

Conditions of Homogeneous Deformation of Poly(ethylene terephthalate) Films during Uniaxially Drawing

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ABSTRACT: Amorphous poly(ethylene terephthalate) film was uniaxially drawn over a wide range of temperatures from below to above the T_g at a constant strain rate. The geometry of the deformation in macroscopic dimensions of the sample demonstrates that homogeneous deformation can be obtained when the drawing temperature (T_{def}) is not lower than 69°C. The change of the cold crystallization peak temperature (T_{cc}) and crystallinity determined by differential scanning calorimetry and density measurement, respectively, were studied in terms of the T_{def} and the draw ratio (λ). The orientation, relaxation, and crystallization during drawing were investigated as a function of T_{def} as well as of λ . The results suggest that 69°C is the critical temperature at which the sample with the highest orientation and the least slippage of the molecular chain and without obvious crystallization can be obtained. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2044–2048, 2000

Key words: poly(ethylene terephthalate); uniaxially draw; orientation; relaxation; crystallization

INTRODUCTION

As an important commercial polymer, poly(ethylene terephthalate) (PET) has been studied extensively. The mechanical properties of PET films and their practical application are directly controlled by the molecular orientation and the morphology produced during film processing. Substantial effort has been directed to the deformation and orientation behavior of amorphous PET using small-angle light scattering,^{1,2} X-ray scattering,^{1–7} Fourier transform infrared spectroscopy,^{8–10} differential scanning calorimetry (DSC),^{2,11,12} and birefringence techniques.^{13–15} The drawing temperature

(T_{def}) and the draw ratio (λ) influence the orientation and crystallization of the PET sample significantly. Despite the large number of investigations, the temperature-dependent behavior of the orientation and relaxation during deformation of amorphous PET in the range from below to above the T_g has not been completely understood yet. The question arises as to how relaxation, orientation, and crystallization influence each other and how their relationship evolved with increasing of T_{def} from below to far above the T_g .

The aim of this article was to give a more detailed description of the influence of T_{def} and λ on the deformation behavior of amorphous PET film below the T_g , around the T_g , and far above ($\sim 20^\circ\text{C}$) the T_g at a constant strain rate. The deformation was investigated in terms of the position, the shape, and the magnitude of the cold crystallization peak in DSC curves as well as the crystallinity of the drawn sample.

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EXPERIMENTAL

Samples

For the uniaxially drawing, a wide (~ 200 mm) sheet of amorphous PET with a thickness of 0.10 mm was produced by melt extrusion at 290°C through a slit die followed by quenching onto a chill roll at 20°C. Its viscosity-average molecular weight was 1.63×10^4 . The density of the sheet was 1.3363 g/cm^3 and the birefringence less than 0.0002, indicating a vanishing amount of crystallinity and orientation. The sheet was dried in a vacuum oven at room temperature for the following uniaxially drawing process.

Uniaxially Drawing

Drawn samples were prepared on a self-made tensile tester equipped with a temperature-programmed chamber. The amorphous film was first heated in the chamber for 5 min at the desired drawing temperature to allow thermal equilibration of the sample. Uniaxial drawing was performed at a constant crosshead speed of 6 mm/min to a predetermined λ and the initial distance between the clamps was 20 mm. T_{def} ranged from 62 to 95°C. After drawing, the chamber's door was opened immediately and the temperature of the sample was allowed to decrease to room temperature quickly in order to freeze the deformation; then, the sample was taken out of the chamber. The actual value of λ of the sample was obtained from the change of the spacing between ink marks placed 1 mm apart on the sample before drawing.

Density Measurements

Density of the sample was measured in a density-gradient column prepared from a mixture of carbon tetrachloride and *n*-heptane at $25 \pm 0.5^\circ\text{C}$. The volume fraction crystallinity was estimated from $X_c = [(\rho - \rho_a)/(\rho_c - \rho_a)] \times 100\%$, with the crystalline region density $\rho_c = 1.455 \text{ g/cm}^3$ and the amorphous region density $\rho_a = 1.335 \text{ g/cm}^3$.

DSC Measurements

The DSC curve was recorded on a TA2910 differential scanning calorimeter from 30 to 200°C with the heating rate of 10°C/min in a N_2 atmosphere. Weight of the sample was 6 ± 0.5 mg.

Recovery Experiments

The deformed PET samples were hung freely in an oven at 88°C for 6 h, at which temperature the

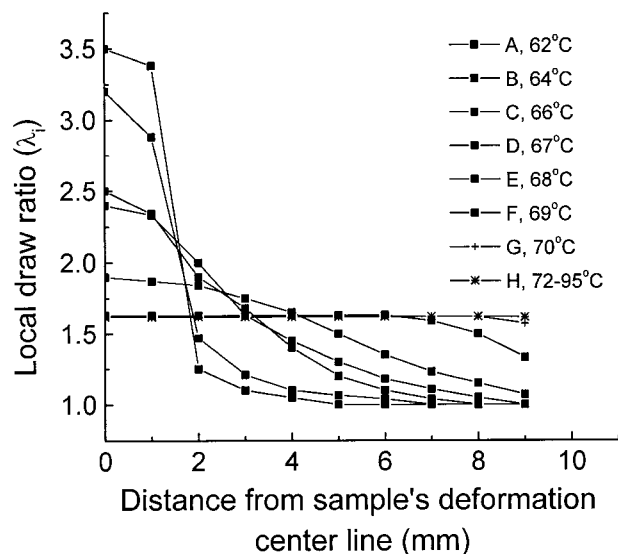


Figure 1 Macrodimensional change of PET film drawn at different temperatures; the whole original length of the sample was 20 mm and the whole length after drawing was 32 mm.

deformed PET recovered much faster and avoided crystallization. After that, the samples were taken out and allowed to decrease to room temperature. The relative residual strain was obtained using the following expression: $\varepsilon = (L_r - L_0)/L_0$, where L_0 is the original length of the undrawn sample, and L_r , the length after recovery.

RESULTS AND DISCUSSION

Local dimensional changes along the drawing direction on the amorphous PET samples uniaxially drawn in the vicinity of the T_g are shown in Figure 1. All the samples in this figure were drawn from original length of 20 mm to final 32 mm. The value of the local λ_i is obtained by dividing the length (mm) between the $i - 1$ th and $i + 1$ th ink mark by 2. When T_{def} is below 66°C, deformation of the sample is almost entirely concentrated on a small, well-defined neck with the actual λ_i up to 3.5. However, in the temperature range from 69 to 70°C, the deformation is homogeneous. In fact, the deformation is always homogeneous in the range from 69 to 95°C. In the range from 66 to 69°C, just near the T_g , the λ shows a gradually decreasing tendency from the deformation center of the sample to the two ends along the drawing direction. These experimental

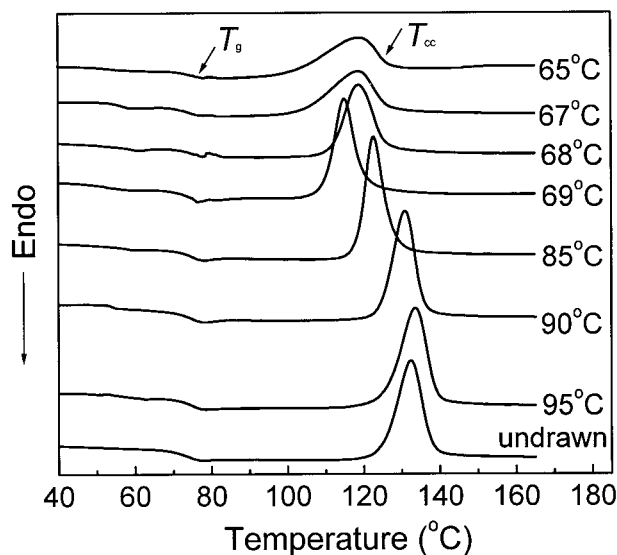


Figure 2 DSC curves of amorphous PET film drawn at different temperatures with $\lambda = 2.0$.

results are in accordance with those done by Ward et al. by birefringence and shrinkage force measurements.¹³ It is demonstrated that the transition from cold drawing through a neck to homogeneous deformation occurs in a narrow temperature range in the vicinity of the T_g . A explanation may be proposed that when drawing below the T_g the molecular chains are frozen in the local regions and the cooperative molecular rearrangements cannot occur, resulting in an aggregate of mechanically anisotropic units aligning along the drawing direction, while deformation above the T_g is consistent with the deformation mechanism of rubberlike network.^{12,16}

DSC results of the samples drawn at a series of temperatures from 65 to 95°C with the λ of 2.0 are shown in Figure 2. The sample drawn at 69°C has the lowest cold crystallization peak temperature, $T_{cc} \approx 117^\circ\text{C}$. When T_{def} is between 69 and 95°C, T_{cc} shifts to the higher temperature with increasing T_{def} . However, for the samples drawn at 65, 67, and 68°C, T_{cc} is always at 120°C. Furthermore, the area of the cold crystallization peak of the samples drawn above 69°C remains invariant. For the samples drawn below 69°C, the shape becomes more diffuse and the area is smaller than that of undrawn sample, indicating an increase of crystallinity.

The crystallinity of the samples in Figure 2 determined by density measurement is shown in Table I. The change of the crystallinity is consistent with the DSC results in Figure 2.

When T_{def} is below the T_g , the motion of the chain segment is frozen and the orientation of the chain during drawing is localized in certain regions, which results in the crystallization instead of cooperative rearrangement with neighboring chain segments; thus, the rest of the amorphous regions have the lower orientation. Broadening of the cold crystalline peak in the DSC curve shows that crystallization occurs in a wide temperature range, implying the existence of some imperfect crystals and the orientation of the crystalline phase.² When the T_{def} is above the T_g , the local chain's relaxation becomes more significant with the increasing of T_{def} , resulting in the lower orientation of the chain. As a result, the sample drawn at T_g should have the highest orientation in amorphous region, demonstrating the lowest T_{cc} in DSC curve. It seems that the PET film's T_g is in the vicinity of 69°C (Fig. 2).

DSC curves of the samples drawn at 69°C in terms of λ are given in Figure 3. T_{cc} decreases remarkably with increasing of λ . When λ exceeds 2.1, the cold crystallization peak becomes smaller and more diffuse, indicating the strain-induced crystallization of amorphous PET film. The deformation of amorphous PET films at a temperature close to or slightly above T_g was described as a rubberlike network resulting from the local intra- or intermolecular interactions.^{12,16} The local chain would rearrange in relation to the tensile stress, and the slippage of the chain could not take place due to the "network." The existence of a molecular network results in a limiting extensibility, λ_c , of the deformed sample. When λ exceeds λ_c , the network would be destroyed and the sample crystallize. From the above experimental results, it seems that when T_{def} is 69°C, λ_c is about 2.1–2.3.

Table I Crystallinity of PET Film Drawn at Different Temperatures, $\lambda = 2.0$

Drawing Temperature (°C)	Crystallinity (%)
65	12.5
67	10.7
68	6.8
69	1.2
70	1.3
74	1.2
85	1.1
90	1.2
95	1.1
Undrawn sample	1.1

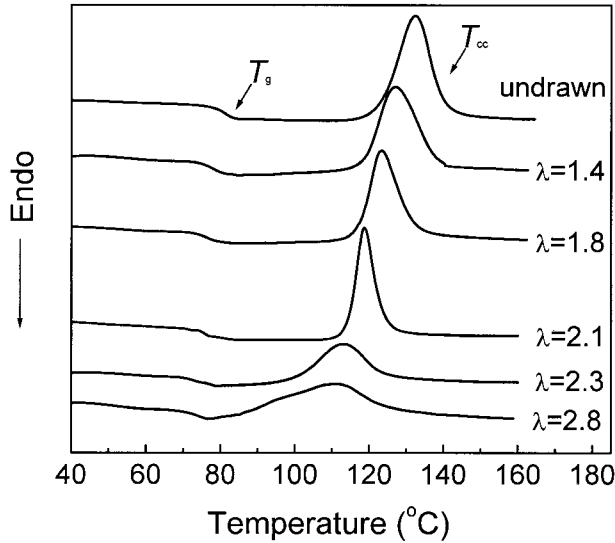


Figure 3 DSC curves of PET film drawn at 69°C with different draw ratios.

DSC curves of the sample drawn at 95°C with λ up to 5.0 are shown in Figure 4. When λ is lower than 3, T_{cc} is always the same as that of the undrawn sample, while T_{cc} begins to decrease with further increasing of the draw ratio. When λ is 5, the magnitude of cold crystallization peak decreases, implying the formation of crystallites during drawing, but the peak does not broaden as in Figure 3. Combined with the DSC results in Figure 3, it could be found that the onset of the

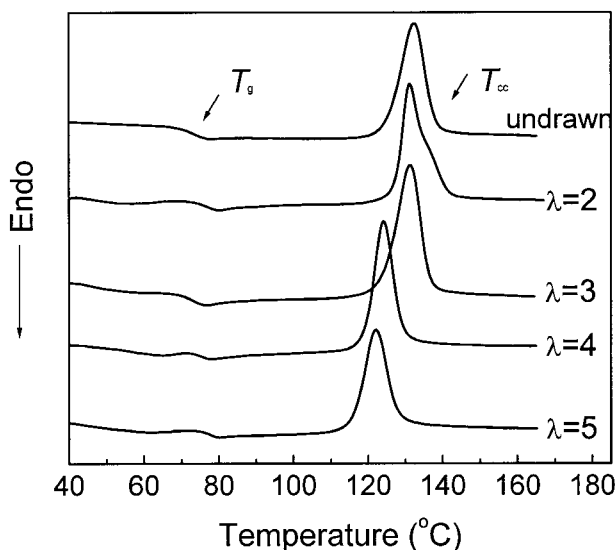


Figure 4 DSC curves of PET film drawn at 95°C with different draw ratios.

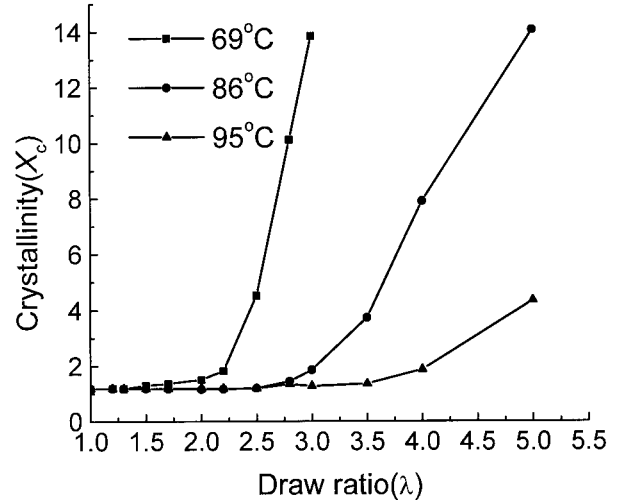


Figure 5 Dependence of crystallinity of PET film on the draw ratio at different drawing temperatures.

crystallization during drawing at 95°C occurred at a higher λ than that at 69°C.

Figure 5 shows the change of crystallinity of the samples with increasing of λ at different temperatures. The results show, obviously, that the λ of the onset crystallization increases with the T_{def} . Relative residual strain as a function of T_{def} is shown in Figure 6. It must be noted that there is no apparent crystallization in these samples after recovery, so the residual strain should be due to the slippage of the chain during drawing. With increase of the T_{def} above the T_g , the slippage of the chain become more

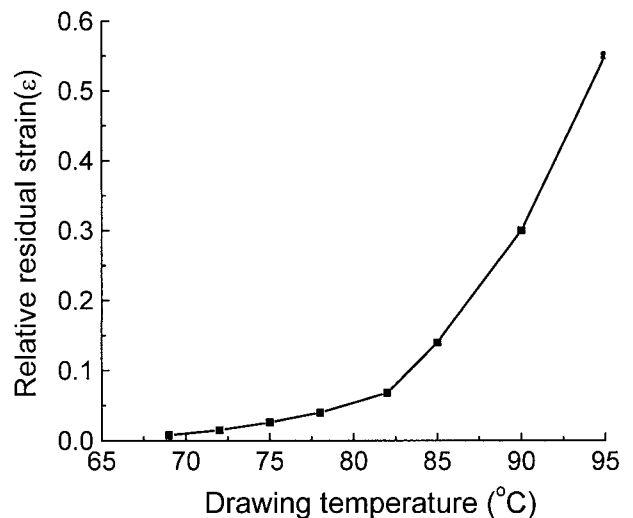


Figure 6 Dependence of relative residual strain of PET film on the drawing temperature with the draw ratio of 2.0.

significant, which results in the lower orientation, and thus the onset of the strain-induced crystallization would happen at higher λ . In fact, drawing at 20°C above the T_g is the often so-called flow-drawing process.¹⁶⁻¹⁸ The sample drawn at 69°C recovers almost completely, while at 95°C, over half of the deformation could not recover, which implies that the deformation mechanism changed from a rubberlike deformation to a flow-drawing deformation from 69 to 95°C.

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