Interaction between thermal shrinkage and crystallization in axially oriented poly(ethylene terephthalate) fibres and films*

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The thermal shrinkage behaviour of poly(ethylene terephthalate) fibres and films with varying amounts of orientation and crystallinity and different degrees of crystal disorder is reported. It is shown that the shrinkage of undrawn and drawn samples with low orientation can be considered as the contraction of a rubber-like network which arises from disorientation of the oriented amorphous phase. However, in the highly drawn samples with significantly higher orientation, interaction between shrinkage and crystallization can occur, particularly in samples produced at low speeds. X-ray diffraction and thermal studies show that these samples have crystals with high defect density and also contain tiny nuclei; these factors can result in rapid crystallization at relatively high temperatures and thus impede shrinkage.

(Keywords: poly(ethylene terephthalate); shrinkage; orientation; crystallization)

INTRODUCTION

A number of studies on the thermal shrinkage of poly(ethylene terephthalate) (PET) fibres and films by various authors[1-12] and an investigation of the associated structural and other aspects, have led to the suggestion that, depending on temperature and time, the overall shrinkage process involves a rapid initial stage of rubber-like contraction of the molecular network, associated with disorientation in the amorphous phase, followed by a crystallization stage during which chain folding may occur. It has also been suggested that the crystallization can occur simultaneously with amorphous disorientation, and once the crystallization starts, further shrinkage is hindered. Studies involving heat treatment of PET partially oriented yarn (POY) under slight tension in the millisecond and longer time periods have shown[13] that during the shrinkage of POY, there is competition between the recoiling of the chains and the crystallization process in the short time range. It has been pointed out[2,8] that at higher temperatures, the separation between shrinkage and crystallization process is not so clear cut.

The present studies originated from the observation that the high-temperature shrinkage of a highly oriented PET film of draw ratio of around 4 with axial symmetry was considerably less than that of the corresponding PET multifilament yarn having similar structural characteristics. In an effort to explain this difference in shrinkage, some studies were made on crystallization kinetics and associated structural changes in the samples. As the studies progressed, it became evident that sample production speed was an important factor as far as the interaction between shrinkage and crystallization was concerned. A more detailed study of the shrinkage and crystallization characteristics of PET fibres and films produced at different speeds and with varying orientation was therefore undertaken. In this article the results for undrawn samples, namely as-spun fibres and as-cast PET films with birefringence in the range of 0 to 0.038, are first presented. These are followed by the results for drawn samples with birefringence up to 0.22. The results are then discussed in terms of the interaction between shrinkage and crystallization in samples of high draw ratio and an attempt is made to identify the structural basis for such interaction. A noteworthy observation from these studies is that, compared with standard commercial PET multifilament yarns which are produced at high speeds and show high shrinkage, oriented PET samples prepared by spinning or casting at very low speeds and then drawing at low strain rates, show very low shrinkage as apparently they can crystallize rapidly when exposed to elevated temperatures. Thermal studies revealed the presence of tiny ordered regions or nuclei in these samples while X-ray diffraction studies revealed that the crystallites had a higher defect density. It is proposed that both these factors promote rapid crystallization at high temperatures which impedes shrinkage.

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EXPERIMENTAL

Starting samples

Fibres.

1. *Monofilament*: Single filaments of 130 denier were spun from fibre-grade PET chips in a laboratory spinning unit. The filaments were quenched in water at around 5°C, 25 cm below the spinneret, before being wound at 10 m min^{-1}.
2. *Low-oriented yarn (LOY)*: Multifilament PET yarns 165/36/0, i.e. of 165 denier, 36 filaments and zero twist, were produced on an industrial unit at 1000 m min^{-1} by M/s Orkay Polyester, Bombay, India.
3. *Partially oriented yarn (POY)*: Multifilament PET yarns 126/36/0, i.e. of 126 denier, 36 filaments and zero twist, were produced on an industrial unit at 3000 m min^{-1} by M/s Modipon Ltd, Modinagar, India.

Film. A film 80 μm thick and 30 mm wide was melt cast from fibre-grade PET chips and wound on chilled rollers at 10 m min^{-1} by M/s Garware Polyester, Aurangabad, India.

Amorphous bulk sample. PET (fibre grade) melt from the laboratory spinning unit was allowed to drop into a liquid nitrogen bath, thus resulting in an amorphous and isotropic bulk sample which was stored in a freezer.

Uniaxial drawing of samples

Drawing of filaments in air at 90°C. The monofilament produced at 10 m min^{-1}, and the LOY and POY multifilament yarns were uniaxially stretched on a laboratory drawing machine at a heater plate temperature of 90°C to different draw ratios up to 5 at strain rates of 2–20 min^{-1}.

Drawing of film and filaments in water at 70°C and in air at 87°C. PET film and the monofilament produced at 10 m min^{-1} were drawn to different draw ratios in water at 70°C in two stages at strain rates between 1 and 3 min^{-1}. They were also drawn to different draw ratios at 87°C in air by passing them over a heater plate at strain rates between 1 and 8 min^{-1}.

Density

The densities of the samples were measured using a density gradient column prepared from n-heptane and carbon tetrachloride.

Birefringence

A polarizing microscope fitted with a tilting compensator was used to measure the sample birefringence. The thickness of the film was measured with the help of a precision digital micrometer, while the diameter of the fibre was measured with the help of an eye-piece micrometer.

X-ray diffraction studies

The X-ray diffraction studies were made to measure crystallinity, crystallite orientation in terms of Hermans' orientation factor, f_c and crystal disorder parameter. The methods used for determining crystallinity and crystallite orientation have been described elsewhere[14]. The crystal disorder parameter was determined following the method suggested by Ruland[15] and subsequently simplified by Vonk[16]. A computer program based on the procedure suggested by Fontaine *et al.*[17] was used for the calculation of the disorder parameter.

Amorphous orientation by infra-red (i.r.) studies

An infra-red spectroscopic study of molecular orientation was made using the attenuated total reflection technique[18] for the filaments and the transmission technique in the case of film. Combining the i.r. data with the X-ray data, the Hermans' amorphous orientation factor, f_{am}, was estimated[19].

Percentage shrinkage

The percentage shrinkage, %S, of different samples was measured in water, hot air, and in silicone oil in the temperature range 50–250°C. Samples were kept for 5 min in water and in air, and for 2 min in silicone oil at different fixed temperatures. The samples were then removed and allowed to come to room temperature. Percentage shrinkage was obtained using the following expression

$$\%S = \frac{(L_0 - L_s)}{L_0} \times 100$$

where L_0 = initial length and L_s = length after shrinkage.

Shrinkage force

Multifilament yarn or film strip of width 2 mm and length 5 cm was clamped with little pre-tension between two grips connected to an Instron load cell. The sample was then quickly heated by raising a cylindrical heater preheated to a desired temperature, so that it surrounded the sample completely. The shrinkage force which was generated as a result of the heating of the sample was recorded on the Instron recorder as a function of time. The maximum value of the stress was taken as the peak shrinkage stress at that particular temperature.

Thermal transitions

A Perkin–Elmer differential scanning calorimeter DSC 7 was used for studying thermal transitions. The film and fibre samples were first cut into very fine pieces and then scanned at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

Crystallization kinetics

The studies on crystallization kinetics were conducted between 85 and 110°C since in this temperature range the crystallization is slow enough for the kinetics to give meaningful data within a reasonable time-scale. The samples were first heat-treated isothermally in the slack condition between 85 and 110°C in silicone oil for time periods varying from 30 s to 72 h, then removed from the silicone oil bath, quenched in air, and washed with carbon tetrachloride and dried. Densities of these samples were measured on the density gradient column.

RESULTS AND DISCUSSION

Undrawn samples

Physical characteristics. Some physical characteristics of the undrawn samples are summarized in *Table 1*. These samples as examined by X-ray are essentially amorphous and have relatively low orientation, the birefringence varying between 0 and 0.038 (a fully oriented PET sample

Table 1 Some physical characteristics of undrawn samples

Sample	Winding speed (m min^{-1})	Birefringence (Δn)	Density (g cm^{-3})	X-ray crystallinity (%)
Film	10	ND	1.336	ND
Monofilament	10	ND	1.339	ND
LOY yarn	1000	0.007	1.342	ND
POY yarn	3000	0.038	1.349	2
Quenched bulk material	–	–	1.335	ND

ND, Not detectable

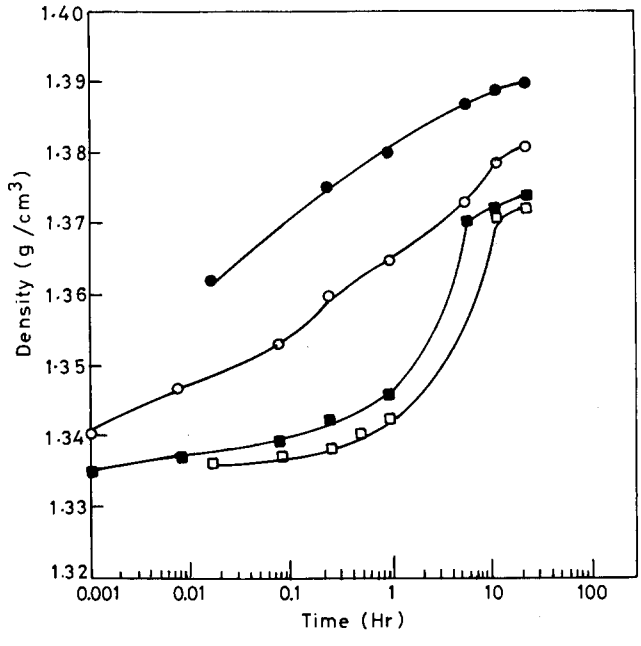

Figure 1 Density of undrawn samples as a function of heat treatment time at 110°C. (●) POY (3000 m min^{-1}); (○) LOY (1000 m min^{-1}); (■) as-cast film; (□) bulk quenched amorphous sample

has a birefringence of $\geqslant 0.16$). The monofilament spun at 10 m min^{-1} and the film cast at 10 m min^{-1} showed no detectable birefringence and their densities were close to the amorphous density, whereas the as-spun POY and LOY yarns were slightly oriented and their densities were also somewhat higher than the amorphous density.

Crystallization kinetics. The crystallization kinetics of some undrawn samples heat-treated at 110°C in silicone oil from 30 s to 24 h were studied, the measured density being taken as a measure of crystallinity. The data are shown in *Figure 1*. The orientation dependence of crystallization kinetics is quite evident from this figure and similar effects for PET fibres, films and sheets are documented in the literature[20–23]. The absence of orientation in the cast film and the amorphous bulk sample results in very slow crystallization during the first hour giving rise to an induction period. This is followed by a significant enhancement of crystallization rate at longer times. The relatively higher orientation of the as-spun POY and LOY yarns results in the crystallization rate being relatively more rapid in these samples right from the beginning.

Shrinkage and shrinkage stress. The shrinkage behaviour of some undrawn samples which were allowed to shrink in silicone oil without any constraint at temperatures varying from 50 to 150°C for 2 min is shown in *Figure 2*. The orientation dependence of shrinkage is quite obvious, a feature also observed for their crystallization kinetics (*Figure 1*). Thus in the glass transition range, say from 70 to 90°C, shrinkage appears to be dominated by the rubber-like contraction of the network for all the samples studied. However, at higher temperatures, crystallization stabilizes the shrinkage in the as-spun POY and LOY multifilament yarns whereas in the other two samples the rubber-like contraction continues to predominate. In all these samples the chain recoil step predominates over crystallization because their crystallization half-times are likely to be quite high because of their relatively low orientation.

The shrinkage stress generated in these samples, when they were held at fixed length in air at elevated temperatures between 60 and 120°C, is shown in *Figure 3*. The as-spun LOY and POY multifilament yarns developed low but significant shrinkage stress whereas the monofilament and film produced at a low speed of 10 m min^{-1} hardly developed any stress. The shrinkage stress correlates well with the orientation as would be expected of a rubber-like network.

Structural basis of shrinkage. The shrinkage and shrinkage stress data on PET fibres spun at different speeds and on flow-drawn PET films have recently been analysed[24] in terms of a rubber network with the entanglements playing the role of crosslinks. It was found that the extension and shrinkage characteristics of the networks in these samples could be described quite satisfactorily in terms of the statistical theory of rubber elasticity.

Drawn samples

Some physical characteristics of the drawn samples. Some physical characteristics of the water- and air-drawn

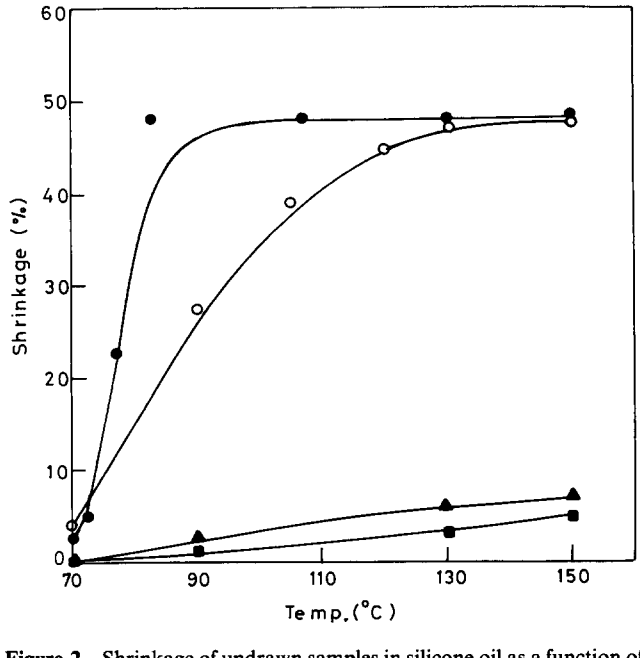

Figure 2 Shrinkage of undrawn samples in silicone oil as a function of temperature. (●) POY (3000 m min^{-1}); (○) LOY (1000 m min^{-1}); (■) as-cast film; (▲) monofilament (10 m min^{-1})

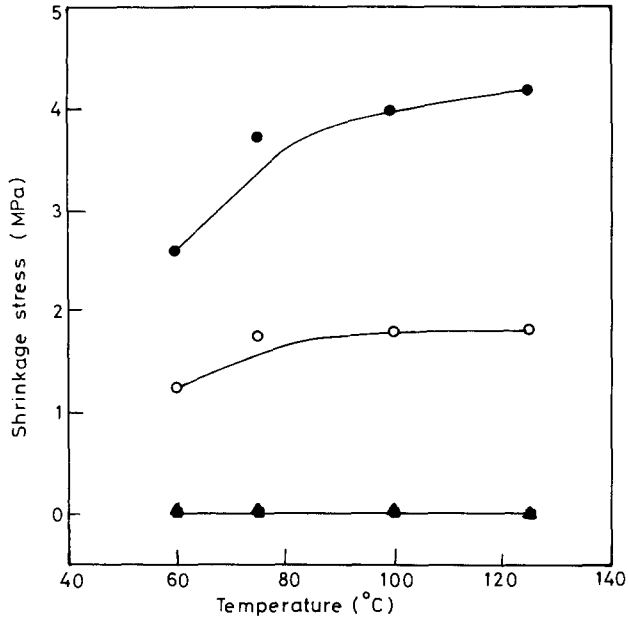

Figure 3 Shrinkage stress of undrawn samples as a function of temperature (symbols as in *Figure 2*)

Table 2 Some physical characteristics of the drawn samples

Sample draw ratio	X-ray crystallinity (%)	Birefringence (Δn)	Density (g cm^{-3})	f_c	f_{am}
Water-drawn film					
2.15	3.3	0.036	1.34	0.89	0.09
2.48	3.4	0.054	1.343	0.88	0.17
2.70	4.4	0.070	–	0.90	0.19
3.03	5.3	0.09	1.346	0.91	0.25
4.16	7.2	0.18	1.36	0.90	0.64
Air-drawn film					
1.56	4.5	0.028	1.34	0.75	0.09
2.11	5.4	0.041	1.342	0.88	0.13
2.49	6.3	0.072	1.347	0.88	0.24
3.0	12.5	0.113	1.355	0.90	0.39
3.70	25.0	0.170	1.366	0.91	0.57
Air-drawn LOY yarns					
1.10	–	–	1.340	–	–
1.30	–	0.008	–	–	–
2.50	–	0.044	1.348	–	–
3.80	24	0.170	1.360	–	–
4.11	27	0.216	1.362	0.940	0.58
5.00	29	0.220	1.370	–	–
Air-drawn POY yarns					
2.60	–	0.040	1.349	–	–
3.30	–	0.100	1.353	–	–
4.16	–	0.160	1.362	–	–
4.80	–	0.184	1.365	–	–
5.20	–	0.200	1.367	–	–

films and air-drawn LOY and POY yarns are listed in *Table 2*. The following features are noteworthy: (1) the trends shown by drawn fibres and films are essentially similar and as expected, both orientation and crystallinity increase with increase in draw ratio; (2) the drawn fibres and films develop significant orientation typical of a commercial fibre only at draw ratios of $\geqslant 3.70$; (3) crystallites orient quite early during drawing but amorphous orientation becomes significant only at high draw ratios; and (4) water-drawn film samples have lower crystallinity than the corresponding air-drawn samples.

Shrinkage behaviour of the drawn samples. The shrinkage studies were first made on the samples prepared by drawing the as-cast film and as-spun LOY and POY yarns to different extents. The percentage shrinkage in boiling water (100°C) and in silicone oil at 220°C was measured and the data are shown in *Figures 4* and *5*. Typical inverted U-shaped curves are obtained in all cases.

The samples in the low and intermediate draw ratio range show high shrinkage and the extent of shrinkage at 100 and 220°C is nearly the same or only slightly different. Thermally induced shrinkage results from disorientation of the oriented non-crystalline phase and is consequently highest in unset fibres of intermediate orientation and low crystallinity. The crystallization half-times for these samples would be relatively high because of low orientation and hence disorientation predominates and, as stated earlier for the undrawn samples, the shrinkage of these samples of intermediate draw ratios can also be considered as the contraction of a rubber-like network[10].

In the samples of high draw ratio, the simple correlation between thermal shrinkage and molecular orientation, which was observed for samples of low orientation, is no longer present. Compared with the highly drawn films, which show a shrinkage of $<20\%$ at 220°C (*Figure 4*), the highly drawn fibres show a shrinkage of over 40% at the same temperature (*Figure 5*). In view of this noteworthy result and also because of the interest in shrinkage characteristics of highly drawn commercial fibres and films, the results for the samples of high draw ratio will be considered in some detail.

Samples of high draw ratio

It is not immediately obvious why the thermal shrinkage values of the highly drawn films and fibres at

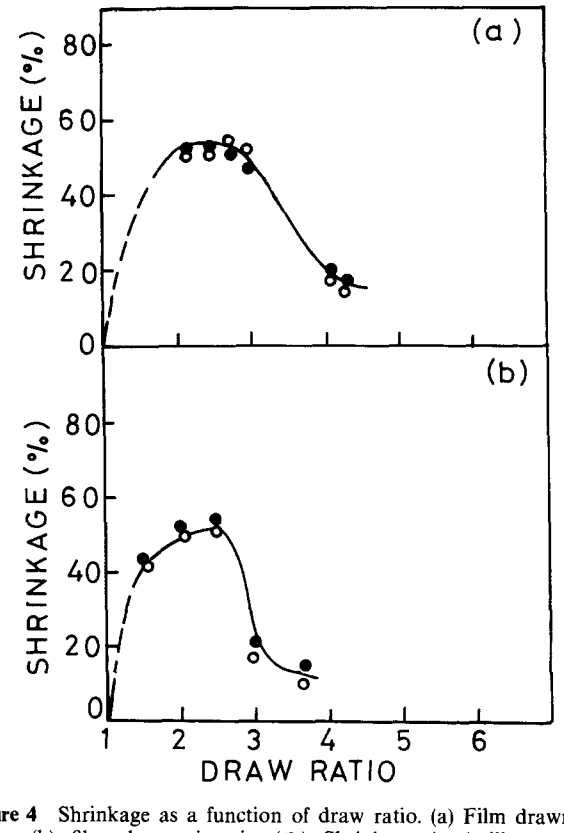

Figure 4 Shrinkage as a function of draw ratio. (a) Film drawn in water; (b) film drawn in air. (○) Shrinkage in boiling water; (●) shrinkage in silicone oil at 220°C

220°C (*Figures 4* and *5*) show such a large difference, in spite of their physical characteristics being quite close. To ensure that this difference in shrinkage was not due to any intrinsic structural differences between fibres and films, PET monofilament was produced in the laboratory under conditions close to those used for producing the film, i.e. by spinning it from the melt, quenching it at 5°C and then winding it at 10 m min^{-1}. The spun filament was then drawn to a draw ratio close to 4.2 at low strain rates in air and also in water, as in the case of the film. The physical characteristics of these new samples are summarized in *Table 3* and are seen to be quite close to the other drawn samples of corresponding draw ratio listed in *Table 2*.

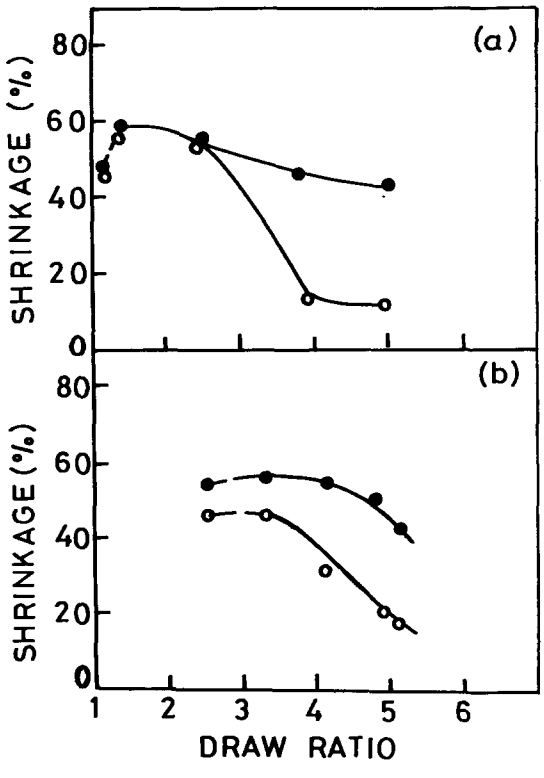

Figure 5 Shrinkage as a function of draw ratio. (a) LOY-based yarn; (b) POY-based yarn; (symbols as in *Figure 4*)

Table 3 Physical characteristics of filaments spun at 10 m min^{-1} and then drawn to draw ratios close to 4

Sample draw ratio	X-ray crystallinity (%)	Birefringence (Δn)	Density (g cm^{-3})
Drawn in water at 70°C			
4.16	7.0	0.188	1.360
Drawn in air at 90°C			
4.11	26.0	0.198	1.361

Shrinkage and shrinkage stress. It is instructive at this stage to examine the shrinkage behaviour of samples of high draw ratio, say between 4 and 4.2. The production parameters and physical characteristics of some of these samples described earlier have been put together in *Table 4*. The shrinkage characteristics of these samples are shown in *Figure 6*. It is interesting to note that, in spite of similar physical characteristics, the samples show wide variations in shrinkage at the higher temperatures. It is worth noting that the film and fibre produced at low speeds, i.e. cast or spun at low speeds and drawn at relatively low strain rates, show the lowest shrinkage. The LOY- and POY-based fibres, which have been produced at higher speeds, show higher shrinkage. The

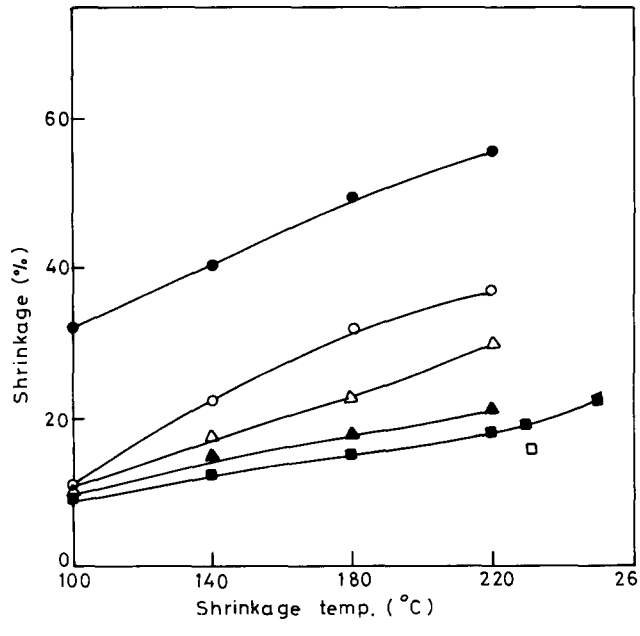

Figure 6 Shrinkage of samples of draw ratio around 4.2 as a function of temperature. (●) POY-based yarn; (○) LOY-based yarn; (△) air-drawn monofilament; (▲) water-drawn monofilament; (■) water-drawn film; (□) air-drawn film of draw ratio 3.7

Table 4 Physical characteristics of drawn film and fibre samples with draw ratios close to 4

Starting sample	Drawing conditions				Characteristics of the drawn samples			
	Medium	Temp. (°C)	Strain rate (min^{-1})	Draw ratio	Density (g cm^{-3})	Birefringence (Δn)	f_c	f_{am}
LOY (yarn spun at 1000 m min^{-1})	Air	90	20	4.1	1.362	0.216	0.940	0.58
Film (cast at 10 m min^{-1})	Air	87	8	4.0	1.365	0.165	0.910	0.57
	Water	70	2	4.16	1.360	0.184	0.90	0.64
Monofilament (spun at 10 m min^{-1})	Air	90	20	4.11	1.361	0.198	–	–
	Water	70	2.5	4.16	1.360	0.188	–	–

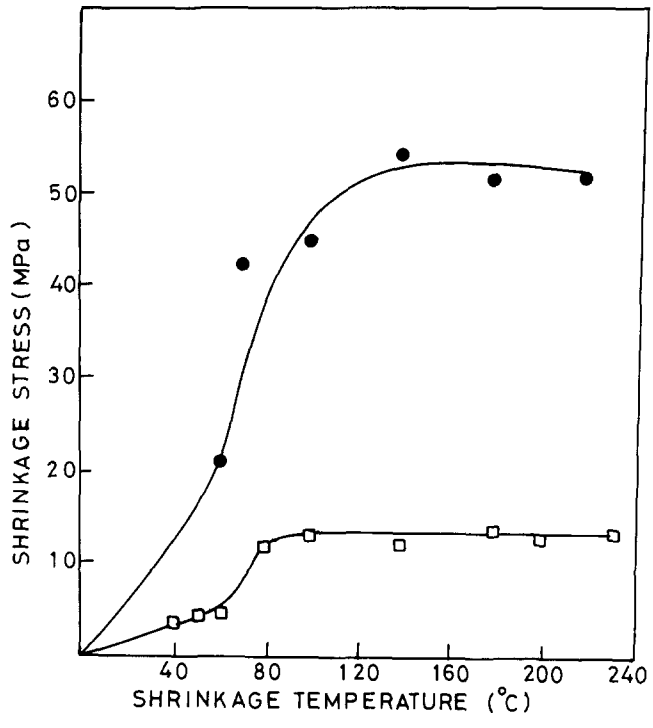

Figure 7 Shrinkage stress as a function of temperature. (□) Film of draw ratio 4.16. (●) LOY-based yarn of draw ratio 4.11

monofilament produced at 10 m min^{-1} and drawn in air at 90°C at relatively high strain rates showed intermediate behaviour. The data on shrinkage stress generated in two of these samples are shown in *Figure 7* and are found to be relatively low in the samples which showed low shrinkage. While shrinkage and shrinkage stress were found to correlate with orientation in the case of samples of low orientation, such was not the case at high draw ratios. Apparently the effect of crystalline reorganization on shrinkage stress would need to be taken into account since such reorganization would lower not only the potential for shrinkage but also the amount of shrinkage tension[25] that develops. The kinetics of crystallization and shrinkage were therefore studied at 220°C starting from an exposure of 1 s. It was observed that at this temperature both crystallization and shrinkage were very fast and values close to the equilibrium were reached within one second[26]. The crystallization kinetics were therefore studied at a lower temperature just above the glass transition temperature over a wide time range to gain an understanding of how the equilibrium values are reached.

Crystallization kinetics. The crystallization kinetics of some of these samples at 85°C are shown in *Figure 8*; the inset shows the short time behaviour more clearly. It is interesting to observe that the samples which were cast or spun at low speeds and drawn at low strain rates crystallize faster than those produced at higher speeds. Recalling that the former samples showed very low shrinkage and shrinkage stress at higher temperature, it is likely that at higher temperatures of treatment, the shrinkage in these samples is hindered because of fast crystallization. It has been suggested[13] that if crystal reorganization is fast during heat treatment, the amount of initial shrinkage and the potential for subsequent shrinkage would be lowered.

Crystallization can occur at two distinct kinetic levels[27]. The first level relates to slow processes involving stress relaxation in the amorphous regions and can be viewed as a release of the strained network of individual molecules. The second level relates to the more rapid processes involving crystallite reorganization, i.e. the formation of new, more stable crystalline structures by crystallite thickening (regularization of chain folds) and other perfection processes. Geil[28] has pointed out that defects within the lattice reduce the energy for molecular motion and their presence can therefore result in faster crystallization. The characterization of the present samples for crystal defects using the X-ray diffraction technique led to some interesting results which are described below.

Crystal disorder parameter. The data on crystal defects for the highly drawn samples in the unset and set states are presented in terms of the disorder parameter, k, in *Figure 9* and show that the crystallites of drawn samples based on the film and low speed monofilament are more disordered. The value of k for the unset film of draw ratio 4.16 is unusually large and is about equal to that reported[29] for Kevlar fibres. In the literature the value of 3–5 has been reported for nylons[30] and 4–6 for polypropylene[15]. The drawn samples based on LOY yarns show low defect density. When subjected to heat treatment in the slack condition, the drawn film samples showed rapid decrease in crystal disorder parameter in the temperature range of 100 to 210°C whereas the conventional fibres showed a small decrease only in the high temperature range. This suggests that the presence of high defect density within the crystal might promote faster reorganization through crystallization.

The potential for structural reorganization at elevated temperatures can also be studied with the help of a differential scanning calorimeter (d.s.c.) and detailed thermal studies were therefore made on the samples under

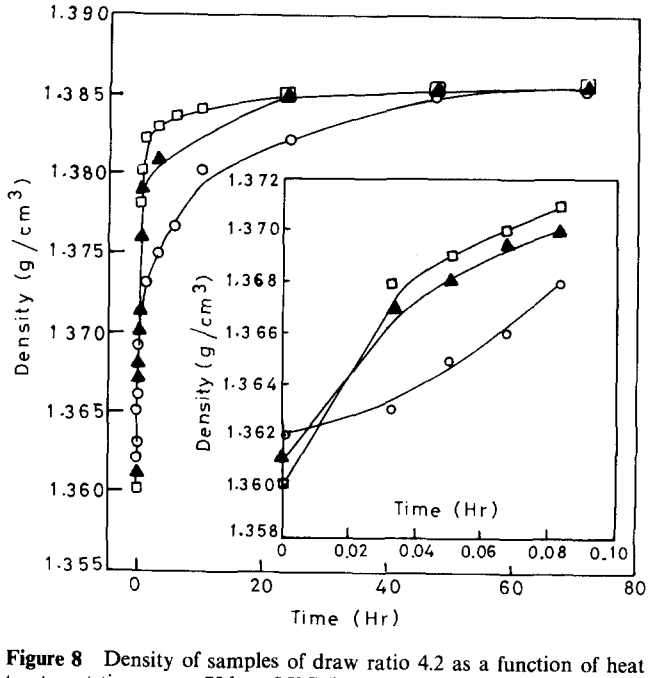

Figure 8 Density of samples of draw ratio 4.2 as a function of heat treatment time up to 72 h at 85°C (inset shows the data up to 5 min). (□) Water-drawn film; (▲) water-drawn monofilament; (○) LOY-based yarn

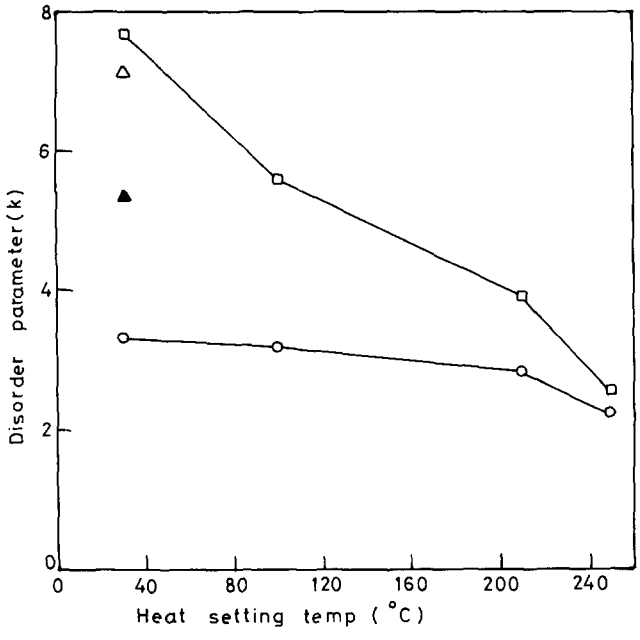

Figure 9 Crystal disorder parameter of samples of draw ratio about 4.2 as a function of heat treatment temperature. (□) Water-drawn film; (△) water-drawn monofilament; (▲) air-drawn monofilament; (○) LOY-based yarn

investigation. Only the relevant data are included in this paper.

Thermal transitions. The melting endotherms of various samples of draw ratios close to 4.2, as obtained on a d.s.c., are shown in *Figure 10*. It is interesting to observe that while the drawn film and monofilament produced at low speed show doublets, the drawn LOY and POY yarns show what are essentially single peaks. It can be recalled that all these samples were drawn at temperatures in the 70–90°C range and were not subsequently subjected to any setting treatment. During the d.s.c. run, they are subjected to a thermal cycle for around 20 min over a variable temperature from 50 to >250°C. During this period the sample is free to shrink and the structural reorganization that can therefore occur in the d.s.c. cell itself will be reflected in the melting endotherm. In a doublet, endotherm 1 at the lower temperature represents the non-crystallizable fraction while endotherm 2 at the higher temperature represents the crystallizable fraction which has formed as a result of crystalline reorganization during the d.s.c. run itself[31]. Thus the presence of a doublet with a relatively large endotherm 2 in the samples produced at low speeds is indicative of the high potential for reorganization of the crystalline structure in these samples.

The d.s.c. investigations were extended to study an interesting aspect arising from an observation made by Sheldon[32], who pointed out that PET film extruded at low extrusion rate showed a high rate of crystallization at 110°C compared with a film extruded at high extrusion rate. To explain this result Sheldon suggested that crystalline remnants in the melt which are capable of acting as nuclei, are disrupted at high speeds of extrusion but retained at low speeds. The existence of microcrystallites or small unstable ordered regions in the amorphous phase has been postulated[33,34] to account for the middle endotherm peak (MEP) with a heat content of around 2 cal g^{-1} in the temperature range 175–200°C observed in the d.s.c. thermograms of PET samples which have been heat-set. It was therefore of obvious interest to attempt to locate such nuclei in the samples under investigation. When the samples were scanned on the d.s.c. under standard settings, no evidence for any endothermic peaks was obtained. However, when the data were analysed at high sensitivity, it was found that both the monofilament and film of draw ratio close to 4.2 showed small endothermic peaks in the 190–210°C range with areas of about 0.03 cal g^{-1} (*Figure 11a*). As shown in this figure, such peaks were not present in the

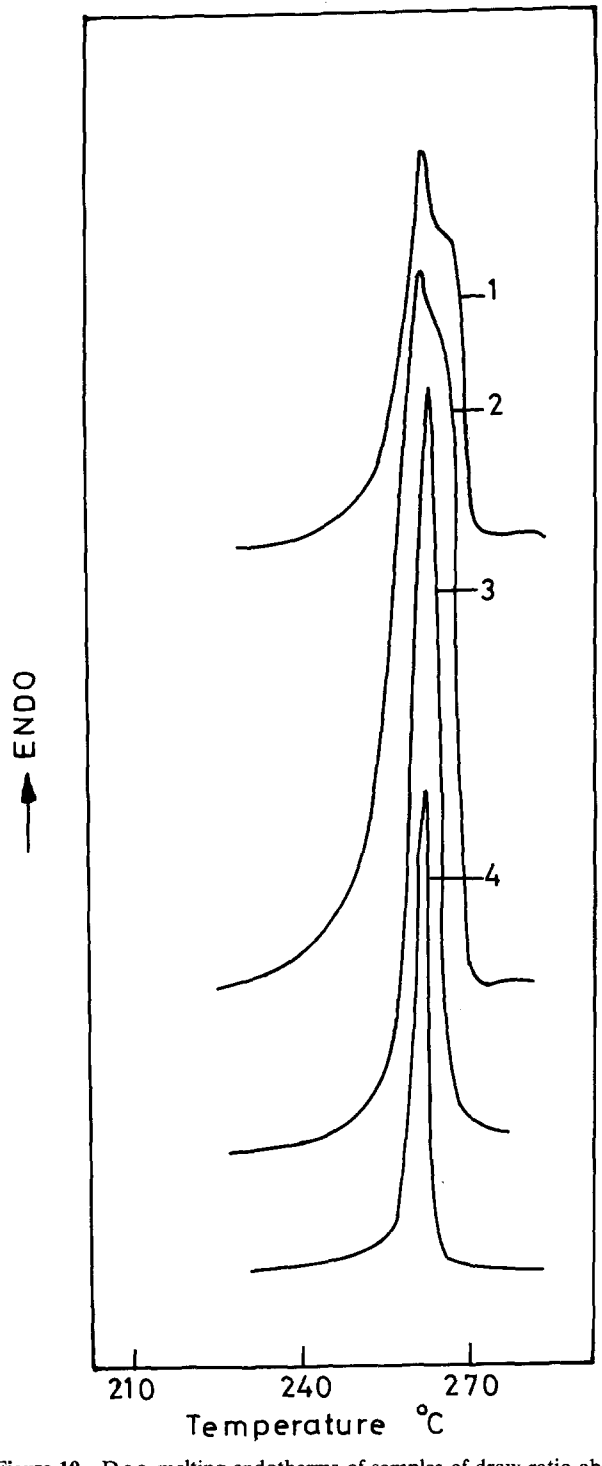

Figure 10 D.s.c. melting endotherms of samples of draw ratio about 4.2. (1) Water-drawn monofilament; (2) water-drawn film; (3) LOY-based yarn; (4) POY-based yarn

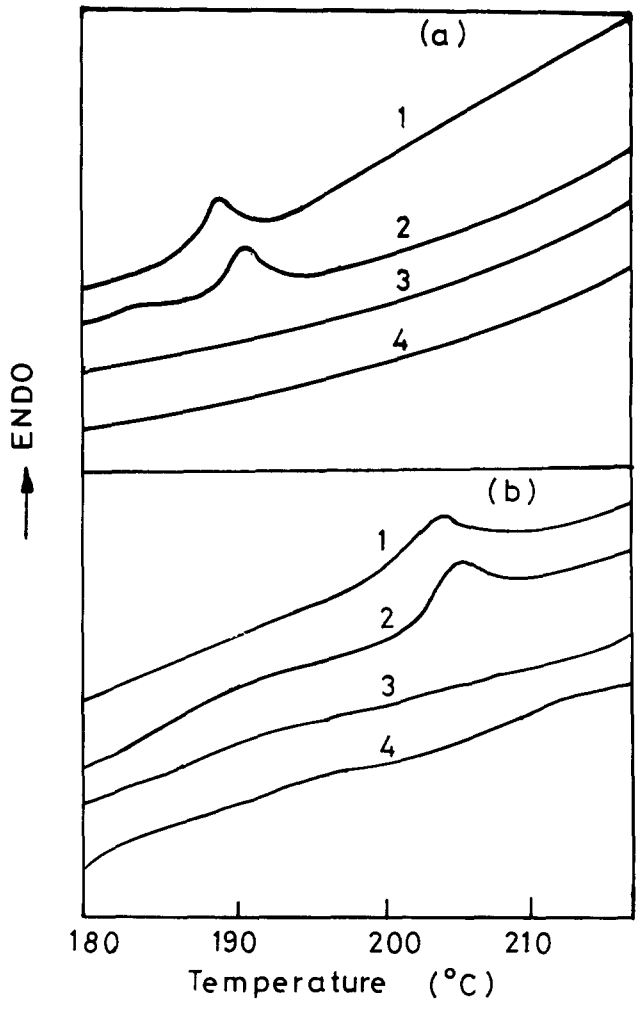

Figure 11 D.s.c. thermograms at higher sensitivity. (a) Samples of draw ratio of about 4.2: (1) water-drawn film; (2) water-drawn monofilament; (3) LOY-based yarn; (4) POY-based yarn. (b) Undrawn samples: (1) as-cast film; (2) monofilament (10 m min^{-1}); (3) LOY; (4) POY

drawn LOY and POY samples of approximately the same draw ratios. When the starting samples were similarly scanned, the as-cast film and as-spun monofilament both showed middle endotherms in the 210–220°C range which are shown in *Figure 11b*. As shown in this figure, the spun LOY and POY samples did not show such middle endotherms. These results provide evidence for the presence of tiny nuclei in both undrawn and drawn samples produced at low speed which may assist in their rapid crystallization. In the starting samples, these nuclei may not be as effective because of the very low orientation of these samples.

Structural basis of shrinkage and shrinkage stress

As a result of detailed studies presented in this article on the shrinkage, crystallization and structural characteristics of PET films and fibres produced at different extrusion and drawing speeds with different orientation and crystallinity levels, some comments can be made on the likely structural origin of shrinkage and shrinkage stress. For this purpose, the samples may be classified in terms of their orientation with respect to the fibre axis as having low, intermediate and high orientation.

In the undrawn amorphous film and fibres that have been studied, orientation is very low and the crystallization half-times will therefore be relatively large. Thus shrinkage, which is associated with the relaxation of internal stress which is generated in the sample during extrusion (casting of film and spinning of fibre) and winding, will be dominated by disorientation of the oriented molecules. The higher shrinkage of samples spun at high speeds is consistent with this postulate. The shrinkage stress also correlates with internal stress or orientation since according to the molecular theory of rubber elasticity, the stress is proportional to the end-to-end distance of the oriented molecule.

When the amorphous as-spun fibres and as-cast film are drawn to low and intermediate draw ratios at relatively low temperatures, as in the present investigation, both the orientation and crystallinity of the drawn samples are quite low. Under these conditions the situation is similar to that for the starting samples described above and both shrinkage and shrinkage stress can be satisfactorily described in terms of a rubber network.

The thermal shrinkage of both fibres and films in the high draw ratio range is less than that of the samples of intermediate draw ratio. This is because as the samples are drawn to a high draw ratio, stress-induced crystallization occurs with the crystallites having their chain direction preferentially oriented parallel to the axis of elongation and the molecular chains in the amorphous phase get anchored between the crystals formed during drawing. This hinders long range motion and reduces shrinkage. However, the films of draw ratio 4.2 show much less shrinkage at 220°C than the corresponding fibres and this difference in shrinkage cannot be explained on the basis of disorientation of molecules in the amorphous phase alone as the amorphous orientation factors for these two samples are quite close. Thus the simple correlation observed earlier between shrinkage and amorphous orientation is no longer present. An attempt was therefore made to identify any additional factors that might be important. It was observed that thermal crystallization is more rapid in the films of draw ratio 4.2 than the corresponding fibres and therefore when considering the shrinkage data at 220°C the interaction between crystallization and shrinkage needs to be taken into account. The thermally induced crystallization will have two consequences. First, it will stabilize the structure by crystal formation in the oriented amorphous phase. Second, since the parallelization of molecules is a prerequisite for crystallization, the formation of the crystals in the fibre axis direction will result in an increase in fibre length[20,35]. Both these factors will reduce shrinkage. The shrinkage stress will also decrease because when a molecular chain is incorporated into a crystallite as a result of oriented crystallization, the average stress that it exerts at its end-points is reduced. However, the distance traversed by the remaining amorphous units is severely reduced because of the disproportionately greater distance taken up by the crystalline units. Consequently, the retractive force exerted is diminished by the crystallization process[35]. Thus in the highly drawn samples both stress-induced crystallization during drawing and thermally induced crystallization during shrinkage should be taken into account and their effect on shrinkage and shrinkage stress considered. In the

present investigation, the rapid crystallization of the as-drawn film of draw ratio close to 4.2 during thermal shrinkage has been attributed to the presence of tiny nuclei and the higher density of crystal defects.

CONCLUSIONS

Comprehensive studies have been made on the thermal shrinkage behaviour of PET fibres and films having different structures and morphologies with varying amounts of orientation and crystallinity and different degrees of crystal disorder. It has been shown that thermal shrinkage of samples with low orientation can be attributed to the rubber-like behaviour of a molecular network. This is apparently because disorientation of the oriented amorphous phase is the predominant mechanism by which shrinkage occurs in these samples and crystallization, being relatively slow because of low orientation, does not compete with shrinkage. In the highly drawn samples with high orientation, however, crystallization can be extremely rapid, particularly at high temperatures, and can impede shrinkage. Compared with conventional samples produced at high speeds, the samples produced at low speeds, by spinning or casting at low speed and drawing at low strain rates, have been shown to undergo rapid crystallization. D.s.c. studies showed that at elevated temperatures these samples have greater potential to reorganize their structure. It is proposed that this may be due to their lattice being more defective, as shown by X-ray diffraction studies, or due to the presence of tiny nuclei in these samples as shown by d.s.c. Both these factors could result in rapid crystallization at relatively high temperatures.

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