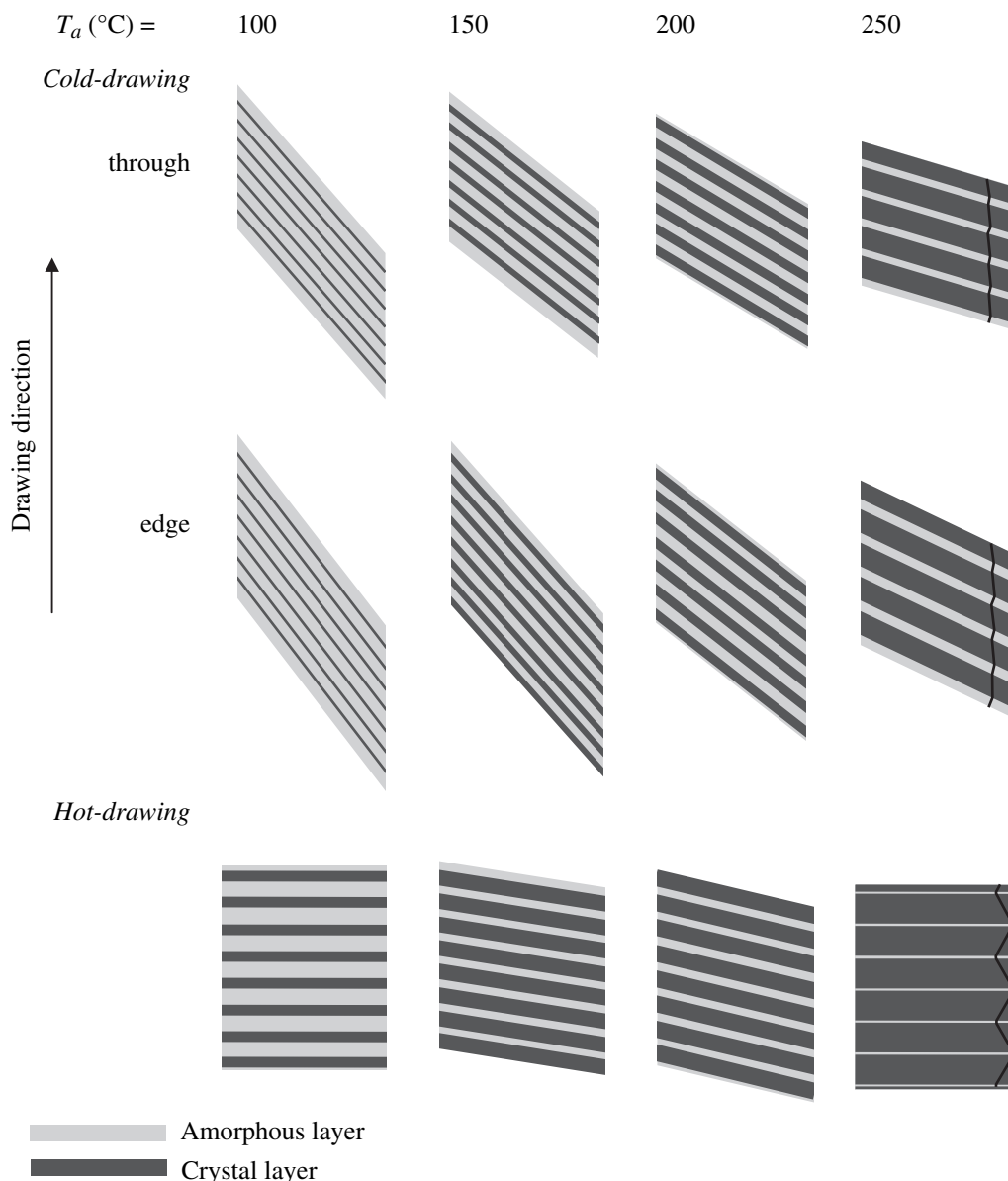


Fig. 8. Schematics of the layer profiles for cold- and hot-drawn PETs developing at different T_a . In the case of cold drawing, a different layer profile has been drawn for the “through” and “edge” directions. For the sake of simplicity, the molecular direction has been schematically represented by one single molecule in the layer profile corresponding to the highest T_a .

ΔH data also fit satisfactorily with our previously published work [5]. The fact that $\Delta H \approx 0$ for the hot-drawn samples and the cold-drawn ones annealed at the highest temperature, while the WAXS and SAXS patterns reveal a significant degree of orientation, suggests that ΔH is governed by the elastic response of the molecules located within the amorphous regions. Indeed, the conspicuous ΔH decrease above $T_a \approx 70$ °C for the cold-drawn material has been previously associated to a relaxation mechanism of the molecules in the amorphous layers. As a result, elastic recovery in the chain direction decreases, and hence ΔH diminishes.

For the un-annealed material, the large difference in microhardness and ΔH between cold- and hot-drawn PET appears to be mainly due to the different degree of molecular orientation (see Fig. 2), the more the oriented material yielding the lower

the H_{\perp} values. In the cold-drawn material, the plastic deformation induced by the indentation in the direction perpendicular to the drawing is mainly due to the separation of molecules bound by van der Waals forces. In contrast, in the hot-drawn material, owing to the lack of good orientation, intramolecular covalent forces may also contribute to the microhardness value. In addition, a slight initial crystallization may as well play a role in the microhardness enhancement for hot drawing.

Let us recall that the initial H_{\perp} increase with T_a for the cold-drawn samples within the interval 25 °C $< T_a < 100$ °C was associated to the gradual appearance of smectic domains with increasing degree of perfection, and the development of crystallinity at $T_a \geq 80$ °C [5]. At $T_a \geq 100$ °C, only the triclinic crystallization takes place and the hardness increase

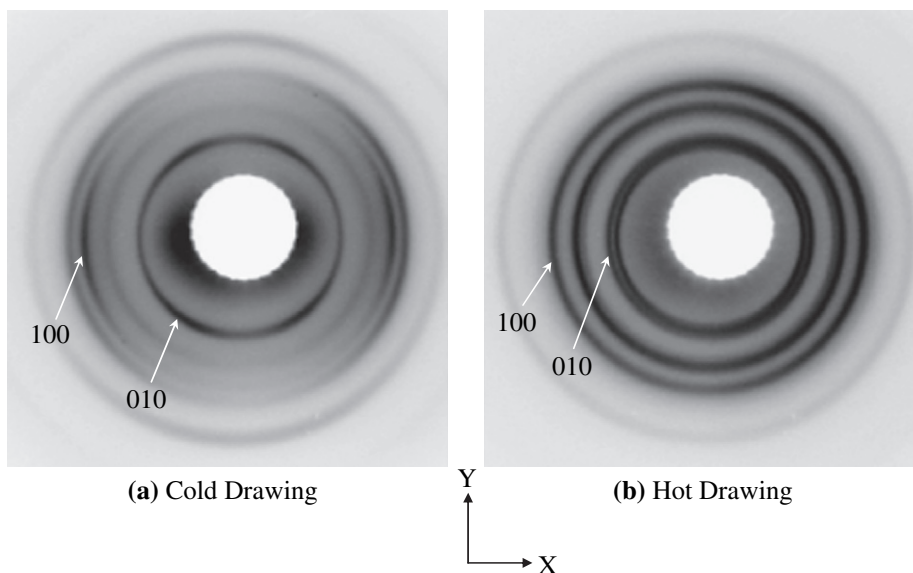


Fig. 9. WAXS end patterns of the cold- and hot-drawn samples annealed at 250 °C.

with increasing T_a for both, hot- and cold-drawn, is directly related to the gradual rise in crystallinity and crystal thickness (see Table 1 and Fig. 7). Moreover, the hardness difference between the hot- and the cold-drawn samples for $T_a \geq 100$ °C is also mainly related to changes in the developing nanostructure. Indeed, the H values for both series can be accounted for by introducing the corresponding α and l_c values (see Table 1) in Eqs. (4) and (5) ($H_{\perp}^{\infty} = 358$ MPa, $H_a = 140$ MPa, $b = 1-8$ nm [5,17–19,22]). A detailed discussion on the influence of the b -parameter on the H values is given below.

3.2.2. Influence of the layer surface on microhardness

In previous studies, we investigated the b -parameter for various PET materials and values of b in the range of 1–8 nm were obtained [17–19,22]. The value of b has been related to the surface perfection of the crystals and modulates accordingly the hardness values. For the calculation of b (using Eqs. (4) and (5)), we have assumed a H_{\perp}^{∞} value of 358 MPa and $H_a = 140$ MPa, which are both derived for oriented PET [5]. Fig. 12 illustrates the variation of the b -parameter with T_a , for the hot- and the cold-drawn samples. It is seen that the small difference found between the b -values for hot- and cold-drawing lies within the experimental error. The notable increase of b at $T_a = 250$ °C resembles the sudden increase of b obtained for isotropic PET samples at $T_a = 240$ °C [22]. In that case, the b -rise has been ascribed to the decrease of Δh due to a chain scission process occurring at high temperature that could result in: (i) a reduction of entanglements within the amorphous intercrystalline layers and (ii) a decrease of tie molecules connecting adjacent lamellae [5].

3.2.3. Microhardness measurements on the film- and along the edge-surface

Fig. 13 comparatively illustrates the microhardness variation with T_a , for the cold- (bottom) and hot-drawn (top)

samples measured on the edge-surface, H_{\perp}^{edge} , and on the film surface, H_{\perp} (results also shown in Fig. 11). It is to be noted that, for cold- and hot-drawn samples, H_{\perp}^{edge} is always smaller than H_{\perp} and both values increase with temperature, similarly as in Fig. 11. It is noteworthy that indentation anisotropy values on the film surface and on the edge (not shown here) are within the error of measurement for both, cold- and hot-drawn samples.

As discussed above, the biaxial orientation found in cold-drawn PET results in a different lamellar inclination in the “through” and “edge” SAXS 4-point patterns. However, it is difficult to explain the difference between H_{\perp} and H_{\perp}^{edge} in the light of the observed structural variations. Moreover, the crystal thickness values obtained for the measurements “through” and “edge” of the cold-drawn material (see Table 1) would only yield a hardness difference of about 1% (see Eq. (5)). On the other hand, no significant variations between the “through” and the “edge” X-ray diffraction measurements have been discussed so far in the case of hot drawing. However, a closer inspection of the SAXS patterns of the cold- and the hot-drawn materials (Figs. 4 and 6) reveals the appearance of an equatorial continuous scattering. The occurrence of this scattering indicates the presence of microvoids (provoking a great density difference), which could act as weak zones during the indentation measurement. Hence, the slightly lower H_{\perp}^{edge} values with respect to H_{\perp} can be attributed to the occurrence of microvoids.

4. Conclusions

1. Hot drawing of glassy PET yields a material with a lower degree of molecular orientation than cold drawing.
2. Crystallized cold-drawn PET exhibits a biaxial orientation normal to the lamellae surface, in contrast to the uniaxial orientation found for crystallized hot-drawn PET.

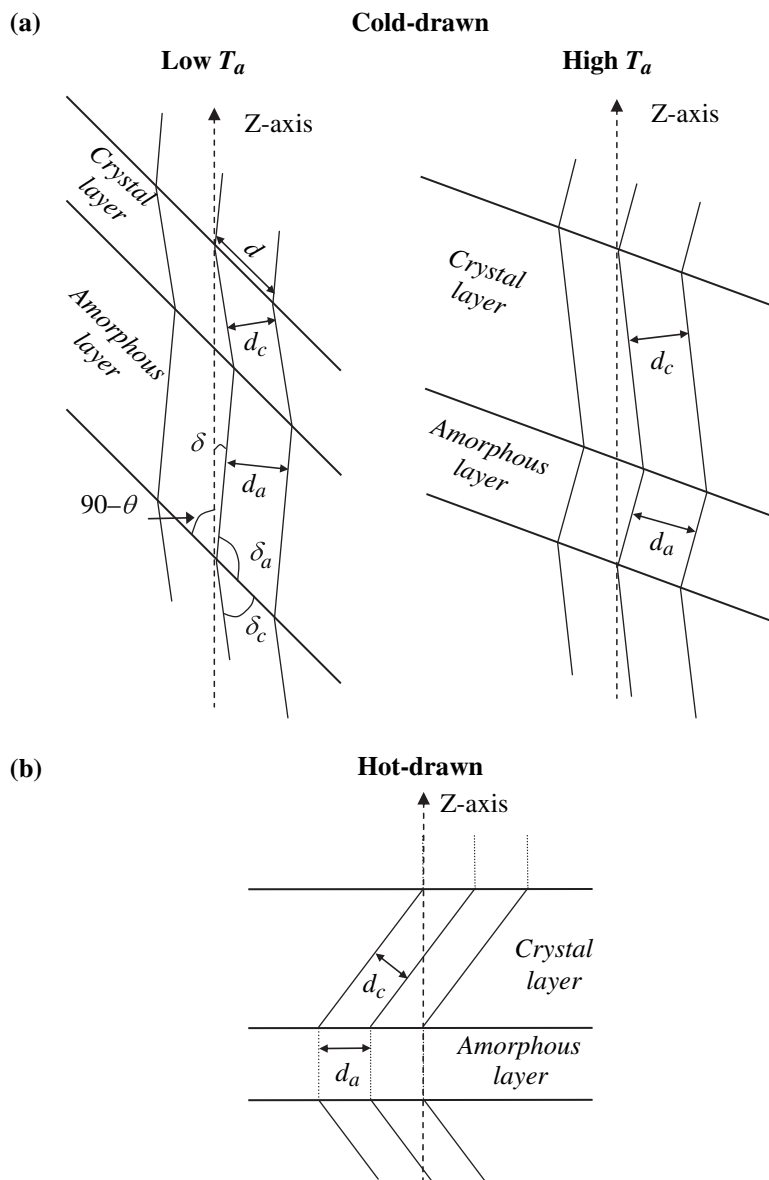


Fig. 10. Schematic representation of the molecular tilting (δ) and the surface layer inclination (θ) for: (a) cold-drawn PET annealed at low and high T_a (left- and right-hand sides, respectively) and (b) hot-drawn PET.

3. In the cold-drawn material, the triclinic c -axis is slightly tilted and the normal to the lamellar surface is largely inclined with respect to the drawing direction (4-point

Table 2

Values of the angle of molecular tilting, δ , obtained using Eq. (10), as a function of the inclination of the layer surface, θ (assuming $\rho_c/\rho_a = 1.062$, see text)

θ ($^\circ$)	δ ($^\circ$)
<i>Cold-drawn PET</i>	
50	1.5
40	2.0
30	3.0
20	4.7
<i>Hot-drawn PET</i>	
10	9.7
5	19
3	30

SAXS pattern). In contrast, in case of hot-drawn PET, the molecular c -axis is largely tilted with respect to the Z-axis and the lamellar normal remains nearly parallel to the Z-axis (2-point pattern).

4. A mutual supplemental relationship is found between the inclination angle of the lamellae and the c -axis tilting. In cold-drawn PET, a conspicuous lamellar inclination is necessary to produce a significant density difference between the crystalline and the non-crystalline domains. In this case, the lamellar surface is largely inclined. For hot drawing, due to a lower degree of molecular orientation, molecules may adopt a larger number of molecular conformations. Hence, a large molecular inclination is induced upon crystallization, leading to the formation of stacks of flat layers (lamellae surface perpendicular to Z-axis).

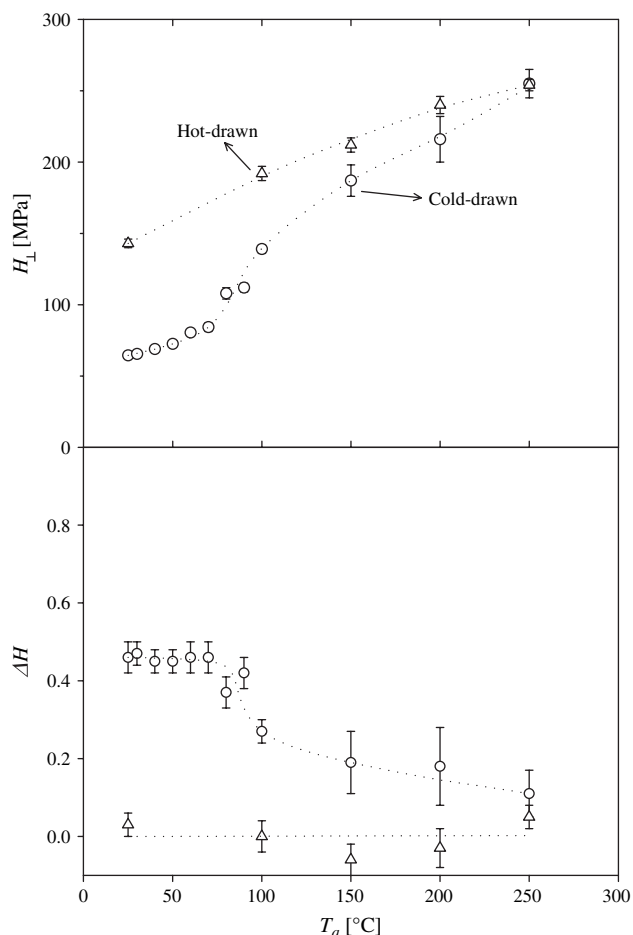


Fig. 11. Variation of microhardness (top) and indentation anisotropy (bottom) values for cold- (○) and hot-drawn (△) PETs with annealing temperature. The dotted lines are guide to the eyes.

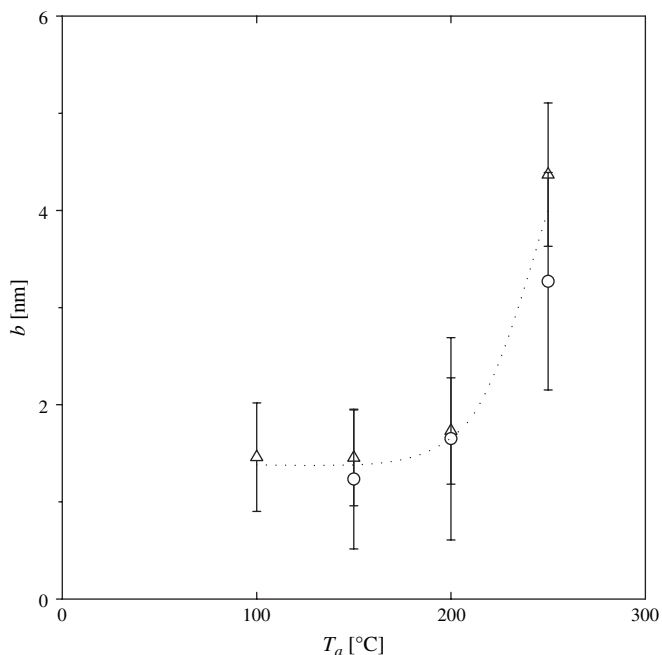


Fig. 12. The b -parameter for cold- (○) and hot-drawn (△) PETs, as a function of T_a .

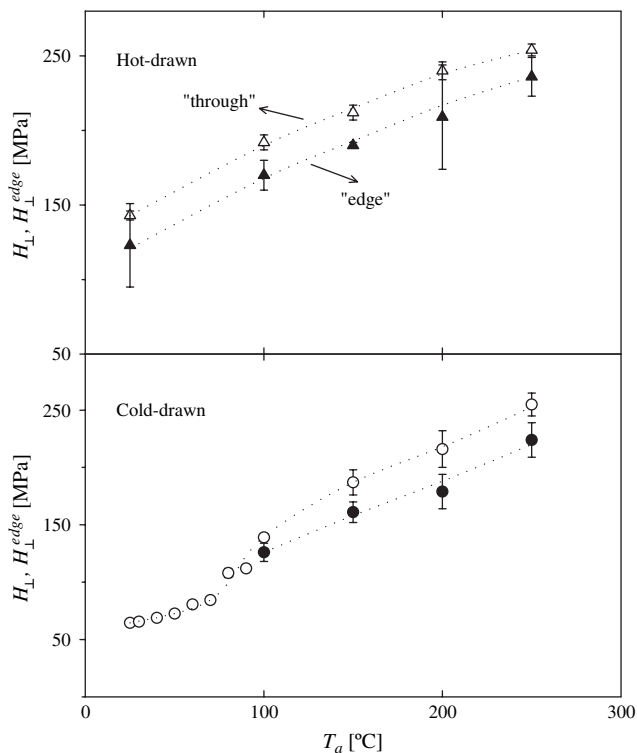


Fig. 13. Microhardness values on the film- (open symbols) and on the edge-surfaces (solid symbols) for the cold- (○, ●) and the hot-drawn (△, ▲) samples, versus T_a .

5. A large difference is found between the H_{\perp} values of the un-annealed cold- and hot-drawn samples due to the occurrence of a higher molecular orientation in the former.
6. The increase in the degree of crystallinity and crystal thickness with increasing T_a gives rise to a parallel increase in H_{\perp} , for both hot- and cold-drawn samples. In addition, the differences in hardness found between hot- and cold-drawing can also be explained in terms of crystallinity and crystal thickness.
7. For cold-drawn samples, the indentation anisotropy ΔH decreases with T_a (for $T_a \geq T_g$) leading to ΔH values converging to those for the hot-drawn material ($\Delta H \approx 0$). The fact that the WAXS and SAXS patterns at high temperature reveal a significant degree of orientation for the cold-drawn material, suggests that ΔH is governed by the elastic response of the molecules located within the amorphous regions.
8. The smaller hardness values found on the edge surface with respect to those measured on the film surface are ascribed to the occurrence of microvoids as revealed by the appearance of continuous equatorial scattering in the SAXS patterns.

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