Extrusion drawn amorphous poly(ethylene terephthalate): 4. Irreversible spontaneous elongation

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Uniaxially-oriented poly(ethylene terephthalate) (PET) films prepared by solid-state co-extrusion exhibit irreversible spontaneous elongation (rather than shrinkage) under specific conditions. Results for these conditions show that marked elongation (up to 20%) can occur during annealing of unconstrained samples. This phenomenon, which is not commonly observed for polymers, depends strongly on the prior conditions of extrusion draw. There is significant increase in length for films prepared with extrusion draw ratio (EDR) at 2.0 in the extrusion draw temperature (T_{ext}) range 80–100°C. The extrusion rate is also significant. Lower extrusion rates favour spontaneous elongation on subsequent heating. In addition, the annealing temperature (T_a) also affects elongation. Samples extruded at T_{ext}=80°C to EDR of 2.0 show maximum elongation at T_a=180–190°C. However at higher temperatures, e.g. at 10°C below the melting temperature and higher, shrinkage occurs instead. Moreover, annealing at T_a=90°C for different periods of time (t_a) shows that prior to the elongation a moderate amount of shrinkage occurs ($t_a \leqslant 30$ s). The results suggest a correlation between spontaneous elongation and crystallization during annealing.

(Keywords: elongation; drawing; poly(ethylene terephthalate); crystallization; annealing; shrinkage)

INTRODUCTION

The dimensional stability of oriented polymers is an important feature in their application. During drawing of amorphous and semicrystalline polymers chain orientation occurs. Depending on drawing conditions, such orientation may be 'frozen-in', resulting in a thermodynamically unfavourable state for the amorphous chains. If the polymer is subsequently heated so that chain mobility is allowed (usually above the glass transition temperature, T_g), the frozen-in stresses and strains may dissipate. As a result, if the polymer is free to relax, it will shrink to a more favourable, random conformation. However, if external constraints are imposed on the sample, a shrinkage force will develop. Parameters such as time, temperature, draw ratio, degree of orientation and crystallinity can be important in control of shrink.

There have been many investigations on thermal shrinkage and heat setting of oriented poly(ethylene terephthalate) (PET)[1-22]. In addition to molecular disorientation, crystallization may also occur during shrinkage. The mechanism of contraction is not well established and controversies exist. For example, Statton et al.[15] have proposed that chain folding is a major influence during shrinkage. Subsequently, however, it has been suggested that the basic mechanism for dimensional changes involves disorientation in the amorphous phase[2,3,10]. Infra-red spectroscopy has shown that chain folding occurs only during crystallization, which may or may not be associated with change in length. However, as

noted by Wilson[3], this does not imply that during shrinkage no crystallization occurs before complete amorphous disorientation. Heffelfinger[16] has shown that the crystalline *trans* content does not change during shrinkage at 100°C for a short period of time. In contrast, the amorphous *trans* content markedly decreases. Consequently, the mechanical and other physical properties are significantly changed.

An anomolous behaviour during annealing of unconstrained PET was reported by Oswald et al.[17] They found that after 1 s exposure at 220°C, the sample shrunk 41% whereas after 20 min it shrank only 34%. This corresponds to a lengthening of 14% with increasing annealing time. In contrast, Liska[22] has observed a lengthening in oriented PET filaments with increasing annealing temperature. However, in both cases the net change in length with respect to the original oriented sample was shrinkage rather than extension. An unusual behaviour related to dimensional changes in oriented polymers is the so-called spontaneous elongation. In this case, under some special conditions, during annealing, the polymer elongates in the orientation direction without the application of external stress. The classical example is the spontaneous elongation of natural rubber described by Smity and Saylor[23]. They found that when strips of rubber were stretched at room temperature and subsequently cooled under strain, a 4% increase in length occurred. The elongation was attributed to chain orientation during cooling, leading to crystallization. Alfrey and Mark[24] proposed a mechanism in which the amorphous chains in

the early stages of crystallization become compressed in the orientation direction, leading to spontaneous elongation. A similar mechanism has been proposed by Bosley[20]. According to his model, prior to heat treatment the polymer chains are moderately oriented, and a few oriented nuclei are also present. On further treatment, crystallization proceeds on these nuclei, leading to a state in which the amorphous chain segments experience axial compression and the specimen elongates. Polyethylene cross-linked in a highly oriented state has also shown spontaneous elongation during recrystallization from the melt[25]. In this case, the cross-links introduced in the oriented PE are a major factor in maintaining the reversibility of the dimensional changes. Triacetate fibre when spun from aqueous acetic acid solution exhibited 15–20% elongation during subsequent heating[26]. The elongation was attributed to the uncoiling of molecules in the wet-drawn fibre. It was shown that as the degree of orientation introduced during drawing increased, the amount of spontaneous elongation decreased. Polycarbonate and PET, when deformed in straight-chain propanol at room temperature, also elongated on subsequent annealing[18]. It was found that the linear dimensions could increase as much as 65%. In this case, the elongation has been associated with the presence of microcracks formed during wet deformation. Pinnock and Ward[19] reporting stress–optical properties of amorphous PET, referred briefly to an 'unusual' behaviour where the fibre exhibited an increase in length. Associated with the elongation they observed a large increase in birefringence. A special process for preparing PET with a potential for spontaneous elongation has been reported in a US patent[21]. The patent shows that annealing of a constrained sample may result in elongation of 3%. However, if the sample is free to relax during heating, shrinkage occurs instead.

This paper reports results obtained during annealing of unconstrained oriented PET films. It is established here that spontaneous elongation of films prepared under special conditions may attain values as high as 20%. Although this effect has been reported previously[18,19,21], this is the first extensive study of the conditions under which spontaneous elongation can occur.

EXPERIMENTAL

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 $[\eta]=0.94$ ($\bar{M}_v=81\,000$) after film preparation. The crystallinity, calculated from density, as measured by gradient column in a carbon tetrachloride–heptane mixture, was $<2\%$. Uniaxially-oriented PET films were prepared by the split billet co-extrusion technique in an Instron capillary rheometer from 50°–105°C, to extrusion draw ratios (EDR) up to 4.4. Commercial polyethylene rods split in two halves were used as the outside billet. Brass conical dies with 20° cone angle and different draw ratios were used. Details of this procedure, density and per cent crystallinity determinations have been described[27]. Except where mentioned, all samples were prepared at 0.2 cm min^{-1} Instron cross-head speed. The annealing tests were carried out in silicone oil (Arthur H. Thomas Co., catalogue No. 6428-R15). Before shrinkage measure-

ments, the bath was pre-heated to the desired temperature and maintained within ±1°C. During annealing, the sample was unconstrained. To facilitate removal from the oil bath, the sample was placed in a wire mesh backet. To minimize friction, the basket was lined by a Teflon film. After a prescribed time in the constant temperature bath, the sample was removed and allowed to attain room temperature. Subsequently, the sample was blotted and rinsed with carbon tetrachloride to remove residual silicone oil, for reliable density measurements. It has been shown previously that carbon tetrachloride does not crystallize PET[28]. Except for experiments where annealing time was investigated, annealing for 5 min was chosen. Preliminary tests showed that, within this time, maximum shrinkage was obtained at all annealing temperatures (T_a). Sample dimensions, before and after annealing, were measured with a caliper to 0.02 mm. Film thickness ranged from 0.30 to 0.20 mm, depending on the EDR. In most cases the initial sample length was ≈ 5 mm. Longer samples reduce end effects and measurement errors, but also exhibit curl upon heating, making measurements difficult. All experiments show good reproducibility, and the values reported are an average of at least two determinations. The per cent shrinkage $(\%S)$ as well as elongation $(\%E)$ in the draw direction, were calculated from the formula

$$\%S, \%E = \frac{\text{initial length} - \text{final length}}{\text{initial length}} \times 100$$

It has been reported previously that the T_g of PET in oil is the same as in air[7]. Some annealing tests were also carried out in hot air as well as in boiling water. The results agree with those carried out with silicone.

RESULTS AND DISCUSSION

Figure 1 shows the changes in shrinkage and crystallinity as a function of EDR for films extrusion drawn at 50°C and annealed at 100°C. As EDR is increased, shrinkage is seen to decrease. This significant reduction in shrinkage is attributed to the increased crystallinity in the more highly drawn films. The crystallites act as immobile cross-links and restrict shrinkage. The crystallinity increases significantly on annealing whereas it remains practically unchanged for the isotropic film, which exhibited negligible shrinkage ($\approx 1\%$). It is established that isotropic PET can crystallize at >100°C[29]. However, if the sample is pre-oriented, the rate of crystallization is significantly enhanced and crystallization may occur at temperatures <100°C[12]. *Figure 2* shows the dimensional changes as well as the changes in crystallinity as a function of EDR, for films prepared at $T_{ext}=90$°C when annealed at 100. Unexpectedly, the samples prepared at lower draw ratios (EDR = 2 and 3) did not shrink. Instead, at EDR = 2, a marked increase in length ($\leq 14\%$) occurred. As noted previously, this 'spontaneous elongation' is not a commonly observed phenomenon. Similar behaviour was observed when these samples were annealed at 150°C. These results show that spontaneous elongation depends on the extent of orientation produced during extrusion drawing. In agreement, the patent reporting the spontaneous elongation of PET[21] shows that the samples which elongate during annealing have initially low birefringence. Comparing *Figures 1* and *2*, the effect of T_{ext} on the subsequent dimensional changes is evident. At EDR = 2, $T_{ext}=50$°C, the annealed sample exhibits 49%

shrink whereas at $T_{ext} = 90°C$, 14% elongation is observed. These samples have similar per cent crystallinity before heat treatment (6 and 7%). However, after heat treatment the sample which elongates shows considerably higher crystallinity (24% *versus* 12%). From this it is concluded that the per cent crystallinity before heat treatment is not an important parameter controlling spontaneous elongation during subsequent annealing. However, the results suggest that there may be a correlation between spontaneous elongation and crystallization during annealing. *Figures 3* and *4* show the dimensional and crystallinity changes as a function of T_{ext} for EDR of 2 during annealing at 100° and 150°C, respectively. Before heat treatment all samples exhibited same crystallinity ($\approx 6\%$), independent of T_{ext}. Only the samples prepared in the T_{ext} range 80°–100°C exhibit spontaneous elongation. In addition, both curves showing the dimensional changes at different annealing temperatures have the same shape, going through a maximum at $T_{ext} = 90°C$. *Figure 3* also shows that the samples which elongate exhibit considerably higher crystallinities after annealing, than those that shrink. Furthermore, the per cent crystallinity curve also shows a maximum at $T_{ext} = 90°C$. These results again suggest a correlation between spontaneous elongation and crystallization during annealing. In *Figure 4*, however, only a slight tendency for a maximum in the per cent crystallinity curve is observed. It can be attributed, in part, to the relatively higher annealing temperature ($T_a = 150°C$) which favours thermal crystallization. This is supported by a comparison of samples extruded drawn at 105°C. For both annealing temperatures the samples
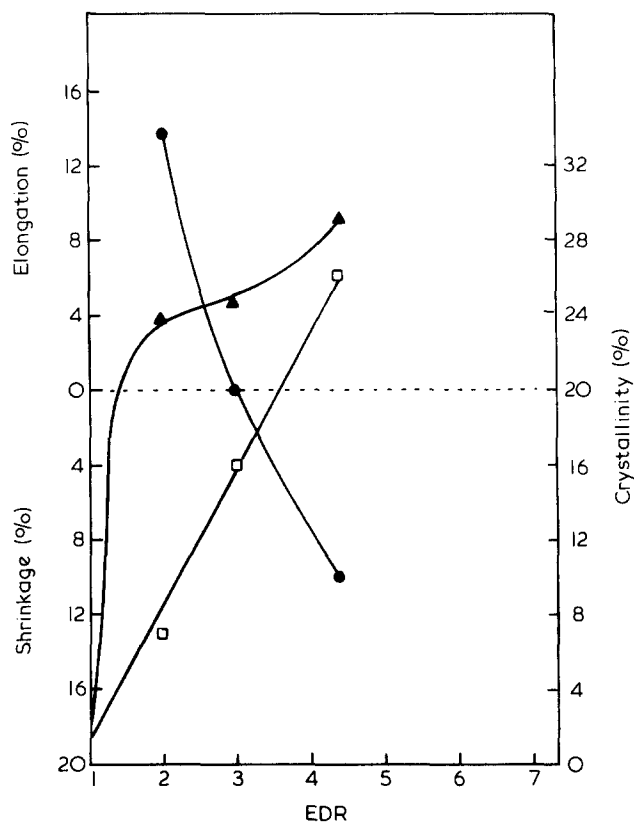
Figure 2 Per cent shrinkage–elongation (●) and per cent crystallinity before (□) and after (▲) annealing *versus* extrusion draw ratio ($T_{ext} = 90°C$; $T_a = 100°C$)
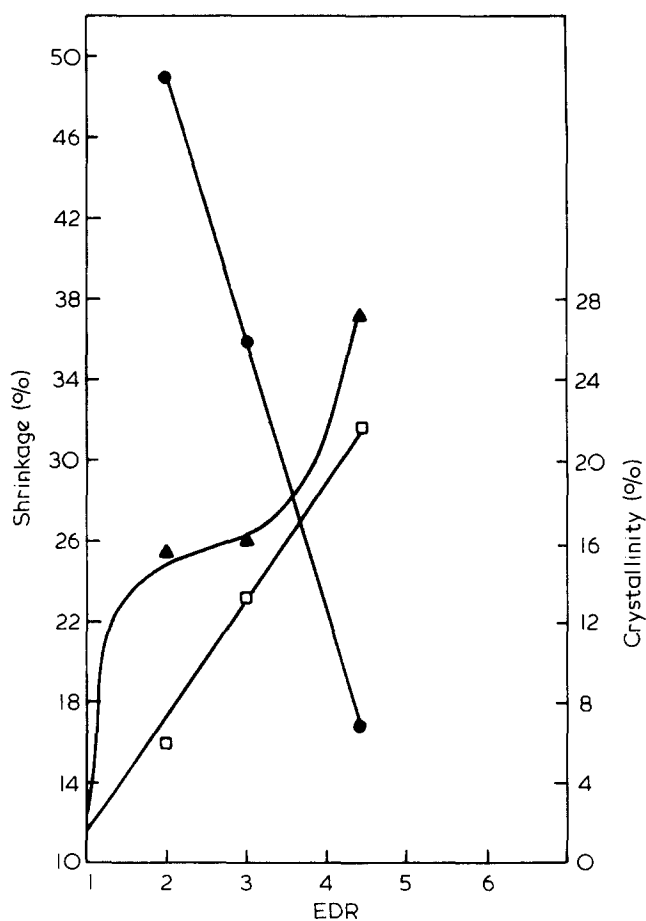
Figure 1 Per cent shrinkage (●) and per cent crystallinity before (□) and after (▲) annealing *versus* extrusion draw ratio ($T_{ext} = 50°C$; $T_a = 100°C$)
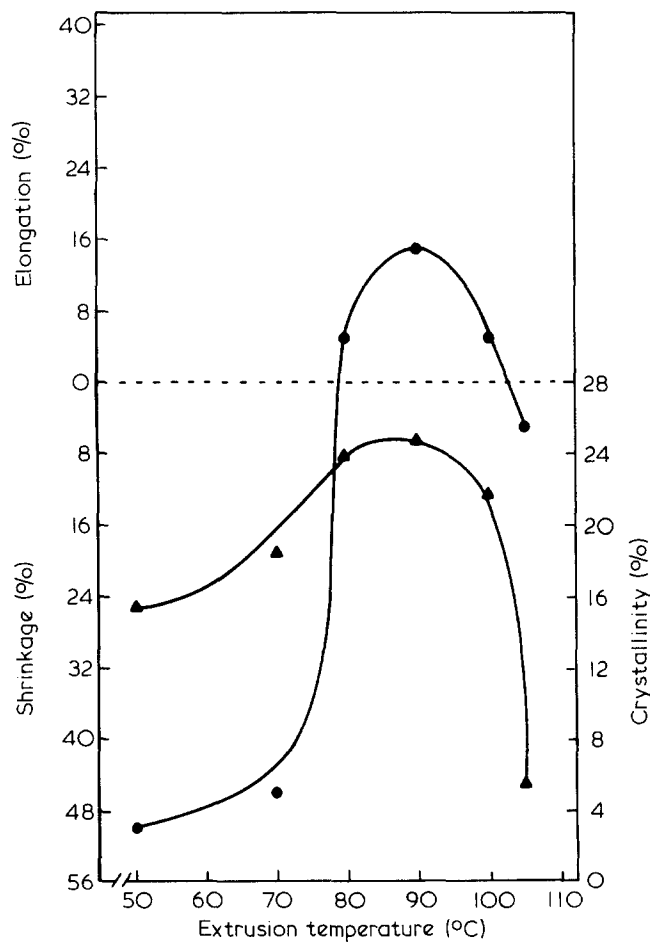
Figure 3 Per cent shrinkage–elongation (●) and per cent crystallinity (▲) after annealing *versus* extrusion temperature (EDR = 2.0; $T_a = 100°C$)
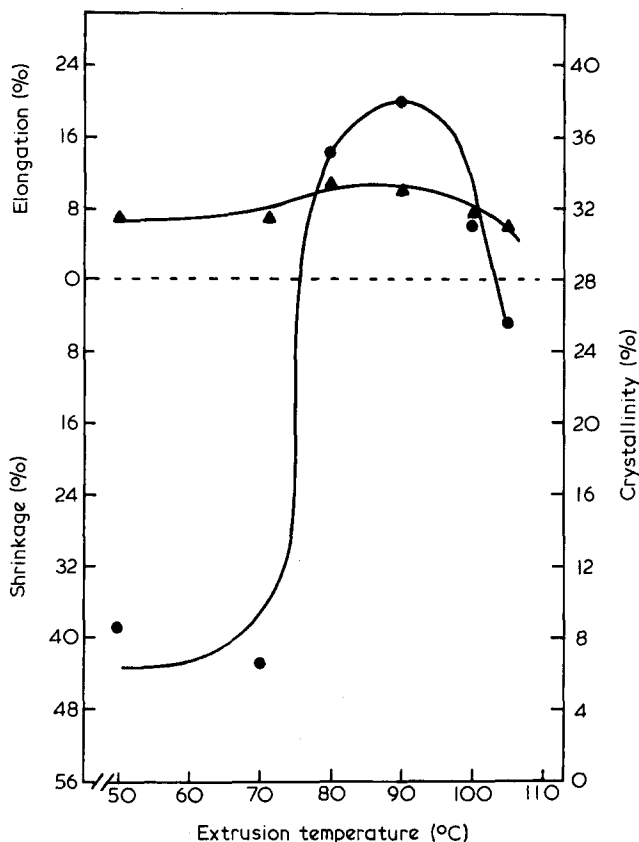
Figure 4 Per cent shrinkage–elongation (●) and per cent crystallinity (▲) after annealing *versus* extrusion temperature (EDR=2.0; T_a=150°C)

show the same amount of shrinkage, but the crystallinities after annealing are markedly different. However, thermal crystallization effects can be reduced at lower annealing temperatures, as shown in *Figure 5*. Both dimensional change and crystallinity curves show the same trends as in *Figures 3* and *4*, except that the absolute values are lower. Once again, the correlation between spontaneous elongation and crystallization is evident. It is noteworthy that in this *Figure* the samples which shrunk ($\approx 48\%$), after annealing exhibited no crystallinity at all. Thus, an apparent decrease in crystallinity from 6% to 0 is observed with annealing. This unusual behaviour for PET has been reported previously[10,11]. It is, however, an important result concerning the mechanism of shrinkage. Clearly, it shows that there is a distinction between shrinkage and crystallization processes, at least at lower annealing temperatures. The basic mechanism responsible for shrinkage involves disorientation of a *trans*-oriented component in the amorphous phase. Only under suitable conditions crystallization occurs. At annealing temperatures <90°C, dimensional changes are negligible, due to the proximity of T_g (*Figure 6*). Again, *Figure 6* suggests a correlation between the changes in per cent crystallinity and elongation. Additional information on spontaneous elongation is shown in *Figure 7*. By increasing the annealing temperature, the amount of elongation increases and reaches a maximum at 180°–190°C (20%). At higher annealing temperatures, elongation decreases, and at 230°C, i.e., 10°C below T_m a moderate amount of shrinkage (5%) occurs. At 240°C the sample melts and shrinks back to its corresponding isotropic length. These results show that the same sample may exhibit both spontaneous elongation and shrinkage, depending on the

annealing temperature. During annealing at 150°C it was observed that, before elongation, the first step in dimensional change was shrinkage, followed by elongation. It was not possible to isolate the sample in its initial shrunk state. However, such isolation was possible in the early
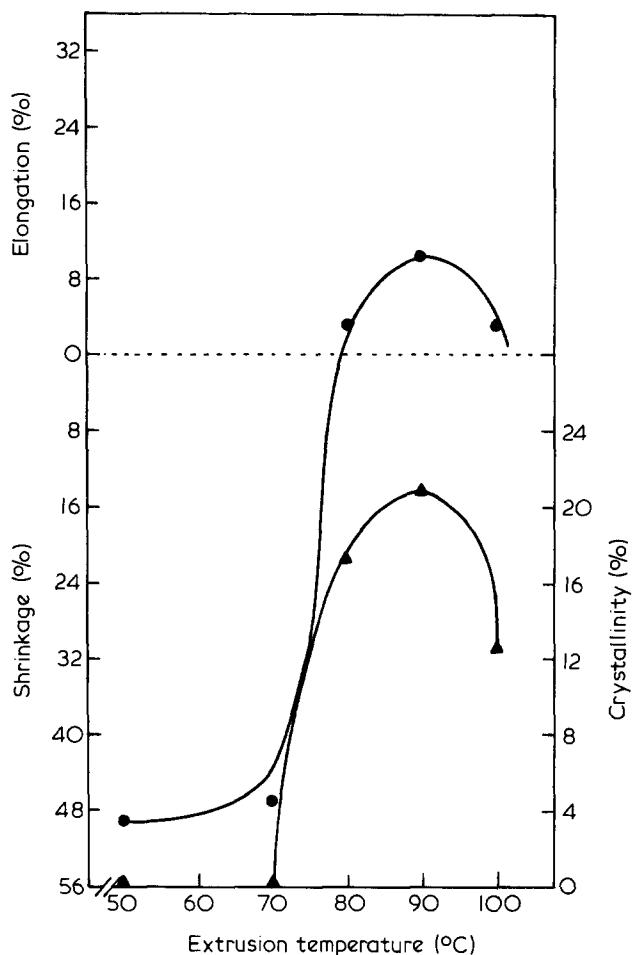

Figure 5 Per cent shrinkage–elongation (●) and per cent crystallinity (▲) after annealing *versus* extrusion temperature (EDR=2.0; T_a=90°C)
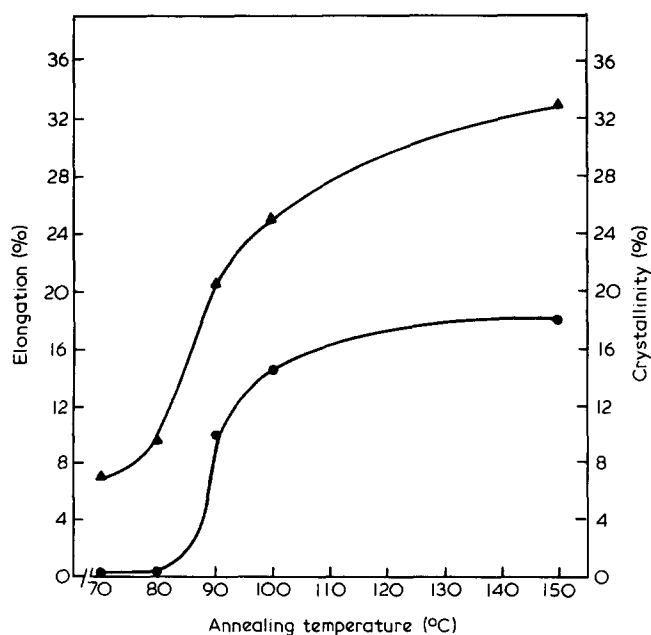

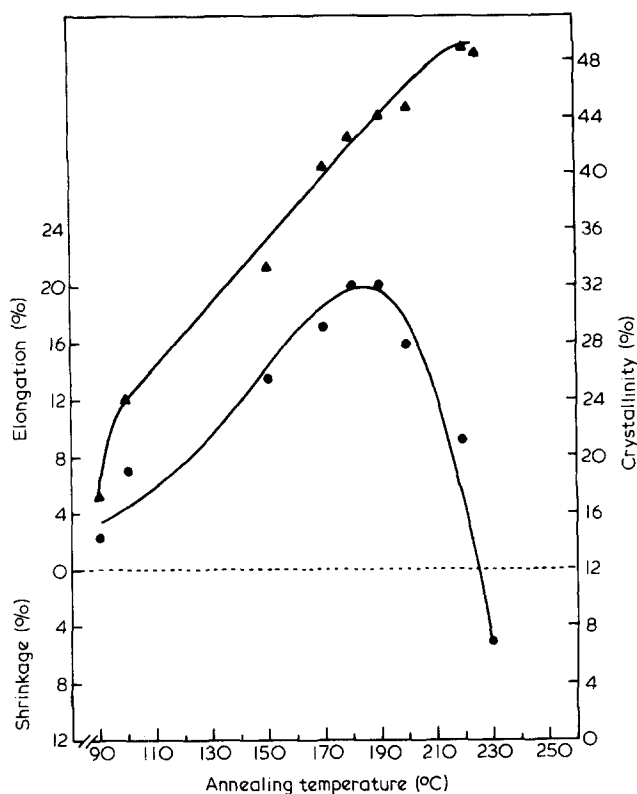**Figure 6** Per cent elongation (●) and per cent crystallinity (▲) *versus* annealing temperature (EDR=2.0; T_{ext}=90°C)

Figure 7 Per cent shrinkage–elongation (●) and per cent crystallinity (▲) *versus* annealing temperature (EDR=2.0; T_{ext}=80°C)
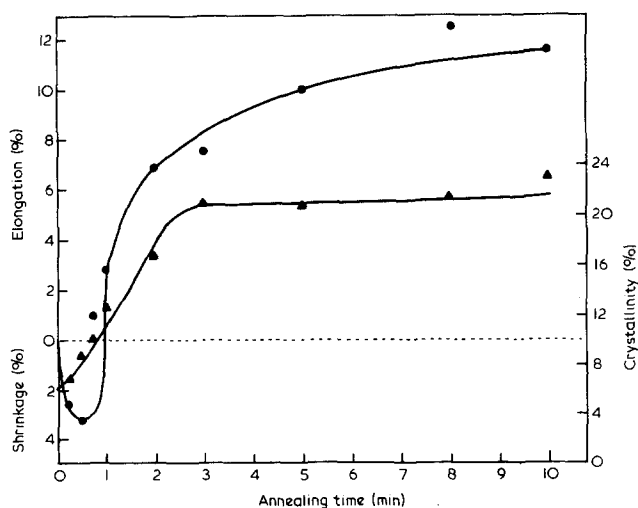

Figure 8 Per cent shrinkage–elongation (●) and per cent crystallinity (▲) *versus* annealing time (EDR=2.0; T_{ext}=90°C; T_a=90°C)

stages ($t_a \leqslant 30$ s) of annealing at 90°C, as shown in *Figure 8*. This result suggests that the initial shrinkage leads to structures which become dimensionally unstable. As mentioned previously, spontaneous elongation has been observed for PET when deformed in straight-chain propanol[18]. In that case, the authors also observed the occurrence of some contraction before elongation. The Instron cross-head speed, i.e., extrusion rate during sample preparation also affects significantly the dimensional changes occurring on subsequent annealing. It was established here that spontaneous elongation was favoured only for samples prepared at cross-head speeds $\leqslant 0.2$ cm min^{-1}. If a small load (≈ 200 g) is attached to the film (1.0 mm^2 cross-sectional area) during extrusion drawing, the amount of elongation on subsequent annealing is

markedly reduced, although EDR remains unchanged. In a few cases when higher loads were used, the samples exhibited shrink rather than elongation, during heat treatment. Thermomechanical analysis[30] (TMA) also revealed elongation in the orientation direction during relaxation at $\approx T_g$.

Much further work is required to elucidate the precise nature and mechanism of spontaneous elongation. It has been shown here that significant elongation ($\leqslant 20\%$) can take place during annealing of PET. Fibres and films are often used in applications where relatively high temperatures are required. Therefore, an understanding of the dimensional changes which may occur at $> T_g$ and $< T_m$ is of practical as well as of scientific importance.

ACKNOWLEDGEMENTS

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