Influence of stress-induced crystallization on the dimensional stability of monoaxially drawn poly(ethylene terephthalate)

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The thermal shrinkage of poly(ethylene terephthalate) (PET) films drawn uniaxially to different draw ratios over a wide range of temperatures was measured and analysed primarily by differential scanning calorimetry (d.s.c.) studies and density measurements, and by recording the load–extension characteristics of the samples associated with the drawing process. The overall orientation of drawn samples was assessed from birefringence measurements. The d.s.c. analysis was found to be an accurate predictor of shrinkage behaviour, particularly with respect to the changes in the exothermic crystallization peak. Furthermore, the analysis has shown that shrinkage is completely suppressed when a degree of crystallinity equal to 43% is reached, which can only be achieved through annealing treatments. A reduction in shrinkage is always manifested by a down-shift and a concomitant flattening of the exothermic crystallization peak.

INTRODUCTION

Stress-induced crystallization phenomena taking place when stretching poly(ethylene terephthalate) (PET) in its amorphous state are widely exploited commercially for the production of fibres, films and bottles. The molecular and morphological orientation resulting from drawing operations in the associated manufacturing processes brings about a state of dimensional instability in the resulting products.

Many studies have been reported on the crystallization of PET occurring in stretching operations[1-4]. Le Bourvellec et al.[5] have indicated that the initial state of orientation of the material and the ambient temperature are the two main parameters that control the kinetics of stress-induced crystallization, which is always much faster than crystallization under stress-free (undrawn) conditions. According to Bragato and Gianotti[6] the mechanism of crystallization changes from a three-dimensional growth to a two-dimensional type and finally to a one-dimensional rod-like growth with increasing level of stretching.

Previous workers[7,8] have shown that the level of crystallinity in drawn PET films does not change appreciably until they have been stretched to at least 150%. Similar observations have been reported by Spruiell[9] for stress-induced crystallization in stretch blow moulding of PET bottles.

Jabarin[10] has shown that the level of orientation in drawn PET products decreases with increasing drawing

temperature, but the extent to which this takes place is less with high-molecular-weight polymers. Nicolas et al.[11] have studied the thermal properties of drawn PET by differential scanning calorimetry and have reported that the crystallization exotherm gradually disappears while the melting endotherm progressively increases with increasing draw ratio. Whereas the heat of fusion was found to be relatively insensitive to draw ratio, the height of the melting endotherm increased sufficiently to be taken as a comparative measure of the level of orientation in the sample.

Studies of the thermal shrinkage of oriented products at temperatures below the melting point of the polymer have been reported by various authors[12-15]. In addition to molecular disorientation, further crystallization has been found to take place during shrinkage, but the underlying mechanism remains unclear. Statton et al.[15] have suggested that crystallization by chain folding is the main event, but the temperatures involved were very near the melting point of the polymer. Other authors[16-19] have indicated that shrinkage is primarily associated with relaxations within the amorphous phase.

Heffelfinger[20] supports the association of shrinkage with relaxation in the amorphous phase by providing evidence for a marked increase in the *trans*-configuration content within the amorphous domains, while no change was found for the crystalline phase.

In the present work, thermal shrinkage in the ambient temperature range of 85–150°C and its dependence on draw ratio were studied on monoaxially drawn samples to elucidate the relationship between dimensional stability and crystallinity.

EXPERIMENTAL

Uniaxial stretching experiments were carried out over a wide range of temperatures and draw ratios using amorphous sheets, 0.98 mm thick, produced from a bottle-grade polymer ($IV = 0.84$). Dumbbell-shaped specimens with a central rectangular section, 4 mm wide and 30 mm long, were punched out from the sheets and stretched monoaxially to different draw ratios using a J. J. Lloyd tensile testing machine fitted with an environmental chamber heated by recirculated hot air. Unless otherwise stated, the rate of clamp separation was kept at 200 mm min^{-1} and the specimens were preheated for 3 min in the stretching device. The specimens were immediately quenched with a wet cloth prior to being removed from the grips and the draw ratio was calculated from measurements of the new distance between the lines previously scribed on the surface of the specimens. The load–displacement curves, on the other hand, were recorded directly on the printer connected to the tensile testing machine.

The dimensional stability of the drawn samples was assessed by measuring the amount of shrinkage taking place after immersing small sections in hot water at temperatures above the T_g of the polymer, i.e. in the range 85–100°C. In another series of experiments shrinkage measurements were carried out in an oven at temperatures between 100 and 150°C.

The effects of annealing the drawn samples at various temperatures under constraints was also investigated. D.s.c. analysis and density measurements were used with the view to establishing the relationship between morphology and dimensional stability. These were in some cases complemented by birefringence measurements on samples exhibiting low and high shrinkage respectively. The latter measurements were carried out using a u.v. spectrophotometer (Beckman Acta MVIII), but the birefringence values could only be calculated for draw ratios up to 4:1.

RESULTS AND DISCUSSION

In *Figure 1* is shown the linear shrinkage in boiling water as a function of draw ratio for samples stretched monoaxially at temperatures above the T_g of the polymer up to 100°C. These data reveal a strong influence of the drawing temperature and draw ratio on the dimensional stability of the drawn samples.

Moreover, the plots in *Figure 2* show that above the T_g of the polymer the ambient temperature plays a minor role, i.e. only a slight increase in shrinkage is observed by raising the temperature to 150°C. The minor influence of ambient temperature on the level of shrinkage is confirmed in annealing experiments, carried out under fixed length conditions. In *Figure 3* it is shown, in fact, that an annealing time of 30 s is sufficient to enhance substantially the dimensional stability of monoaxially drawn products even at a temperature as low as 100°C. Furthermore, a maximum in the level of shrinkage is always observed for samples drawn at around 110°C and a minimum at 80°C, rising again quite rapidly when the drawing temperature is taken below the T_g of the polymer.

The d.s.c. traces in *Figure 4* show a depression of the exotherm peak for samples exhibiting low shrinkage, particularly for samples drawn at 80 and 150°C. The importance of stress-induced crystallization is highlighted by the suppression of the exothermic peak in samples
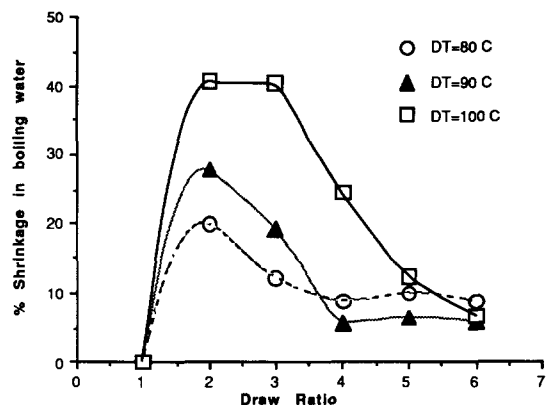
Figure 1 Effect of drawing conditions on shrinkage for samples drawn (uniaxially) at 500 mm min^{-1} at various drawing temperatures (DT)
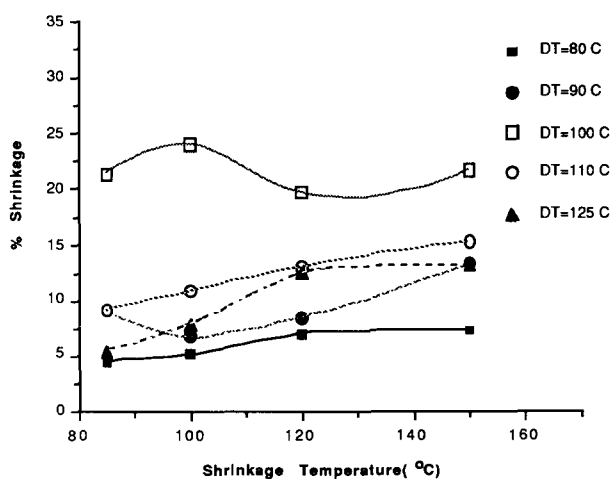

Figure 2 Effect of shrinkage temperature on percentage shrinkage for samples drawn (uniaxially) to 4:1 at various drawing temperatures (DT)
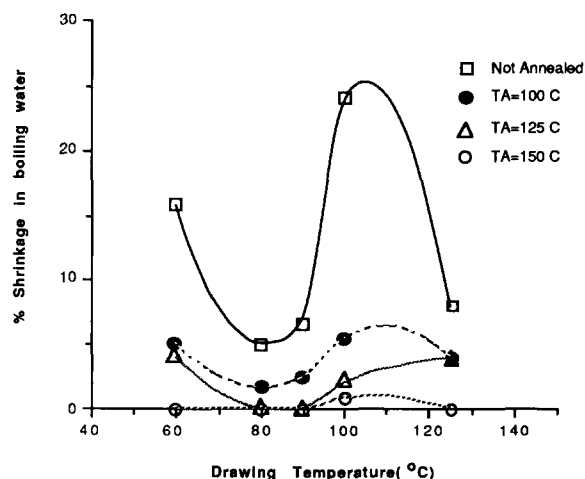

Figure 3 Effect of drawing temperature on shrinkage for samples drawn (uniaxially) to 4:1 and annealed at various temperatures (TA)

drawn 4:1 at 80°C and by the re-emergence of such a peak when the draw ratio is reduced from 4:1 to 2:1 (compare this trend with the shrinkage data in *Figure 1*). Thermal crystallization, on the other hand, appears to be the major factor responsible for the reduction of shrinkage in samples drawn above 100°C. The d.s.c. data
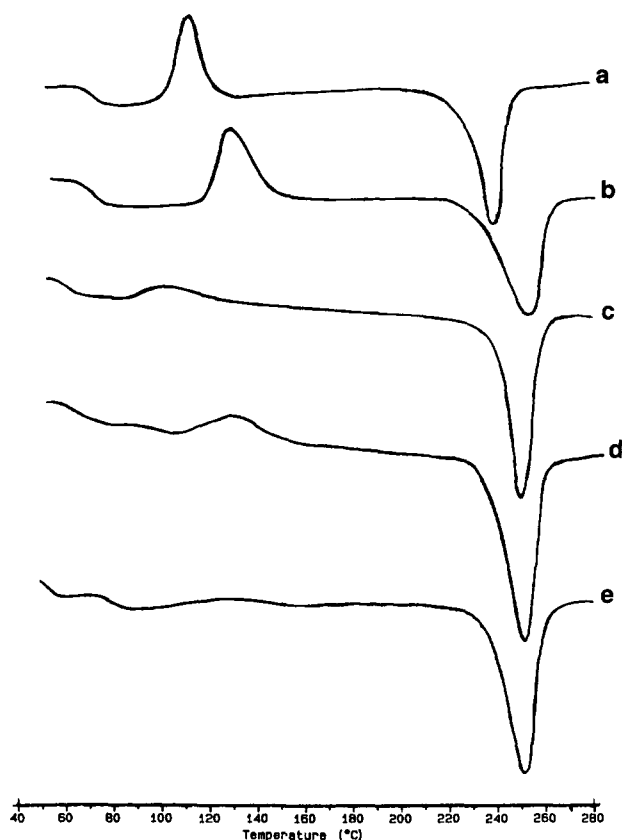
Figure 4 D.s.c. traces at 20°C min^{-1} for samples drawn uniaxially at different drawing temperatures (*TD*) to various draw ratios (*DR*): (a) *TD* = 100°C, *DR* = 4:1; (b) *TD* = 80°C, *DR* = 2:1; (c) *TD* = 80°C, *DR* = 4:1; (d) *TD* = 125°C, *DR* = 4:1; (e) *TD* = 150°C, *DR* = 4:1
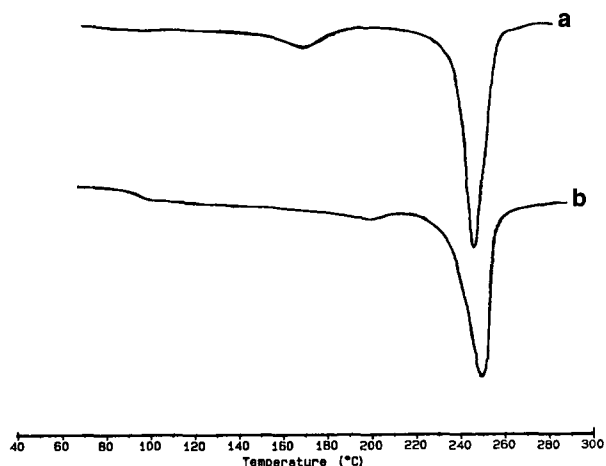
Figure 5 D.s.c. traces at 20°C min^{-1} for annealed samples showing zero shrinkage: (a) *TD* = 80°C, *DR* = 4:1, annealed at 125°C; (b) *TD* = 100°C, *DR* = 2:1, annealed at 180°C

on annealed samples (*Figure 5*) show, in fact, a similar absence of crystallization exotherms, irrespective of the previous history of the samples. Note that the samples chosen for comparison exhibit a widely different behaviour before annealing and that the annealing conditions used were chosen to represent extreme cases, i.e. 125 and 180°C respectively.

Evidence for the importance of both thermal crystallization and stress-induced crystallization in controlling the shrinkage behaviour of drawn samples is

also obtainable from observations of strain-hardening phenomena during stretching and from the values of the birefringence recorded on the drawn samples. In *Table 1* it is shown that at temperatures between 80 and 100°C the yield stress is approximately constant but a strain-hardening behaviour is noted on samples drawn at the lowest temperature. However, an increase in yield stress, due to thermal crystallization in the preheating cycle, is observed above 100°C and becomes very pronounced at 125°C.

The strong strain-hardening behaviour experienced at the upper temperature is undoubtedly associated with the continuation of thermal crystallization, which is, at the same time, responsible for the large reduction in shrinkage through annealing effects. Orientation of polymer crystals has to be considered also a significant contributory factor for the observed strain-hardening effects. Comparing, in fact, the data for samples drawn at 80°C with those at 125°C one notes large birefringence values in both cases, in comparison to those recorded on samples drawn at intermediate temperatures.

The density data shown in *Figure 6* indicate that the density of the drawn samples is related primarily to drawing temperature, while the draw ratio has a less significant effect.

The plots of percentage crystallinity in the drawn samples, calculated respectively from d.s.c. data and density measurements, as a function of drawing temperature in *Figure 7* show a good agreement only at the higher drawing temperatures, i.e. the conditions where

Table 1 Comparison of stresses recorded in stretching monoaxially PET sheets to 4:1 with properties of drawn samples[a]

	Drawing temperature (°C)				
	80	90	100	110	125
Stress recorded in stretching samples					
Yield stress (MPa)	0.17	0.15	0.16	0.23	0.77
Final stress (MPa)	0.22	0.14	0.13	0.17	1.27
Properties of drawn samples					
Shrinkage in boiling water (%)	5.1	7.3	27.2	10–15 (I)	7.9
Birefringence ($\times 10^{-3}$)	86.3	64.5	64.5	(ND)	93.0

[a] ND = not measured; I = interpolated
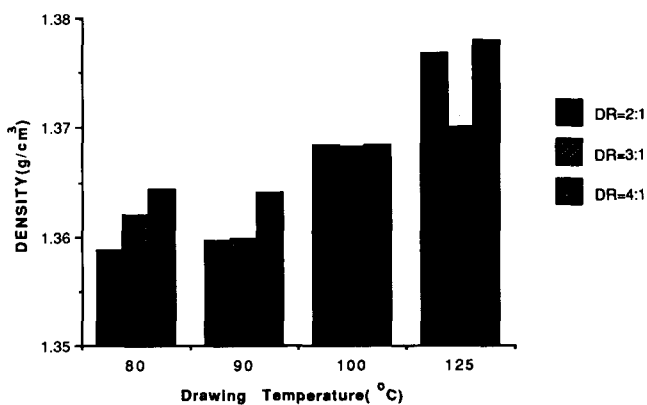
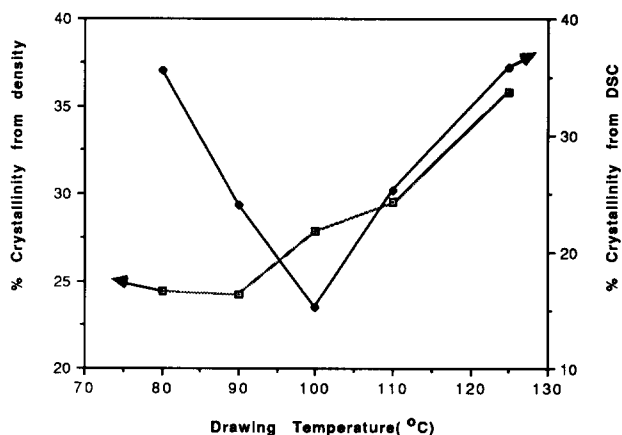Figure 6 Relationship between drawing conditions and density for uniaxially drawn samples

Figure 7 Effects of drawing temperature on crystallinity (from d.s.c. and density measurements) of uniaxially drawn samples at $DR = 4{:}1$

thermal crystallization events are significant. (Note that the percentage crystallinity from d.s.c. data was calculated by subtracting the heat of crystallization developed during the d.s.c. run from the total heat of fusion recorded.)

At the lower end of the temperature range, where phenomena are dominated by stress-induced crystallization, the d.s.c. gives substantially higher estimates. As the samples drawn at 60°C were hazy in appearance, clearly indicating the presence of voids, it is likely that the discrepancy between the crystallinity values obtained from d.s.c. data and those from density measurements on samples drawn at 80°C may also have resulted from the formation of microvoids. (Note that the obvious presence of voids and the unevenness of the samples drawn at 60°C made it pointless to record d.s.c. data and density values on these samples.)

Although the samples drawn at 80°C were transparent, one cannot exclude the possibility of microvoids being present, particularly if these are in the form of elongated ellipsoids with their major axis lying in the drawing direction, thereby producing a scattering site smaller than the wavelength of visible light.

Contrary to the above, the discrepancy in level of crystallinity recorded by the two methods in question on samples drawn at 100°C is more difficult to explain. Owing to the high level of shrinkage exhibited by the samples and the obvious association of shrinkage with relaxations within the amorphous phase[16–19], it is tempting to suggest that the crystallinity calculated from d.s.c. measurements may have been overestimated by the substantial amount of orientation within the amorphous phase. The small bump in the curve at this temperature, in fact, is supportive of such an argument, but it may be difficult to account entirely for the observed discrepancy in view of the suggestion by Nobbs et al.[17] that such overestimates in level of crystallinity are generally small.

A very good correlation is found between birefringence and percentage crystallinity calculated from d.s.c. data (*Figure 8*), confirming the overall accuracy of d.s.c. data.

The conclusion that emerges, therefore, from the above discussion is that d.s.c. analysis predicts quite well the shrinkage behaviour of monoaxially drawn PET. Extrapolation to 0% shrinkage in *Figure 9*, in fact, leads to the deduction that the required level of crystallinity (as defined in terms of d.s.c. data) is 43%, a value coinciding exactly with that obtained on samples

annealed at 150°C in which shrinkage was completely eliminated. Even an approximate extrapolation of the data in *Figure 10* suggests that shrinkage is suppressed when the peak exotherm temperature is displaced to about 75–80°C, i.e. the range for the glass transition of the polymer, at which thermal crystallization cannot take place. This is in good agreement with the extrapolation in *Figure 11*, which predicts a zero value for the heat of crystallization for samples exhibiting 0% shrinkage.
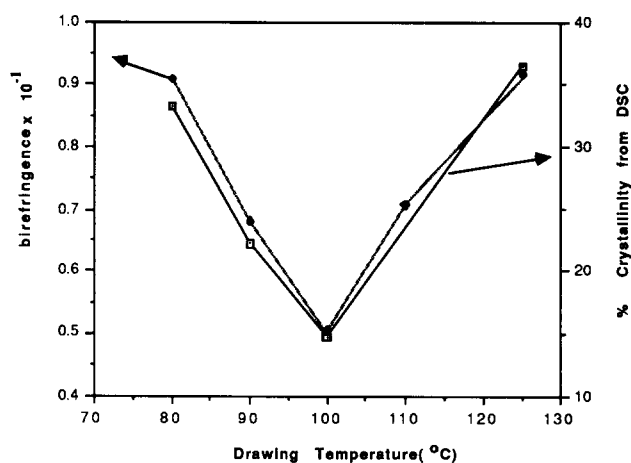

Figure 8 Comparison of effect of drawing temperature on crystallinity (measured by d.s.c.) and birefringence at $DR = 4{:}1$
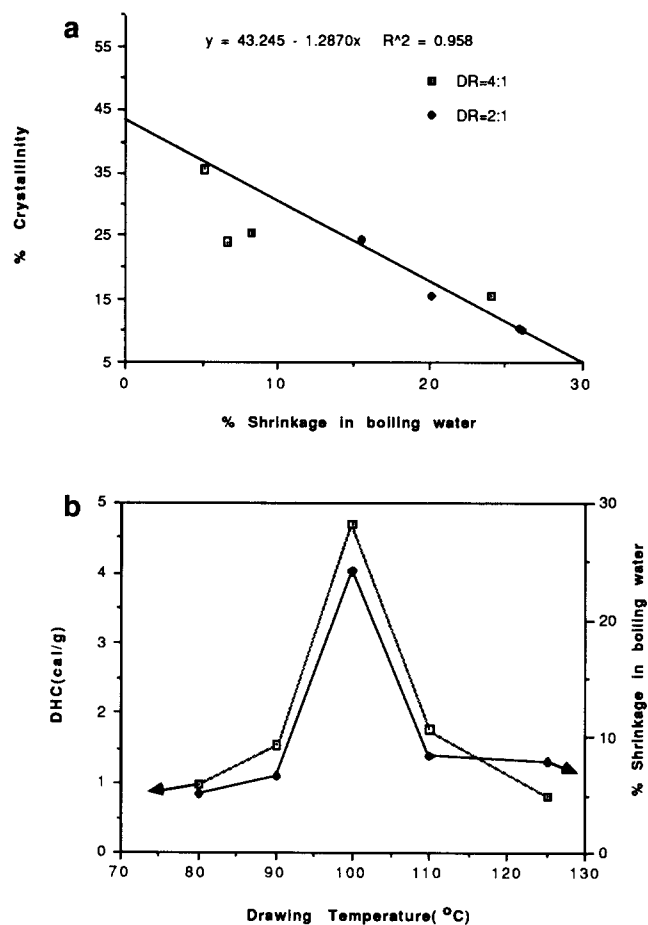

Figure 9 Correlation between (a) shrinkage and crystallinity and (b) shrinkage and heat of crystallization (*DHC*) at various drawing temperatures (both from d.s.c. measurements)
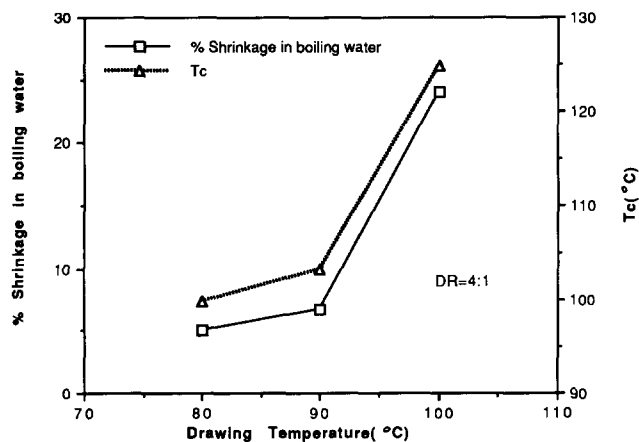
Figure 10 Correlation between shrinkage and cold crystallization temperature (T_c) at various drawing temperatures
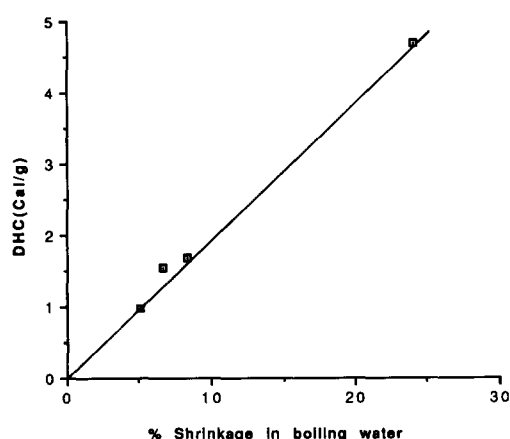

Figure 11 Correlation between shrinkage and heat of cold crystallization (DHC) for samples drawn uniaxially to 4:1 at different temperatures

CONCLUSIONS

From the analysis of the results of this study the conclusions that can be derived for the thermal shrinkage of monoaxially drawn PET are as follows:

The level of shrinkage of monoaxially oriented PET is largely independent of the ambient temperature up to 150°C.

Thermal shrinkage is highest at a draw ratio of about 2:1 and for drawing temperatures around 100°C and below the T_g of the polymer.

D.s.c. data can be used to predict thermal shrinkage, i.e. drawn samples are dimensionally stable when (1) the enthalpy associated with the endothermic peak approaches a limiting value, corresponding to a calculated percentage crystallinity of 43%, and (2) the exothermic peak is completely suppressed.

The percentage crystallinity calculated from d.s.c. data coincides with the values estimated from density measurements only for samples drawn at the higher temperatures, i.e. when thermal crystallization is significant. At lower temperatures the formation of microvoids in the samples is likely to result in lower densities, giving rise to underestimates in the calculated degree of crystallinity. The accuracy of d.s.c. data is confirmed by the very high correlation between total birefringence and the recorded exothermic enthalpy for all drawing conditions.

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