

Extrusion drawn amorphous and semi-crystalline poly(ethylene terephthalate): 3. Linear thermal expansion analysis

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Thermal expansion analysis of uniaxially-oriented poly(ethylene terephthalate) (PET) films has been carried out from 123 K up to the PET glass transition temperature, T_g . The films are prepared by solid-state co-extrusion, from different premorphologies (amorphous, 33% and 50% crystalline), to draw ratios (EDR) up to 4.4, over a wide temperature range (T_{ext}). The coefficients of linear thermal expansion exhibit anisotropy: normal to the draw direction (α_{\perp}) it increases, whereas along the draw direction (α_{\parallel}) it always decreases with draw, independent of the initial morphology. Results are interpreted by treating PET as a simple two-phase composite structure. Tie-molecules occurring in the amorphous domains and bridging adjacent crystallites have a major influence. At EDR=4.4, a significant number of taut tie-molecules are developed, resulting in α_{\parallel} becoming negative ($\alpha_{\parallel}^{max} = -1.0 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$) at temperatures below ambient. This appears to be the first report of a negative α for a polymer of relatively low crystallinity. Temperature for extrusion draw significantly affects α . Normal to the draw direction, α_{\perp} decreases with T_{ext} whereas α_{\parallel} increases. The results show that the thermal expansion of PET depends primarily on orientational effects. Only in the absence of anisotropy does per cent crystallinity have a dominant influence. In addition, the TMA thermograms display sharp transitions which are attributed to irreversible shrinkage of the oriented films. The shrinkage temperature (T_s) shows a strong dependence on both orientation and crystallinity, and it is discussed in association with T_g .

(Keywords: poly(ethylene terephthalate); expansion; drawing; morphology; crystallinity)

INTRODUCTION

The coefficient of linear thermal expansion, α , as defined by:

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_p$$

for polymers usually shows a strong dependence on temperature¹⁻⁵, at $\approx T_g$. In general, the glassy and rubbery states of a polymer exhibit different expansivities⁶, and T_g can be readily determined from linear thermal expansion measurements, i.e., the classic T_g determination. In addition, it has been observed^{3,4,7} that the expansivity of oriented polymers show marked anisotropy. For both amorphous and semicrystalline polymers, the thermal expansion along the draw direction (α_{\parallel}) decreases with increasing deformation. Conversely, in the direction perpendicular to orientation, α_{\perp} increases with draw. Although thermal expansivity provides useful morphological information, very little has been reported using this technique. Choy *et al.*^{3,4} have reported recently a significant study of expansivity for oriented semicrystalline polymers of low and high crystallinities. In contrast to PET^{8,9}, polyethylene (PE) is one of the few polymers which has been investigated extensively. Porter

et al.^{1,2} have found a negative coefficient of thermal expansion, $\alpha_{\parallel} \approx -1.0 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, for a highly oriented PE. Choy *et al.*⁴ observed that α_{\parallel} becomes negative at a characteristic draw ratio; DR=3 for PE, DR=7 for PP and DR=9 for POM. However, for polymers of lower crystallinity, including PET, they found* that α_{\parallel} becomes negative only at temperatures $> T_g$. As shown later, α_{\parallel} is negative below room temperature, for PET films extruded to a draw ratio (EDR) of 4.4. To explain the polymer expansivity along and perpendicular to the draw direction, a model based on a simple two-phase composite structure has been used.

EXPERIMENTAL

An amorphous PET film was prepared by melt pressing commercial PET pellets (VFR 5041 AS from Goodyear Tire and Rubber Company) in a Pasadena hydraulic press maintained at 270°C. After 1 h the film was removed from the press and quenched in ice-water. The intrinsic viscosity in trifluoroacetic acid, at 30°C, was $[\eta] = 0.94$ ($M_v = 81\,000$). The crystallinity, as established with a density gradient column using a carbon tetrachloride-heptane mixture was $< 2\%$. Isotropic 33% crystalline PET

* See C. L. Choy *et al.* *J. Polym. Sci. Polym. Phys. Edn.* 1983, **21**, 1427

film was prepared by annealing the amorphous film at 110°C for 3 h *in vacuo*. A 50% crystalline film was also prepared by melt compression of PET pellets, but allowing the pressed melt to cool slowly to room temperature. Uniaxially-oriented PET films were prepared by solid-state co-extrusion in the range 40°–120°C, to an EDR ≤ 4.4 . The films were allowed to attain room temperature as they exited the Rheometric barrel. Film thickness ranged from 0.30 to 0.20 mm, depending on EDR. Apparent crystallinities were also evaluated with a density gradient column using the same mixture mentioned previously. Details of the extrusion draw procedure, density and per cent crystallinity determinations have been described¹⁰.

The thermal expansion measurements were carried out using a thermomechanical analyser, TMS-1, together with a differential scanning calorimeter, DSC-1B, both by Perkin Elmer Corporation, Norwalk, Conn. The PET film was placed between a quartz stage and a flat-tipped quartz probe. A 'zero load condition' on the probe was used, i.e., a minimum load for the probe to follow dimensional changes. The probe was zeroed on the sample using the maximum instrument sensitivity so that changes in sample dimension could be accurately sensed by a linear variable differential transformer (LVDT). A plot of displacement *versus* temperature was recorded, and α was calculated from the tangent to the thermogram (slope) at the desired temperature, divided by the sample thickness. Expansion measurements were carried out at 123 K (under liquid nitrogen) up to T_g , at a heating rate of 20°C min⁻¹. A chromel–alumel thermocouple placed next to the sample was used to monitor the temperature.

The aim of this study was to investigate the thermal expansion behaviour of PET films as prepared by solid-state extrusion. Thus, the oriented films were not conditioned (annealed) and, therefore, discussion of α is limited to temperatures below ambient. In this lower temperature range α is reversible with temperature, a condition that has to be met for reliable measurements. As the temperature approaches T_g shrinkage may also occur, thus affecting significantly the expansion coefficient data.

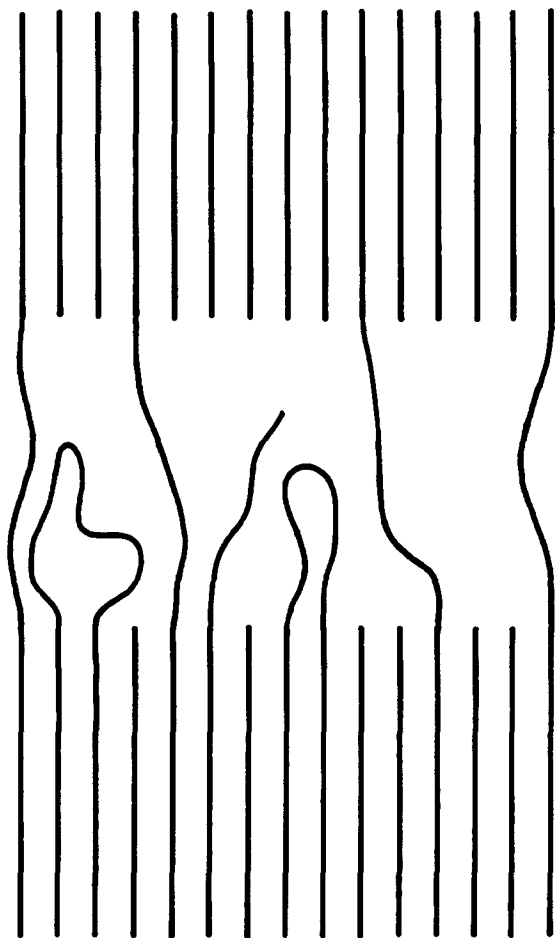
RESULTS AND DISCUSSION

Coefficients of linear thermal expansion— α_{\perp} and α_{\parallel}

To analyse the effect of draw on α , a suitable morphological model is required. The structure of unoriented amorphous, semicrystalline and oriented polymers, as well as their deformation mechanism has been extensively reviewed. Amorphous PET is expected to exhibit 'random coils' which are extensively entangled. However, a paracrystalline ball-like structure has also been suggested¹¹. In contrast, unoriented crystalline polymers prepared from the melt and glassy states exhibit a high degree of chain folded crystals¹². The basic element of the spherulitic structure is the folded chain lamellae packed into many layer stacks and interconnected by a few tie-molecules¹². Zachmann and Stuart¹³, using polarizing microscopy, observed spherulitic growth in glassy PET when annealed at temperatures $> 110^\circ\text{C}$. The morphology of oriented polymers is still a subject of many controversies. Generally, the proposed structural models are based on studies of deformation of highly crystalline polymers, such as PE and PP. Takayanagi and Kajiyama¹⁴ proposed a model for drawn crystalline polymers, wherein the dominant mechanism of deformation is the breakdown of

lamellar crystals into mosaic blocks. The models of Peterlin¹⁵ and Prevorsek^{16,17} are similar. They propose a two-step deformation process involving the destruction of the original spherulitic structure followed by the deformation of a new fibre structure. Microfibrils are formed and their structure contain oriented and folded chain crystalline blocks alternating with amorphous layers in the orientation direction. Amorphous tie chains are formed due to partial chain unfolding during separation of blocks. However, this type of model seems not to be suitable for oriented polymers of low crystallinity, such as PET. In addition, during drawing from the amorphous state, PET crystallizes. The morphology produced by strain-induced crystallization differs from that produced by isothermal crystallization, and appropriate models have been proposed^{18–22}. Although strain-induced crystallization has been extensively observed, the detailed morphology has not yet been well defined. Misra and Stein^{19,20} suggest that imperfect extended-chain crystals are formed, similar to the model of Starron and Sismore for nylon-6,6²³. Koenig²⁴ proposed that strain-induced crystals contain long-loop types of folds, which are not measured by the 988 cm⁻¹ band assigned to regular folds. However, Prevorsek and Sibila²⁵ reported that on drawing, the i.r. absorption band at 988 cm⁻¹ does not disappear completely. It is generally agreed, however, that in drawn PET the polymer molecules are extended and oriented in the draw direction. *Gauche* to *trans* isomerism is the main mechanism leading to crystallization. With draw, chain segments between crystallites become highly strained acting as tie-molecules bridging adjacent crystallites. To interpret the results here, a two-phase model consisting of a crystalline phase and a lower density amorphous phase is used. The amorphous and crystalline domains are assumed to be coupled in series in the draw direction, as shown in *Figure 1*. In the crystalline phase the chains assume *trans* conformation whereas in the amorphous phase the ethylene glycol units may occur in both *gauche* and *trans* conformations²⁶. Their relative amount will depend on the extent of drawing as well as on the extrusion temperature²⁶. Cilia and loose loops are also likely to occur. As mentioned previously, to avoid interference of shrinkage in the coefficient of thermal expansion the analysis is limited to temperatures below room temperature. For discussion and comparison the expansion coefficients were estimated at 7°C. This temperature has been arbitrarily chosen. *Figures 2–4* show the dependence of α on EDR for all samples studied. The first observation is that α_{\perp} increases with draw and α_{\parallel} decreases, both approaching a limit. It is known⁴ that polymer crystals along the draw direction (usually the \hat{c} -axis) have a negative coefficient of thermal expansion (α_{\parallel}^c). However, perpendicular to the draw direction, α_{\perp}^c is positive and approaches in magnitude the expansivity of the amorphous phase at low temperatures⁴. According to *Figure 1* the crystals will expand in series with the amorphous chains along the draw direction. Consequently, α_{\parallel} decreases on drawing because of the greater contribution of α_{\parallel}^c . In the perpendicular direction the situation is reversed, and α_{\perp} increases as a result of a greater contribution of α_{\perp}^c to the sample expansivity⁴. Although the crystal expansivity (α_{\parallel}^c , α_{\perp}^c) contributes significantly to the macroscopic expansion, the amorphous chains also have significance. The results reveal that, for oriented PET, per cent crystallinity *per se* may have only a secondary effect. The changes in per cent

Extrusion direction



A

B

A

Figure 1 Schematic diagram showing crystalline (A) and amorphous (B) domains in oriented PET

crystallinity with draw are shown in Figures 5-7 and they have been discussed previously¹⁰. Figures 2-4 show that with increasing EDR, α_{\parallel} decreases, no matter how per cent crystallinity changes. This suggests that the amorphous chain orientation as well as tie-molecules bridging crystallites have a dominant effect on the macroscopic expansion. As draw ratio increases more strained tie-molecules are likely to form. At an EDR of 4.4 a significant fraction of these tie segments must occur because α_{\parallel} becomes negative, approaching in magnitude the polymer crystal expansivity. For Dacron, $\alpha_{\parallel}^c = -2.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ has been reported²⁷. According to Choy *et al.*⁴ polymers of lower crystallinities such as PET, nylon-6, and poly(vinylidene fluoride) show $\alpha_{\parallel} < 0$ only at temperatures $> T_g$. They attributed this mainly to the rubber elasticity of the stretched tie-molecules. In the case of PET, their sample was stretched to DR=3.2. So far, a negative α_{\parallel} at low

temperatures has been reported only for more highly crystalline polymers, such as PE, PP and POM. In these cases, it has been attributed to the occurrence of crystalline bridges or continuous crystals which formed on drawing^{4,28}. There is no evidence in the literature that crystalline bridges are formed during deformation of

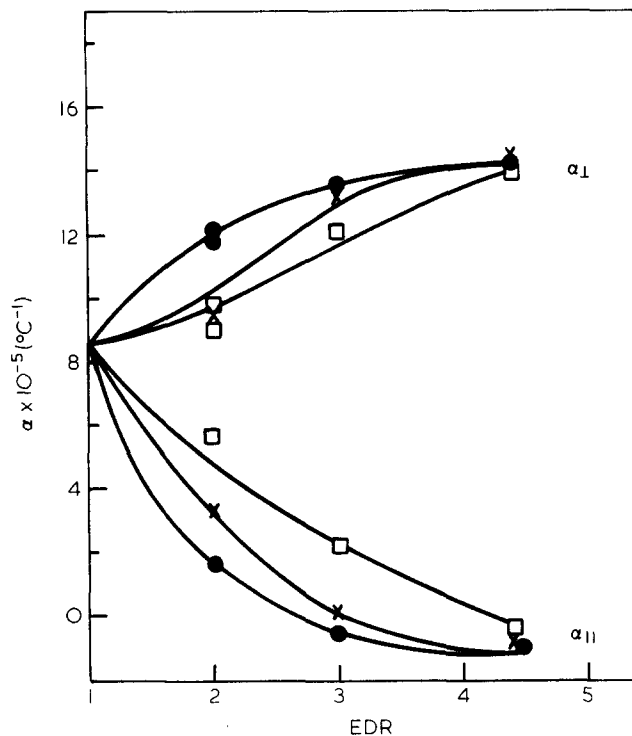


Figure 2 Linear expansion coefficient along (α_{\parallel}) and normal (α_{\perp}) to the extrusion direction versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=1.4%). T_{ext} : ●, 50; ×, 70; □, 90°C

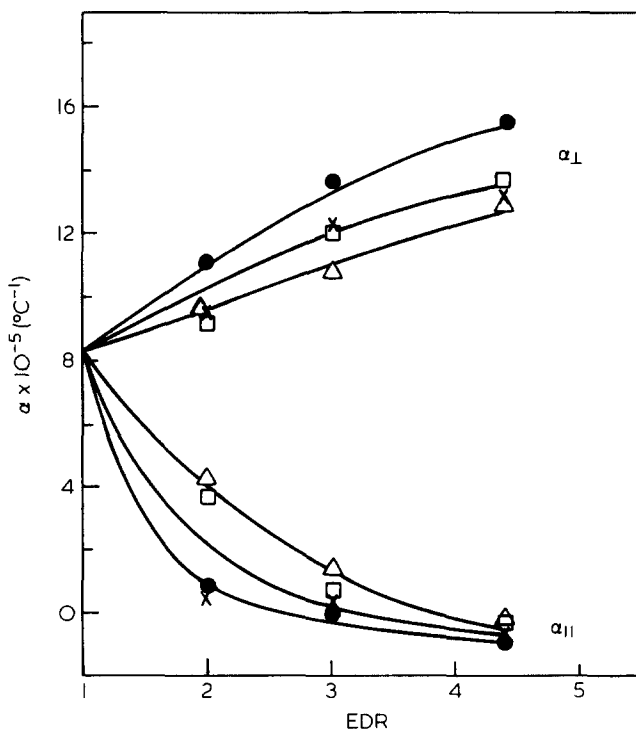


Figure 3 Linear expansion coefficient along (α_{\parallel}) and normal (α_{\perp}) to the extrusion direction versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=33%). T_{ext} : ●, 50; ×, 70; □, 90; △, 110°C

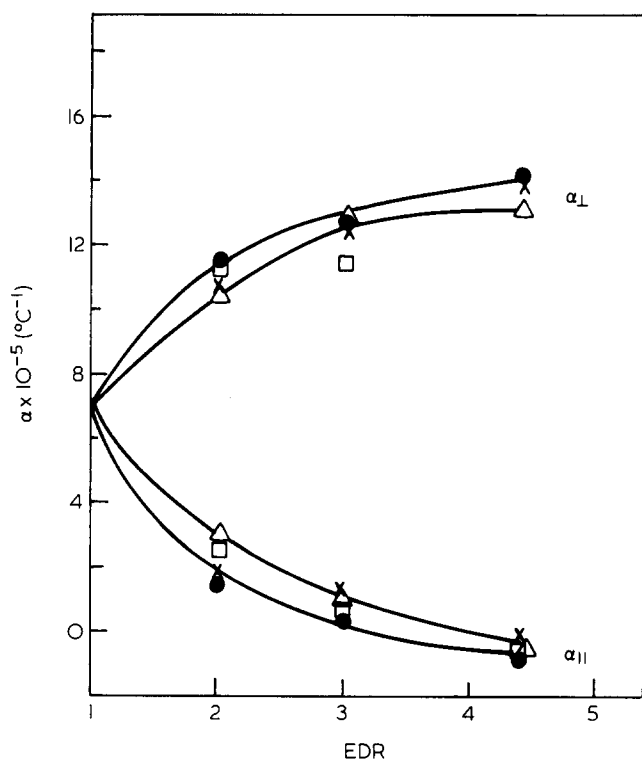


Figure 4 Linear expansion coefficient along (α_{\parallel}) and normal (α_{\perp}) to the extrusion direction versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=50%). T_{ext} : ●, 50; ×, 70; □, 90; △, 110°C

PET. There is also evidence that crystalline bridges are not present in the samples here. This was indirectly revealed by the anomalous decrease in α_{\parallel} at T_g to values much lower than α_{\perp} . Such a decrease can be attributed only to the rubber elastic contraction of the tie-molecules⁴. According to these observations it is likely, however, that the effects of crystalline bridges and tie-molecules on α are similar below T_g , i.e., they are equivalent to fully-extended and crystalline tie molecules.

Figures 2–4 also show that for a given EDR, independent of the initial premorphology, α_{\perp} decreases with increasing T_{ext} whereas α_{\parallel} always increases. According to the previous discussion, an increase in α_{\parallel} reflects a smaller contribution of α_{\parallel}^c to the macroscopic expansion. However, as shown in Figure 8, per cent crystallinity increases with increasing T_{ext} . This way, a film prepared from 33% crystalline PET and extruded to EDR=2 at 110°C shows a 33.5% crystallinity and $\alpha_{\parallel}=4.3 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. This sample extruded at 50°C forms 25% crystallinity but exhibits lower $\alpha_{\parallel}=1.3 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. This reveals that although the crystallinity is higher, the influence of the crystal expansivity, α_{\parallel}^c , on the macroscopic expansion is less. Once again it is evident that α depends primarily on the organization of both crystalline and amorphous domains. Previous FTi.r. results²⁶ have shown that the overall chain orientation decreases when T_{ext} increases. In addition, a smaller fraction of taut tie-molecules should occur due to increased thermal vibrations at higher temperatures. In contrast to the oriented films, isotropic PET exhibited lower α at higher crystallinity: $\alpha_{\text{am}}=8.5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$; $\alpha_{33\%}=8.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$; $\alpha_{50\%}=7.0 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. Buckley and McCrum²⁹ have also observed the same behaviour for isotropic linear polyethylene.

Glass transition and shrinkage temperature

Polymers pass through a transition with temperature, known as T_g , between glassy and rubbery states. At T_g , molecular mobility increases markedly and properties such as viscosity, expansion coefficient, specific heat, etc. undergo abrupt changes. In addition, oriented polymers will dissipate orientation³⁰ when heated up to temperatures in the region of the T_g . As a consequence, shrinkage occurs. Highly crystalline polymers, however, may be dimensionally stable at temperatures $> T_g$.

Considerable confusion exists concerning the T_g of many semicrystalline polymers³¹. Many factors are known to affect T_g , and in the case of PET temperatures ranging from 51° to 127°C are reported³². As mentioned by Boyer³¹, the basic problem is that the amorphous phase of semicrystalline polymers, in which T_g occurs, is not uniform. Crystalline elements subdivide the amorphous phase into a number of species differing in length and/or in local volume, as well as in physical restraint. As a consequence, more than one T_g can be observed or an average temperature is observed, depending on the morphology present. In addition, different techniques usually give different measures of T_g . The effect of drawing on T_g for semicrystalline polymers is still confused. So far there

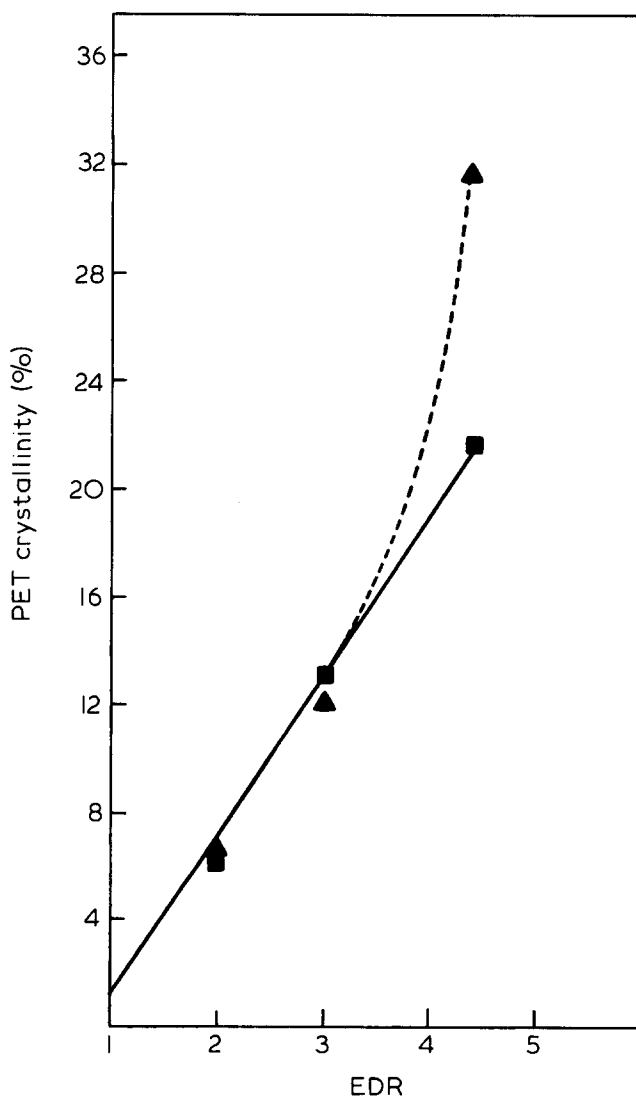


Figure 5 Per cent crystallinity versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=1.4%). T_{ext} : ■, 50; ▲, 100°C

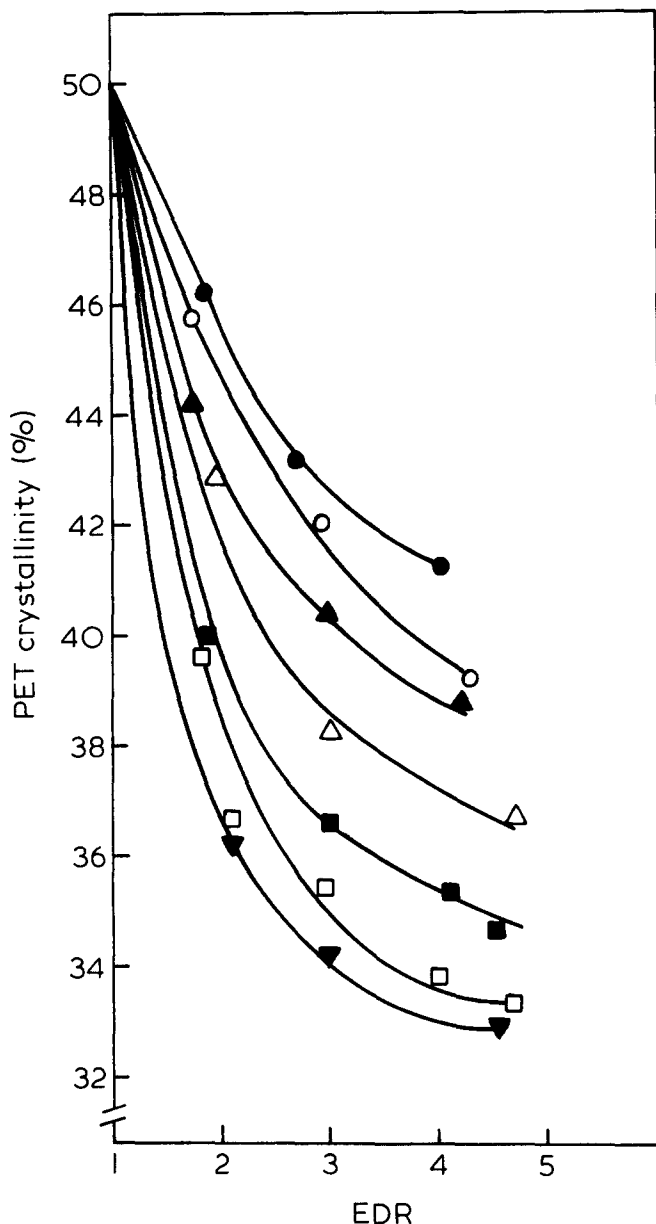


Figure 6 Per cent crystallinity versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=50%). T_{ext} : \blacktriangle , 40, 50 and 60; \square , 70; \blacksquare , 80; \triangle , 90; \blacktriangle , 100; \circ , 110; \bullet , 120°C

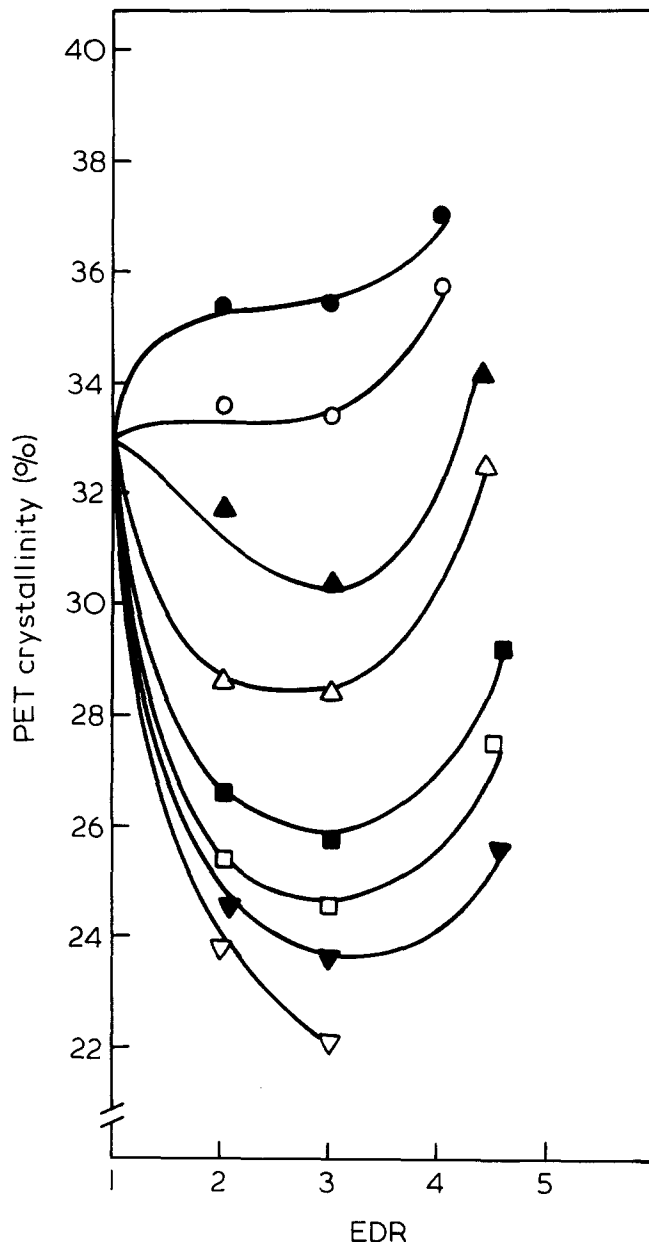


Figure 7 Per cent crystallinity versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=33%). T_{ext} : \triangle , 40; \blacktriangle , 50; \square , 70; \blacksquare , 80; \triangle , 90; \blacktriangle , 100; \circ , 110; \bullet , 120°C

is no definitive evidence relating T_g with orientation³³; it may be lowered, increased or be unaffected. For crystallizable polymers, such as PET, further complications arise. Usually an increase in crystallinity is accompanied by an increase in orientation, making it difficult to separate the individual effects on T_g . It has been established here, however, that this is not always the case, as shown in Figures 6 and 7. In this sense, the samples here are suitable for study. Previously¹⁰, it was noted that extrudates from semicrystalline PET did not reveal a T_g during d.s.c. scans. Only in the case of the isotropic films could a clear transition in the glass region be detected. For these samples there is good agreement between both d.s.c. and TMS techniques. However, during the expansivity measurements in the direction perpendicular to orientation (α_{\perp}), an abrupt change in α was always observed. As shown in Figure 9, the transition takes place in a narrow temperature range and it is suggestive of a glass transition. In contrast, the magnitude and anisotropy of the observed

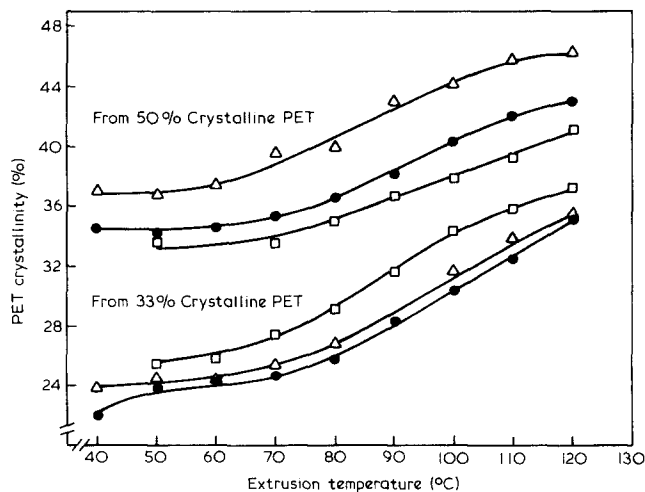


Figure 8 Per cent crystallinity versus extrusion temperature at different extrusion draw ratios. EDR: \triangle , 2; \bullet , 3; \square , 4.4

transition also suggests that it is associated with shrinkage of the oriented film. However, these samples exhibit relatively low crystallinities, and it is assumed that both shrinkage and glass transition occur at approximately the same temperature. As a consequence, the transition shown in Figure 9 must be a result of both shrinkage and glass transition. For simplicity, the temperature where it occurs will be referred to as shrinkage temperature, T_s . Along the draw direction (α_1) the transition was usually broader and appeared systematically about 10°–15°C lower than that of α_2 . This is probably due to the sample geometry, i.e., thin films which probably start bending under the probe as the temperature approaches T_g .

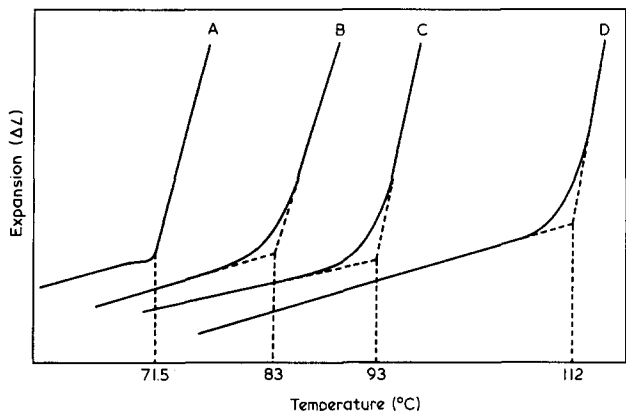


Figure 9 Typical TMA thermograms normal to the extrusion direction of PET films extruded to draw ratio of 3.0 (from 50% crystalline PET) at different extrusion temperatures (heating rate = 20°C min⁻¹). T_{ext} : A, 50; B, 70; C, 90; D, 110°C

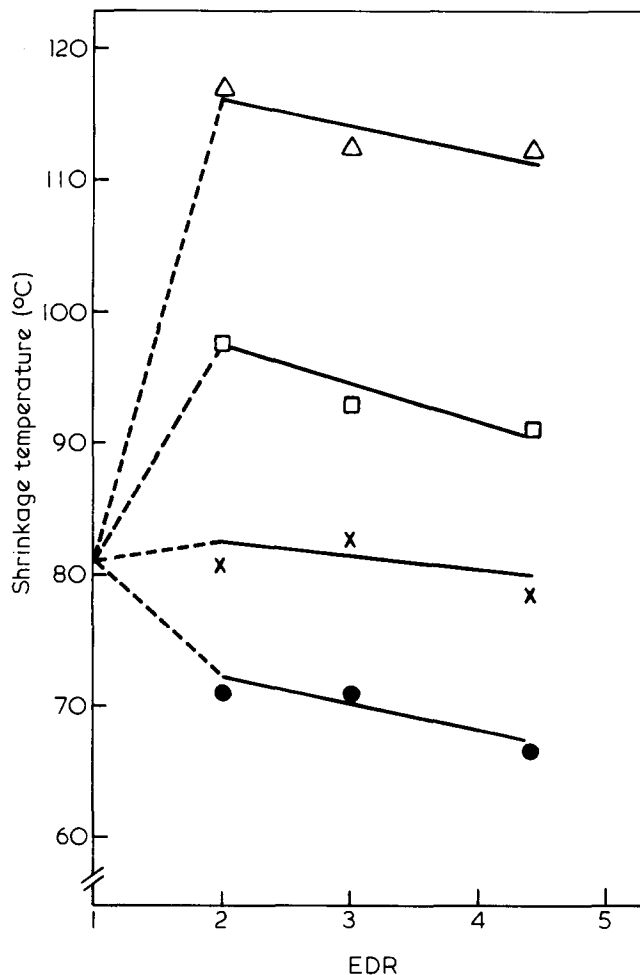


Figure 11 Shrinkage temperature versus extrusion draw ratio at different extrusion temperatures (initial crystallinity = 50%). T_{ext} : ●, 50; ×, 70; □, 90; △, 110°C

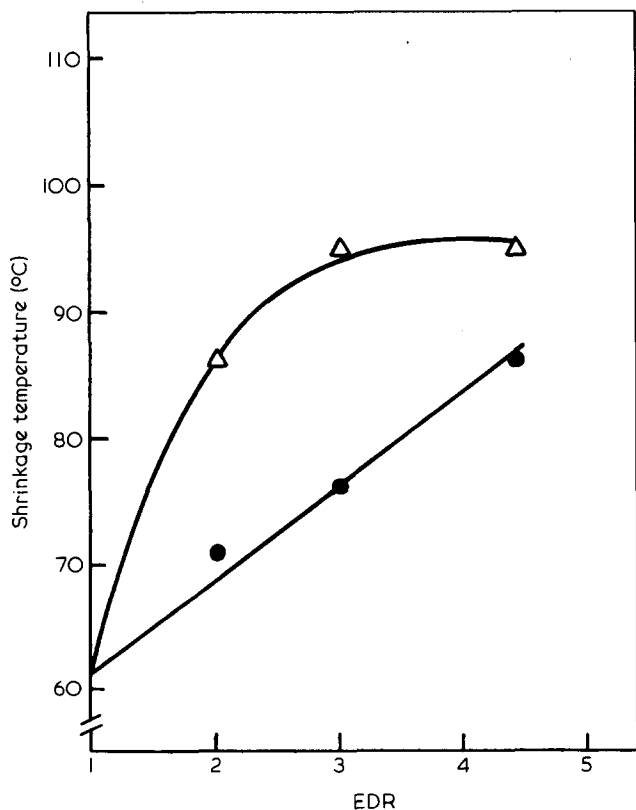


Figure 10 Shrinkage temperature versus extrusion draw ratio at different extrusion temperatures (initial crystallinity = 1.4%). T_{ext} : ●, 50; △, 90°C

For the isotropic PET films, the following T_g 's have been established: amorphous, 61°C; 33% crystalline, 83°C and 50% crystalline, 81°C. Thus, T_g increases considerably with crystallinity, except when comparison is made between both semicrystalline films. Illers and Breuer³⁴ have investigated molecular motions in PET samples of different crystallinity. In agreement, they found that T_g goes through a maximum with increasing crystallinity at $\approx 30\%$. Their X-ray results revealed that many small crystallites were formed for PET crystallized between 90°–170°C. Samples crystallized above this temperature range exhibited higher crystallinity (up to 46%), larger but relatively less crystallites. They concluded that as crystallites decrease in number, amorphous chain motions become easier, and T_g decreases. Figure 10 shows the T_s dependence on EDR for films prepared from amorphous PET. A significant increase in T_s occurs with draw. In the extreme, an increase of 34°C is observed. Simultaneously, the per cent crystallinity also increases (Figure 5), and the combined effects of orientation and crystallinity increase T_s , as expected. It is noteworthy that at EDR of 2 (Figure 10) there is a significant increase in T_s compared to a relatively low increase in crystallinity (Figure 5). This suggests that at low draw, chain orientation is dominant in increasing T_s . This effect can also be seen in Figures 11 and 12. In these later cases, per cent crystallinity and orientation are not affected in the same way (see Figures 6 and 7). Although crystallinity is reduced, at EDR = 2 a

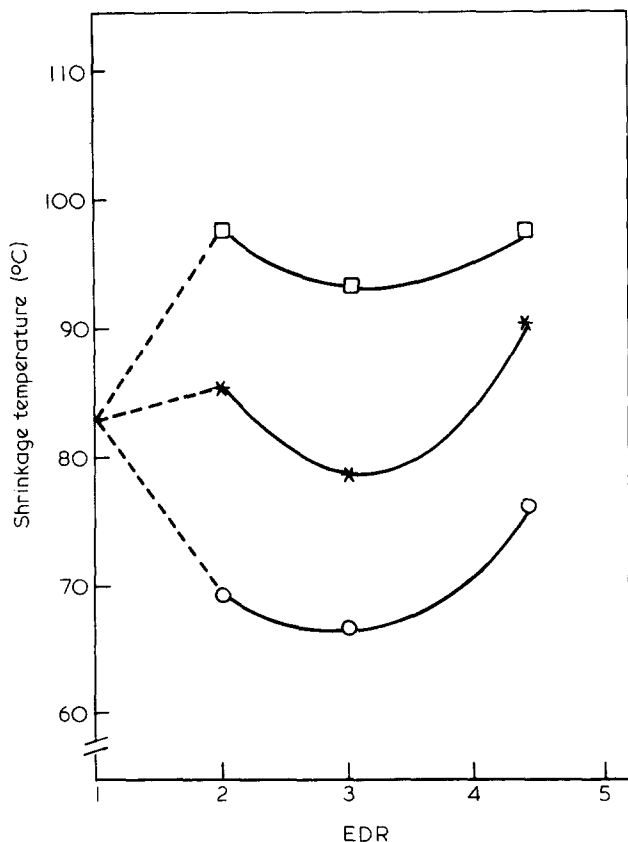


Figure 12 Shrinkage temperature versus extrusion draw ratio at different extrusion temperatures (initial crystallinity=33%). T_{ext} : O, 50; x, 70; □, 90°C

marked increase in T_s is observed for $T_{\text{ext}} \geq 90^\circ\text{C}$. Such increase can be attributable only to the orientation effect. In contrast, at this same EDR of 2, but for $T_{\text{ext}} = 50^\circ\text{C}$ the oriented films exhibit T_s lower than the corresponding isotropic films. However, at this temperature a considerable decrease in crystallinity occurs upon drawing. So far, the birefringence of these samples has not been determined. Nonetheless, FTi.r. analysis²⁶ revealed that the overall chain orientation increases with draw over the entire range of T_{ext} investigated. Figures 11 and 12 also show that at EDR > 2 the changes in T_s with EDR follow the same pattern as per cent crystallinity. Therefore, the results suggest that, within this EDR range, the effect of crystallinity on T_s is dominant. This is supported by analysis of the effect of extrusion temperature on T_s , shown in Figures 13–15. For a given EDR, with increasing T_{ext} , T_s increases markedly. Simultaneously, the per cent crystallinity also increases with T_{ext} (Figure 8). However, FTi.r. analysis²⁶ has shown that the overall chain orientation decreases as T_{ext} increases. Again, this is in agreement with a dominant effect of crystallinity on T_s at EDT > 2. Therefore, for this EDR range, the effect of orientation on T_s may only be secondary.

The heating rate dependence of T_s was investigated for one of the samples, and it was found that T_s increased with the rate of the test, in agreement with the literature⁹. However, the expansion coefficient was approximately constant at all rates.

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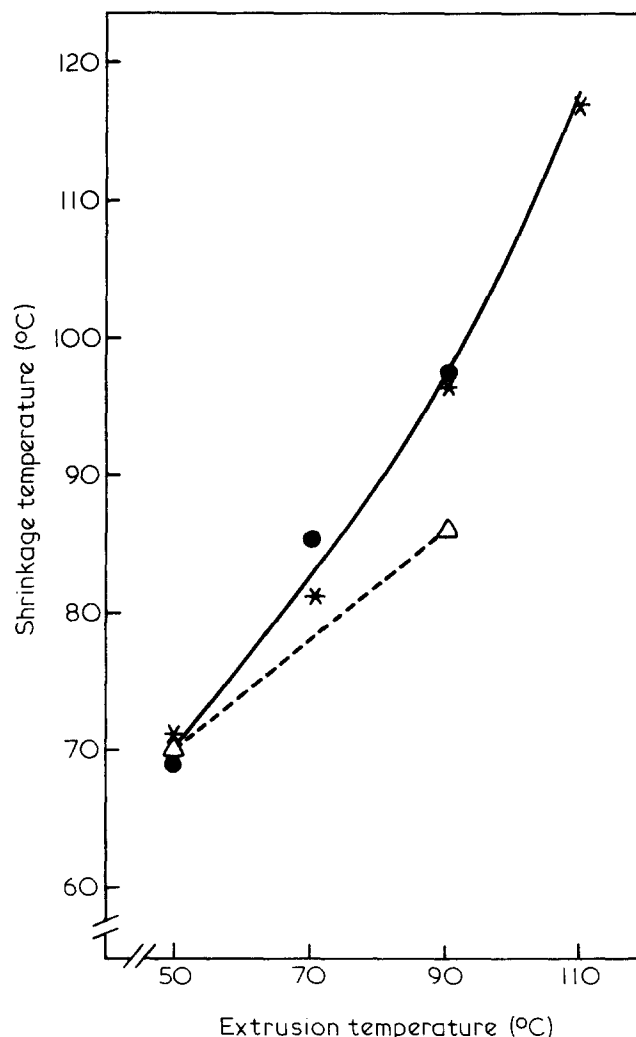


Figure 13 Shrinkage temperature versus extrusion temperature for different PET premorphologies extruded to draw ratio 2.0. Δ, From 'amorphous'; ●, from 33% crystalline; x, from 50% crystalline PET

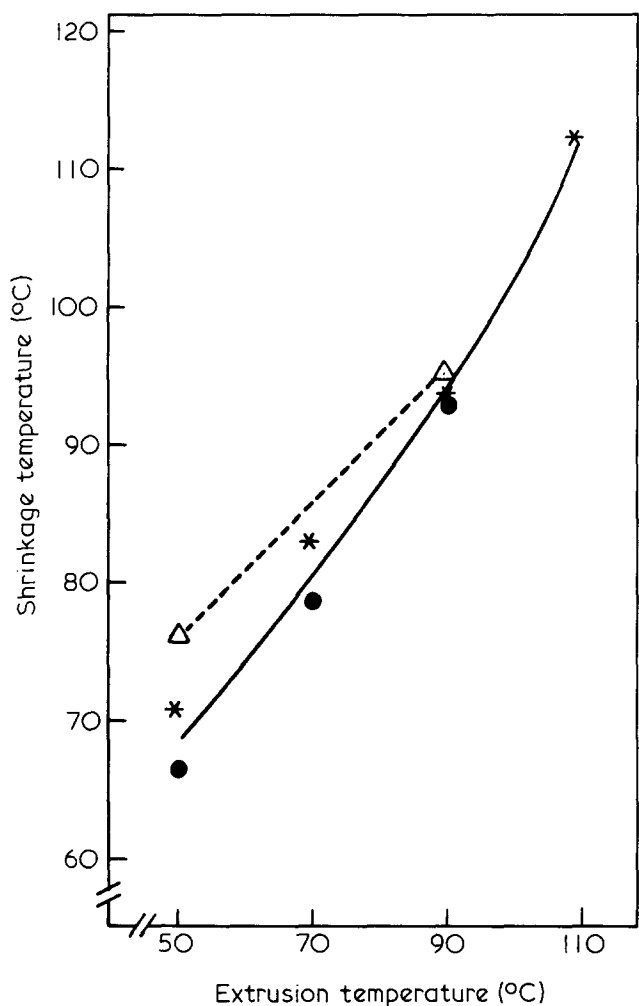


Figure 14 Shrinkage temperature versus extrusion temperature for different PET premorphologies extruded to draw ratio 3.0. Δ, From 'amorphous'; ●, from 33% crystalline; *, from 50% crystalline PET

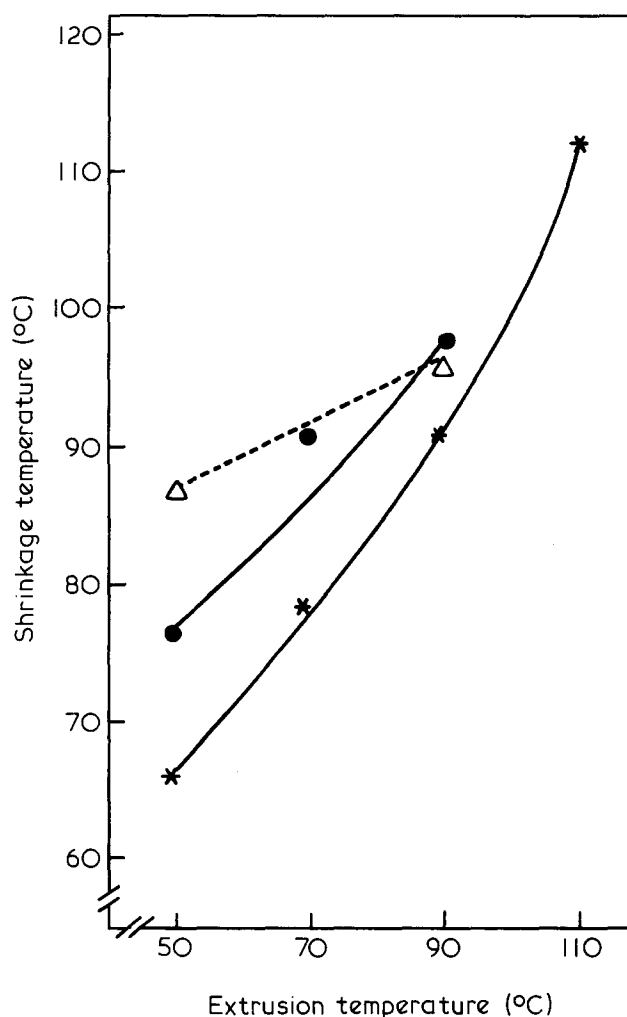


Figure 15 Shrinkage temperature versus extrusion temperature for different PET premorphologies extruded to draw ratio 4.4. Δ, From 'amorphous'; ●, from 33% crystalline; *, from 50% crystalline PET

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