

Shrinkage Behavior after the Heat Setting of Biaxially Stretched Poly(ethylene 2,6-naphthalate) Films and Bottles

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Received 26 October 2001; accepted 13 May 2002

ABSTRACT: Amorphous preforms of poly(ethylene 2,6-naphthalate) (PEN) were biaxially drawn into bottles up to the desired volume under industrial conditions. These bottles were used to characterize the shrinkage behavior of the drawn bottles with or without heat treatment and to study structural variations during heat setting. During drawing, a rigid phase structure was induced, and the amount of the induced rigid phase structure was linearly related to the square root of the extra first strain invariant under equilibrium conditions. During the production of these bottles, this equilibrium was not attained because of high stretching conditions and rapid cooling after stretching. The structure after orientation contained a rigid amorphous phase and an oriented amorphous phase. The shrinkage behavior was a function of the temperature and time of heat setting. Long heat-setting times, around 30 min, were used to characterize the possible structural variations of the oriented PEN after heat setting at equilibrium. Under the equilibrium conditions of heat setting, the start temperature of the shrinkage was directly related to the heat-setting temperature and moved from 60°C without heat treatment up to a temperature of 255°C by a heat-setting temperature of 255°C; this contrasted with poly(ethylene terephthalate) (PET), for which the start temperature of shrinkage was always around 80°C. For heat-setting temperatures higher than 220°C, the structural variations changed rapidly as a function of the heat-setting time, and the corresponding shrinkage of the

heat-set samples sank below 1% in a timescale of 30–60 s for a film thickness of 500 μm . The heat treatment of the oriented films taken out of the bottle walls with fixed ends stabilized the induced structures, and the shrinkage of these heat-set films was zero for temperatures up to the heat-setting temperature, between 220 and 265°C, if the heat-setting time was sufficient. According to the results obtained, a heat-setting time of 30 s, for a film thickness of 500 μm , was sufficient at a heat-setting temperature of 255°C to stabilize the produced biaxially oriented PEN bottles and to take them out the mold without further shrinkage. During the drawing of PEN, two different types of rigid amorphous phases seemed to be induced, one with a mean shrinkage temperature of 151°C and another rigid amorphous phase, more temperature-stable than the first one, that shrank in the temperature range of 200–310°C. During heat setting at high temperatures, a continuous transformation of the less stable phase into the very stable phase took place. The heat-set method after blow molding is industrially possible with PEN, without the complicated process of subsequent cooling before the molds are opened, in contrast to PET. This constitutes a big advantage for the blow molding of PEN bottles and the production of oriented PEN films. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1462–1473, 2003

Key words: polyesters; stabilization; annealing; orientation; structure–property relations

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) is a polyester for which the preparation was first reported as long ago as 1948.¹ PEN is produced by the condensation polymerization of 2,6-naphthalenedicarboxylic acid and ethylene glycol.^{2–4} There has, however, been increasing interest in its commercial use because of recent indications^{5,6} that the dicarboxylic acid monomer will become available in large quantities. PEN molecules contain naphthalene rings, which are stiffer than those of poly(ethylene terephthalate) (PET). The important aspect of PEN is the influence of an increased chain

stiffness on the mechanical and thermal properties of the polymer. This polymer, like PET, can be formed into an amorphous form by being quenched from the melt, or it can be crystallized either by slow cooling from the melt or by stretching between the glass-transition temperature (T_g) and the cold-crystallization temperature. PEN exhibits a T_g value of about 120°C, and this makes it quite attractive as a high-temperature polymer for film, tape, and molding applications. PEN possesses oxygen barrier properties four to five times higher than those of PET, and this makes PEN attractive for packaging applications.

One of the unusual characteristics of PEN, obtained by melt polycondensation without solid-phase post-polycondensation, is that it shows necking behavior upon stretching from the amorphous state above T_g .^{7,8} Some authors have reported that this neck formation is a result of a highly cooperative orientation of the

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naphthalene planes parallel to the surface of the film. This behavior resembles an isotropic–nematic structural transition that occurs at highly localized regions of the sample.

It has been reported that PEN also has two crystal forms (α and β), and both are triclinic, depending on the crystallization temperature.⁹ Crystallizing at 180°C yields the α form, as reported by Mencik,² whereas crystallizing at 240°C yields the β form. Recent X-ray work¹⁰ has suggested the presence of a mesophase in addition to the crystal form. In this mesophase structure, the molecular chains are in registry with each other in the meridional direction but not fully crystallized in the equatorial direction. The emergence of this structure is due to the drawing of PEN at temperatures of 120 or 150°C.¹¹ This structure persists upon annealing at 180 or 200°C, and this leads to the conclusion that this mesophase structure is stable at high temperatures.

In previous articles,^{12,13} we represented the amount of the rigid phase structure, f_r , as a function of I_{1e} , the extra first strain invariant, which is equal to $I_1 - 3$, and a correlation between these two was experimentally obtained, so that f_r varied between 0 and 1 with the square root of I_{1e} . The first strain invariant I_1 equals $\lambda_1^2 + \lambda_2^2 + \lambda_3^2$, with λ_i being the draw ratios in the three principal directions and I_{1e} equaling $I_1 - 3$.

This relationship can be expressed with the following equation:

$$f_r = I_{1e}^{0.5} / I_{1e,\max}^{0.5}$$

The value of $I_{1e,\max}$ corresponded to the maximum attainable draw ratio, which equaled 6.9 at 145°C in the material studied therein.

In the same article, we compared the stress–strain curve with f_r during drawing. We observed that when f_r was reaching 50%, for a draw ratio of 4, a dramatic increase in the stress was measured. Actually, the dramatic increase in stress suggested a critical degree of the rigid phase structure, similar to a percolation threshold accompanied by an inversion of the continuous phase, above which the rigid phase structure was drawn. When f_r was less than 50%, the amorphous phase was the continuous phase, with the rigid phase dispersed therein. If f_r was greater than 50%, phase inversion took place, and the rigid phase formed the continuous phase, with an amorphous phase dispersed therein.

There have been several other reports^{14,15} of a mesophase occurring in both oriented PET and PEN prepared under specific conditions. Both nematic and smectic states were recognized in a series of stretching experiments on PET,¹⁶ and these mesophase states characterized stages in the crystallization process. During the cold drawing of PET under various conditions, all-nematic or all-smectic forms were pro-

duced.¹⁷ An annealing of cold-drawn PET fibers demonstrated a progression from nematic order to smectic order and from smectic order to crystalline order.¹⁸

More recently, a mesophase in PEN fibers prepared by spinning at a windup speed of 500 mm/min followed by drawing at 120°C was reported. In a further study of this mesophase,¹⁹ it was reported that a low temperature and a high strain encouraged the mesophase formation. However, the mesophase was not very stable and could be removed by annealing. The observed PEN mesophase was interpreted as a nematic structure in which substantial lengths of individual chains were fully extended but did not pack laterally in the crystalline register, with a random conformational disorder along the PEN chains.

Shrinkage or shrinkage stress is generated through an entropic retraction. When the internal energy of an oriented polymer is elevated by an increase in the temperature, polymer molecules tend to relax the orientation by retracting from an ordered, extended conformation to a disordered, random coil. This eventually produces a change in the length or contraction force. Shrinkage can be observed through the measurement of the change in a sample length with free ends as a function of time or temperature.

The shrinkage behavior of PET is rather complicated but well documented, and an increased dimensional stability of biaxially oriented PET containers and films can be obtained by heat setting.²⁰ Even with heat setting, the hot-fill temperature of PET containers has been reported to be limited to 85–95°C,^{21,22} and for certain applications, such as hot-fill applications, shrinkage properties are inadequate.

A two-color laser photometric measurement system has been used to follow birefringence changes in the annealing of prestretched films.^{23,24} At high stretch rates, comparable to industrial stretch rates, with which substantially oriented and strain-induced structures are obtained, the initial relaxation stage disappears, and birefringence continues to increase throughout the heat-setting process even at temperatures very close to T_g . The kinetics of the structural changes exhibit a complex behavior, and the largest rates of structural changes have been observed in PET films exhibiting intermediate birefringence levels. As a result, the shrinkage behavior of oriented polyester films is rather complex, and its relation to structural variations is still not clarified.

As already described, the drawing behavior of amorphous PEN, obtained by melt polycondensation without solid-phase postpolycondensation, is characterized by a necking behavior, and the end of the yielding or necking is reached when the amount of the induced rigid phase is 50%. The stretching behavior of PEN is more characterized by strain-induced rigid phase formation¹² than by stress- or strain-induced crystallization.

The shrinkage behavior is characterized by two regimes.¹³ The first one is for draw ratios below the necking behavior in which films shrink back to their original length, comparable to the shrinkage behavior of PET at small draw ratios. The second regime, for draw ratios above the necking behavior, is characterized by a shrinkage behavior that is different in many aspects from the shrinkage behavior of PET. Uniaxially drawn samples are characterized by a small value of shrinkage for temperatures between 120 and 160°C and by no further shrinkage for higher temperatures. The films never shrink back below the draw ratio corresponding to necking, and a linear relationship can be obtained between the initial draw ratio and the final draw ratio after shrinkage at temperatures above 160°C. From differential scanning calorimetry (DSC) measurements, a structure change can be observed by which a part of the induced rigid phase is transformed into a crystalline structure, and the sample drawn at a draw ratio corresponding to the necking behavior, with no shrinkage even with free ends, undergoes a quasicomplete transformation of the rigid amorphous phase into a crystalline phase.

A heat treatment of oriented films with fixed ends stabilizes the induced structures, and the shrinkage of these heat-set films is zero for temperatures approaching the heat-setting temperature. The heat setting of oriented PEN films can completely eliminate shrinkage for temperatures up to the heat-setting temperature.

With this study, we have aimed to clarify how heat treatment under the specific conditions of the heat-setting temperature and time influences the shrinkage behavior of industrially produced PEN bottles. This could lead to a better understanding of shrinkage behavior.

In this article, we present our results on the shrinkage behavior of oriented PEN films taken out of the bottles, as influenced by heat treatment, using a fixed geometry at different temperatures and times of heat setting and using density and DSC measurements in addition to the shrinkage curves to perform a structural analysis.

EXPERIMENTAL

Materials

The poly(ethylene 2,6-naphthalene) (PEN) bottles used in this study were provided by Rexam Petainer AB. The bottle thickness for the cylindrical part was 0.5 mm, and the volume was 380 mL. These bottles are industrially used for the packaging of beer.

Thermal analysis

The thermal properties of unoriented and oriented PEN films were determined with a Universal V1.6I TA

Instruments apparatus at a heating rate of 10°C/min under a dry nitrogen atmosphere. T_g for an unoriented PEN sample was observed around 129°C, the cold-crystallization peak temperature was observed around 197°C, and the melting temperature was observed at 280°C. The heat of cold crystallization was around 35 J/g, and the heat of fusion was 40.55 J/g with a heat capacity increase at T_g of 0.3360 J/(g K) or 84 J/(K mol).

Crystallinity

The crystallinity of the films before and after orientation was determined with DSC thermograms. The crystallization exothermic enthalpy, $\Delta H_{\text{cold crystallization}}$ or ΔH_c , was subtracted from that of the melting endotherm, $\Delta H_{\text{melting}}$ or ΔH_m , to determine the amount of the apparent crystallinity initially present in the samples. The crystallinity of the films was calculated as follows:

$$\text{Crystallinity (\%)} = \Delta H_{\text{exp}} \times 100 / \Delta H_f$$

where ΔH_{exp} is equal to $\Delta H_{\text{melting}} - \Delta H_{\text{cold crystallization}}$ and ΔH_f is the heat of fusion for 100% crystalline PEN (103.4 J/g).^{25,26}

Heat setting

Samples cut from the walls of the industrially produced bottles were mounted with a fixed geometry in a circular steel frame with an internal diameter of 55 mm. The mounted samples were then placed in a circulating air oven for 30 min at the desired temperature (120–240°C). After 30 min, the frame with the fixed samples was removed from the circulating air oven and allowed to cool to room temperature before the samples were removed from the frame. Previous studies have shown that a treatment time of 30 min is sufficient to attain the desired temperature in a circulating air oven and to obtain a constant density value for heat-set films.

To simulate the heat setting of bottle blow molding, we used a heat-setting process. A cylindrical aluminum block with an internal diameter of 54 mm (1 mm less than the internal diameter of the circular steel frame) and a height of 150 mm was constructed. This aluminum block was preheated in the circulating air oven during 30 min at the desired temperature. A PEN sample, taken out of a bottle wall, was fixed in the circular steel frame and put in the circulating air oven at the top of the preheated aluminum block for the desired heat-setting time. One surface of the sheet touched the aluminum block, and the other surface was exposed to air. Therefore, this test with the aluminum block simulated a blow-mold system with different heat-set times. The sample was heated because

of the contact with the aluminum block on the one surface, and the mass of the aluminum block was sufficient to keep the temperature of that block constant. During the heat-setting experiments at short heat-setting times, up to a maximum of 20 s, the air oven was opened, and the temperature of the air approached the ambient temperature.

After heat setting at the desired temperature and heat-setting time, the sample, which was still fixed in the circular steel frame, was taken off the aluminum block, and it was cooled with compressed air. After cooling to ambient temperature, the sample was taken out of the frame, and the circular sample, which was in contact with the aluminum block, was cut out of the total sample. This circular sample, with a diameter of 50 mm, was used for the shrinkage measurements and for the structural characterization.

Temperature rise during heat setting in the oriented films

The polymer sample taken out of the cylindrical part of the bottle was considered a slab of thickness l , bounded by a parallel plane (the surface of the aluminum block) on the one side, with practically no heat transfer on the other side. The transfer of heat through the thickness of the slab was assumed to occur by linear heat conduction. This transfer of heat corresponded to the same case in which a slab of thickness $2l$ was bounded by a pair of parallel planes on both sides of the slab. An equation describing one-dimensional transient heat transfer may be written as follows:

$$\frac{\delta T}{\delta t} = \kappa \frac{\delta^2 T}{\delta x^2} \quad (-1 < x < 1)$$

where T is the temperature at time t , x is the distance from the center of the slab in the thickness direction, and κ is the thermal diffusivity:

$$\kappa = \frac{k}{\rho C_p}$$

where k is the thermal conductivity, ρ is the density, and C_p is the specific heat of the sample.

The boundary conditions for the heat-transfer equation are

$$T = T_a, \text{ when } x = -1$$

$$T = T_a, \text{ when } x = 1$$

$$T = T_0, \text{ when } t = 0$$

where T_a is the temperature of the aluminum block, and T_0 is the starting temperature of the slab.

The equation for transient heat transfer with the defined boundary conditions has been solved,²⁷ and the solution for this case has the following form:

$$\frac{T - T_0}{T_a - T_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \times \exp \left[- \frac{(2n+1)^2 \pi^2 \Theta}{4} \right] \cos \frac{(2n+1)\pi \xi}{2}$$

Θ and ξ are dimensionless parameters described as follows:

$$\Theta = \frac{\kappa t}{l^2}$$

$$\xi = \frac{x}{l}$$

The solution of the dimensionless heat-transfer equation may be obtained for various values of t and x .

The values of k , ρ , and C_p for PEN were taken to be 0.14 J/m s K, 1350 kg/m³, and 1600 J/kg K, respectively.²⁵ The thickness of the PEN sample was 500 μ m.

Shrinkage

The oriented samples, without or with heat setting, were placed unconstrained in a circulating air oven at the selected temperature. After 30 min, the samples were removed and allowed to cool to room temperature, and the displacement of the ink marks on the samples was measured and controlled by the thickness variation of the samples. The influence of the shrinkage behavior was expressed by the measured length variation and was equal to the ratio of the length variation between the ink marks after shrinkage on the original length.

The thermal shrinkage can be represented as follows:

$$\frac{(L_0 - L)}{L_0} \times 100\%$$

where L_0 is the sample length along the measured direction and L is the sample length after thermal treatment.

RESULTS AND DISCUSSION

Shrinkage of the bottles

We measured the shrinkage of the bottles by putting them into a circulating air oven at the desired temper-

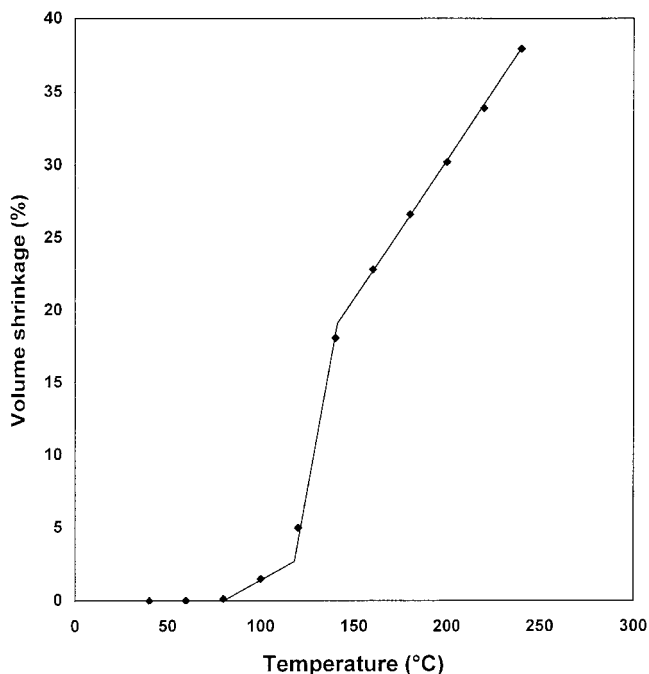


Figure 1 Free-volume shrinkage of the PEN bottles as a function of the heat-shrinkage temperature.

ature, ranging from 40 to 240°C, for 15 min to obtain an equilibrium value of the shrinkage. After the bottles cooled to ambient temperature, we measured the volume by filling them with water, and we measured the lengths between the ink marks on the bottles in the height and circumferential directions. The differences between the measured lengths and volumes and the original values characterized the shrinkage behavior.

The measured values of the volume shrinkage, expressed as a percentage of the original volume, as a function of the temperature are given in Figure 1.

The square root of the extra first strain invariant was calculated from the measured lengths and corresponding shrinkage in both directions with an original stretch ratio of 3 in both directions. These calculated values are given in Figure 2.

For both curves, there are three zones. A first zone, from 60 to 120°C, is characterized by a small variation of the volume, 2.7% at 118°C, and of the square root of the extra first strain invariant. For the second zone, from 110 to 150°C, a strong volume shrinkage, 19.1% at 141°C, can be observed, accompanied by a strong decrease in the square root of the extra first strain invariant. For temperatures exceeding 150°C, continuous decreases in the bottle volume, 38% at 240°C, and in the square root of the extra first strain invariant can be observed.

Shrinkage after heat setting under equilibrium

We next heat-set samples taken from the cylindrical part of the bottle wall with a fixed geometry at tem-

peratures ranging from 120 to 240°C for 30 min to obtain an equilibrium structure after the heat setting. The shrinkage behavior of the heat-set samples was measured with free ends in both directions in a circulating air oven by the temperature being increased from 40 to 240°C in steps of 20°C. The measured shrinkage behavior in both directions was used to calculate the square root of the extra first strain invariant as a function of the heat-setting temperature and the temperature used for the shrinkage measurements. The obtained results of the square root of the extra first strain invariant are represented on Figure 3.

After the heat setting, two different zones were observed in the shrinkage behavior. One interesting parameter in the figure and in the shrinkage behavior of the heat-set PEN samples was the increase in the starting temperature of the shrinkage of those heat-set samples. Once the heat-set temperature was 215°C, the starting temperature of the shrinkage was higher than the heat-setting temperature. This meant that the PEN bottles or films could be heat-set at temperatures higher than 215°C without any shrinkage at that temperature. The bottles could be heat-set after blow molding at temperatures higher than 215°C and be taken out of the molds without further cooling. This was a very interesting phenomenon in the heat setting of oriented PEN. The time of heat setting was 30 min, a value too high for industrial applications. In the next section, we study the effect of the heat-setting time on the stability of the heat-set oriented PEN bottles and films to study the possibility of using the process of heat setting for PEN bottles under industrial conditions.

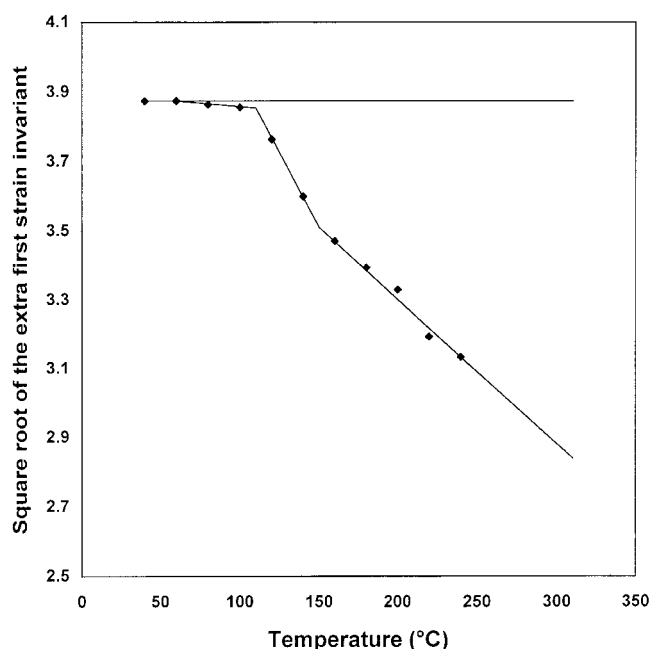


Figure 2 Calculated square root of the extra first strain invariant as a function of the shrinkage temperature.

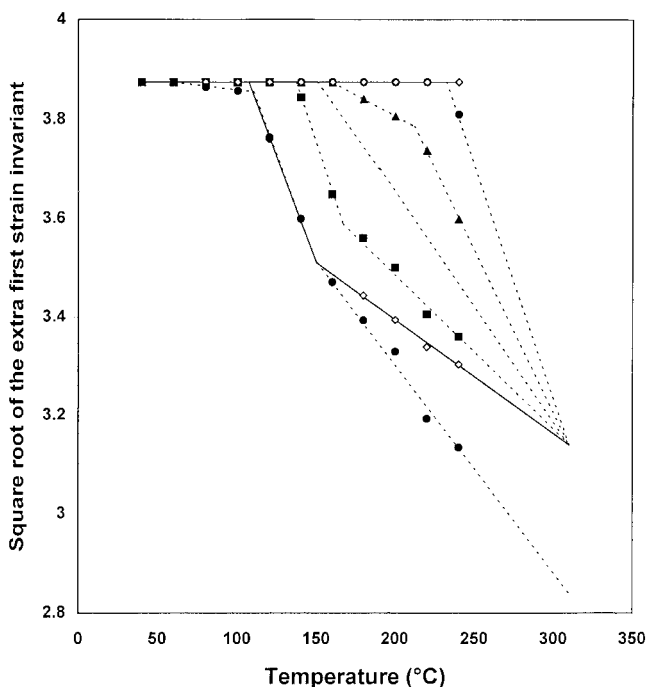


Figure 3 Square root of the extra first strain invariant as a function of the heat-setting temperature: (●) original sample, (◇) heat-setting temperature = 120°C, (■) heat-setting temperature = 160°C, (△) heat-setting temperature = 180°C, (▲) heat-setting temperature = 200°C, and (●) heat-setting temperature = 220°C.

Another characteristic of the shrinkage behavior was observed at high temperatures. The values of the square root of the extra first strain invariant, a parameter characterizing the stretch ratio under multiaxial orientation, all converged to a constant value of 3.15 at 310°C. This shrinkage behavior of heat-set PEN was totally different from the shrinkage behavior of heat-set PET, as shown in Figure 4. The stretch ratio in the height direction was 2.6 and in the circumferential direction was 3.6 in the original samples. These PET samples were taken from industrially produced PET bottles with a volume of 1500 mL.

For PET samples heat-set up to heat-setting temperatures of 220°C, the values of the square root of the extra first strain invariant converged to a value of zero at 310°C. This means that the original induced orientation was completely recovered at 310°C and is an indication that no slip occurred during the stretching of PET. For PET, the starting temperature of the shrinkage for heat-set samples was practically constant for all heat-setting temperatures and was equal to 80°C.

The residual elongation curves, corresponding to the square root of the extra first strain invariant, all converged in the high-temperature range to a temperature of 310°C for PET and PEN. This seemed to be a characteristic temperature for the polyesters studied and corresponded to the equilibrium melting temper-

ature of heat-set PET samples.²⁸ At that temperature, the induced elongation of the rigid amorphous phase completely recovered for PET, whereas for PEN, a limiting value of 3.15 was measured. This corresponded to a residual draw ratio of 3.6.

This behavior corresponded to the shrinkage behavior of drawn PEN samples with necking¹³ measured on PEN obtained by melt polycondensation without solid-phase postpolycondensation. For the drawn sample with a draw ratio of 4, just after necking, the shrinkage was practically zero for temperatures up to 240°C. No shrinkage was measured for the drawn sample at the end of the necking zone, accompanied by a phase inversion from the amorphous phase to the rigid amorphous phase as a continuous phase. This could be explained as follows: the rigid amorphous phase was stable up to 240°C and was not in a stretched state at the moment of phase inversion.

A linear relationship between the calculated draw ratios after shrinkage for temperatures greater than 170°C and the initial draw ratio, related to samples with a draw ratio above the necking behavior, was also observed and the final draw ratio after shrinkage was 60% of the initial draw ratio with a corresponding constant shrinkage value of 40%. In this case, the rigid amorphous phase seemed to be elongated after phase inversion, and 40% of the induced supplemental elongation was recovered during shrinkage at high temperatures.

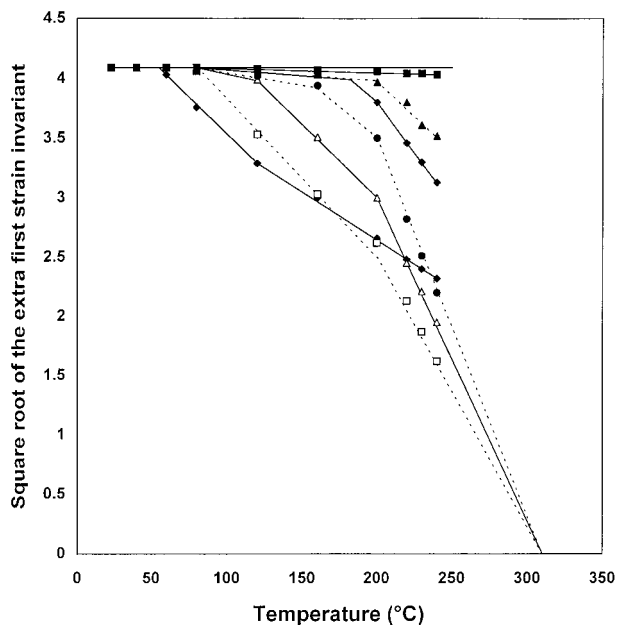


Figure 4 Square root of the extra first strain invariant of the heat-set PET samples as a function of the heat-setting temperature: (◆) original sample (no heat setting), (□) heat-setting temperature = 120°C, (△) heat-setting temperature = 160°C, (●) heat-setting temperature = 200°C, (◆) heat-setting temperature = 220°C, (▲) heat-setting temperature = 230°C, and (■) heat-setting temperature = 240°C.

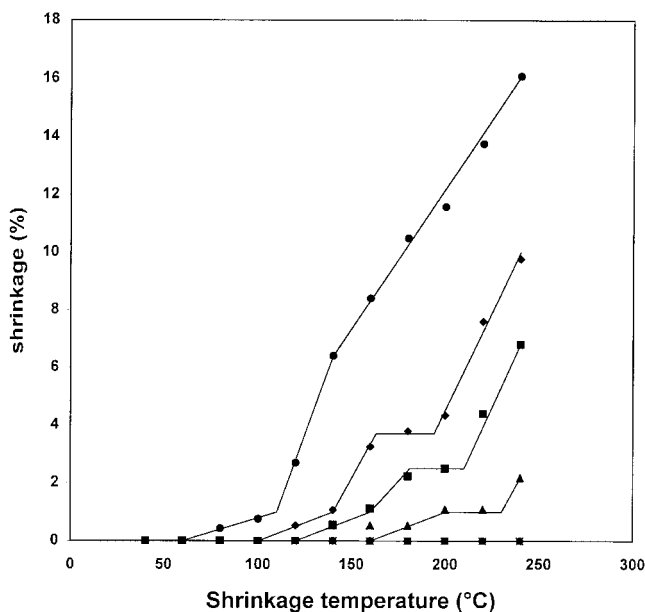


Figure 5 Shrinkage of the heat-set samples in the circumferential direction after a contact time of 20 s on the heated metal surface: (●) original sample (no heat setting), (◆) heat-setting temperature = 200°C, (■) heat-setting temperature = 220°C, (▲) heat-setting temperature = 240°C, and (▣) heat-setting temperature = 255°C (lowest).

The value of 3.6, measured for PEN samples with solid-phase postpolycondensation, was lower than the values obtained for PEN samples without solid-phase postpolycondensation, for which the values of the final draw ratios in all cases were higher than 4.

The effect of the solid-state postpolycondensation seemed to diminish the draw ratio of the induced rigid amorphous phase, accompanied by an elimination of the necking behavior. As a result, the process of solid-phase postpolycondensation diminished the draw ratio of the induced rigid amorphous phase, and there was an increasing force at lower draw ratios during the orientation process of PEN and PET. This lower value of the draw ratio of the induced rigid amorphous phase was measurable for PEN and was not directly measurable for PET. For PET, the natural draw ratio went to lower values with an increased process of solid-phase postpolycondensation, which was characterized by a higher value of the molecular weight of PET. The process of solid-phase postpolycondensation was rather complicated, inducing an higher value of the molecular weight and a lower value of the draw ratio of the induced rigid amorphous phase.

For the original PEN samples, without heat setting, the corresponding value of the extra first strain invariant was 2.86 or a draw ratio of 3.3, lower than the value of 3.6 after the stabilization of the induced structures during drawing. This was a result of the high stretching rate during the process of blow molding

and the very rapid cooling after drawing. The resulting structure was still not in equilibrium, and some orientation was still present in the amorphous phase. After the stabilization of the induced structures through heat setting at 120°C, the orientation of the amorphous phase was further transformed into an increase in the rigid amorphous phase, as characterized by a higher draw ratio of the rigid amorphous phase.

Shrinkage after heat setting under transient conditions

The results of the shrinkage after 20 s of heat setting are reproduced in Figures 5 and 6. As explained in the Experimental section, these experiments simulated the heat-setting process after bottle blow molding.

The measured shrinkage of the heat-set samples was a function of the heat-setting temperature and became smaller with the increasing heat-setting temperature. This can be more clearly seen in Figure 7, in which the measured value of the shrinkage in the height direction is represented as a function of the heat-setting temperature. From a heat-setting temperature of 170°C, the measured shrinkage at 240°C became smaller, and the shrinkage at 240°C was zero at a heat-setting temperature of 260°C.

As already mentioned in the Experimental section, there was a temperature profile in a heat-set film

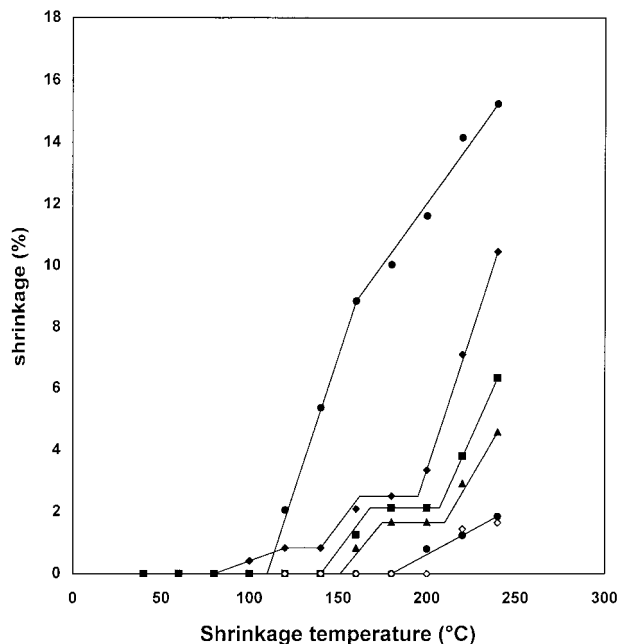


Figure 6 Shrinkage of the heat-set samples in the height direction after a contact time of 20 s on the heated metal surface: (●) original sample (no heat setting), (◆) heat-setting temperature = 200°C, (■) heat-setting temperature = 220°C, (▲) heat-setting temperature = 240°C, and (○) heat-setting temperature = 255°C.

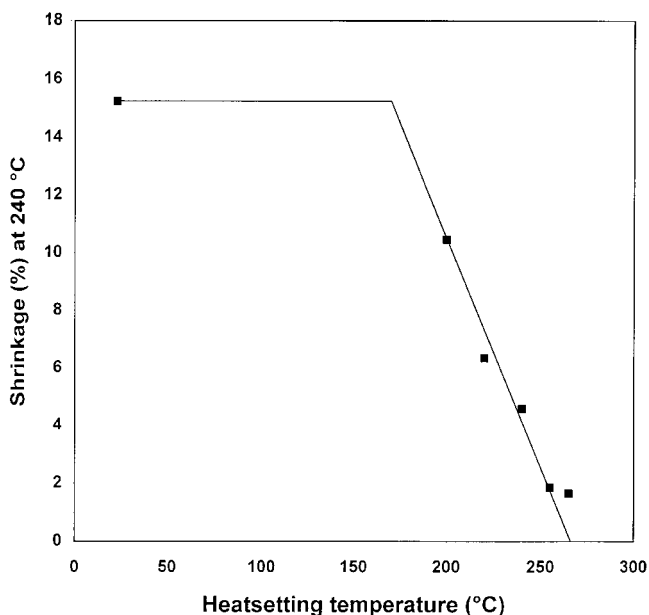


Figure 7 Measured shrinkage at 240°C in the height direction as a function of the heat-setting temperature for a contact time of 20 s.

during those short contact times. The temperature of the surface of the film in direct contact with the aluminum block equaled the temperature of the aluminum block, and the outer surface of the film was at the lowest temperature, with a cosine variation of the temperature between the two temperatures, for contact times greater than 3 s and for a sample thickness of 500 μm .

An interesting temperature for a temperature profile is the mean temperature of a heat-set film as a function of the heat-setting temperature and contact time, and it can be calculated from the equation of transient heat transfer. For the geometry used and for contact times greater than 3 s, this mean value of the temperature can be approximated with the following relation:

$$\frac{T_{\text{mean}} - T_0}{T_a - T_0} = 1 - 0.811 \times \exp(-0.1615 \times t)$$

As an example, for a contact time of 20 s and for a heat-setting temperature of 220°C, the mean temperature of the heat-set sample was 194°C; for a heat-setting temperature of 220°C, it was 213°C; for a heat-setting temperature of 240°C, it was 233°C; and for a heat-setting temperature of 260°C, it was 252°C. After a heat-setting time of 20 s, the mean temperature of the heat-set samples was 6–7°C lower than the used heat-setting temperature.

For the different heat-setting experiments, contact times of 3–20 s were used with heat-setting temperatures of 200–265°C. For all those experiments, the

mean temperature of the samples at the end of the heat setting was calculated, and the measured values of the shrinkage in both directions was used to calculate the corresponding values of the square root of the extra first strain invariant. In this way, a global view could be obtained of the resulting shrinkage of the heat-set samples as a function of the reached mean temperature of the heat-set sample. The use of such a representation made it possible to use it for other sample thicknesses. The obtained results are given in Figures 8 and 9.

Different and interesting results were obtained from these two graphical representations of the shrinkage behavior during the transient heat-setting process.

The shrinkage behavior from 80 to 120°C, corresponding to the shrinkage of the amorphous phase, was constant for mean heat-setting temperatures up to 194°C. This shrinkage behavior went to a value of zero as the mean heat-setting temperature increased from 194 to 213°C. For a mean heat-setting temperature of 213°C, the shrinkage due to the orientation of the amorphous phase was completely eliminated.

A second zone in the shrinkage behavior was observed at 130–167°C. A mean heat-setting temperature of 120 or 150°C produced the same effect on the

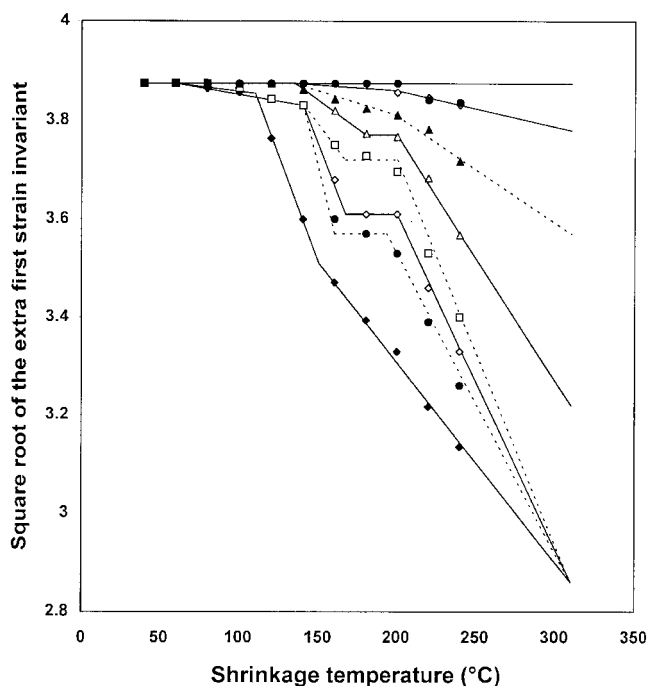


Figure 8 Square root of the extra first strain invariant as a function of the shrinkage temperature for different values of the obtained mean temperature of the heat-set samples: (◆) original sample, (●) mean heat-setting temperature = 120 and 150°C, (◇) mean heat-setting temperature = 170°C, (□) mean heat-setting temperature = 194°C, (△) mean heat-setting temperature = 213°C, (▲) mean heat-setting temperature = 232°C, and (●) mean heat-setting temperature = 248°C.

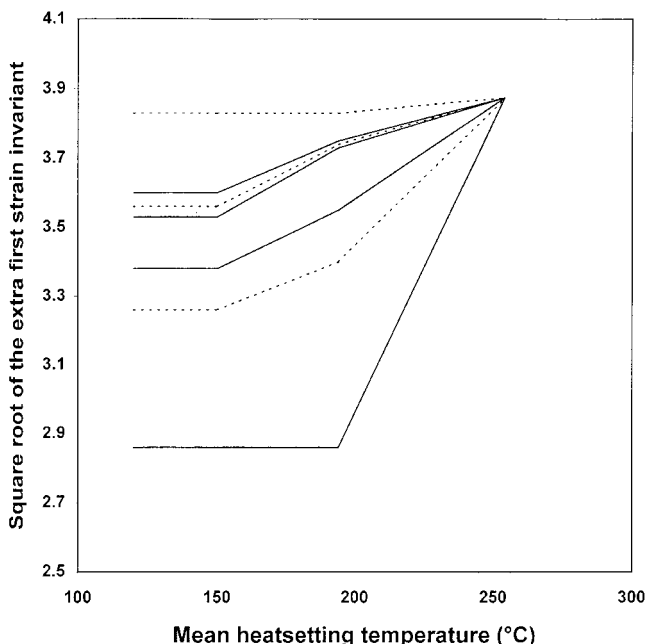


Figure 9 Square root of the extra first strain invariant as a function of the mean temperature of the heat-set samples for shrinkage temperatures (from bottom to top) of 310, 240, 220, 200, 180, 160, and 140°C.

shrinkage behavior. The shrinkage became lower if the heat-setting temperature was higher than 150°C, with the first zone going up to a temperature of 194°C with a relatively strong variation and with a second zone going from 194 to 254°C with a relatively slower variation of the measured shrinkage behavior. For the lowest values of the mean heat-setting temperature, from 120 to 194°C, a temperature zone of constant shrinkage behavior and a corresponding constant value of the extra first strain invariant were observed between 167 and 200°C.

The last zone of the shrinkage behavior was observed from 200°C to the extrapolated value of 310°C. In this zone, the shrinkage became lower with an increasing mean temperature of the heat-set samples and reached a value of zero at 254°C. The extrapolated value of the square root of the extra first strain invariant was constant at a value of 2.86 for temperatures up to 194°C and went to the initial value at 254°C.

The shrinkage behavior started at a constant temperature of 135°C if the mean heat-setting temperature was higher than 213°C.

For practical applications, the measured shrinkage at a heat-setting temperature of 255°C after 10 and 20 s is important to study with respect to the time limit necessary to obtain a heat-set bottle without shrinkage after heat setting that can be taken out of the mold without further cooling. The measured shrinkage in both directions is represented in Figure 10. For this heat-setting temperature, the shrinkage in the height direction was more critical than that in the circumfer-

ential direction. The shrinkage in the circumferential direction was already zero for a contact time of 20 s. The appearance of three different zones in the shrinkage behavior for a contact time of 10 s can be clearly observed in the graphical representation of the shrinkage behavior. A contact time of 30 s was sufficient to obtain a zero value of the shrinkage in the height direction at that heat-setting temperature.

The measured results can be explained by the possible occurrences of two types of rigid amorphous phases: an induced rigid amorphous phase with a mean shrinkage temperature of 151°C and another induced rigid amorphous phase with a shrinkage behavior between 200 and 310°C, with a final value of the elongation at 310°C increasing from 2.86 up to the initial multiaxial elongation of 3.87. This corresponds to a draw ratio of 3.3 for the lowest heat-setting temperatures and to a draw ratio of 4.25 for the initial samples, the value also reached for a heat-setting temperature of 254°C.

This shrinkage behavior of the heat-set samples corresponded to the shrinkage behavior of the previously studied PEN samples,¹³ which were obtained by melt polycondensation without solid-phase postpolycondensation. The shrinkage behavior for oriented PEN, obtained with solid-phase postpolycondensation, was more complicated than the previous one, but the same general lines were observed. In both cases, the shrinkage behavior in the temperature zone of 130–170°C

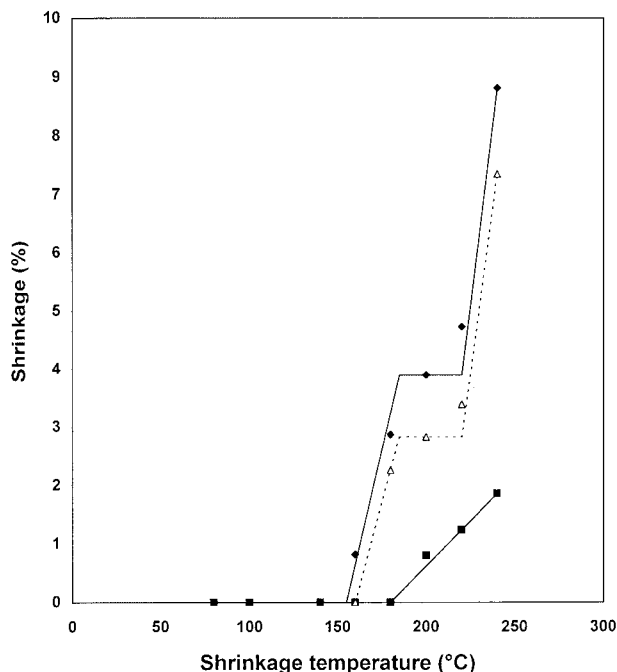


Figure 10 Shrinkage in both directions after heat setting at 255°C for 10 and 20 s: (◆) shrinkage in the height direction after a contact time of 10 s, (△) shrinkage in the circumferential direction after a contact time of 10 s, and (■) shrinkage in the height direction after a contact time of 20 s.

was measured, and this was followed by a constant value of the square root of the extra first strain invariant for the heat-set PEN samples without solid-phase postpolycondensation up to a temperature of 240°C and extra shrinkage behavior in the temperature zone of 200–310°C for the PEN samples with solid-phase postpolycondensation. These two zones in the shrinkage behavior can be explained by the presence of two different structures of the rigid amorphous phase. For the drawn PEN samples without solid-phase postpolycondensation, necking behavior during drawing was observed, and the drawn sample obtained just after necking was stable up to 240°C. This means that the induced rigid amorphous phase was the most stable. For samples further drawn after the necking behavior, 60% of the extra draw ratio was stable during the shrinkage behavior, and 40% was recovered from 120 to 170°C. Of the extra induced rigid amorphous phase, after necking, 40% was the less stable structure, and 60% was the most stable structure. This also corresponds to the shrinkage behavior measured in this study for PEN samples obtained after solid-phase postpolycondensation. The possible presence of two different forms of the induced rigid amorphous phase, probably nematic and smectic, is possibly linked to the two possible crystal forms (α and β) of PEN in its semicrystalline structure. If the mean heat-setting temperature was higher than 194°C, a continuous transformation of the less stable rigid amorphous phase into the more stable rigid amorphous phase was observed, accompanied by an extrapolated higher stable draw ratio at 310°C. Further studies are necessary to clarify this equivalence and to characterize the different induced rigid amorphous phases as well as the possible induced crystalline structure as folded lamellar, fibrillar, or fringed micellar crystalline structures.

Density

As for PET, a parameter indicating structural variations is the density of heat-set samples. The measured density as a function of the heat-setting temperature is given in Figure 11.

For PET, a constant variation of the density as a function of the heat-setting temperature was measured.²⁰ For PEN, the density was increasing at 100°C from 1.3453 g/cm³ for the initial sample to 1.3575 g/cm³ at 155°C. The density values remained constant from 155 to 215°C, after which the density slowly increased up to 1.3665 g/cm³ at 258°C. This behavior of the density variations was different from that of PET and was another difference between the heat setting of PET and PEN. The measured densities of the heat-set samples after shrinkage at 240°C followed the same behavior, with a nearly constant density difference of 0.0025 g/cm³.

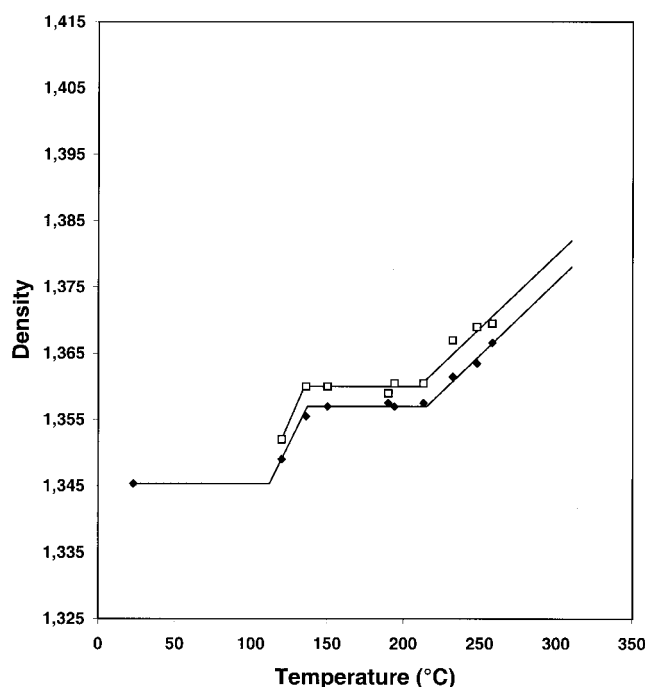


Figure 11 Density of the heat-set samples as a function of the reached mean temperature during the heat-setting process: (◆) after heat setting and (□) after heat setting and free shrinkage at 240°C.

As previously explained, PEN provides a new example of a polymer that may possess in the oriented state an amorphous fraction and a rigid amorphous fraction, which may be a nematic structure, a smectic structure, or both. The rigid amorphous fraction does not contribute to the increase in the heat capacity at T_g and devitrifies only at temperatures well above T_g . Similar behavior was found in several high-melting-temperature polymers with phenylene groups in the main chain. The overall rigid fraction, f_r , constituting the rigid amorphous phase and the crystalline phase, is computed from the heat capacity, C_{pr} , as follows:

$$f_r = 1 - [\Delta C_p(m) / \Delta C_p(a)]$$

where $\Delta C_p(m)$ and $\Delta C_p(a)$ represent the measured and total amorphous heat capacity increases at T_g , respectively. In the nonoriented state, for which the two-phase model of amorphous and crystalline phases is valid, the fraction f_r is equal to the fraction of the crystalline phase. In the oriented state, with or without heat setting, if we suppose a two-phase model of amorphous and rigid amorphous phases, f_r is equal to the fraction of the rigid amorphous phase and can be quantified. From the measured value of the heat capacity increase at T_g , a value of 0.59 for f_r was calculated. From the measured value of the density of the amorphous phase of the used PEN, equal to 1.3250 g/cm³ and a fraction of 41% of the amorphous phase,

the calculated density of the rigid amorphous phase was 1.36 g/cm^3 . After the heat setting of the oriented PEN samples and after mean heat-setting temperatures were reached of $155\text{--}210^\circ\text{C}$, the density was 1.3575 g/cm^3 , the fraction of the rigid amorphous phase remained constant at 59%, and the density of the rigid amorphous phase was increasing to 1.3780 g/cm^3 . This is the same value as that of the density of the oriented heat-set samples extrapolated to the characteristic temperature of 310°C . This is an indication that this density may be the density of the most stable rigid amorphous phase. For mean heat-setting temperatures higher than 210°C , the fraction of the rigid amorphous phase increased and reached a value of 100% by a temperature of 310°C . These extrapolated densities were different from the densities of the two crystal structures of PEN. The unit cell densities of the α and β forms were 1.407^2 and 1.439 g/cm^3 .⁹ Further studies have been undertaken to correlate these structural variations with the infrared absorption spectra of oriented and heat-set samples. These results will be published in a forthcoming article.

CONCLUSIONS

Amorphous preforms of PEN were biaxially drawn into bottles up to the desired volume under industrial conditions. These bottles were used to characterize the shrinkage behavior of the drawn bottles with or without heat treatment and to study structural variations during heat setting. During drawing, a rigid phase structure was induced, and the amount of the induced rigid phase structure was linearly related to the square root of the extra first strain invariant under equilibrium conditions. During the production of these bottles, this equilibrium was not attained because of the high stretching conditions and the rapid cooling after stretching. The structure after orientation contained a rigid amorphous phase and an oriented amorphous phase.

The shrinkage behavior was a function of the temperature and time of heat setting. Long heat-setting times, around 30 min, were used to characterize the possible structural variations of the oriented PEN after heat setting at equilibrium. Under the equilibrium conditions of heat setting, the start temperature of the shrinkage was directly related to the heat-setting temperature and moved from 60°C without heat treatment up to a temperature of 255°C by a heat-setting temperature of 255°C ; this was in contrast to PET, for which the start temperature of shrinkage was always around 80°C . For heat-setting temperatures higher than 220°C , the structural variations changed rapidly as a function of the heat-setting time, and the corresponding shrinkage of the heat-set samples sank to values below 1% in a timescale of 30–60 s for a film thickness of $500 \mu\text{m}$.

A heat treatment of the oriented films taken out of the bottle walls with fixed ends stabilized the induced structures, and the shrinkage of these heat-set films was zero for temperatures up to the heat-setting temperature, in the temperature range of $220\text{--}265^\circ\text{C}$, if the heat-setting time was sufficient. According to the results obtained, a heat-setting time of 30 s for a film thickness of $500 \mu\text{m}$ was sufficient at a heat-setting temperature of 255°C to stabilize the produced biaxially oriented PEN bottles and to take them out the mold without further shrinkage. During the drawing of PEN, two different types of rigid amorphous phases seemed to be induced, one with a mean shrinkage temperature of 151°C and another rigid amorphous phase, more temperature stable than the first one, that shrank from 200 to 310°C . During heat setting at high temperatures, a continuous transformation of the less stable induced rigid amorphous phase into the high stable phase took place.

The heat-set method after blow molding is industrially possible with PEN, without the complicated process of subsequent cooling before the molds are opened, in contrast to PET. This constitutes a big advantage for the blow molding of PEN bottles and the production of oriented PEN films.

Even if there are many similarities between PET and PEN, the shrinkage behavior of PEN is quite different from that of PET, and the presence of the naphthalene rings seems to be the dominant parameter for this behavior. After orientation, PEN more approaches the behavior of a liquid-crystalline polymer than PET does.

The authors are very grateful to Rexam Petainer Co., which kindly supplied the PEN bottles, and to E. Schacht (Faculty of Sciences, University of Ghent), who provided the DSC measurement facilities.

References

1. Cook, J. G.; Huggill, H. P. W.; Lowe, A. R. Br. Pat. GB604073 (1948).
2. Mencik, Z. Chem Prim 1967, 17, 78.
3. Cakmak, M.; Wang, Y. D.; Simhambhatla, M. Polym Eng Sci 1990, 30, 721.
4. Desai, A. B.; Wilkes, G. L. J Polym Sci Polym Symp 1974, 46, 291.
5. Chemistry Weekly, March 6, 1991, p 7.
6. Chemistry Marketing Reporter, July 12, 1993.
7. Cakmak, M.; Lee, S. W. Polymer 1995, 36, 4039.
8. Murakami, S.; Yamakawa, M.; Tsuji, M.; Kohjiya, S. Polymer 1996, 37, 3945.
9. Buchner, S.; Wiswe, D.; Zachmann, H. G. Polymer 1989, 30, 480.
10. Jakeways, R.; Klien, J. L.; Ward, I. M. Polymer 1996, 37, 3761.
11. Saw, C. K.; Menczel, J.; Choe, E. W.; Hughes, U. R. Soc Plast Eng Annu Conf Tech Pap 1997, 2, 1610.
12. Schoukens, G. Polymer 1999, 40, 5637.
13. Schoukens, G.; Verschuere, M. Polymer 1999, 40, 3753.
14. Mahendrasingam, A.; Martin, C.; Fuller, W.; Blundell, D. J.; Oldman, R. J.; Mackeron, D. H.; Harvie, J. L.; Riekel, C. Polymer 2000, 41, 1217.

15. Welsh, G. E.; Blundell, D. J.; Windle, A. H. *Macromolecules* 1998, 31, 7562.
16. Bonart, R. *Kolloid Z Z* 1966, 213, 1.
17. Bonart, R. *Kolloid Z Z* 1968, 231, 16.
18. Asano, T.; Balta Calleja, F. J.; Flores, A.; Tanigaki, M.; Mina, M. F.; Sawatari, C.; Itagaki, H.; Takahashi, H.; Hatta, I. *Polymer* 1999, 40, 6475.
19. Carr, P. L.; Nicholson, T. M.; Ward, I. M. *Polym Adv Technol* 1997, 8, 592.
20. Jabarin, S. A. Presented at the 11th Annual High Performance Blow Molding Conference of the Society of Plastics Engineers, Cleveland Section, Cleveland, OH, Oct 17–18, 1995.
21. Maruhashi, Y.; Asada, T. *Polym Eng Sci* 1992, 32, 481.
22. Maruhashi, Y.; Asada, T. *Polym Eng Sci* 1996, 36, 483.
23. Venkatesvaran, H.; Cakmak, M. *Polym Eng Sci* 2001, 41, 341.
24. Galay, J.; Cakmak, M. *J Polym Sci Part B: Polym Phys* 2001, 39, 1107.
25. Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* 1988, 21, 789.
26. Cheng, S. Z. D.; Janimak, J. J.; Zhang, A.; Guan, J.; Chu, A. L. *Polym Bull (Berlin)* 1988, 20, 449.
27. Carslaw, H. S.; Jaeger, J. C. *Conduction of Heat in Solids*; Oxford University Press: London, 1959.
28. Fakirov, S.; Fischer, E. W.; Hoffmann, R.; Schmidt, G. F. *Polymer* 1977, 18, 1121.