JOURNAL OF MATERIALS SCIENCE 6 (1971) 1447–1464

Mechanical and Structural Studies of Low Density Polyethylene

Part 2 *Tensile Creep Behaviour of Uniaxially Oriented Material*

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This paper is one of a series concerned with the complete characterisation of the creep behaviour of oriented polymers, the correlation of creep behaviour with other mechanical properties and the interpretation of such data in the light of present structural knowledge. Sheets of oriented low-density polyethylene were prepared from initially isotropic sheets by cold-drawing, cold-drawing followed by heat-treatment at 55°C, drawing at a temperature of 55°C and hot-drawing at temperatures in the range 90 to 100°C. At each draw ratio, specimens were cut at angles of 0°, 45° and 90° to the draw direction. For each specimen, the variation of longitudinal and lateral strain with time, during uniaxial tensile creep at 20°C, was measured simultaneously by direct extensometer methods, for a wide range of applied stresses. All the materials exhibited complex anisotropic non-linear viscoelastic behaviour. The methods of presenting such data are discussed and the results are presented in some detail. Many similarities in the creep behaviour of the cold- and hot-drawn materials are noted. However, marked differences are apparent in the non-linearity and creep rate of the 45° specimens from these two materials at high draw ratio. These, and other effects found at high draw ratio, are discussed with reference to the structural studies reported in part 1. At low draw ratio, it is shown that the anomalous behaviour of the modulus in the draw direction, reported previously for cold-drawn material, may also be found in the hot-drawn material, although at a different creep time. On the basis of obvious differences in wide-angle X-ray patterns other workers had previously predicted that the anomalous mechanical behaviour of cold-drawn LDPE was probably unique. The anomalous behaviour of the hot-drawn material is also explained in terms of the structures discussed in part 1.†

1. Introduction

A detailed study of the mechanical anisotropy of cold-drawn low density polyethylene (LDPE), carried out by Raumann and Saunders [1], yielded several features of considerable interest. These were:

(i) an anomalous decrease, at low draw ratios, in the tensile moduli at 0° and 90° to the draw direction (referred to below as E_0 and E_{90}) such that $E_0 < E_{90} \simeq E_{45}$, and

(ii) a change of anisotropy at high draw ratios to give $E_0 > E_{90} \gg E_{45}$. Both aspects appeared unique to LDPE [2].

In order to extend this work to study the time and strain dependence of the five pseudo-elastic compliance "constants" necessary to fully describe the creep behaviour of this transversely isotropic material, sensitive tensile creep apparatus was developed which permitted simultaneous measurement of lateral and longitudinal strain [3]. An initial study on high draw ratio, cold-drawn LDPE showed that, in addition to their help in the determination of compliance "constants", the lateral strain measurements provided useful additional evidence for identifying deformation mechanisms suggested by the

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†*J. Mater. Sci.* 6 (1971) 572.

tensile strain data. Thus this study confirmed that the very low value of E_{45} at high draw ratio could be attributed to an easy shear mechanism parallel to the oriented chains for a wide range of tensile strains [4, 5].

The creep apparatus was then used to study cold-drawn LDPE over a wide range of draw ratios from 1.0 (isotropic) to 4.2 [6, 7]. The inclusion of torsional creep studies enabled the five compliance "constants" to be obtained by direct measurement and tabulated for the entire range of draw ratios. In addition, the variation of the "constants" with time and strain was studied in detail and several interesting trends found. These included a large anisotropy of creep rate at low draw ratio and a systematic variation of non-linear behaviour with angle and draw ratio for tensile strains as low as 0.1%.

Wide-angle X-ray diffraction studies have shown that, at low draw ratios, the *c*-axes of the crystals do not gradually align in the draw direction with increasing draw ratio, but tend to a cone distribution about the draw direction, the cone angle then decreasing as the draw ratio increases (see part 1). Gupta *et al* [8, 9] proposed that the cone distribution of *c*-axes was intimately connected with the mechanical deformation, for when a stress is applied in the draw direction there is a high resolved shear component along the chain direction, so "easy-shear" can occur. The shear component rapidly diminishes as the angle between the draw direction and test direction increases, leading to the observed anisotropy of modulus. The large anisotropy of creep rate mentioned above [6, 7] was also in agreement with this proposal. Gupta *et al* [8] also examined the wide-angle X-ray diffraction patterns for LDPE drawn at 105°C. At this temperature they considered that drawing proceeded with a continual reorientation of the *c*-poles toward the draw direction. They concluded that the anomalous pattern of mechanical anisotropy shown by cold-drawn LDPE at low draw ratios was probably unique. No measurement of mechanical properties was reported for the hot-drawn LDPE, so this was a pertinent area for an extension of the creep studies.

Considerable additional interest in hot-drawn LDPE was provided by some preliminary studies in this laboratory on LDPE drawn at 90°C[10]. It was found that, at high draw ratio, E_0 (hot-drawn) was considerably lower than E_0 (cold-drawn) with much smaller differences in E_{45} and E_{90}, while E_{45} for the hot-drawn LDPE showed a large increase in creep rate and degree of non-linearity when compared with the cold-drawn LDPE.

The main aim of the present work was, therefore, to examine the creep behaviour of hot-drawn LDPE in detail, for a wide range of draw ratios, and attempt to correlate it with the structural differences resulting from hot- and cold-drawing. The creep behaviour may also be correlated with dynamic mechanical measurements, made over a wide temperature range, and structural studies on high draw ratio, cold-drawn LDPE, as prepared and after annealing at 105°C [11].

As more than one structural factor is altered simultaneously by hot-drawing, we have also studied the creep behaviour of highly drawn LDPE after various treatments at 55°C. Other workers have shown that, at this temperature, there should be a significant relaxation of the amorphous regions (compared to the highly strained state in cold-drawn material) with little effect on the crystalline regions [12, 13].

Full details of the structural studies on all the materials discussed here are given in part 1. For convenience, a summary of the relevant conclusions is given in section 4.

Because of a slight difference in the method of preparation of the isotropic sheets used here we have made a few repeat measurements on cold-drawn LDPE prepared from the new isotropic sheets for comparison with our creep data on the hot-drawn LDPE. Although not the main concern of this paper, the close similarity of the non-linear behaviour between the cold-drawn LDPE (as reported in detail elsewhere [7] and the few measurements reported here) and the hot-drawn LDPE is indicated in some detail. This behaviour is discussed elsewhere [7], but is particularly relevant as other workers have claimed that cold-drawn LDPE is linear below tensile strains of approximately 0.8% [14].

It will be apparent that the data reported here allows the compliance "constants" of the anisotropic materials to be tabulated for a wide range of draw ratios and preparation methods. However, such tables are not particularly helpful to the discussion and are therefore omitted from this paper. Full details of such a presentation and the manipulation of the data within the framework of elasticity theory may be found elsewhere [7].

2. Experimental

2.1. Sample Preparation

Isotropic sheets of LDPE (ICI Alkathene, grade WJG 11) were prepared from granules by compression moulding at 160°C, followed by quenching in water at room temperature. The resulting sheets were approximately 0.18 cm thick and isotropy was confirmed by optical and X-ray analysis.

Samples up to 25 × 8 cm were cut from the pressed sheets and ruled with a 1 cm square grid. Some of these samples were then drawn at room temperature (cold-drawn) at an extension rate of 6 cm/min. The remainder were drawn at the same extension rate in an air oven with the temperature controlled to within ± 2°C, in the range 90 to 100°C (hot-drawn). On completion of drawing, the oven door was opened and sheets left to cool to room temperature at constant length. On release from the drawing machine all the drawn sheets retracted to some extent. In order to obtain relatively stable materials all sheets were allowed to relax freely at room temperature for at least three weeks [1]. The draw ratio for each stabilised sheet was then determined from the measured grid dimensions. X-ray analysis confirmed that the drawn sheets were transversely isotropic over the range of draw ratios investigated (1.2 to 4.2.)

The effect of the thermal cycles occurring during hot-drawing, on the quenched isotropic material was investigated by subjecting isotropic sheets to the same thermal cycles while suspended freely in the oven. The resulting material will be referred to as the annealed isotropic material.

Further sets of drawn sheets were produced by each of the following schedules, involving thermal treatments at 55°C and resulting in final draw ratios of about 3.0 or 3.5:

(i) 55°C annealed – a sheet that had previously been cold-drawn to high draw ratio was held at constant length in an air oven at a temperature of 55°C for 30 min.

(ii) 55°C relaxed – sheets that had been cold-drawn to draw ratios of 3.4 and 4.0 were allowed to relax freely in an air oven at a temperature of 55°C for 30 min. This gave stable final draw ratios of 3.0 and 3.55 respectively.

(iii) 55°C drawn – a quenched isotropic sheet was drawn in the oven with an air temperature of 55°C and held at constant length until cool.

2.2. Tensile Creep Measurements

For the creep studies, dumbell-shaped specimens 3.8 cm long were cut from the drawn sheets (using a micro-tensile specimen cutter ASTM type D.1708-59T) with their long axes at 0°, 45° and 90° to the draw direction. Specimens were also cut from the isotropic sheets using the same cutter.

The apparatus developed for the measurement of creep of small specimens has been described in detail elsewhere [3] and also discussed in connection with other recent creep studies [5, 7]. It allows simultaneous measurement of the lateral strain in the thickness direction and the longitudinal strain during tensile creep. The tensile extensometer works on a gauge length of 1.2 cm and the lateral extensometer monitors thickness changes within this gauge length. The loads applied to the specimen by the extensometer are negligible. The sensitive element in each extensometer is a linear-displacement, differential capacitor transducer (Rank Taylor Hobson) which, with its associated electronics, has a sensitivity of better than 2×10^{-5} cm. Examples of the reproducibility of the system for tensile strains from 0.1 to 3.0% are given in section 3.1.1 The apparatus is situated in a controlled atmosphere laboratory and all the creep measurements were made at a temperature of 20.2 ± 0.7°C and relative humidity of (50 ± 5)%.

Two types of experiment were carried out on the creep apparatus, namely isochronous and time-dependent.

The first consisted of subjecting each specimen to a series of successively increasing loads in the manner described elsewhere for producing 100 sec isochronous stress-strain curves [15]. This procedure allows for relaxation of the specimen under zero load, between each test, for a time equal to or greater than four times the creep time. (At the lower creep loads complete strain recovery is normally achieved during each relaxation cycle.) The longitudinal and lateral strains were monitored from 5 to 115 sec, the strain values at a creep time of 100 sec being used when calculating the isochronous data. The creep loads were chosen to give tensile creep strains in the range 0.1 to 4.0%. The applied tensile creep stress was calculated using the original area of cross section in all cases and is thus the "nominal stress".

Some time after completion of the isochronous experiments a set of long term creep experiments were performed; the tensile and lateral strains being monitored from 5 to 1000 sec after application of the load. As the materials under investigation exhibit not only anisotropy of modulus but also anisotropy of non-linearity (exemplified by the dependence of modulus on stress or strain), there is no unique way of comparing the creep curves at different angles and draw ratios. A comparison at small tensile strains (where the materials are pseudo-linear) theoretically reduces these difficulties to a negligible level, but involves unacceptable errors in the creep curve shapes with the present accuracy of strain measurement (especially for the lateral strains). Other work on cold-drawn LDPE in this laboratory [7] has compared the creep curve shapes over 1000 sec, for a given angle and draw ratio, obtained with loads which gave 100 sec tensile strains of 0.5 and 1.0%. For a wide range of non-linear and time-dependent behaviour the *shapes* of the two creep curves were found to be very similar. In the present work the creep load was therefore chosen to give a tensile strain at 100 sec of approximately 1.0% to enable the creep curves in a uniform strain range to be compared. Owing to the anisotropy of modulus encountered in these studies it follows that the applied stress varies widely between individual curves. The appropriate tensile stress for each specimen was determined from the 100 sec data obtained during the isochronous series of experiments.

An alternative procedure would be to compare creep curves obtained at a single value of tensile stress. However, at the higher draw ratios, this would result in some creep tests being carried out with tensile strains of $< 0.2\%$ in order that some of the other specimens were not tested in the highly non-linear region ($> 2\%$ tensile strain). This would result in poor accuracy for some of the creep curves, whereas the uniform strain approach allows a controlled and uniform accuracy to be achieved. Furthermore, if correlation of creep behaviour with deformation mechanism is sought, it may be desirable to compare the polymer response when the different mechanisms produce equal strains.

2.3. Structural Studies

Wide- and low-angle X-ray techniques were used to investigate the structural changes resulting from the various drawing procedures. Full details are given in part 1. A summary of the major conclusions from this work is given in section 4.

The birefringence of the drawn materials was also measured at room temperature, using a Berek compensator. The specimens for these measurements were, however, prepared from very thin isotropic sheets as large phase differences and excessive scattering of the light on passing through the relatively thick creep specimens made them difficult to examine optically.

3. Results

The results from the tensile creep experiments only are described in this section. For convenience, the main results and conclusions from the X-ray and birefringence studies are summarised in section 4.

For the materials under investigation, the variation of creep compliance with time depends on the applied stress; this non-linear behaviour itself depending on the direction in the sheet at which the specimen is cut. The method of presentation used below has been chosen to emphasise the main trends in the data.

3.1. 100 Second Isochronous Behaviour

In this section the variations of creep behaviour with time are ignored by taking all measurements of strain 100 sec after application of the tensile creep stress to the specimen. The data described were obtained using the isochronous procedure described in section 2.2. The 100 sec tensile creep modulus, E_θ, is defined as the (nominal) tensile creep stress divided by the tensile strain at 100 sec, for a specimen cut at an angle, θ, to the draw direction. The 100 sec lateral compliance, $S_{t\theta}$, is defined as the lateral strain (perpendicular to the plane of the sheet, i.e. the thickness direction) at 100 sec divided by the (nominal) tensile creep stress. The 100 sec thickness contraction ratio, $\nu_{t\theta}$, is defined as the ratio of the lateral strain (in the thickness direction) to the longitudinal strain, both being measured 100 sec after application of the tensile creep stress.

3.1.1. *Isotropic Material*

The variations of 100 sec tensile creep modulus, lateral compliance and thickness contraction ratio with the 100 sec tensile strain, for four specimens of quenched isotropic LDPE, are shown in figs. 1, 2 and 3 respectively. It is apparent that, even at tensile strains as low as 0.1% the material exhibits non-linear behaviour (i.e. strain dependence of modulus and compliance). On each graph a $\pm 2\%$ error bar is plotted at 1% tensile strain to illustrate the degree of reproducibility achieved.

Fig. 4 shows that, within experimental accu-

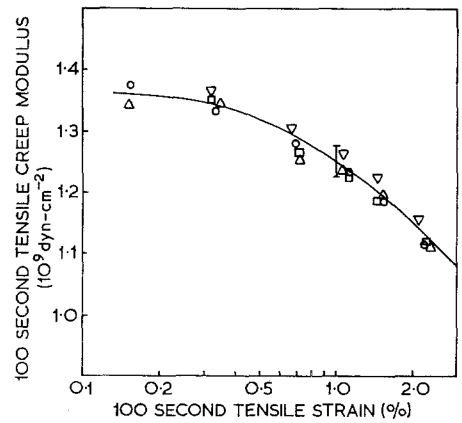

Figure 1 Variation of 100 sec tensile creep modulus with 100 sec tensile strain for four specimens of quenched isotropic LDPE (± 2% error bar at 1% tensile strain).

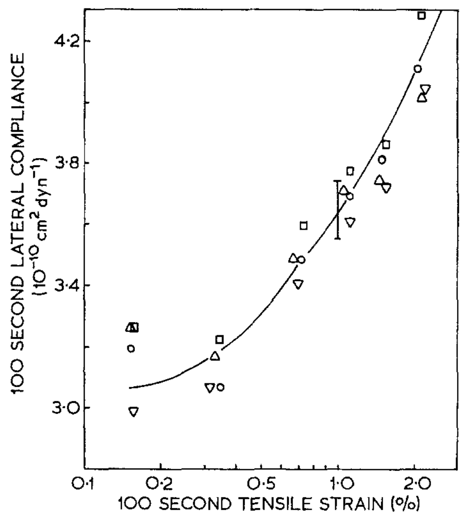

Figure 2 Variation of 100 sec lateral compliance with 100 sec tensile strain for four specimens of quenched isotropic LDPE (± 2% error bar at 1%) tensile strain).

racy, the 100 sec tensile creep modulus of the quenched LDPE is not altered by annealing treatment. In addition, equal non-linearity

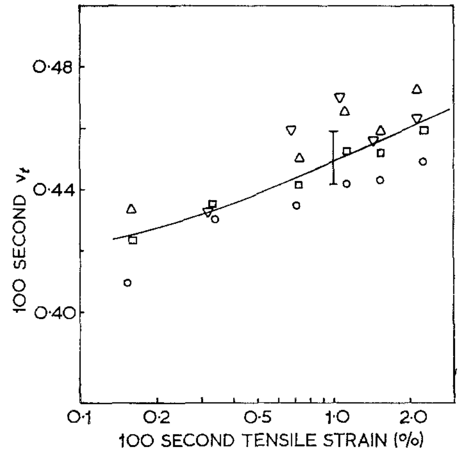

Figure 3 Variation of 100 sec thickness contraction ratio, ν_t, with 100 sec tensile strain for four specimens of quenched isotropic LDPE (± 2% error bar at 1% tensile strain).

(shown by 0.3 and 1% strain data) is retained throughout the temperature range. The 100 sec lateral compliance and thickness contraction ratio of the quenched LDPE show small increases with annealing temperature. Data for all three parameters for the quenched isotropic LDPE is summarised in table I.

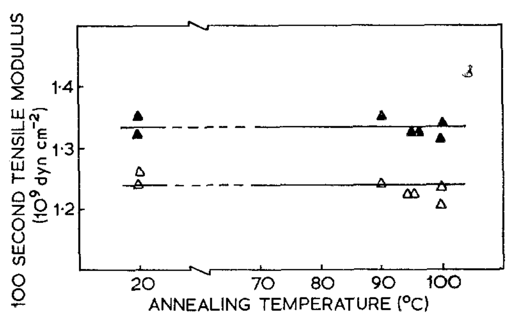

Figure 4 Effect of annealing on the 100 sec tensile creep modulus of quenched isotropic LDPE. ▲ = 100 sec tensile strain of 0.3%. △ = 100 sec tensile strain of 1.0%.

TABLE I Variation of mechanical properties with thermal treatment for quenched isotropic LDPE (100 sec creep data)

	Tensile strain (%)	Annealing Temperature 20°C	90°C	100°C
Tensile modulus (10^9 dyn cm^{-2})	0.3	1.38	1.36	1.35
	1.0	1.25	1.24	1.23
Lateral compliance (10^{-10} cm^2 dyn^{-1})	0.3	3.22	3.42	3.45
	1.0	3.65	3.86	3.85
Thickness contraction ratio	0.3	0.43	0.45	0.45
	1.0	0.45	0.47	0.47

3.1.2. Cold-drawn Material

For cold-drawn (and hot-drawn) LDPE the 100 sec tensile creep modulus and lateral compliance exhibit variations with the 100 sec tensile strain that depend on the angle, θ. Thus, there is anisotropy of non-linear behaviour in addition to the expected anisotropy of modulus and lateral compliance themselves. Typical variations at three draw ratios for tensile modulus and lateral compliance are shown in figs. 5 and 6 respectively. From fig. 5 it is apparent that, for modulus, the order of increasing linearity is $90° < 45° < 0°$ at all three draw ratios, with the non-linear behaviour of the isotropic material intermediate between that for the 90° and 45° specimens. There is also very little change in non-linear behaviour with draw ratio, for each angle, although the non-linear response of the 45° specimens does decrease slightly with increasing draw ratio, becoming similar to that for the 0° material at the highest draw ratio. The lateral compliance data in fig. 6 shows similar trends with angle. The 45° and 90° specimens appear to show a greater reduction in non-linear behaviour as the draw ratio increases, but it must be emphasised that, at least for the 45° specimen, the lateral strains are very small at high draw ratio, so leading to large possible errors in the variation with tensile strain.

3.1.3. Hot-drawn Material

As with the cold-drawn polymer, drawing at a temperature of 90 to 100°C causes anisotropy of the compliances and of their non-linearity. The non-linearity of the 100 sec tensile creep modulus

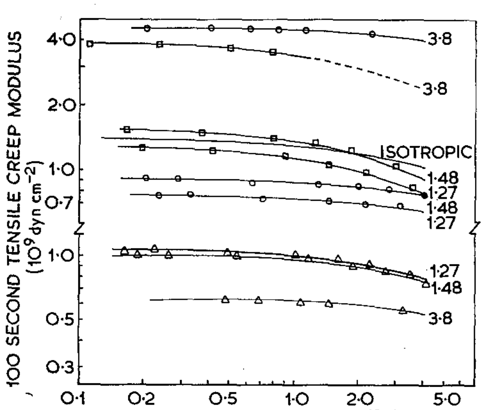

Figure 5 100 sec isochronous modulus-strain data for cold-drawn LDPE of various draw ratios. ○ = 0° specimens. △ = 45° specimens. □ = 90° specimens.

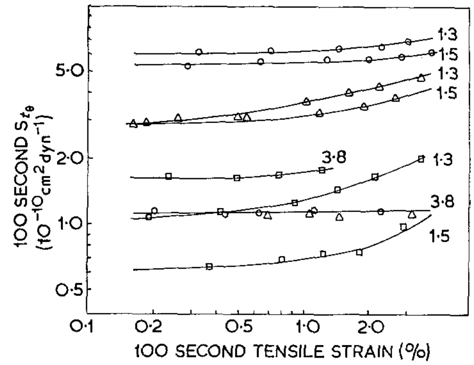

Figure 6 100 sec lateral compliance (S_{t_θ}) – tensile strain data for cold-drawn LDPE of various draw ratios. (Symbols as for fig. 5).

as a function of angle and draw ratio is shown in fig. 7. As for the cold-drawn material, the non-linearity of the 0° and 90° specimens remains fairly constant over the range of draw ratios. However, the 45° specimens become more non-linear as draw ratio increases. Thus for the hot-drawn material the order of increasing linearity of modulus changes from $45° \simeq 90° \simeq 0°$ at low draw ratio to $45° < 90° < 0°$ at high draw ratio.

The strain dependence of the lateral compliances is illustrated in fig. 8. Again the non-linearity of the 0° and 90° specimens remains fairly constant over the range of draw ratios. However, the lateral compliance at 45° is highly non-linear at low draw ratio and linear at high draw ratio which is the direct opposite of the trend shown by the 45° modulus data (fig. 7). Thus for the hot-drawn material the order of increasing linearity of later compliance changes from $45° < 90° \simeq 0°$ at low draw ratio to $90° \simeq 0° < 45°$ at high draw ratio.

3.1.4. Comparisons Between the Non-linear Behaviour of Cold- and Hot-drawn Material

The general trends in the modulus and lateral compliance behaviour of the 0° and 90° specimens are very similar for the cold- and hot-drawn materials. An interesting feature in the modulus data is the reasonably linear behaviour at 0° compared with the highly non-linear behaviour at 90° (with the behaviour of the isotropic material lying between these two extremes).

At low draw ratio the general trends in the modulus and lateral compliance of the 45°

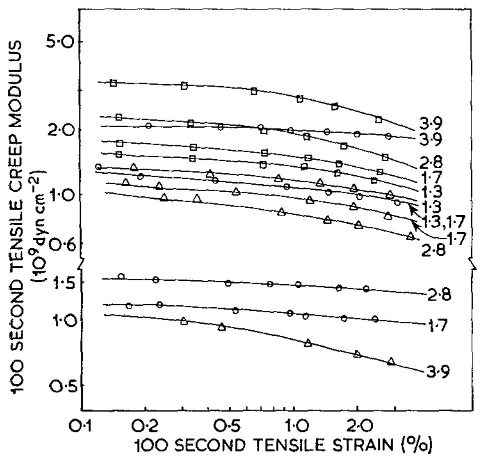

Figure 7 100 sec isochronous modulus – strain data for hot-drawn LDPE of various draw ratios. (Symbols as for fig. 5).

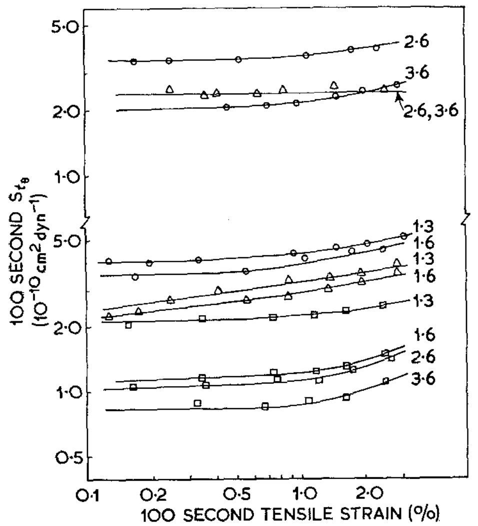

Figure 8 100 sec isochronous lateral compliance ($S_{t\theta}$) – tensile strain data for hot-drawn LDPE of various draw ratios (Symbols as for fig. 5).

specimens for the cold-drawn and hot-drawn materials are also very similar. However, at high draw ratio an unexpected difference is encountered. Thus whilst the lateral compliance is reasonably linear in both materials, the modulus is reasonably linear in the cold-drawn material but highly non-linear in the hot-drawn material (Compare figs. 6 and 8, 5 and 7 respectively).

It must be emphasised that the patterns of non-linear behaviour given above apply when the variations of a parameter with tensile strain are considered. If the variations of a parameter with tensile stress are considered the trends will be different due to the anisotropy of the tensile modulus itself [6]. However, this will not affect the comparison between the two 45° specimens since their moduli are very similar.

3.1.5. Variation of Parameters at 0.3% Tensile Strain with Draw Ratio

The isochronous data presented above may be used to determine the values of the various parameters at a 100 sec tensile strain of exactly 0.3%. The variations of the 100 sec tensile creep moduli, lateral compliances and creep contraction ratios, determined in this manner, for both cold- and hot-drawn LDPE are shown in figs. 9, 10 and 11 respectively. The few results on the cold-drawn material reported here show all the major features reported in other more detailed studies [1, 7].

Comparison of the modulus behaviour in figs. 9a and b yields three major differences: the minimum in E_0 at low draw ratio is far less pronounced in the hot-drawn material; above a draw ratio of 1.5, E_0 for the cold-drawn material rises rapidly with increasing draw ratio and becomes greater than E_{90} at high draw ratios, whereas in the hot drawn material E_0 only rises slowly with increasing draw ratio and is always less than E_{90}; the minimum in E_{90} at low draw ratios for the cold-drawn material is absent in the hot-drawn material.

Comparison of the lateral compliance curves in figs. 10a and b shows that the peak in S_{t0} at low draw ratio in the cold-drawn material is far less pronounced in the hot-drawn material and that above a draw ratio of 1.5, S_{t0} decreases with increasing draw ratio at a slower rate in the hot drawn material (corresponding very closely to the changes in E_0). It is also apparent that as draw ratio increases, S_{t45} for the cold-drawn material falls steadily to a value of approximately 10^{-10} cm^2 dyne^{-1} whilst S_{t45} for the hot-drawn material falls quickly to a value of 2.4×10^{-10} cm^2 dyne^{-1} at a draw ratio of 1.7 and then remains constant. The behaviour of S_{t90} is, however, broadly similar for the hot- and cold-drawn materials.

The combined effects of the variations of E and S_t with draw ratio are reflected in the creep contraction ratio data of fig. 11. Note that although $S_{t\theta}$ at high draw ratio is very low at all angles, $\nu_{t\theta}$ is only very low at 45°.

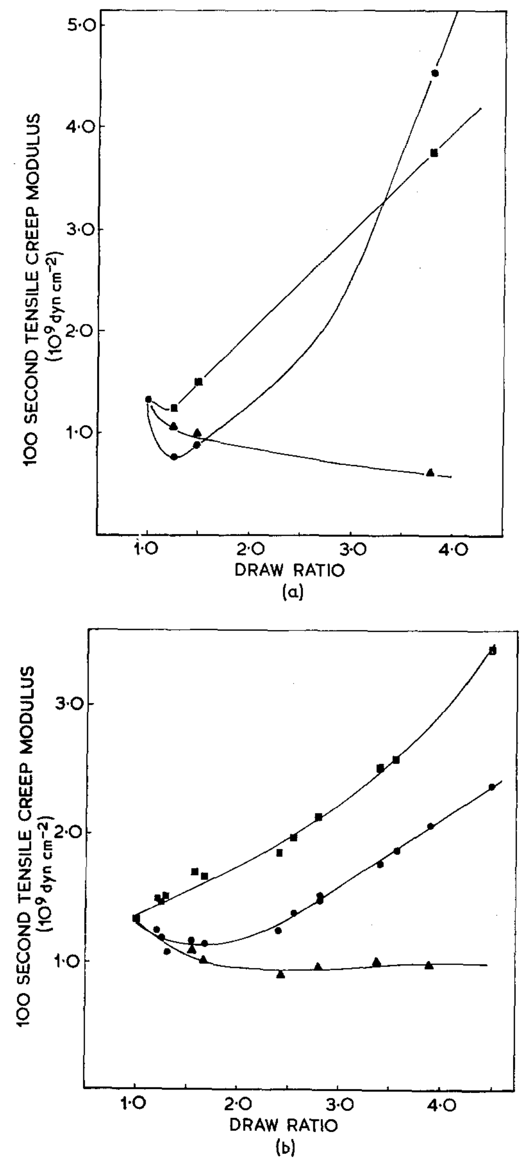

Figure 9 Variation of 100 sec tensile creep modulus with draw ratio for (a) cold-drawn LDPE and (b) hot-drawn LDPE. (100 sec tensile strains of 0.3%). ● = 0° specimens ▲ = 45° specimens. ■ = 90° specimens.

3.1.6. Behaviour of Materials given Thermal Treatments at 55° C

Data on tensile modulus and lateral compliance for 100 sec tensile strains of 0.3% are presented in tables II and III respectively. (The results are independent of the annealing time (see [12].) Values for the cold-drawn and hot-drawn (95°C) materials at the same draw ratios are included in each table to facilitate comparisons.

The thermal treatments at 55°C resulted principally in a marked change in the anisotropy of tensile modulus (at a draw ratio of 3.5) from that of the cold-drawn polymer ($E_{45} < E_{90} < E_0$) to that of the hot-drawn polymer ($E_{45} < E_0 < E_{90}$) and this is seen to be due especially to a large decrease in E_0. E_{45} for the 55°C material remained equal to the cold-drawn value. The modulus variations would appear to be representative of the "intensity" of the thermal treatment since the moduli for the 55°C materials lie between those of the cold- and hot-drawn polymer. Although the differences are, in some cases, of the order of the experimental error, there appears to be a trend towards decreased moduli in the order annealing, relaxing and

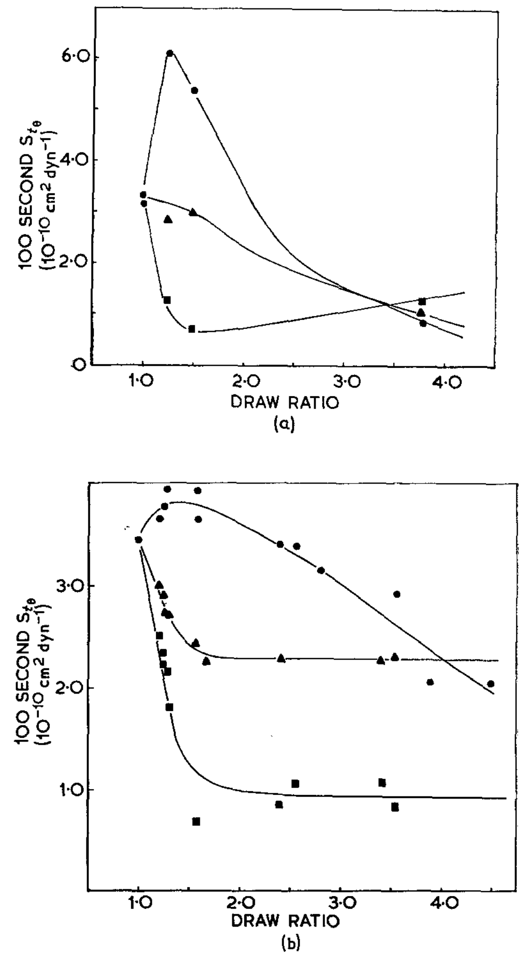

Figure 10 Variation of 100 sec lateral compliance (St_θ) with draw ratio for (a) cold-drawn LDPE and (b) hot-drawn LDPE. (100 sec tensile strains of 0.3%. Symbols as for fig. 9).

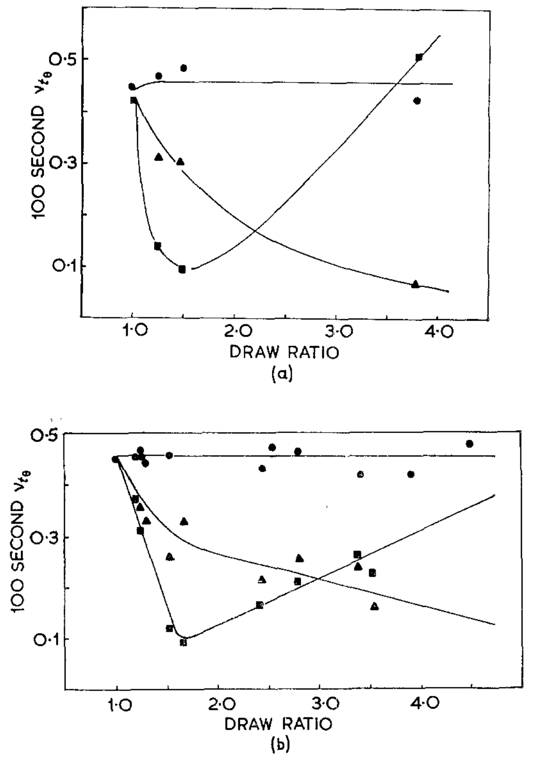

Figure 11 Variation of 100 sec lateral contraction ratio (ν_{t_θ}) with draw ratio for (a) cold-drawn LDPE and (b) hot-drawn LDPE. (100 sec tensile strains of 0.3%. Symbols as for fig. 9).

drawing at 55°C. Thus the effect of the thermal treatment does depend to some extent on the process applied.

The lateral compliances given in table III show that there is insufficient difference in S_{t90} between the cold- and hot-drawn specimens to detect any difference due to the 55°C thermal treatments. Of the other 55°C compliances, S_{t45} is, within experimental error, the same as S_{t45} for the cold-drawn material, but S_{t0} is intermediate between the cold- and hot-drawn values. It would also appear that S_{t0} is slightly larger for the 55°C drawn material than for the other treatments at 55°C.

TABLE II Summary of tensile creep modulus data for a 100 sec tensile strain of 0.3%. (CD = drawn at 20°C)

Drawing procedure	Draw ratio	E_0 (10^9 dyn cm^{-2})	E_{90}	E_{45}
Drawn at 20°C	3.0	2.50	2.96	0.70
	3.5	3.70	3.45	0.64
CD-annealed 55°C	3.5	3.03	3.36	—
CD-relaxed 55°C	3.0	2.13	2.68	—
	3.5	2.98	3.16	0.61
Drawn at 55°C	3.0	1.98	2.66	—
Drawn at 95°C	3.0	1.52	2.12	0.86
	3.5	1.80	2.42	0.86

TABLE III Summary of lateral compliance data for a 100 sec tensile strain of 0.3%. (CD = drawn at 20°C)

Drawing procedure	Draw ratio	S_{t0} (10^{-10} cm^2 dyn^{-1})	S_{t90}	S_{t45}
Drawn at 20°C	3.0	1.40	1.05	1.50
	3.5	1.10	1.25	1.25
CD-annealed 55°C	3.5	1.49	1.13	—
CD-relaxed 55°C	3.0	1.97	1.07	—
	3.5	1.36	0.98	1.30
Drawn at 55°C	3.0	2.43	1.26	—
Drawn at 95°C	3.0	3.03	0.94	2.28
	3.5	2.68	0.93	2.28

In view of the comments in section 3.1.4 it is of interest here to record that the degree of non-linearity of E_{45} and S_{t45} for the 55°C relaxed material was similar to that found for the cold-drawn material.

3.2. Time-dependent Behaviour

The creep data presented in this section were obtained from tests in which the tensile strain at 100 sec was in the range 0.9 to 1.1% (see section 2.2). The tensile creep compliance used in this section is defined as the tensile creep strain divided by the applied (nominal) tensile creep stress. It is thus directly proportional to the creep strain and is the inverse of the tensile creep modulus at the same instant of time.

The long term creep experiments were performed several months after the isochronous experiments. Due to ageing processes the 100 sec compliances in this section are lower than those given in section 3.1, although the relative values within any group of measurements are preserved.

It should be noted that the rates of change of compliance with time, for the quenched isotropic and low draw ratio, cold-drawn LDPE, differ from those reported previously [7]. This has been attributed to a slight difference in the method of preparation of the isotropic sheets [16].

3.2.1. Tensile Creep Compliance

The variations of tensile creep compliance with

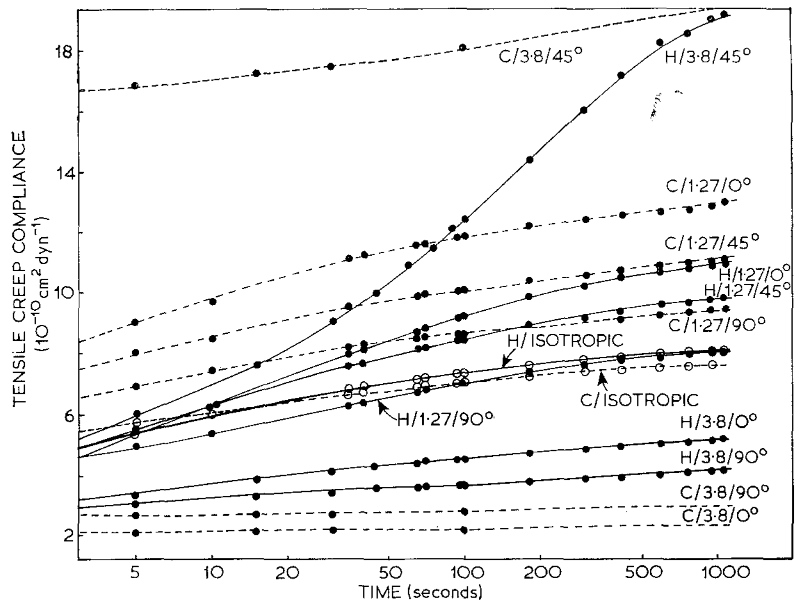

Figure 12 Time dependence of the tensile creep compliances of isotropic, cold-drawn and hot-drawn LDPE. (For each curve the tensile strain after 100 sec was approximately 1.0%).
C/ISOTROPIC – quenched isotropic sheet
H/ISOTROPIC – quenched isotropic sheet annealed at 90°C
--- and label C/$\times$/θ – cold-drawn
—— and label H/$\times$/θ – hot-drawn
(where $\times$ is the draw ratio and θ the specimen angle).

time for both cold- and hot-drawn material at several draw ratios are shown in fig. 12. The creep behaviour for specimens cut at angles of 0°, 45° and 90° to the draw direction is shown for each draw ratio.

The creep behaviour of the quenched isotropic sheet, as prepared, and after annealing at 90°C, is also shown in fig. 12. The creep rate of the annealed isotropic sheet appears to be slightly higher than that for the material as quenched.

At low draw ratio (1.27) the cold-drawn polymer shows a marked anisotropy at the shortest times, with compliance increasing with θ in the order $90° < 45° < 0°$. This is followed by small creep rates (of similar magnitude to the isotropic state) which increase slightly with angle, in the same order as above, but decrease with time. In contrast, for the hot-drawn polymer the anisotropy of tensile compliance is very small at short times, but quickly develops during our time scale owing to moderate creep rates, which increase in the same order as for the cold-drawn material. The creep rates are higher than those from cold-drawing.

At high draw ratios (3.8) even greater differences result from cold- and hot-drawing. As at low draw ratios the cold-drawn specimens already possess their typical anisotropyof compliance ($0° < 90 \leqslant 45$) at the shortest time, but have extremely low creep rates at all angles to the draw direction. For the hot-drawn material the compliances at angles of 0° and 90° to the draw direction show small creep rates with the 0° specimen creeping faster than the 90° one. At short times the 0° and 90° compliances are nearly equal. The 45° specimen is, however, markedly more compliant at all times and possesses a very large creep rate which decreases rapidly at the longest times. Curves, not shown in fig. 12, for creep at intermediate draw ratios, clearly reveal that this extremely facile creep develops steadily upon drawing above draw ratios of about 2.0.

The effects of the thermal treatments at 55°C are compared with the above creep patterns in fig. 13. The creep behaviour of the "55°C" specimens is, in every case, identical to that of the cold-drawn polymer, i.e. anisotropy is already developed at short times and creep rates are low.

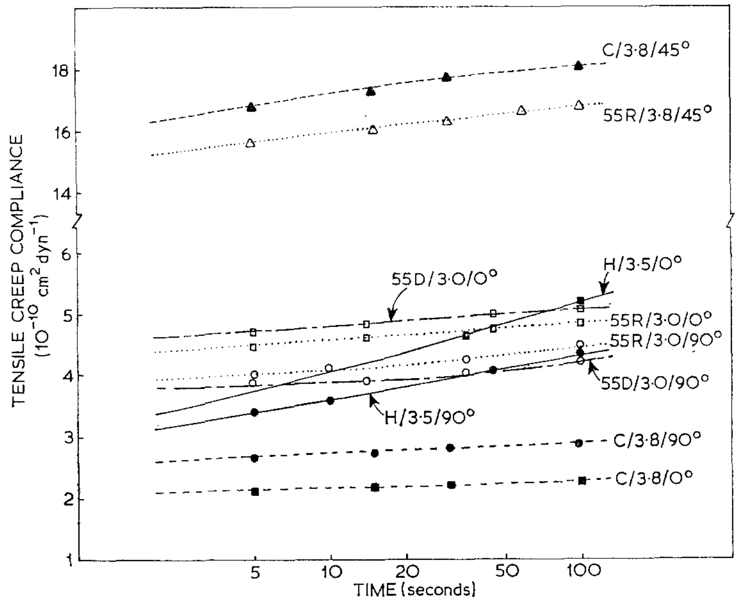

Figure 13 Comparison of the tensile creep behaviour of LDPE treated at 55°C with cold- and hot-drawn LDPE. (For each curve the tensile strain after 100 sec was approximately 1.0%).
...... and label 55R/×/θ – cold-drawn, relaxed at 55°C
— — — and label 55D/×/θ – drawn at 55°C
- - - - and label C/×/θ – cold-drawn
——— and label H/×/θ – hot-drawn
(where × is draw ratio and θ the specimen angle).

It is worth noting that this creep pattern persists whilst the 100 sec tensile compliance in the draw direction is significantly increased from the cold-drawn value (see modulus data in section 3.1.6). Creep rates for the 55°C annealed material were not measured.

3.2.2. *Lateral Compliance*

The variation of lateral compliance with time during tensile creep for the same selection of specimens discussed in section 3.2.1 is shown in fig. 14.

As with the tensile creep compliances, the annealed isotropic sheet appears to have a slightly higher rate of change of lateral compliance than the isotropic sheet as quenched.

At low draw ratios the lateral compliance of cold-drawn LDPE shows a well developed anisotropy at the shortest times (as found with the tensile compliance), with the same anisotropy as the tensile compliance ($90° < 45° < 0°$). The rates of change however, vary widely: S_{t0} increases at a moderate rate, $S_{t45°}$ increases at about the same rate as the quenched isotropic material, but $S_{t90°}$ exhibits a most unusual feature, namely an instantaneous lateral contraction is followed by a slow *expansion* in the thickness direction. It is considered that this effect is not an experimental artefact, having been observed independently in more detailed studies on cold-drawn LDPE in our laboratories [7]. It has been found to occur over a wide range of tensile strains for intermediate draw ratios.

For the hot-drawn material (at low draw ratio) the anisotropy of lateral compliance is very small at short times and the observed lateral compliance anisotropy of $90° < 45° < 0°$ at larger times results from the rapid increase in S_{t0}. As with the cold-drawn material, $S_{t45°}$ increases at approximately the same rate as S_t for the annealed isotropic material and $S_{t90°}$ again exhibits anomalous expansion.

As in the tensile creep behaviour, changes in lateral compliance with time for the hot-drawn material are greater than for the cold-drawn material.

At high draw ratio, very low lateral compliances are obtained by cold-drawing. Very

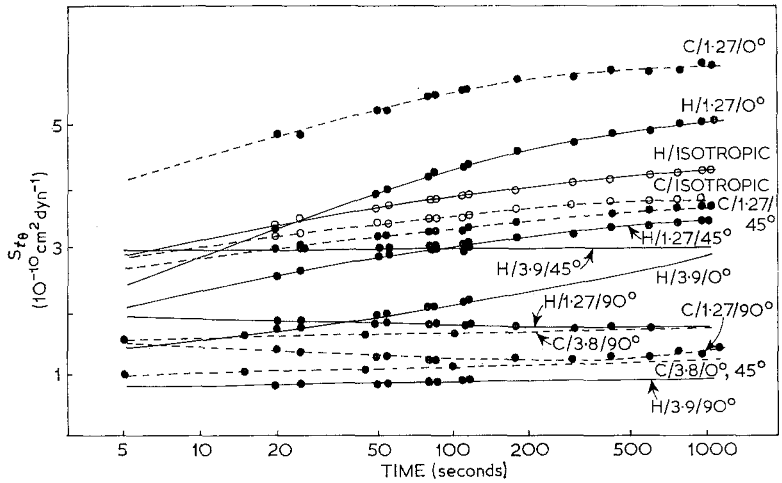

Figure 14 Time dependence of the lateral compliances of isotropic, cold-drawn and hot-drawn LDPE. (For each curve the tensile strain after 100 sec was approximately 1.0%.) (Labels as for fig. 12.)

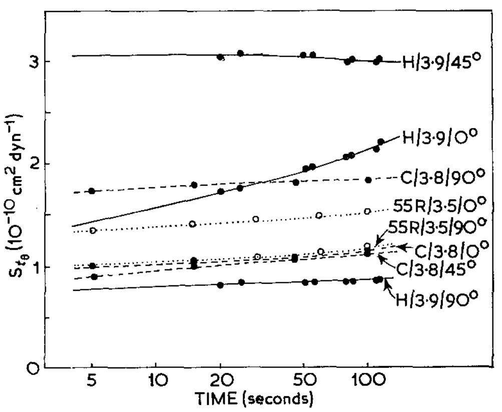

Figure 15 Comparison of the time dependence of the lateral compliances of 55°C relaxed, cold-drawn and hot-drawn LDPE. (For each curve the tensile strain after 100 sec was approximately 1.0%.) (Labels as for fig. 13.)

little increase with time occurs at all angles and the anisotropy 0° 45≃° < 90° is present over the entire time scale studied. For the hot-drawn material, however, there is a moderate increase in $S_{t0°}$, but a very small increase in $S_{t90°}$. The very small change in $S_{t45°}$ for the hot-drawn specimen is worthy of special note in view of the very high creep rate of the tensile compliance for this specimen. At short times the anisotropy of the lateral compliance for the hot-drawn material follows closely the pattern for tensile compliance with 90° ≃ 0° < 45°.

The rates of change of lateral compliance for the 55°C relaxed sheet are compared with the above patterns in fig. 15. (Measurements for the other treatments at 55°C were not made.) The rate of change of $S_{t0°}$ for the 55°C relaxed material follows closely the behaviour of the cold-drawn specimen despite the change in anisotropy of lateral compliance from 0° < 90° (cold-drawn) to 90° <0° in the 55°C relaxed material. The rates of change of lateral compliance of both hot- and cold-drawn material are extremely low for directions away from the draw direction, so no variation with material treatment can be detected.

3.2.3. *Isochronous Data from the Creep Curves*

It is readily apparent from the creep data for hot-drawn LDPE in fig. 12 that the shape of the modulus/draw ratio curves (as given in fig. 9) for each angle must vary with the time chosen for the isochronous plots. The curves given in fig. 16 were obtained from the data of fig. 12 for creep times of 5 and 1000 sec. (1% tensile strain at 100 sec.) It will be seen that the *shapes* of the curves in fig. 9b (100 sec data) lie between the two sets of curves in fig. 16.

It is obvious from fig. 12 that no such major changes of *shape* with time occur in the modulus/draw ratio curves for the cold-drawn material. Thus the modulus/draw ratio behaviour at the lower draw ratios for the cold- and hot-drawn material is very similar when compared at moderately different creep times. In particular the minima in E_0 and E_{90} may be found in both materials.

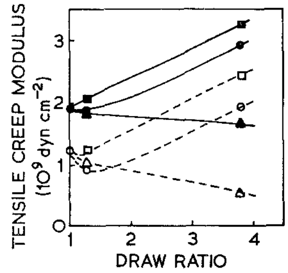

Figure 16 Variation of tensile creep modulus with draw ratio for hot-drawn LDPE. Filled symbols – 5 sec data. Open symbols – 1000 sec data. ● and ○ = 0° specimens. ▲ and △ = 45° specimens. ■ and □ = 90° specimens. (All data taken from creep curves where the tensile strain after 100 sec was approximately 1.0%.)

Examination of fig. 14 shows that the basic shape of the lateral compliance/draw ratio curve for the 0° hot-drawn specimen is similarly affected by time. Thus at short times the lateral compliance is a maximum for the isotropic material while at long times the shape of the curve at low draw ratio tends to that for the cold-drawn 0° specimen.

No other significant changes of shape of the draw ratio curves occur with time.

3.3. Recovery

Complete strain recovery can be achieved even from tensile strains as high as 3% and this recovery behaviour has already been studied in detail for cold-drawn LDPE [7]. In the present work the strain recoveries achieved after five times the creep period were invariably better than 97% of the creep strain just prior to removal of the creep load, for creep strains of up to 2%.

4. Summary of Results from Structural Studies

Only the conclusions relevant to the ensuing discussion will be given here. Full details may be found in part 1 and elsewhere [17].

4.1. Low Draw Ratio

Cold-drawn material. There is a marked cone-distribution of the crystalline c-axes about the draw direction, with the maximum of the distribution at approximately 35° to the draw direction.

Hot-drawn material. The distribution of c-axes shows a relatively flat maximum in the draw direction with a width at half-peak height, $W(\frac{1}{2})$, which is close to the value for the cold-drawn material. The distribution appears to be made up of two parts: the cone distribution of the cold-drawn material plus a relatively narrow distribution with a maximum in the draw direction. (It is interesting to note that a hint of this axial component also occurring in cold-drawn LDPE may be seen in fig. 1 of [9].)

4.2. High Draw Ratio

Cold-drawn material. The crystalline c-axes are highly aligned parallel to the draw direction, with the a- and b-axes randomly aligned in the plane perpendicular to the draw-direction. There is some evidence of a residual lamellar texture with lamellar surface normals at 30° to the draw direction. The tie molecules of the amorphous regions are in a highly strained state.

Hot-drawn material. The same pattern of alignment of the crystalline a-, b- and c-axes is obtained, as with cold-drawing, but with less perfection of alignment at equal draw ratio. Thus examination of the data summarised in figs. 1 and 2 of part 1 shows that the distribution of [110] poles is similar for the hot- and cold-drawn materials at the same draw ratio (i.e. similar values of $W(\frac{1}{2})$). However, plots of $W(\frac{1}{2})$ against draw ratio for the [200] poles give almost parallel but well separated straight lines, and indicate that $W(\frac{1}{2})$ at a draw ratio of 4.2 for the hot-drawn material is equal to $W(\frac{1}{2})$ at a draw ratio of only 2.8 for the cold-drawn material. In view of the similarity of the [110] distributions for the two materials, it would seem reasonable to expect that the c-axes distributions would show similar trends to the a-axis distributions.

There is evidence of a reasonably defined lamellar texture in the hot-drawn material, with a relatively wide distribution of lamellar surface normals, centred in the draw direction.

The combination of wide-angle X-ray and birefringence measurements shows that the amorphous regions of the cold-drawn material are considerably more oriented than those of the hot-drawn material [17].

Material treated at 55°C. The material that was allowed to relax at 55°C after cold-drawing possesses almost identical distributions of [200] and [110] poles to the cold-drawn material. The lamellar texture is somewhat better defined, but has a similar orientation distribution to that shown by the cold-drawn material.

In the case of the material drawn at 55°C, the

[200] distribution is also very similar to that for the cold-drawn material, but the [110] distribution is wider and very flat in the central region. The orientation distribution of the lamellae is closer to that of the hot-drawn material than of the cold-drawn or 55°C relaxed materials.

5. Discussion

Stachurski and Ward [11] have suggested that there are two major relaxation processes of interest in oriented LDPE. They have labelled them β^* and β' in order of decreasing temperature and have attributed them to intracrystalline and interlamellar shear processes respectively. These labels are used in the following discussion.

5.1. Processes at High Draw Ratio

5.1.1. Shear Processes for 45° Tensile Tests

In the cold-drawn material little creep occurs at all angles, indicating that the relaxation mechanisms producing the observed anisotropy occurred before our time scale. The high tensile compliance of the 45° specimens, coupled with the very low value of the lateral compliance in the thickness direction (and hence extremely low value of thickness contraction ratio) has been identified previously as due to easy shear in the aligned chain direction [5]. From dynamic loss work this β^* relaxation occurs at temperatures around 10°C at a frequency of about 250 cps for high draw ratio, cold-drawn LDPE [11].

In the hot-drawn material, significant creep does occur during the time scale of our experiments and this can be correlated with the dynamic loss data which showed that, after heat treatment at 95°C, the β^* relaxation moved to higher temperatures (75°C at a frequency of about 100 cps) [11]. Identification with this process is satisfactorily confirmed by the 45° creep curves, where the tensile creep rate is very high and passes through a distinct maximum (with little creep at 0° and 90°) whereas S_{t45} shows no change with time, so confirming the shear nature of the deformation. At long times the values of E_{45} for the hot- and cold-drawn specimens are approximately equal. Furthermore the values of the compliance at 1000 sec for shear parallel to the draw direction (one of the five independent compliances for this material and labelled S_{44} in [5]) are 76×10^{-10} and 70×10^{-10} cm^2 dyn^{-1} for the hot- and cold-drawn specimens respectively. (These S_{44} values were calculated using the present creep data and equation 2 of [5].) This suggests that precisely the same easy shear process occurs in both hot- and cold-drawn LDPE although at different times.

There are, however, some differences in the behaviour of the two 45° specimens which require explanation:

(i) E_{45} for the cold-drawn material (and hence the easy-shear mechanism) is relatively independent of the tensile strain, at least for tensile strains up to 2%. However, E_{45} for the hot-drawn material exhibits extremely non-linear behaviour over the same strain range.

The creep data obtained during the "isochronous" experiments described in section 2.2 may be used to obtain a tensile strain (and hence a tensile creep modulus) at 5 sec after application of the load, for each load applied. The variation of this 5 sec modulus with the tensile strain at 5 sec for the 45° hot-drawn specimen (draw ratio 3.9) is shown in fig. 17. Comparison of this curve with the 100 sec curve for the same specimen (replotted from fig. 7) shows that the slope of the log modulus – log strain curve at 5 sec does not differ significantly from that at 100 sec. The easy shear mechanism is therefore reasonably linear in the hot-drawn material, but there must be a deformation mechanism occurring at shorter times in the hot-drawn material which exhibits highly non-linear behaviour. This short time mechanism must be absent from the cold-drawn material in view of its linear behaviour.

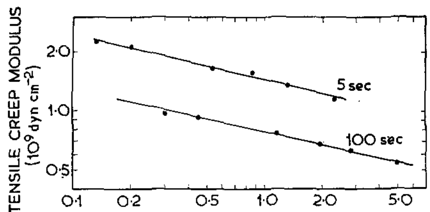

Figure 17 Variation of tensile creep modulus with tensile strain, at creep times of 5 and 100 sec, for a 45° specimen from a sheet of hot-drawn LDPE of draw ratio 3.9.

The structural studies (see part 1) have shown that in the hot-drawn LDPE there are not only aligned crystal chains, but also perpendicularly oriented lamellae. Thus application of a tensile stress at 45° to the draw direction might induce interlamellar shear. Such a process would not be expected in the cold-drawn material in view of the absence of a well defined lamellar texture. Support for a lamellar shear process at short times is provided by the dynamic loss studies [11] which associate the β' relaxation in annealed cold-drawn LDPE with interlamellar shear (this process occurs at $-20°$C at a frequency of about 300 cps). It must, however, be noted that the orientation distribution of lamellae in our hot-drawn material is fairly wide and shear on conically disposed lamellae could occur during a test on a 0° specimen (compare with *c*-axis shear at low draw ratios). It is then difficult to reconcile the highly non-linear behaviour of E_{45} with the linear behaviour of E_0.

(ii) The lateral compliance S_{t45} of the hot-drawn material is in the region of 2.5 to 3.0×10^{-10} cm^2 dyne^{-1} compared with a very low value in the region of 10^{-10} cm^2 dyne^{-1} for the cold-drawn material.

If the short time process in the hot-drawn material was simply an interlamellar easy shear process the lateral compliance would be very low, providing the lamellar surfaces are perpendicular to the draw direction. Since, however, there is a wide distribution of the angle between the normal to the lamellar surface and the draw direction, the easy-shear process would usually involve a thickness change.

A further part of the apparent difference between the two compliance values could be accounted for by the observation that the degree of chain alignment in the hot-drawn material at a high draw ratio is only equivalent to that found at a lower draw ratio in the cold-drawn material, thus comparison at equal draw ratio may be irrelevant here.

No further information can be obtained, regarding the deformation mechanisms at 45°, from the 55°C relaxed material since the non-linear and time dependent behaviour follows closely that for the cold-drawn material. The structure also appears to be similar to that for the cold-drawn material.

5.1.2. Deformation Mechanisms for 0° and 90° Tensile Tests

The anisotropy of moduli $E_0 > E_{90}$ for the cold-drawn high draw ratio material has been associated with the highly strained nature of the oriented non-crystalline regions [5, 18]. Very little contribution to the deformation at 0° would be expected from lamellar shear processes in view of the poorly defined low-angle X-ray patterns for the cold-drawn material.

A complete reversal of anisotropy occurs in the hot-drawn material, to give $E_{90} > E_0$. This reversal is due, primarily, to a large drop in E_0, which has also been observed by Ward *et al* in cold-drawn LDPE when annealed at 105°C [11,18].

The time dependence of the 0° tensile compliance of the hot drawn material deserves comment at this point (fig. 12). It was stated in section 5.1.1 that the mechanism occurring in our time scale was easy-shear parallel to the aligned chain direction. The small, but significant creep rate at 0° (with very low creep rate at 90°) could then be due to shear on chains which are not yet fully aligned in the draw direction. (The chain axes being slower to orient with increasing draw ratio in the hot drawn material – see section 4.)

At short times, before this easy shear deformation has occurred, the difference between E_0 and E_{90} is very small and, to some extent, the difference between E_0 for the hot- and cold-drawn sheets, at the same draw ratio is decreased. The remainder of the large drop in E_0 could be solely due to relaxation of the amorphous tie molecules in the hot-drawn material. However, Ward *et al* [11, 18] attributed part of the drop in E_0 to shear on lamellar planes which were at 35° to the draw direction (with fibre symmetry) in their annealed sheet. Although the low angle X-ray pattern for our hot-drawn material is different to that for Ward's sheet, it is obvious that we cannot entirely exclude the possibility of lamella shear effects contributing to the drop in E_0 in our material.

However, comparison at equal draw ratio may not be particularly relevant when the degree of crystalline orientation differs between the two materials (see section 4). On this basis, the high draw ratio, hot-drawn material should be compared with a lower draw ratio cold-drawn sheet and this again reduces the difference in E_0.

A comparison between the cold-drawn and the 55°C relaxed material may be of greater interest. Thus the wide-angle X-ray data shows that the distribution of [110] poles and crystalline *a*-axes are almost identical and the low angle X-ray photographs indicate great similarity of structure. However, the modulus data in table II shows that at a draw ratio of 3.5 there is a significant drop in E_0 from the cold-drawn to the 55°C relaxed material with a much smaller drop in E_{90} and E_{45}. Furthermore, the non-linearity of E_{45} for the 55°C material is similar to that for the cold-drawn material (section 3.1.6). In the absence of changes in lamellar or chain orientation it would appear that the drop in E_0 must be largely due to a relaxation of the amorphous tie molecules in the 55°C material. Unfortunately the cumulative errors in the determination of the amorphous orientation from birefringence and X-ray measurements are too large for us to obtain a positive indication that the 55°C heat treatment does result in partial relaxation of the strained tie molecules in the amorphous regions of the cold-drawn material [17]. However, relaxing the cold-drawn material at 55°C did cause a shrinkage in the draw direction of 15% and this together with work in other laboratories supports the suggestion that partial relaxation does occur during the 55°C heat treatment [13].

It is apparent that the magnitude of the drop in E_0 for the hot-drawn material (when compared with cold-drawn material) is similar to that observed, even when lamellar shear processes are expected to be operative (see [11, 18]). From this and the above observations on the 55°C relaxed material it appears that the behaviour of oriented LDPE in the draw direction is dominated by the degree of alignment and elongation of the tie molecules of the amorphous regions. In suitably oriented materials interlamellar shear can result from relaxation of the tie molecules, but it would appear that such shear processes alone form a minor part of the total strain response to a stress applied in the direction of chain alignment. (see also [19]).

The obvious extension of this work to low temperatures is planned, in order to examine lamellar shear mechanisms in more detail.

5.2. Processes at Low Draw Ratio

In cold-drawn LDPE at low draw ratio the curious tensile modulus anisotropy of $E_0 < E_{45} < E_{90}$ has been explained on the basis of the particular distribution about the draw direction assumed by the crystalline chains (see section 1). This explanation is consistent with the large value of S_{t0} observed and with the anisotropy of tensile creep rate described in detail elsewhere [7].

The wide-angle X-ray diffraction data reported in part 1 showed distinct differences in the orientation of the crystal axes at low draw ratio, with apparently the cone distribution of c-axes in the cold-drawn material being replaced by a relatively flat distribution with approximately the same angular spread in the hot-drawn material. (It must be stressed that the c-axis orientation distribution has not been measured directly. However, the above observations are in qualitative agreement with those based on direct observation [8].) It is therefore of considerable interest to recall that a large minimum in E_0 at low draw ratio is found with the hot-drawn material when compared with the isotropic value at long times, (1000 sec). This drop in E_0 below the isotropic value for the hot-drawn material is just over half that for the cold-drawn material at the same draw ratio, while the difference between E_0 and E_{90} is approximately the same for the two materials. There is of course no reason why the drop in E_0 should be the same for both materials at the same draw ratio. Thus examination of fig. 9 shows that the minimum in E_0 occurs at draw ratios of 1.3 and 1.5 for the cold- and hot-drawn materials respectively.

The occurrence of the c-axis shear mechanism at longer times for the hot-drawn material is probably associated with an improvement in crystal perfection resulting from annealing the quenched LDPE at 95°C. A similar effect has been found when the creep behaviour of quenched LDPE is compared with LDPE that has been cooled from the melt at a slightly slower rate [16].

It therefore appears that at low draw ratio the creep behaviour of drawn LDPE is not necessarily directly related to the obvious features of the X-ray diffraction patterns. Nor is the behaviour of cold-drawn LDPE unique as suggested elsewhere [8]. The behaviour of E_0 nevertheless remains closely related to the orientation distribution of the crystalline c-axes. Thus the model of the hot-drawn material at low draw ratio given in part 1 proposes that the relatively flat distribution of c-axes still contains a substantial "conical" component. It is suggested that this conical component is again responsible for the anomalous behaviour of E_0 at low draw ratio. The decrease in magnitude of the effect could then be due simply to a reduction in the number of suitably oriented crystalline chains in the hot drawn material (due to the presence of a second, axial, component in the hot-drawn distribution).

6. General Conclusions

The major points emerging from this study may be summarised as follows:

Previous work has shown that the anomalous behaviour of E_0 at low draw ratio in cold-drawn LDPE is closely associated with a "cone-distribution" of the crystalline c-axes. However, contrary to the suggestion of other workers, the absence of a marked cone-distribution (i.e. absence of four distinct intensity maxima in the relevant wide-angle X-ray diffraction pattern) in hot-drawn LDPE does not mean that the anomaly must completely disappear, as the *c*-axis distribution in the hot-drawn material still contains a "conical" component.

In connection with the above anomaly it has also been shown that it is misleading to view isochronous data in isolation when comparing materials. Allowance must be made for possible changes in the retardation times of the molecular mechanisms involved, especially when the preparation methods of the materials being compared involve differing temperature histories.

The patterns of non-linear behaviour for the 0° and 90° specimens from the hot-drawn material are very similar to those found previously for the cold-drawn material, despite differences in the state of the amorphous regions and the lamellar textures. The highly non-linear behaviour of E_{45} for the hot-drawn material at high draw ratio (compared with the relatively linear response of the cold-drawn specimen) is associated with an extra deformation process occurring at creep times of less than 5 sec at 20°C. It is suggested that this extra mechanism involves the lamellae, as they are better defined and suitably oriented in the hot drawn material.

For the materials studied here it is considered that the large drop in E_0 for the hot-drawn material at high draw ratio (compared with the cold-drawn material at equal draw ratio) is due more to the relaxation of the tie molecules of the amorphous regions than to interlamellar shear processes. However, it is stressed that comparisons between such materials at equal draw ratio are not particularly relevant in this context owing to the differences in degree of crystalline orientation at equal draw ratio. The specimens prepared so as to control both the lamellar and crystalline chain orientations (such as the cold-drawn and 55°C heat treated specimens) are therefore of particular value in delineating these effects. Creep studies on these materials at low temperatues should prove interesting.

The very high creep rate of the 45° specimen from the hot-drawn material at high draw ratio is associated with an easy shear process parallel to the aligned molecular chains. The shift of this process, from very short times for the cold-drawn material to our time scale for the hot-drawn material, must be due to the structural differences resulting from the different drawing procedures. Thus the activation energy for the same molecular process could be higher in the hot-drawn material or the deformation process could be different in the two materials (e.g. interfibrillar shear in the cold-drawn material but intracrystalline shear in the hot-drawn material). In this connection the relatively linear behaviour of the shear process in both the hot- and cold-drawn sheets, and the similarity in the values of S_{44} (see section 5.1.1.) should be noted.

The value of studying the time *and* strain (or stress) dependence of moduli and lateral compliances in the manner outlined above is readily apparent.

Acknowledgements

B.H.M. acknowledges the generous contribution of his employer, Fibremakers Ltd (Australia), in arranging the period of study leave during which this work was carried out. M.W.D. gratefully acknowledges the award of a Research Assistantship from the Science Research Council. The creep apparatus was developed under the sponsorship of the Department of Trade and Industry.

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Received 29 March and accepted 19 April 1971.