Creep behavior and elastic properties of annealed cold-drawn poly(ethylene terephthalate): the role of the smectic structure as a precursor of crystallization

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ABSTRACT

The creep behavior and elastic properties of cold-drawn poly(ethylene terephthalate) (PET) films, annealed in the range 60°C-240°C have been investigated by means of microindentation testing. Two indentation methods have been used. The imaging method has been employed to examine the visco-plastic properties of the polymer materials while the depth-sensing method was used for the determination of Young's modulus values. The creep behavior (plastic flow) of cold-drawn PET is shown to be intimately correlated to the nanostructural changes occurring upon annealing. The observed decrease in the rate of creep, when the glassy material is annealed at 60°C, has been associated to the emerging smectic structure which confers to the material a higher mechanical performance. The elastic properties of the smectic phase are found to be comparable to those of the glassy state. Young's modulus E -values of the semicrystalline samples are discussed in the light of the parallel model of crystalline and amorphous layers. E -values are shown to depend on the crystalline lamellar thickness and the degree of crystallinity. Results suggest that Young's modulus values of the amorphous constrained regions within the crystals are higher than the E -value of the fully amorphous material.

Keywords. PET, smectic, triclinic, microindentation, depth-sensing, creep, crystal thickness

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I. INTRODUCTION

It is well known that cold-drawing of isotropic poly(ethylene terephthalate) (PET) films induces a highly oriented material ¹. A mesomorphic form for PET has been found to develop under certain hot-drawing conditions or by annealing after cold-drawing ²⁻⁵. We have recently reported the structural changes occurring when glassy cold-drawn PET is annealed at temperatures in the range 50°C-240°C ⁶. X-ray results reveal the appearance of a sharp layer reflection at 50°C. The spacing of this meridional reflection is of 1.07 nm and it has been associated to the occurrence of a smectic structure ⁶. In the smectic state, benzene rings are arranged on planes perpendicular to the draw direction, whereas the lateral packing of the neighboring molecules shows no crystalline order. Annealing above 80°C induces a gradual transformation of the smectic phase into a triclinic structure ⁶. At 100°C, the smectic phase completely disappears and the structural changes occurring are associated to an increase in the degree of crystallinity and to a thickening of the lamellae crystals. This structural rearrangement has been correlated to the mechanical behavior of the material as revealed by microindentation hardness ⁶.

Microindentation hardness has been shown to provide a valuable information of the polymer nanostructure ⁷⁻⁹. This method relies on the local deformation induced on a polymer surface with a sharp indenter under the application of a given load. In an indentation experiment, the yield stress is exceeded and the indentation depth variation is a combination of both, the viscoelastic and the viscoplastic contribution to the total indentation depth. There are two main methods for the acquisition of indentation hardness data. In the first one, microhardness values are determined from the optical measurement of the residual impression left behind upon load release (imaging method). Microhardness determined in this way is an indicator of the irreversible plastic deformation processes while the information about the viscoelastic behavior is mostly lost ⁹. The second method is

based on the continuous monitoring of the penetration depth as the indenter is driven into and withdrawn from the film at a constant rate (depth-sensing method). Continuous depth-sensing recording does not provide hardness values directly. However, the loading/unloading data can be processed on the basis of well-established assumptions to yield, not only hardness data but also Young's modulus values^{10, 11}. In the depth-sensing method, smaller loads can be applied with respect to those employed in the imaging method, thus, allowing for the investigation of the mechanical properties of the materials at the near-surface. The depth-sensing method has been recently applied to the study of polymers¹²⁻¹⁵.

The microhardness behavior of annealed cold-drawn PET films has been investigated using the imaging method⁶. Due to sample orientation, two different hardness values emerge. The hardness value derived from the measurement of the indentation diagonal perpendicular to the orientation direction, $H_{\perp}$, was shown to be intimately related to the different morphologies emerging upon annealing. On the other hand, the hardness values derived from the indentation diagonal parallel to the draw direction, $H_{\parallel}$, were shown to be more affected by instant elastic releases along the orientation direction⁶.

The aim of the present paper is to extend the above studies to the investigation of the creep behavior and the elastic properties of annealed cold-drawn PET, as revealed by imaging and depth-sensing microindentation hardness techniques respectively. Of special interest is the study of the mechanical properties of the smectic PET mesophase, which appears as a precursor of the crystallization process. In oriented samples, the imaging method provides a direct and rapid procedure to examine the visco-plastic properties of a material, which are directly related to the time-dependent behavior of $H_{\perp}$. On the other hand, the depth-sensing method is needed to provide information about the elastic recovery of the sample in the direction perpendicular to the orientation of the molecular chains.

II. EXPERIMENTAL

A. Materials

Amorphous PET was synthesized by Toray Co. Ltd. Japan ($M_n=18,000$ g/mol). The isotropic sample film was drawn at room temperature following the procedure described in reference 6. The film thickness after drawing is of 0.15 mm. Cold drawn PET samples were annealed with fixed ends at temperatures, T_a , in the range 60-240°C for 10^4 s as described in reference 6. Table 1 lists the different structures appearing as the annealing temperature is raised, together with the crystalline lamellar thickness values, l_c , and the degree of crystallinity values, α_c , for the samples annealed at $T_a \geq 100^\circ\text{C}$ ⁶.

B. Techniques

Microindentation imaging experiments were carried out at room temperature ($\sim 23^\circ\text{C}$) using a Leitz tester and a Vickers square-based diamond pyramid. $H_\perp$ values are calculated following ⁹: $H_\perp = 1.854 P/d_\perp^2$, where P is the load applied and $d_\perp$ is the measured diagonal of the residual impression in the direction perpendicular to drawing. The load applied was of 980 mN, which was held for different periods of time, Δt , in the range 0.1-100 min.

Depth-sensing experiments were carried out using a Shimadzu ultramicroindentation tester. A Vickers diamond pyramid was used to make indentations. The polymer films were glued onto a metal holder to avoid air gaps between the sample and the test piece stage. The specimens were then positioned on the test stage of the ultramicroindenter and tightened with the help of two band fasteners. The draw direction is parallel to the sample surface and hence, perpendicular to the direction of the application of the load. The maximum load applied, $P_{\max}$, was of 0.245 N. The penetration depth is

recorded with an accuracy of 10^{-3} μm . The load is incremented at constant velocity, $\dot{P}$, up to P_{max} , held thereafter for a period of time Δt_{hold} and subsequently reduced at the same rate as in the loading cycle. As an example, a typical load-hold-unloading curve for cold-drawn PET annealed at 220°C is shown in Figure 1. Experiments were carried out using a loading/unloading rate of 0.0014 N/s and $\Delta t_{\text{hold}} = 200$ s. By using these long indentation cycles, the measured elastic deformation is close to its limiting value at infinite time¹⁵. The viscoelastic response of amorphous PET has been the object of a previous study, where E was investigated as a function of loading and holding times¹⁵.

To evaluate E from the compliance curves, we have followed the procedure of Oliver and Pharr¹¹. This method has been proved to be successful on evaluating the elastic-plastic properties of glassy PET and of starch^{15, 16}. The procedure makes use of the following equation:

$$E_r = \sqrt{\frac{\pi}{A_c}} \frac{S}{2} \quad (1)$$

$$\text{where } \frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_o^2}{E_o} \quad (2)$$

and where:

- E_r is the reduced modulus. E and ν are Young's modulus and Poisson's ratio of the material respectively and E_o and ν_o Young's modulus and Poisson's ratio of the indenter respectively ($\nu_o = 0.07$ and $E_o = 1141$ GPa for diamond¹⁷). In our case, the contribution of the deformation of the indenter to the total measured displacement is not significant and one can neglect the $(1 - \nu_o^2)/E_o$ term in equation 2. Poisson's ratio for all samples was approximated to 0.3¹⁸.
- $S = (\partial P / \partial h)_{\text{max}}$ is the initial unloading stiffness (see Figure 1). The upper one third of the unloading curve was fitted to a second order polynomial. The initial unloading stiffness is

determined by analytically differentiating the second polynomial fit and calculating the derivative at the peak load and displacement.

- A_c is the projected area of contact at maximum load. For a perfect Vickers geometry, $A_c = 24.5 h_c^2$, where h_c is the contact penetration depth at peak load. The h_c value is evaluated from the intercept of the initial unloading slope with the displacement axis, and the maximum displacement reached by the indenter ¹¹.

To minimize the error on the determination of the true zero of indentation depth, the experimental loading curve was fitted to a power law function of the type ¹⁴:

$$P = m (h - h_0)^n \quad (3)$$

m is here a material constant, n is the index of the deformation and h_0 is the true zero point (see Figure 1).

III. RESULTS AND DISCUSSION

A. Creep Behavior

Figure 2 shows the double logarithmic plot of the $H_\perp$ values as a function of indentation time for cold-drawn PET samples annealed at different temperatures. The time dependent part of the plastic deformation is known to follow a function of the type ⁹:

$$H_\perp = H_0 \Delta t^{-k} \quad (4)$$

where H_0 is the hardness measured at $\Delta t = 1$ min and k is the creep constant. Indeed, Figure 2 shows that microhardness follows a power-law function of indentation time for all the samples investigated. The k -parameter gives a measure of the rate at which the material creeps under the indenter and is equal to the value of the slope of each straight line in Figure 2. Figure 3 illustrates the variation of the creep constant as a function of the crystalline lamellar thickness values. The periodicity of the meridional reflection associated

to the smectic phase has been also included in Figure 3 (1.07 nm). The rate of creep of the glassy material is shown to diminish with the appearance of smectic domains, which confer to the material a higher structural order. This result is in agreement with previous microindentation hardness studies on amorphous PET films with different degrees of internal order ¹⁹. Here, it was suggested that the creep behavior of amorphous PET is considerably reduced by the presence of “ordered” nanoregions that may play the role of “embryos” or nuclei of precrystallization. Figure 3 shows that a further decrease in the creep constant is observed first, with the development of triclinic crystalline order and thereafter, with the increase of crystal lamellar thickness. The smectic phase appears to yield under the indenter at a higher rate than the triclinic structure. The k values steeply decrease with increasing crystal thickness for small l_c values while a leveling-off occurs for large crystal thickness values (see Figure 3). Previous studies on chain-extended polyethylene, chain-folded polyethylene and a series of paraffins, report a similar creep dependence with crystal thickness ²⁰.

B. Young’s modulus: influence of degree of crystallinity and crystal thickness

Figure 4 illustrates the variation of Young’s modulus values as a function of the degree of crystallinity for the cold-drawn samples annealed at $T_a \geq 100^\circ\text{C}$ (see table 1). Results reveal a rise of E with increasing α_c . On the other hand, the E -values for samples annealed below 100°C are shown to remain nearly constant (see inset of Figure 4). The appearance of the smectic domains does not seem to influence Young’s modulus values. In contrast, in the preceding section, we highlighted the k -decrease observed with the development of the smectic mesophase (see also Figure 3). The fact that changes from the glassy to the smectic morphology are monitored by k and not by E should be related to the different deformation modes. While the plastic properties of the smectic phase are mainly controlled by the

degree of structural order within the oriented domains, the E -values seem to be more influenced by other factors such as chain connectedness and local chain elongation ²¹.

Figure 4 also includes the E -value for infinitely thick crystalline regions, $E \approx 6$ GPa, derived from indentation depth-sensing experiments on PET microfibrils ²². One can see that there is a clear deviation of the experimental data with respect to a simple parallel (line 1) or a series model (curve 2) of crystalline and amorphous layers having E_c and E_a respectively ($E_a = 2.8$ GPa, $E_c = 6$ GPa). The same situation applies if a series-parallel model (Takayanagi model) is considered ²³. Thus, it seems that there is not a unique E_c value for all the samples investigated, i. e., the E_c value depends on the thickness of the crystals. It is now accepted that Young's modulus of polymers depends on the degree of crystallinity ²³. It is also known that the modulus parallel to the draw direction increases with increasing average crystal thickness on drawn high-pressure annealed polyethylene ²⁴. However, to our knowledge, so far, there is no experimental evidence on the variation of the elastic modulus in the direction perpendicular to drawing with the thickness of the lamellar polymer crystals.

Let us assume the simplest case, in which the elastic modulus follows a parallel model of crystalline and amorphous layers. This situation conforms to a simple model in which the modulus is measured in the direction perpendicular to the molecular orientation ^{23, 25}. Figure 4 illustrates a series of straight lines (dashed lines) passing through each one of the E experimental values. The straight lines in Figure 4 follow a parallel model, with $E_a = 2.8$ GPa and E_c given by the intersection of the corresponding line with the right-hand y-axis. With increasing annealing temperature, the l_c value increases giving rise to gradually larger crystal modulus values, the upper limit value for E_c being ≈ 6 GPa ²². The observed E rise with increasing T_a may be immediately explained in terms of a double increase of α_c and l_c (see table 1). A similar behavior has been previously found for the indentation hardness of these materials ⁶. Figure 4 reveals, however, that in the range $l_c = 3.5\text{-}7.0$ nm ($T_a = 160^\circ\text{C}$ -

220°C), the modulus-increase appears to be mainly due to an increase of crystallinity. The fact that the E -modulus is apparently insensitive to lamellar thickness at these annealing temperatures could be interpreted in terms of a reinforcing contribution of the chain segments in the amorphous layers which are more constrained than in the low- α_c amorphous regions. Increasing the constraints of the amorphous phase would lead to higher E_a -values than the starting one for the amorphous oriented material. Thus, a gradual increase of E_a with increasing l_c value (in contrast to the assumed constant value of $E_a = 2.8$ GPa in Figure 4) would imply that E_c increases with l_c on the high T_a range.

IV. CONCLUSIONS

- The study of the visco-plastic properties of annealed cold-drawn PET films reveals that the glassy unannealed material flows at the highest rate. The rate of creep is found to diminish with increasing thickness of the crystalline lamellae.
- The creep constant value for the smectic phase lies in between that corresponding to the glassy material and those associated to the triclinic structure. This finding suggests that the visco-plastic flow of cold drawn PET diminishes with increasing structural order of the material and supports the concept of the smectic phase being a precursor state of crystallization.
- Young's modulus values of the smectic phase are found to be comparable to those of the glassy material.
- The elastic modulus of cold drawn PET is found to increase with the temperature of annealing, T_a . This result is associated to an increase in, both, the degree of crystallinity and the crystalline lamellar thickness with increasing T_a . In addition, the fact that at high annealing temperatures ($160^\circ\text{C} \leq T_a \leq 220^\circ\text{C}$) the E -modulus is independent of lamellar

thickness, has been interpreted in terms of an enhancement in the elastic properties of the amorphous regions which are more constrained than in the low- α_c amorphous phase.

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TABLE I. The emerging structure, crystal lamellar thickness, l_c , degree of crystallinity, α_c (from reference 6) and elastic modulus values for cold-drawn PET annealed at different temperatures T_a for 10^4 s.

T_a (°C)	<i>Structure</i>	l_c (nm)	α_c	E (GPa)
Room	Glass	—	—	2.82
60	Smectic	—	—	2.66
80	Smectic + Triclinic	—	—	2.79
100	Triclinic	1.4	0.22	2.96
120	Triclinic	2.0	0.28	3.09
140	Triclinic	2.8	0.35	3.24
160	Triclinic	3.5	0.41	3.34
180	Triclinic	4.4	0.48	3.52
200	Triclinic	5.2	0.55	3.49
220	Triclinic	7.0	0.63	3.72
240	Triclinic	9.1	0.72	4.37

CAPTIONS TO FIGURES

FIG. 1. Depth-sensing curve (load, P , versus displacement, h) for cold drawn PET annealed at 220°C for 10^4 s. The solid line fitted to the experimental data on the loading cycle follows a power law function of the type shown in equation 3.

FIG. 2. Double logarithmic plot of $H_{\perp}$ vs. Δt for cold drawn PET (○) and the same material annealed at the following temperatures: (●) 60°C, (▽) 100°C, (▼) 140°C, (△) 200°C and (▲) 220°C.

FIG. 3. Variation of the creep constant as a function of crystal thickness. The solid triangle corresponds to the periodicity of the meridional reflection associated to the smectic phase. The solid curve is a guide line for the eyes.

FIG. 4. Plot of E as a function of α_c . The dotted lines follow the parallel (line 1) and the series model (curve 2) respectively, having $E_a = 2.8$ GPa and $E_c = 6$ GPa²². The dashed lines follow a parallel model of crystalline and amorphous layers with $E_a = 2.8$ GPa and E_c values which depend upon crystal thickness, l_c . The inset shows Young's modulus values as a function of annealing temperature for $T_a \leq 120^\circ\text{C}$.