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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The creep behavior and elastic properties of cold-drawn poly(ethylene terephthalate) (PET) films, annealed in the range 60–240 °C have been investigated by means of microindentation testing. Two indentation methods have been used. The imaging method has been employed to examine the viscoplastic 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 with 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 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. © 2001 American Institute of Physics. [DOI: 10.1063/1.1418000]

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 50–240 °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 with 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 with 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 valuable information on 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 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 polymers.12–15

The microhardness behavior of annealed cold-drawn PET films has been investigated using the imaging method.5 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
TABLE I. The emerging structure, crystal lamellar thickness $l_c$, degree of crystallinity $\alpha_c$ (from Ref. 6) and elastic modulus values for cold-drawn PET annealed at different temperatures $T_a$ for $10^4$ s.

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

hand, the hardness values derived from the indentation diagonal parallel to the draw direction $H_D$ were shown to be more affected by instant elastic releases along the orientation direction.6

The aim of the present article 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 viscoelastic properties of a material, which are directly related to the time-dependent behavior of $H_D$. 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. EXPERIMENT

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 Ref. 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 Ref. 6. Table I 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 $\alpha_c$ for the samples annealed at $T_a \approx 100$ °C.6

B. Techniques

Microindentation imaging experiments were carried out at room temperature (~23 °C) using a Leitz tester and a Vickers square-based diamond pyramid. $H_D$ values are calculated following $^9$: $H_D = 1.854 P/d_i^2$, where $P$ is the load applied and $d_i$ is the measured diagonal of the residual impression in the direction perpendicular to the drawing. The load applied was of 980 mN, which was held for different periods of time $\Delta t$ in the range of 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 $P_{\text{max}}$ was of 0.245 N. The penetration depth is recorded with an accuracy of $10^{-3}$ μm. The load is incremented at constant velocity $P$ up to $P_{\text{max}}$, held thereafter for a period of time $\Delta t_{\text{hold}}$, 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 Fig. 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 time.15 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 times.15

To evaluate $E$ from the compliance curves, we have followed the procedure of Oliver and Pharr.11 This method has been proved to be successful in evaluating the elastic–plastic properties of glassy PET and of starch.15,16 The procedure makes use of the following equation:

$$E_i = \sqrt{\frac{\pi S}{A_c}}$$  \hspace{1cm} (1)$$

where

$$E_i = \frac{1}{E} \left[ \frac{1 - \nu_i^2}{E_0} \right]$$  \hspace{1cm} (2)$$

and where

![FIG. 1. Depth-sensing curve (load $P$ vs 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 Eq. (3).](image-url)
(i) $E_r$ is the reduced modulus. $E$ and $\nu$ are Young’s modulus and Poisson’s ratio of the material, respectively, and $E_0$ and $\nu_0$ Young’s modulus and Poisson’s ratio of the indenter, respectively. ($\nu_0=0.07$ and $E_0=1141$ GPa for diamond). In our case, the contribution of the deformation of the indenter to the total measured displacement is not significant and one can neglect the $(1-\nu_0^2)/E_0$ term in Eq. (2). Poisson’s ratio for all samples was approximated to 0.3.18

(ii) $S_0=(\partial P/\partial h)_{max}$ is the initial unloading stiffness (see Fig. 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.

(iii) $A_c$ 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 type14

$$ P = m (h - h_0)^n, $$

where $H_0$ is the hardness measured at $\Delta t=1$ min and $k$ is the creep constant. Indeed, Fig. 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 Fig. 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 with the smectic phase has also been included in Fig. 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. 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 Fig. 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 $T_a\geq 100$ °C (see Table I). Results reveal a rise of $E$ with increasing $\alpha_c$. On the other hand, the $E$ values for samples annealed below 100 °C are shown to remain nearly constant (see inset of Fig. 4). The appearance

![FIG. 2. Double logarithmic plot of $H_i$ vs $\Delta t$ for cold drawn PET (○) and the same material annealed at the following temperatures: (●) 60 °C, (▼) 100 °C, (▲) 140 °C, (△) 200 °C, and (▲) 220 °C.](Image 79x545 to 270x739)

![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 with the smectic phase. The solid curve is a guide for the eyes.](Image 354x575 to 522x739)
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 Fig. 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 controlled mainly by the degree of structural order within the oriented domains, the $E$ values seem to be more influenced by other factors such as chain connectivity and local chain elongation.  

Figure 4 also includes the $E$ value for infinitely thick crystalline regions, $E \approx 6$ GPa, derived from indentation depth-sensing experiments on PET microfibris.  

![Graph showing Young’s modulus as a function of annealing temperature for $T_a = 120^\circ$C.](Image)

**FIG. 4.** Plot of $E$ as a function of $\alpha_c$. The dotted lines follow the parallel (line 1) and the series model (curve 2) respectively, having $E_a=2.8$ GPa and $E_c=6$ GPa (Ref. 22). 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 $T_a=120^\circ$C.

which the modulus is measured in the direction perpendicular to the molecular orientation.  

The study of the viscoplastic 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 viscoplastic 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 with 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 ($160^\circ C \leq T_a \leq 220^\circ C$) 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-$\alpha_c$ amorphous phase.

**IV. CONCLUSIONS**

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