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Thermal expansion behaviour of hydrostatically extruded linear polyethylene

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The thermal expansion behaviour of a series of oriented linear polyethylenes has been measured over the temperature range − 180 to + 70° C. With increasing deformation ratio the axial thermal expansion coefficient approaches that of the crystal unit cell, and the transverse expansion coefficient approaches that of the average in the crystal *a*- and *b*-axis directions. The implications of these results are discussed in terms of present understanding of the structure of these materials.

1. Introduction

In a recent publication [1] it was shown that the observed correlation between the mechanical modulus of oriented linear polyethylene (LPE) and the longitudinal crystal thickness can be explained in terms of a model in which the lamellar stacks present at low draw ratios become increasingly linked by randomly spaced intercrystalline bridges as drawing proceeds. On this model, the modulus relates to the properties of crystalline material involved in linking at least two adjacent lamellae, and the X-ray measurements showed that even at comparatively low draw ratios there was a significant degree of crystal continuity in this sense.

The central role which this random bridge model now plays in our understanding of the structure and mechanical properties of LPE, provides an incentive to examine carefully other properties which would be strongly influenced by the degree of crystal continuity. Thermal expansion is clearly a suitable candidate. Therefore, we have examined the thermal expansion behaviour of a series of oriented LPE samples produced by hydrostatic extrusion. The results are of some direct technological importance, quite apart from the contribution which they make to our understanding of these remarkable materials.

2. Experimental

2.1. Sample preparation

Rods of Rigidex 50 LPE, 2.5 mm diameter, were produced at deformation ratios (λ) of 5, 10, 15 and 20 by hydrostatic extrusion at 100° C. Details of the extrusion procedure have been described elsewhere [2, 3]. The rods were taken from a batch of extruded samples which have been well characterized in previous publications [1, 3–5].

The "deformation ratio" in hydrostatic extrusion is equivalent to the "draw ratio" used to describe drawn samples and in general, the hydrostatically extruded rods have comparable properties to drawn samples [1, 3, 5]. The conclusions reached here should, therefore, be equally applicable to both types of product. The advantage of hydrostatic extrusion is that it can be used to produce rods of more substantial cross-section than can be obtained by drawing and this facilitates the measurement of some properties (such as transverse thermal expansion) which would be difficult with small diameter specimens.

2.2. Thermal expansion measurements

The thermal expansion measurements were made using a Perkin Elmer Thermo Mechanical Analyser (TMA). The scanning rate (both heating and cooling) was 10° C min^{-1}, the highest at which results were found to be independent of scanning rate. Data were recorded using the following thermal cycle: 0 to − 180, − 180 to + 70, and + 70 to 0° C. It was found convenient to tabulate the raw data at 10° C intervals for subsequent processing.

Primary calibration was achieved by measure-

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ments on a pure aluminium sample over the same scanning cycle. The correction for thermal expansion of the apparatus was quite small. The calibration was checked with slip gauges, and also by checking that measurements on an isotropic LPE sample agreed with the results of Buckley and McCrum [6].

The samples were in the form of 9 mm long cylinders machined from the extruded rod. At temperatures above 100° C it has been found that solid-state deformed LPE samples undergo irreversible dimension changes [7], and in the present investigation it was found that small changes take place at temperatures as low as 70° C. The aim of this work is to discuss the properties of unannealed samples so this temperature region was avoided. Short excursions up to 70° C were not found to have a measurable effect on the subsequent thermal behaviour. Thermal strain (referred to a datum of 0° C) may be defined as

$$e = \frac{l_T - l_0}{l_0}, \tag{1}$$

where l_T and l_0 refer to specimen dimensions at T and 0° C, respectively.

Since the rods possess fibre symmetry about the extrusion direction, the behaviour can be completely characterized by measuring the thermal strains $e_{\parallel}$ and $e_{\perp}$, parallel and perpendicular to this direction. Over a moderate temperature range (provided the overall thermal strain is not too large), the "volumetric" thermal strain is given by

$$e_{\mathrm{v}} = e_{\parallel} + 2e_{\perp}, \tag{2}$$

and the "average" linear thermal strain, $\bar{e}$, can be defined as

$$\bar{e} = \tfrac{1}{3}e_{\mathrm{v}} = \tfrac{1}{3}(e_{\parallel} + 2e_{\perp}). \tag{3}$$

We shall be interested in comparing the macroscopic dimensional changes with those observed for the crystalline unit cell of LPE [8], which is orthorhombic. The thermal strains for the unit cell will be designated e_a^{cr}, e_b^{cr} and e_c^{cr} for the respective crystallographic directions. An average value $\bar{e}^{\mathrm{cr}}$ is given by

$$\bar{e}^{\mathrm{cr}} = \tfrac{1}{3}(e_a^{\mathrm{cr}} + e_b^{\mathrm{cr}} + e_c^{\mathrm{cr}}) = \tfrac{1}{3}\bar{e}_{\mathrm{v}}^{\mathrm{cr}}. \tag{4}$$

Although the hydrostatically extruded samples show substantial c-axis orientation (at deformation ratios of 10 and above the c-axes can be considered to be perfectly aligned parallel to the deformation direction [9]), there is no preferred orientation of the a- and b-axis in the transverse direction. It will, therefore, be assumed that the crystalline phase is an aggregate of domains in which the a- and b-axes are randomly rotated about the c direction. Since the Young's moduli in the a and b directions are not vastly dissimilar [10], the effective transverse thermal strain of the crystalline phase can be assumed to be close to the average $(e_a^{\mathrm{cr}} + e_b^{\mathrm{cr}})/2$. The expansion coefficient is customarily defined as

$$\alpha = \frac{1}{l_T}\frac{\mathrm{d}l_T}{\mathrm{d}T}. \tag{5}$$

For polymers, α is usually a strong function of temperature (i.e. graphs of e versus temperature show pronounced curvature). It is possible to measure $e_{\parallel}$ and $e_{\perp}$ with reasonable accuracy, but the differentiation required to obtain the corresponding values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ results in some loss of precision. Therefore, it is preferable to present and discuss results in terms of e rather than α. However, in the temperature region − 50° C up to 0° C the curvature of e–T plots is not too great, so some average values of α in this region will be discussed.

The level of experimental error associated with the present measurements is approximately $\pm 0.4 \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$ in expansion coefficient, and it should be noted that the error in thermal strain measurement can be expected to increase with distance from the reference temperature (0° C).

3. Results and discussion

Fig. 1 shows $e_{\parallel}$, the thermal strain parallel to the extrusion direction, versus temperature. As observed by Mead and Porter for capillary extruded LPE [7], the expansion coefficient is negative. The curves of $e_{\parallel}$ approach a limiting envelope with increasing deformation ratio, but it should be pointed out that the overall values of thermal strain are quite small, the difference between the curves for extrusion ratio 5 and extrusion ratio 20 being only about twice the expected experimental error.

By contrast with the $e_{\parallel}$ results, the transverse expansion coefficient is positive and the values of $e_{\perp}$, shown in Fig. 2, are much larger, although the overall changes in $e_{\perp}$ in the range of extrusion ratios from 5 up to 20 are remarkably small. The plots of $e_{\parallel}$ and $e_{\perp}$ both show curvature, but neither set of curves shows the

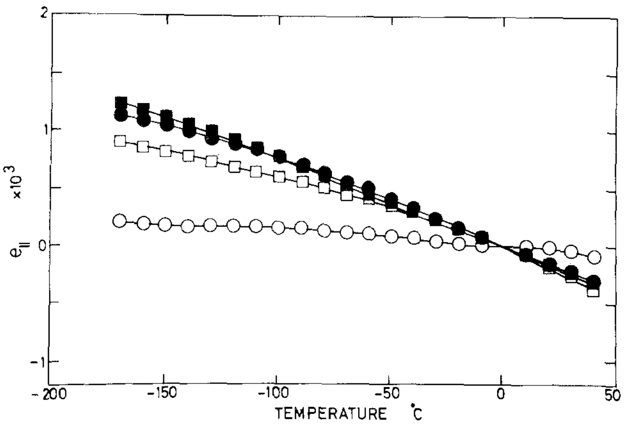

Figure 1 Thermal strain, $e_{\parallel}$, parallel to the extrusion direction versus temperature. ○ $\lambda = 5$, □ $\lambda = 10$, ● $\lambda = 15$, ■ $\lambda = 20$.

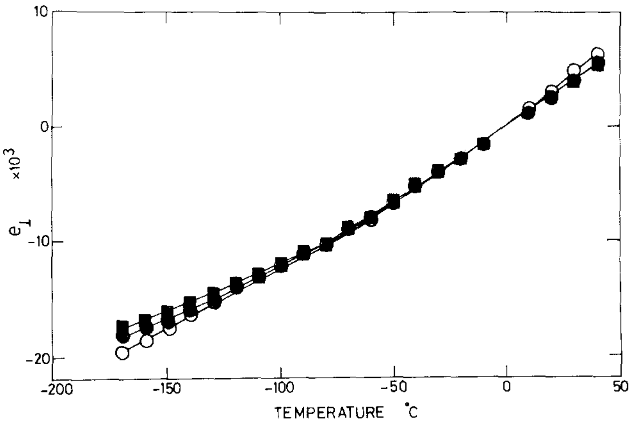

Figure 2 Transverse thermal strain, $e_{\perp}$, versus temperature. ○ $\lambda = 5$, ● $\lambda = 10$, ■ $\lambda = 20$.

inflection at −120° C which is observed in isotropic and single-crystal texture samples [6], and which has been attributed to the glass transition of the amorphous phase.

In Fig. 3, $e_{\parallel}$ and $e_{\perp}$ for the sample at extrusion ratio 20 are compared with thermal strain values for the crystalline unit cell, the latter being calculated* from the X-ray data of Davis *et al.* [8]. The values of $e_{\parallel}$ are quite close to those of e_c^{cr} for the unit cell c direction, the difference being of the same order as the experimental error. This result supports the idea proposed previously that the intercrystalline bridges produce a structure in which the crystalline phase can be regarded as continuous in the c direction.

The experimental points for $e_{\perp}$ lie between the crystal values e_a^{cr} and e_b^{cr}, and can be seen to fit the average crystal values $(e_a^{\text{cr}} + e_b^{\text{cr}})/2$ very closely indeed. At first sight this would appear to imply that the crystalline phase is continuous in the transverse as well as the axial direction. It should, however, be borne in mind that the lamellar crystallites must be present in domains of coherent a- and b-axis orientation. The lateral size of these regions, estimated from the integral breadth of the (1 0 0) and (1 1 0) X-ray reflections [4] is about 10 nm. Since the crystallinity is of the order of 75% (from density) it would be possible to account for the whole of the amorphous phase in terms of a layer about 0.8 nm thick separating crystallites in the transverse direction. This grain boundary-like material would be expected to possess completely different thermal and mechanical properties from conventional "amorphous" polyethylene.

Fig. 4 shows the variation of the thermal expansion coefficients $\alpha_{\parallel}$ and $\alpha_{\perp}$ with deformation ratio.

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*In the expression given by Davis *et al.* [8] for the unit cell parameters as a function of temperature, the a and b parameters depend slightly on long period. We assume a long period of 20 nm, but this is not critical to our conclusions.

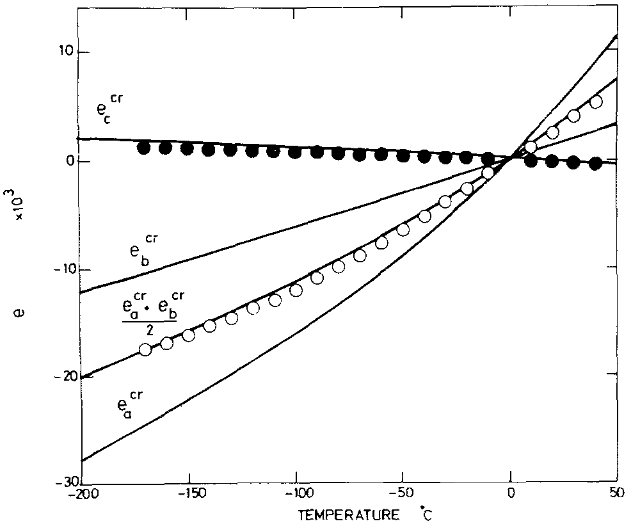

Figure 3 Comparison of parallel and transverse thermal strains (● $e_{\|}$ and ○ $e_{\perp}$) for $\lambda = 20$ sample with values for the crystalline unit cell (calculated from Davis *et al.* [8]) as a function of temperature.

These expansion coefficients are average values for the region −50 to 0° C, where the curvature of the thermal strain plots is relatively small.

As could be anticipated from the structural measurements, which suggest that there is a high degree of crystal continuity at high deformation ratios, $\alpha_{\|}$ and $\alpha_{\perp}$ approach steady values with increasing deformation ratio. It is somewhat surprising that this occurs at comparatively low deformation ratios ($\lambda \sim 10$ to 15). For quite a small proportion of intercrystalline bridge material there appears to be effective crystal continuity as far as the thermal expansion behaviour is concerned. In fact we can conclude that the anisotropy of thermal expansion closely follows the level of crystalline orientation and as soon as this reaches a high value (at around $\lambda = 5$ to 10), and the average longitudinal crystal thickness exceeds the long period [1], the axial thermal expansion reaches that of the crystal unit cell.

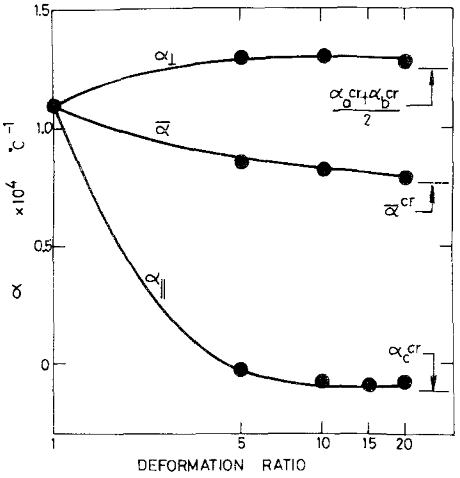

Figure 4 Linear expansion coefficients $\alpha_{\|}$, $\alpha_{\perp}$ and $\bar{\alpha}$ versus deformation ratio. Values of α_c^{cr}, $(\alpha_a^{\mathrm{cr}} + \alpha_b^{\mathrm{cr}})/2$ and $\bar{\alpha}^{\mathrm{cr}}$ for the crystalline unit cell (calculated from Davis *et al.* [8]) have been added for comparison. All values are average values over the temperature interval −50 to 0° C.

Values of the average expansion coefficient, $\bar{\alpha}$, where

$$\bar{\alpha} = \tfrac{1}{3}\alpha_{\|} + \tfrac{2}{3}\alpha_{\perp},$$

have been calculated in Fig. 4 and it can be seen that $\bar{\alpha}$ falls with increasing deformation ratio from the isotropic value, to approach the crystalline $\bar{\alpha}^{\mathrm{cr}}$ value at high deformation ratios, where

$$\bar{\alpha}^{\mathrm{cr}} = \tfrac{1}{3}(\alpha_a^{\mathrm{cr}} + \alpha_b^{\mathrm{cr}} + \alpha_c^{\mathrm{cr}}). \qquad (6)$$

This is quite surprising, considering that the crystallinity changes very little with changing deformation ratio, and is in contrast to the behaviour of single-crystal texture samples where Buckley and McCrum [6] found that the average thermal strain was always close to the linear thermal strain in an isotropic sample of similar crystallinity.

In the case of isotropic samples the crystalline phase can be regarded as being embedded in a matrix of amorphous material. Above T_g, the amorphous phase can deform to accommodate differential thermal strains, so the overall thermal strain follows the rule of mixtures, the expansion coefficients of the crystalline and amorphous phases being about 0.8×10^{-4} and 2×10^{-4} °C^{-1}, respectively, in the temperature region −50 to 0° C.

The fact that $\bar{\alpha}$ in hydrostatically extruded samples is less than the "rule of mixtures" value and approaches $\bar{\alpha}^{cr}$ implies one of two possibilities. Either (i) The amorphous phase is surrounded and constrained by the crystalline phase, and has a low enough bulk modulus to allow the overall strain to equal that in the crystalline phase, or (ii) the amorphous phase has a value of α which is different from that in the isotropic state and which is close to $\bar{\alpha}^{cr}$.

In fact, there are arguments to support both these possibilities. In the first place, at high draw ratios the degree of crystal continuity estimated from the X-ray diffraction data suggests that it is equally valid to regard the structure either as a series of lamellar stacks with a large number of randomly placed intercrystalline bridges or as a paracrystal with a periodic distribution of small disordered regions. This supports (i) above.

Both (i) and (ii) imply that the amorphous phase must be radically different from that present in isotropic samples, but (i) is more in keeping with the fact that $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are so close to the crystalline values. Furthermore, it is reasonable to expect the amorphous phase in ultra-oriented samples to display unusual properties. NMR [9] and bi-refringence [5] measurements both suggest that the disordered material is fairly highly oriented in such samples. Indeed, when taut-tie molecules and random crystalline bridges are both present, the demarcation between the two entities may well be quite broad: single-tie molecules will behave as oriented amorphous material, bundles of 10 or 20 closely packed chains will behave as crystalline bridges, but bundles of only a few chains can be expected to display intermediate behaviour. Such a blurred distinction between crystalline and oriented amorphous material could well account for the discrepancies observed in "crystallinity" values deduced from NMR, density, and X-ray crystal strain measurements.

4. Conclusions

The changes produced in the thermal expansion behaviour of Rigidex 50 LPE as a result of solid state extrusion to high deformation ratios are as follows:

(1) The axial thermal strain approaches that of the crystal unit cell in the c direction. This is in keeping with a highly oriented lamellar texture where crystallites are linked in the c direction by crystalline bridges.

(2) The transverse thermal strain approaches the average of the crystal a- and b-axis thermal strains. This suggests that the lamellar crystals constitute regions of coherent a- and b-axis orientation which are separated laterally by thin grain boundary-like layers of disordered material.

(3) As a result of (1) and (2) the average (or volume) thermal expansion deviates from the "rule of mixtures" expression and approaches that of the crystalline unit cell. This is consistent with the view that at high degrees of crystal continuity the oriented structure can equally be regarded as a paracrystal, where the regions of disorder ("the amorphous regions") are embedded in the crystalline phase. It seems likely that the amorphous phase then has different characteristics from that in the isotropic case, because it is surrounded and constrained by the crystalline phase.

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