Relationship between thermal shrinkage and morphology of zone-drawn polyethylene*

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Shrinkage was investigated in polyethylene drawn in the solid state and in the melt. The findings indicate the formation of a crystalline skeleton at draw ratios above 5–10. The skeleton raises the resistance of the drawn samples to shrinkage and its quality increases with the draw ratio. The possible structure of the skeleton is discussed. Regeneration of the drawn polymer to the isotropic state was also investigated. This was found to depend on the heating procedure; in the case of gradually increased temperature the reversibility of plastic deformation is restricted by annealing effects, while immediate melting at 150°C showed the reversibility to be substantially higher and even total recovery could be achieved. These differences are explained in terms of disturbed continuity of the stretched molecular network.

(Keywords: drawn polyethylene; thermal shrinkage; reversibility of deformation; morphology)

INTRODUCTION

The shrinkage behaviour of drawn semicrystalline polymers has been studied previously. In general, shrinkability increases with annealing temperature[1–3], a decrease in shrinkage was observed with increasing draw ratio[2] and with increasing temperature at which the polymer was drawn[1,2].

Heating the unconstrained samples above the melting point allows the regeneration of the polymer to the isotropic state to be determined[2–5]. However, total recovery (fully reversible plastic deformation) has rarely been reported, and may depend on the experimental procedure[4]. If the fixed sample is heated, relaxation of the stretched molecular network[6] is reflected in high retractive forces[2,3,7].

Different mechanisms for the shrinkage process have been suggested by various authors. Peterlin suggested the relaxation of taut tie molecules to be responsible for shrinkage[8], while other authors believe in the relaxation of melted extended-chain fibrillar cores of shish-kebabs[4]. Capaccio and Ward reported two stages of shrinkage for highly drawn polyethylene[2]: a small contraction of the amorphous chain at lower temperature and consecutive large-scale shrinkage due to reorganization of the crystalline phase before the polymer melts.

This study is a continuation of earlier work describing the method of zone drawing with constant load[9] and the morphology of drawn polyethylene[10].

EXPERIMENTAL

The drawing method in non-isothermal (NR) and isothermal (IR) regimes has been described elsewhere[9]. The temperature of the plates in the heating zone was taken as the drawing temperature T_D.

The material used was a blown, slightly preoriented film (birefringence $\Delta n = 0.0028 \pm 8.1 \times 10^{-5}$) of linear polyethylene (Liten VB 33; Chemical Works Litvinov, Czechoslovakia; density $958\,kg\,m^{-3}$; $\bar{M}_w = 197\,000$). The melting point, determined from the disappearance of birefringence, was in the range 130–132°C.

The draw ratio was defined as $\lambda = \lambda_0 A_0 / A$ where A_0 and A, respectively, are the cross-sections of the original and drawn samples, and λ_0 $(= 1.37 \pm 3.7 \times 10^{-3})$ is the deformation ratio of the starting film[10].

A strip was cut from the drawn polymer and placed between microscope slides in silicone oil which prevents the polymer from adhering to glass at high temperatures.

In the gradual annealing experiment the sample was thermostatically controlled at the annealing temperature T_A until it shrank to constant length and then the magnitude of shrinkage S was measured as the percentage of the original length. The procedure was repeated with increasing T_A from room temperature until the polymer melted. The reversibility of plastic deformation was evaluated from $S_{rev,g}$ measured for the most shrunken sample.

For the experiment of fast shrinkage the sample was subjected to immediate melting at 150°C and the shrinkage value $S_{rev,f}$ was determined after recrystallization at room temperature.

RESULTS

Gradual annealing

For the drawn polymer various types of shrinkage curves $S = f(T_A)$ were measured (*Figure 1*). Their shape depends on the λ values and the morphology of the polymer and thus on temperature T_D and the stress affecting the sample during drawing, irrespective of whether the polymer was drawn in IR or in NR.

Samples drawn in the solid state[10] to $\lambda < 15$–20 are represented by curve 1; the reduction in the rate of increase of S at $T_A \sim 128$–129°C disappears when the draw

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* Dedicated to Dr Karel Dušek on the occasion of his 60th birthday

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ratio reaches values of 15–30 (curve 2). At draw ratios of 25–30 even a dilatation near the melting point disappears, shrinkage is only slowed down before melting (curve 3). When $\lambda > 30$–35 the shrinkage curves become convex (curve 4). Samples drawn in the melt[10] to $\lambda < 10$–30, when annealed in the T_A range 60–130°C, show dilatation before shrinkage (curves 5 and 6). Also, there is dilatation near the melting point, gradually disappearing as the draw ratio increases (curve 6). At very high λ values the shrinkage curve is convex (curve 7). The boundaries between the individual ranges of λ are considerably diffuse.

The effect of the draw ratio on shrinkage at given T_A is shown in *Figure 2*. The basic feature is the existence of shrinkage maxima at $\lambda \sim 5$–10, except the samples drawn in the melt, where there is a trend of dilatation at lower T_A predominating over shrinkage. It can also be seen that melt-drawn samples show a lower shrinkage at high λ values, than those drawn in the solid state.

The dependence of shrinkage on drawing temperature and initial stress σ_0 is illustrated in *Figure 3*. Different symbols are used to denote various T_D values for which the range of initial stress is restricted by its lowest threshold value[9,10]. With decreasing stress shrinkage remains at the same level up to $\sigma_0 \sim 3$–4 MPa, when there is a transition from solid-state to melt drawing[10]. A further decrease in stress results in lower S values. The essential feature is that shrinkage (within scatter of experimental data) does not depend on T_D. Furthermore, the shrinkage of solid-state-drawn samples is a function of the λ values only, although drawing conditions affect the morphology to some extent[10]. With melt drawing, however, the effect of initial stress on the structure becomes so pronounced that it causes a change in shrinkage.

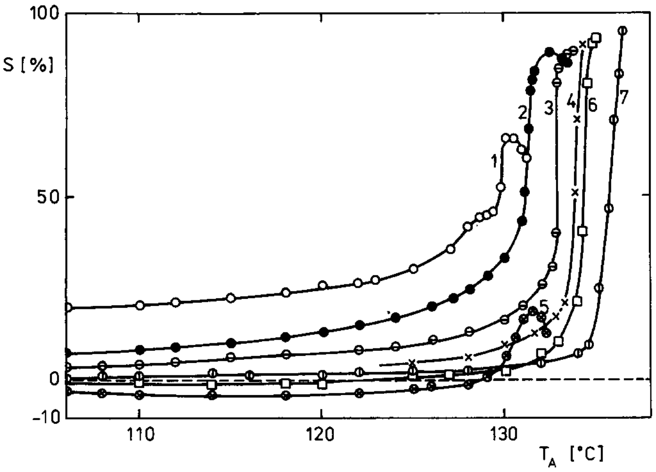

Figure 1 Characteristic curves of the process of shrinkage S as a function of the annealing temperature T_A of the polymer drawn in NR and IR (gradual annealing). Curve 1: IR, $T_D = 112.5$°C, $\sigma_0 = 11$ MPa, $\lambda = 1.8$; curve 2: IR, $T_D = 104$°C, $\sigma_0 = 13$ MPa, $\lambda = 16.8$; curve 3: IR, $T_D = 121$°C, $\sigma_0 = 7$ MPa, $\lambda = 31.4$; curve 4: IR, $T_D = 129.5$°C, $\sigma_0 = 3.6$ MPa, $\lambda = 57$; curve 5: IR, $T_D = 138$°C, $\sigma_0 = 0.8$ MPa, $\lambda = 1.5$; curve 6: NR, $T_D = 135.2$°C, $\sigma_0 = 0.8$ MPa, $\lambda = 29$; curve: NR, $T_D = 141.2$°C, $\sigma_0 = 0.8$ MPa, $\lambda = 144$

From the $S_{rev,g}$ values the shrinkage ratio $\lambda_{rev,g}$ can be determined according to:

$$\lambda_{rev,g} = 100/(100 - S_{rev,g}) \qquad (1)$$

This corresponds to the reversible fraction of plastic deformation. The remaining fraction $\lambda_{ir,g}$ is irreversible, fulfilling:

$$\lambda = \lambda_{rev,g}\lambda_{ir,g} \qquad (2)$$

The effect of draw ratio and drawing conditions on $S_{rev,g}$ is shown in *Figure 4*, where the broken curve corresponds to total recovery ($\lambda_{ir,g} = 1$). The solid-state-drawn polymer possesses total recovery only at draw ratios below ~ 5–10. Above this limit the deviation from total recovery increases with initial stress, increasing more with higher λ. Moreover, within the scatter $S_{rev,g}$ is independent of T_D. If the polymer is drawn in the melt, no total recovery occurs even at low λ values and, at the same time, the reversible fraction of deformation decreases with increasing T_D. Thus, for a sample drawn to $\lambda_0 = 7$ at $T_D = 132$°C and $\sigma_0 = 1.5$ MPa, $\lambda_{rev,g} = 4.8$, while at $T_D = 138$°C, $\lambda_{rev,g} = 3.1$.

Fast shrinkage above the melting point

From the $S_{rev,p}$ values it is possible to determine the shrinkage ratio $\lambda_{rev,f}$ analogous to equations (1) and (2).

With quickly molten samples there is total recovery up to $\lambda \sim 20$ (*Figure 5*). At $\lambda > 20$, recovery of the polymer is incomplete, but higher than with gradually annealed samples, as shown in *Table 1*; the $\lambda_{rev,f}$ values are as

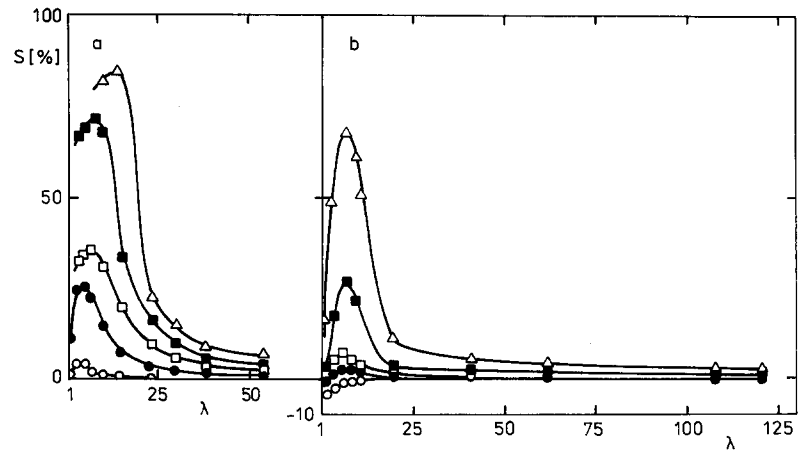

Figure 2 Dependence of shrinkage S on the draw ratio λ at various annealing temperatures T_A (gradual annealing). The polymer was drawn in IR in the solid state (a) at $T_D = 112.5$°C and $\sigma_0 = 7$ MPa and in the melt (*b*) at $T_D = 138$°C and $\sigma_0 = 0.8$ MPa. $T_A = 60$ (○), 110 (●), 125 (□), 130 (■) and 132 (△) °C

much as five-fold higher compared with the $\lambda_{rev,g}$ values and are always higher than $\lambda_{ir,f}$. At gradual annealing, $\lambda_{rev,g} < \lambda_{ir,g}$ is also possible.

Extensibility of a polyethylene chain is given by the value of λ_{ext} according to the relation[5,11]:

$$\lambda_{ext} = I_0/2R_g \sim 0.39\sqrt{n} \quad (3)$$

where I_0 is the contour length of the chain, R_g is its radius of gyration in the fully relaxed melt and n is the number of monomer units. For the polymer used, $\lambda_{ext} \sim 46$. In

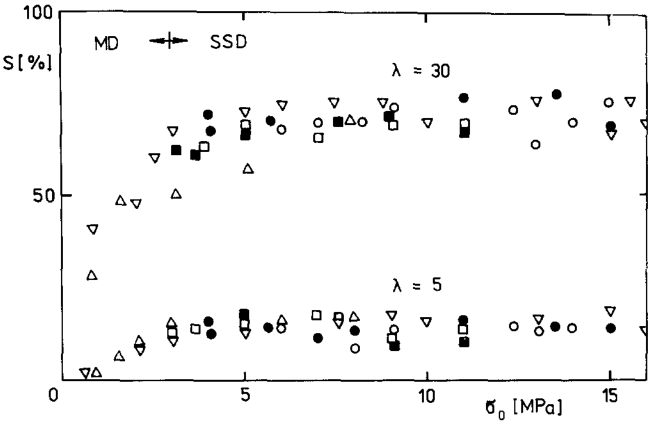

Figure 3 Effect of thermomechanical drawing conditions on the shrinkage S of the polymer (gradual annealing). The initial stress is σ_0; the polymer was drawn isothermally at $T_D = 104$ (○), 112.5 (●), 121 (□), 129.5 (■), 138 (△) °C and non-isothermally (▽); $T_A = 130$°C. MD (SSD) denotes the melt drawing (solid-state drawing) region

Table 1 Comparison between the reversible (λ_{rev}) and irreversible (λ_{ir}) fraction of the draw ratio λ revealed by gradual annealing experiments (g) and fast shrinkage experiments above the melting point (f); T_D is the drawing temperature and σ_0 is the initial stress

			λ_{rev}		λ_{ir}	
T_D (°C)	σ_0	λ	g	f	g	f
112.5	4	20	12.5	18.5	1.6	1.08
	7	20	9.5	16.1	2.1	1.24
	7	53.5	11.8	38.5	4.5	1.39
	15	20	6.9	17.2	2.9	1.16
	15	30	4.9	24.4	6.2	1.23
138	0.8	20	8.0	14.9	2.5	1.34
	0.8	126	26.3	45.5	4.8	2.77
	2.5	20	6.6	16.7	3.0	1.20
	2.5	30	6.7	27.0	4.5	1.11
	10	20	4.5	20.0	4.4	1.00
	10	23.5	4.4	23.5	5.3	1.00

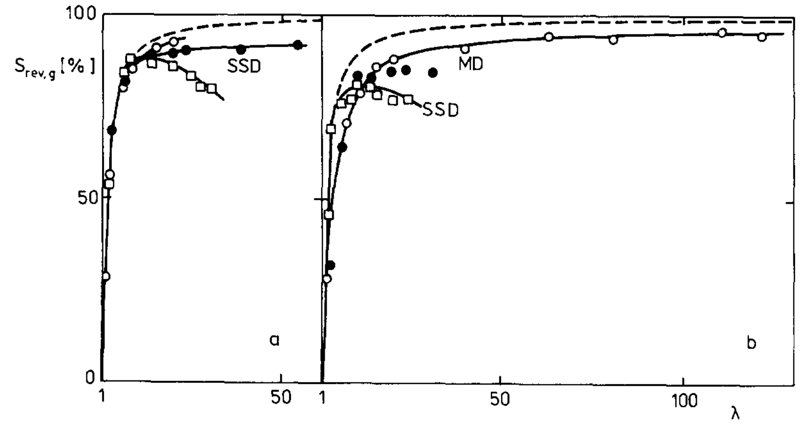

Figure 4 Shrinkage $S_{rev,g}$ at gradual annealing as a function of the draw ratio λ. (a) IR, $T_D = 112.5$°C, $\sigma_0 = 4$ (○), 7 (●) and 15 (□) MPa; (b) IR, $T_D = 138$°C, $\sigma_0 = 0.8$ (○), 2.5 (●) and 10 (□) MPa. Broken curves hold for total recovery; MD (SSD) denotes the melt drawing (solid-state drawing) region

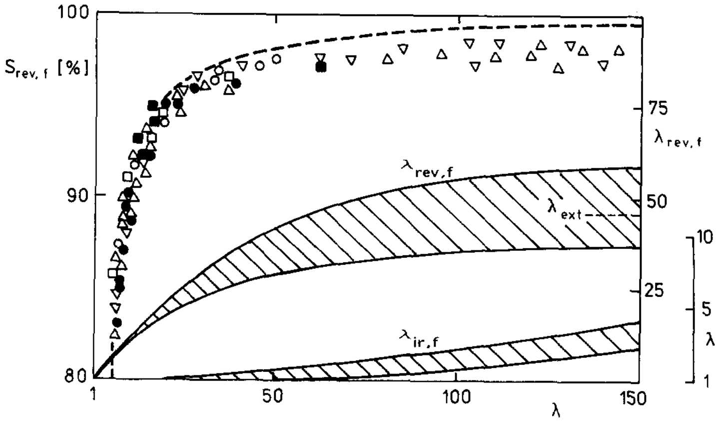

Figure 5 Effect of the draw ratio λ on shrinkage $S_{rev,f}$ of the polymer in the fast shrinkage experiment (heating at 150°C, 15 min). Samples drawn at $T_D = 104$ (○), 112.5 (●), 121 (□), 129.5 (■) and 138 (△) °C and non-isothermally (▽). Broken curve for total recovery; $\lambda_{rev,f}$ ($\lambda_{ir,f}$) denote the reversible (irreversible) fraction of the draw ratio, and λ_{ext} is the highest draw ratio which can be theoretically reached with a polyethylene chain having a molecular weight of 197 000 according to equation (3). Hatched area represents the extent of scatter of the individual quantities

Figure 5 it can be seen that at high λ values $\lambda_{rev,f} \sim \lambda_{ext}$ holds within the scatter, which is evidence for high chain extension.

DISCUSSION

During gradual annealing two competitive processes must be considered, namely, entropic shrinkage of stretched macromolecules and reorganization of the heated crystalline phase[12]. Our previous findings[10] showed that the plastic deformation of polyethylene may proceed simultaneously via mechanical destruction of the lamellae[13,14] and by their melting and recrystallization[15,16]. Hence, the polymer may contain both oriented fragments of the original lamellae in microfibrils and shish-kebabs.

Effect of morphology on shrinkage

In our view, the slowing down of shrinkage in the range $T_A \sim 128$–129°C in the case of the solid-state-drawn polymer at lower draw ratios is a consequence of the thickening of the oriented lamellae[12] in the direction of orientation, acting against shrinkage. These lamellae are assumed to be predominantly the remnants of the original ones incorporated into microfibrils during necking since, irrespective of T_D, the T_A interval of the slowing-down effect remains unchanged. Dilatation of the samples before melting predominates over the completed process of shrinkage. Besides the rest of the original lamellae, there may also be folded-chain components of recrystallized shish-kebabs and cross-oriented lamellae transformed from fibrils during the annealing[17], the thickening of which contributes to the dilatation tendency.

In the melt-drawn polymer dilatation is due to the thickening of recrystallized lamellae only; residues of the original crystals can be excluded. Dilatation to negative S values at lower T_A indicates a considerable fraction of lamellar crystals present particularly in the polymer drawn at lower draw ratios[10].

Both in the solid-state drawn and melt-drawn polymer, the lamellar fraction decreases with increasing draw ratio[10], and its effect on shrinkage gradually disappears.

Heat stability of drawn polymer and the formation of a crystalline skeleton

The influence of the draw ratio on the heat stability of the polymeric structure is shown by the S *versus* λ dependences (*Figure 2*). At low draw ratios the oriented structure is not sufficiently fixed and shrinkage increases with λ. The existence of maxima suggests that at $\lambda \sim 5$–10 a certain crystalline skeleton may be formed, for which the completion of orientation of the crystalline phase is necessary as indicated by birefringence measurements[18]. Stability and continuity of the skeleton in the orientation axis, which increases with draw ratio, will then affect the heat stability of the polymer.

According to the individual structural models of drawn polyethylene, the skeleton components may be:

1. Microfibrils composed of crystalline fragments of the original lamellae[13].
2. Fibrillar cores of recrystallized shish-kebabs[15].
3. Protrusions of deformed crystalline blocks in the microfibrils[19] and intercrystalline axial bridges[20].
4. Lamellar components of shish-kebabs acting as interfibrillar links[10] fixing laterally fibrillar elements of the skeleton.

The assumption of the two-stage shrinkage process below and above 130°C reported by Capaccio and Ward[2] with highly drawn polyethylene (see Introduction) cannot hold at low draw ratios when shrinkage becomes pronounced at much lower T_A (curve 1 in *Figure 1*). The reinforcing crystalline skeleton has not been created yet and does not prevent shrinkage. In this case, relaxation of stretched tie molecules and slip of microfibrils is probably responsible for shrinkage[8].

If the skeleton has already been created, it begins to collapse at T_A close to 130°C by partial melting, and only then does shrinkage steeply increase being affected only by the possible dilatation effect. Hence, at high λ values only the melting of the skeleton releases retractive forces of the stretched molecules. The stability of the structure increases with λ more quickly if the polymer is drawn in the melt than in the solid state (cf. *Figure 3*).

The heat stability of the skeleton may be affected by the following factors:

1. The content and degree of orientation of the amorphous phase. The higher the amorphous fraction and the degree of stretching of amorphous chains, the higher the retractive forces, thus imposing stricter requirements on the quality of the skeleton.
2. Perfection of its individual components. Less perfect components melt at lower T_A and in the amorphous phase contribute to the increase in the retractive forces acting upon the remaining part of the skeleton.

The higher heat stability of the melt-drawn polymer is in agreement with these facts, because it shows a higher crystallinity and a lower degree of amorphous orientation[18].

The heat stability of the solid-state-drawn polymer does not depend on processing conditions; obviously the morphology does not markedly vary with T_D and σ_0 at a comparable λ. The S *versus* σ_0 decrease in the melt-drawn polymer is attributed to an improved stability of the structure due to the increased crystalline fraction[20] and to the reinforcing of the skeleton by fibrillar shish-kebab cores which possess considerable heat stability[21].

Reversibility of plastic deformation

The fast shrinkage experiments have proved high reversibility of plastic deformation. The low fraction of incomplete recovery at $\lambda > 20$ should be attributed to the irreversible, orientationally ineffective viscous flow, when chains may be disentangled from the network joints. Nevertheless, the effective draw ratio reaches the maximum for the macromolecule of the given molecular weight. After the material has passed through the heating zone, the orientation is fixed by fast recrystallization, and no or only small relaxation of stretched chains and their refolding take place.

During gradual annealing, there are several possible phenomena hampering shrinkage which may become operative:

1. Oriented amorphous chains and chains in less perfect, partly melted parts of the skeleton may relax from the entanglements and, thus, perturb network continuity.

This restricts the resulting shrinkage, as has already been predicted[4].

2. Thickening of lamellar crystals in the orientation axis accompanied by the axial slip of chains in them[22] may also contribute to perturbing the network continuity by loosening chains from entanglements.
3. At high stresses acting upon the polymer during drawing, cross cracks formed due to rupture of extremely stretched amorphous chains, as described elsewhere[10], may act as network perturbance sites.

The decrease in the $S_{\mathrm{rev,g}}$ values with increasing σ_0 at higher draw ratios (*Figure 4*) can be successfully explained using the mechanisms described in 1 and 3. At high stresses, high amorphous orientation obviously contributing to retractive forces[18] and increasing concentration of microcracks[10], were observed, both perturbing the molecular network. Mechanism 2 may explain why in the case of the melt-drawn polymer no total recovery takes place even at $\lambda < 5$–10. The shish-kebabs contain a considerable number of folded-chain crystals[10], the thickening of which has a negative effect on the recovery.

CONCLUSIONS

On gradual-annealing shrinkage experiments, competitive processes are operative: entropic shrinkage and dilatation of oriented lamellae due to their thickening. With increasing draw ratio the lamellar fraction decreases and dilatation disappears.

At $\lambda > 5$–10, a crystalline skeleton is formed in the polymer, which improves with increasing draw ratio. This also increases the resistance of the polymer to shrinkage.

Evidence has been given for the high orientational effectiveness of the zone-drawing technique with constant load with a high degree of recovery. The extension of chains at high λ values is comparable with theoretical estimates.

A lower degree of recovery via gradual annealing is probably due to the effects causing the partially perturbed continuity of the molecular network, which restricts the shrinkage process.

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