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The mechanical properties of anisotropic polymers

Progress Report No. 6

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A report of work carried out during the period

1st April, 1968 to 30th September, 1968

Contents

Part 1

General Developments

The basic development work on the tensile creep apparatus was completed by March, 1968. A description of the latest 'heavy-duty' creep rig and two types of contraction extensometer, together with the relevant creep trials, was given in Progress Report No. 5. Since then two further 'heavy-duty' creep rigs have been assembled and tested and are now ready for use with rigid plastics. In addition, further trials of the double transducer contraction extensometer described in Report No. 5 have been carried out. These trials are described in part 2 of this report The trials were considered reasonably satisfactory and each of the three heavy-duty creep rigs has now been fitted with a device of this type in addition to the normal tensile extensometer. The polythene creep rig described in Progress Report No. 3 has been working satisfactorily for over a year and no further modifications have been made in the period under review. At the conclusion of the above-mentioned trials it was considered that the creep apparatus was unlikely to require any further major changes. A detailed report of all the apparatus has therefore been prepared with the intention of submitting it for publication to the Journal of Scientific Instruments. It is at present being examined at the Ministry of Technology. (CoA Memo. No. 158).

A detailed study of the creep properties of isotropic and uniaxially oriented Perspex had been scheduled for the present period, and the heavy-duty creep rigs were prepared for the study. In addition a suitable method for preparing uniformly oriented Perspex sheets has been developed. This is described in part 3 of this report. Unfortunately the Perspex material did not arrive in time for any creep data to be included in this report.

Results of an extensive study on the creep behaviour of isotropic and highly oriented low-density polyethylene have been given in Progress Reports Nos. 4 and 5. A preliminary report of the investigation has been published in 'Nature' (Saunders and Darlington, 1968). A detailed description and analysis of the results has now been prepared in a form suitable for publication and will be submitted to the Ministry in the near future. In view of this no details will be given in this report.

The above investigation yielded many interesting trends and demonstrated the usefulness of making combined thickness contraction and longitudinal extension measurements during tensile creep. In an attempt to gain a greater understanding of the structural implications of some of the results, studies have been carried out on low-density polyethylene oriented by hot-drawing as well as further studies on fresh, cold-drawn material. The results are given in part 4 of this report.

Part 2

APPARATUS DEVELOPMENTS

2.1 Introduction

The development of the creep apparatus up to March, 1968, was summarised in Progress Report No. 5. By then, two types of rig had been built: one for work on the softer plastics such as low-density polyethylene ('polythene' creep rig) and one for work on rigid polymers such as perspex ('heavy-duty' creep rig). Identical extensometers were used on the rigs for the measurement of the longitudinal extension of the specimens during creep. Following extensive trials it was concluded that both rigs were operating satisfactorily. In the period under review two further 'heavy-duty' rigs have been assembled and tested and are now ready for use.

The problem of measuring thickness contraction during tensile creep was also discussed in detail in Report No. 5. Two types of contraction measuring device were described: a single transducer type suitable for soft or rigid specimens with gauge lengths down to 1.3 cms. and a double transducer type intended only for rigid specimens with gauge lengths greater than 2 cms. The former type was obviously to be preferred but creep trials on low-density polyethylene showed that the reliability of the measurements was not sufficient for the determination of absolute values of the creep contraction ratio. It has however been used with some success to study the variation of creep contraction ratio with angle in highly oriented, low-density polyethylene. (See Saunders and Darlington, 1968 or Progress Report No. 5). Further trials of the single-transducer contraction device on low-density polyethylene are in progress at present with the aim of improving the absolute accuracy of the device when used with soft materials. So far a significant improvement appears to have been made simply by repositioning the vibrator and reducing the pressure exerted on the specimen by the extensometer. Some comments on this system are given in section 2.3. It is possible that some of the problems associated with the use of the single transducer extensometer on low-density polyethylene will disappear when the device is used with rigid plastics. This has yet to be investigated.

Verification of the absolute validity of the contraction measurements made with the single-transducer device has been hampered by the lack of a relatively soft plastic for which reliable contraction data exists. The two-transducer device was therefore built to enable comparative measurements on a material to be made using the two devices. Owing to less stringent requirements it was possible to use a very simple design. Trials with this extensometer were reported in Progress Report No. 5. The results were sufficiently promising to warrant further investigation. For this purpose a piece of polypropylene was kindly supplied by Mr. S. Turner of I.C.I. Plastics Ltd. Creep contraction ratio measurements had already been made on samples cut from the same block of material. The results of trials on this material, using the two-transducer device, are given below.

2 2 Two-Transducer Contraction Extensometer Trials

Four specimens were machined from the block of polypropylene supplied by I.C.I. The specimens were of the type shown in fig. 2.1 of Progress Report No. 4, i.e. dumbell shape with parallel centre section of 1.0 inch. They were mounted in the heavy-duty creep rigs with the tensile extensometers set for a gauge length of 0.8 inch. The majority of the tests were of the 100 second isochronous stress-strain type used during the previous polythene studies. (See Progress Report No. 3, page 10 for a typical procedure). For each specimen the contraction extensometer was mounted after some initial tensile tests, in order to check that the addition of the contraction device did not affect the tensile behaviour of the specimen. No adverse effects were detected during these trials. The tensile behaviour of the polypropylene specimens was examined in the strain range 0.05% to 2.5%, with the lowest combined extension-contraction test at a tensile strain of 0.3%. The recovery of the specimens (lateral and longitudinal) was monitored after several of the creep tests.

The results may be used to calculate the value of the creep contraction ratio for the thickness direction, ν_t. This is defined as the ratio of the lateral contraction (thickness direction) strain to the longitudinal tensile strain at the same instant of time, during a creep test. The variation of ν_t, after 100 seconds of creep, with tensile strain is shown in figure 1. The interspecimen reproducibility is regarded as very satisfactory at this stage. The results may be compared with those obtained by McCammond at Queen's University, Belfast and Turner and co-workers at I.C.I. Plastics Ltd. The former could not detect a variation of ν_t with strain outside the scatter of results and therefore gave a mean value of 0.45, independent of tensile strain in the strain range 0.26% to 1.4%. In view of this, the variation of ν_t with strain obtained by us is possibly a product of our method itself. Thus the two transducer springs may be pushing the ends of the transducer shafts into the surface of the specimen. The slight movement of the specimen through the contact points of the contraction device which occurs on application of the creep load, will then cause a reduction in the total effective contraction measured by an amount which depends on the translational movement (i.e. the tensile strain). Whether or not this would lead to a significant error would depend on the magnitude of the dimples made in the specimen and the time necessary to produce the dimples. If the latter was reasonably short (say less than 50 seconds) the specimen would be quickly dimpled in the new position so producing little error in the 100 second reading. However, during a single creep test this would still cause an overall variation of ν_t with time that was larger than the true value. Tests with the improved single-transducer contraction device (lower contact pressure) may be of use here. The problem should not arise during tests on rigid thermoplastics and the two-transducer device is considered satisfactory for this purpose.

It is of interest here to note that Turner has obtained a value for ν_t for our material of 0.34 at a tensile strain in the region of 0.1%. This agrees remarkably closely with our results if they are extrapolated to low strains, and therefore lends support to the variation of ν_t with strain.

However, Turner's result was obtained from tests in flexure and torsion and the reliability of the measurements is not certain at present.

2.3 Comments on the Single-Transducer Contraction Extensometer

In view of the possible effects of pressure exerted on the specimen by the contact pieces of the contraction extensometer, it is obviously desirable to reduce the pressure as much as possible. However, in the single-transducer device, this increases the possibility that stiction effects will prevent the contact pieces from maintaining contact with the specimen. This will lead to low values for ν_t with possibly a large scatter in the results.

On re-examination of the trials described in Progress Report No. 5 it was considered that the peculiar time effects described there may well have been due to pressure effects. Further trials using polythene specimens are therefore in progress at present in an attempt to eliminate the effect and improve the reproducibility. A very low contact pressure is being used. Initially considerable scatter was obtained in the results, presumably due to stiction effects. The vibrator position was therefore varied in an attempt to overcome the stiction. The area of the extensometer arm which makes contact with the transducer was also polished and lubricated with Rocol powder A considerable improvement in the reproducibility has just been obtained with the vibrator acting on the transducer holder itself. Furthermore the latest results do not appear to depend on the time interval between mounting the extensometer on the sample and taking the first measurement. Further comment will be delayed until the next report.

Part 3

Preliminary Studies On Perspex

As mentioned in part 2, three heavy-duty creep rigs have been built and tested in preparation for creep testing on Perspex or other rigid plastics. In addition, all three rigs have been equipped with extensometers for the measurement of lateral contraction during tensile creep.

The development of suitable apparatus for producing uniaxially oriented Perspex has also been carried out in the period under review. The apparatus consists essentially of a fixed upper grip plus a lower grip driven at constant extension rate by electric motor. The grips are completely enclosed in a temperature controlled box. Hot air from two separate fan heaters is blown into the top and bottom of the box. Thermocouple-relay systems are used to control the heater supplies. Three mercury thermometers are used to monitor the temperature. Temperatures in excess of 150°C can be obtained and maintained constant to better than 3°C. The variation in reading of the three thermometers at any given time is also less than 3°C.

Considerable difficulty was experienced initially with the specimen grips: the specimen either tearing in the grips or simply pulling out of them during drawing. The design of the latest grips is shown in figure 2. This design allows the grip faces to move as the specimen contracts during drawing, so maintaining firm contact at all times. The threaded bolts enable the grip faces to be forced onto the specimen during assembly. The grip anti-rotation guides and springs assist in the initial mounting of the specimen.

With this apparatus draw ratios in excess of 3:1 have been obtained at temperatures in the range 120°C to 130°C. Rectangular sheets are used in preference to those with dumbell ends as the latter were found to be prone to fracture at the radius. Shrinkage tests on the oriented specimens have confirmed that negligible flow has occurred during the hot-drawing process.

Part 4

Tensile Creep Studies on Oriented Low-Density Polyethylene

4.1 Introduction

A detailed study of the tensile creep and thickness contraction behaviour of isotropic and highly oriented low-density polyethylene has been reported in Progress Reports Nos. 4 and 5. A full description and analysis of the results has been prepared and is about to be submitted to the Ministry of Technology. The oriented material in the above study was prepared by cold-drawing initially isotropic sheets to a draw ratio above that corresponding to the 'natural draw ratio'. On subsequent relaxation at room temperature for several months a draw ratio of approximately 4.2 was obtained. There is a growing body of evidence which suggests that the amorphous regions of such cold-drawn material contain many molecules that are in a highly strained state, whereas annealing or hot-drawing at a sufficiently high temperature produces relaxed amorphous regions. In both cases highly oriented crystalline regions are obtained. (See Peterlin, 1966). Some preliminary work on the creep properties of hot-drawn low-density polyethylene (draw ratio = 3.5) has therefore been carried out to examine the effects of the structural differences on mechanical properties. Material drawn, at room temperature, to the natural drawn state, has also been studied for comparative purposes. Wide angle X-rays photographs have been taken of all the materials. The creep results are reported below.

4.2 Specimen Preparation and Experimental Methods

The grade of low-density polyethylene used was I.C.I. 'Alkathene' WJG 11. The isotropic sheets were prepared in the manner described in Progress Report No. 2 (page 4) with the exception that the chromium plated steel press plates were replaced by aluminium plates.

The oriented sheets were prepared in the hot drawing machine described in part 3 of this report. The new grips had not then been built and some difficulty was experienced initially in preparing the hot drawn sheets. Finally sheets with dumbell ends were used in order to decrease the chances of slippage from the grips. A temperature of 90 ± 2°C was used during preparation of the hot-drawn sheets. After drawing, the sheets were cooled to room temperature (before being released from the grips) by switching off the heaters and opening the large door of the hot drawing machine. This method of cooling is not as rapid as that used when preparing the isotropic sheets. As the properties of all the sheets will be dependent on the cooling method it would be preferable to cool the isotropic sheets at the same rate for comparison purposes.

The cold-drawn sheets were prepared on the same drawing machine; the heaters being switched off throughout the operation. The sheets were drawn until there was just a small portion of the material in the un-necked state. This ensured reproducibility of the draw ratio in the necked part of the material.

The draw ratio of the hot-drawn sheets appeared to be stable at room temperature after storage for one day (draw ratio = 3.55 ± 0.05) whereas the draw ratio of the cold drawn material was still decreasing very slowly. The cold drawn specimens were tested after only several days storage and it is therefore probable that the material was not completely stable. The draw ratio at the time of testing was 3.55 ± 0.05.

The test specimens were cut from the anisotropic sheets using the usual A.S.T.M. microtensile specimen cutter.

The creep apparatus and measuring procedures were identical to those used during the previous polyethylene studies. The majority of the work was of the 100 second isochronous type; the recovery of the specimens being monitored in many cases. No contraction measurements were made. All measurements were made at 20.5 ± 0.5°C.

4.3 Results

The tensile creep and recovery properties of seven anisotropic and two isotropic specimens have been studied. For the anisotropic sheets, specimens cut at the following angles, θ, to the draw direction were used:

Hot-drawn material	1 at 0°, 2 at 45°, 1 at 90°.
Cold-drawn material	1 at 0°, 45° and 90°.

The variation of the 100 second tensile creep modulus with strain, for specimens cut at the various angles from the hot- and cold-drawn material, is shown in fig. 3. It will be seen that the curves for the 0° and 90° hot-drawn specimens are similar in shape to those for 0° and 90° cold-drawn specimens respectively. The curve for the 45° hot-drawn specimen is noticeably different from the other curves. In view of the large difference a second specimen was studied in detail but the results appeared to be genuine. No immediate explanation for the curve can be advanced.

The shapes of the three curves for the cold-drawn material are almost identical to those obtained previously for a draw ratio of 4.2. The absolute values are however quite different. This was expected on the basis of the results given by Raumann and Saunders (1961) for the variation of modulus with draw ratio from cyclic tests.

The tensile strain-time curves of the various specimens in the region of low and high strains are given in figures 4 and 5 respectively. Again the behaviour of the 45° hot-drawn specimen differs considerably from that of the other specimens. The only 1000 second creep test carried out during the programme was on the 45° hot-drawn specimen. It is included in figure 4. It is of interest in that it shows a point of inflection. The importance of extending the time scale of these creep experiments is thus obvious. Over the short time interval of the present tests, the shapes of the tensile strain-time curves of the three cold-drawn specimens at low strains (Figure 4) are almost identical. The same applies to the 0° and 45° cold-drawn specimens at high strains (Figure 5). The 90° cold-drawn specimen fractured above a strain of 1.5%. This is identical to the pattern observed in the creep results of the previous study (cold drawn to draw ratio of 4.2). Furthermore the creep rates of the latter specimens were only slightly less than those in the present study. The hot-drawn material shows no such uniformity of behaviour. The 90° hot-drawn specimen was still undamaged after a test which reached a tensile strain of 2.8%. The creep rates of the hot-drawn specimens are greater than the corresponding rates of the cold-drawn specimens in all cases.

The recovery of each of the specimens was monitored after at least one of the 100 second creep tests. Some typical results for hot- and cold-drawn materials are given in figures 6 and 7 respectively. The fractional recovered strain is defined as

$$1 - \left(\frac{\text{residual strain}}{\text{strain at start of recovery experiment}}\right)$$

and the reduced time as

$$\left(\frac{\text{recovery time}}{\text{duration of preceeding creep}}\right)$$

The relevant experimental data are given in table 1.

As expected, the recovery behaviour of the 45° hot-drawn specimen is markedly different from that of the other specimens. It is apparent however that at least 99% of the final creep strain is recoverable. The unusual behaviour of this specimen is not therefore due to deformation by flow.

It is of interest that the recovery of the 90° hot- and cold-drawn specimens does not appear to be as good as that of the other specimens. This may be connected with the molecular rearrangement mechanisms postulated during the previous study on highly oriented material; the initial rearrangement being non-recoverable. Further contraction measurements are obviously needed on these materials.

4.4 Discussion

The results presented above illustrate the large variations in creep behaviour that are produced by varying the heat treatment during preparation of the anisotropic samples. Unfortunately the hot drawing procedure described here not only produces relaxed amorphous regions (the desired effect) but also causes changes in the crystalline phase. (See Peterlin, 1967). At present the relative importance of the various changes is not certain. To complete this study the following measurements would be of use:

(i) Birefringence of the anisotropic sheets

(ii) Creep behaviour of an isotropic sheet that has been subjected to the heating and cooling cycle experienced by the hot-drawn sheets.

(iii) Creep behaviour of cold-drawn material of lower draw ratio.

This will enable a comparison of the creep rates to be made on materials with the same moduli. (In the present study it is apparent that the moduli of the hot drawn material correspond approximately with those for a cold-drawn sheet of draw ratio 2.5).

It is also intended to extend the time range of the creep tests and determine the variation of ν_t with time and strain.

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Progress Report No. 2 - October, 1966. CoA Memo. No. 115.
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SPECIMEN	APPLIED TENSILE STRESS (10^6 dynes/cm^2)	CREEP TIME (Seconds)	FINAL CREEP STRAIN
0°-H-1	0.251	105	0.2%
0°-H-2	6.13	105	4.3%
45°-H-1	0.444	105	0.5%
45°-H-2	0.731	1,000	1.5%
90°-H	4.6	105	2.8%
0°-C	8.2	105	3.4%
45°-C	0.455	105	0.7%
90°-C	3.96	105	1.5%

TABLE 1. Experimental data relevant to the recovery results given in figures 6 and 7.

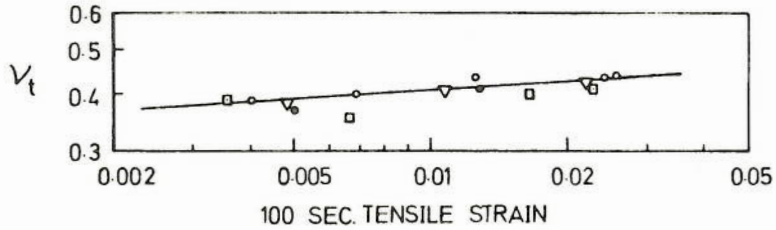

FIG.1. Variation of 100 second creep contraction ratio, ν_t, with 100 second tensile strain for four polypropylene specimens.

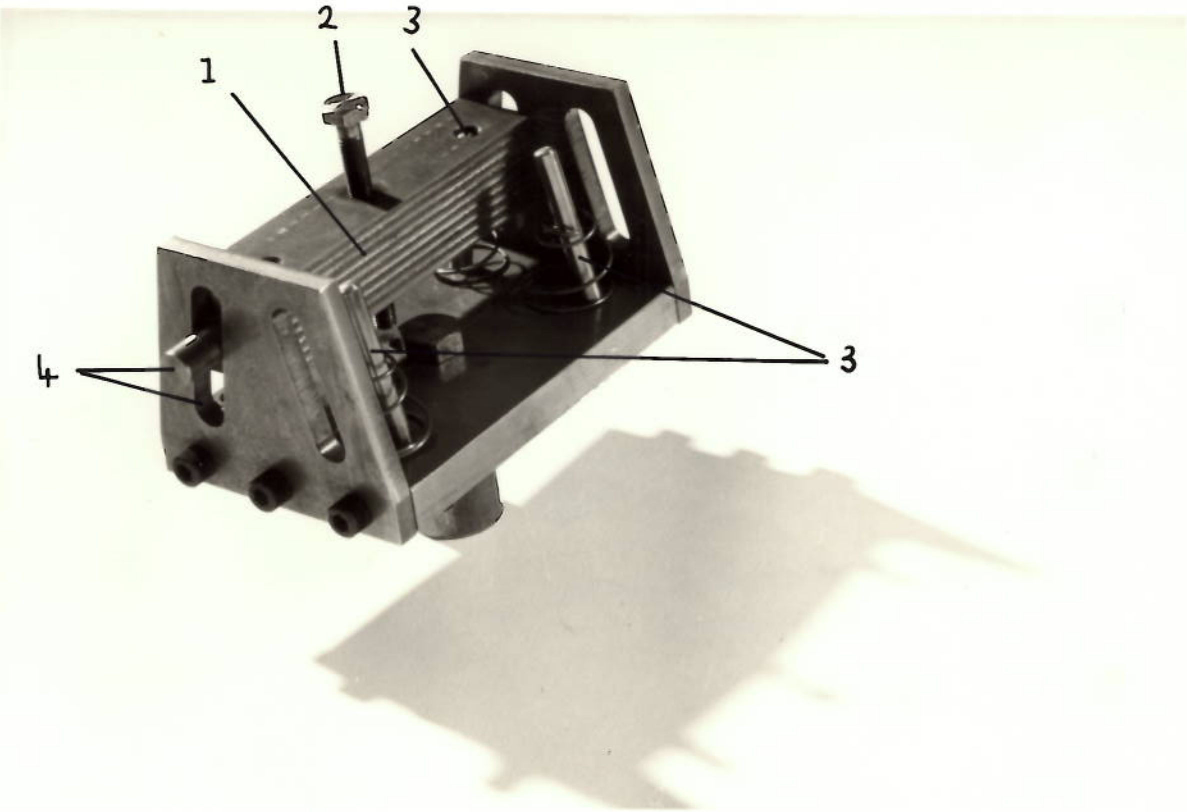

Figure 2. The hot-drawing machine grip construction. (One of the grip faces removed).

1, grooved grip face; 2, threaded bolt;
3, grip anti-rotation guide 4, main grip guide.

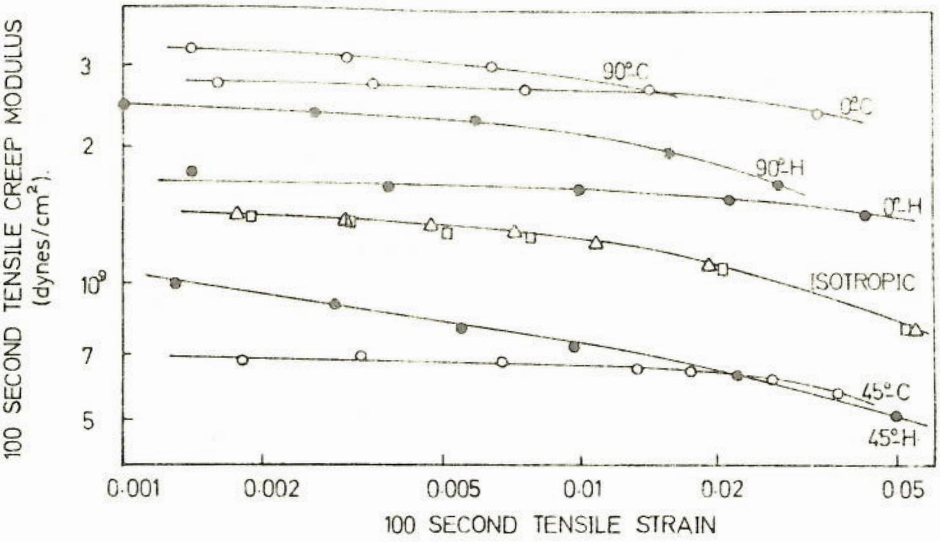

FIG. 3. Variation of 100 second tensile creep modulus with 100 second tensile strain for isotropic and anisotropic polyethylene.
(H= hot-drawn C=cold-drawn).

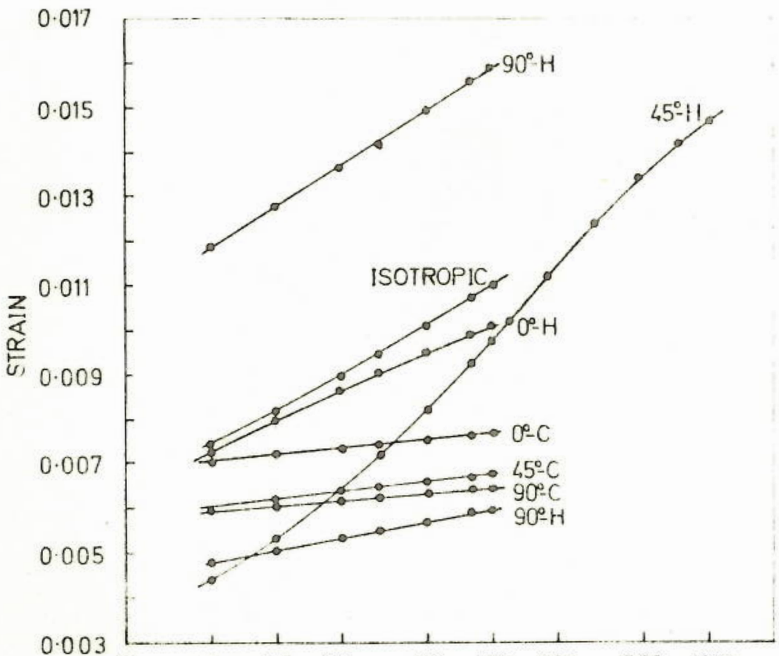

FIG. 4 Variation of tensile strain with time for isotropic and anisotropic polyethylene, in the low strain region.
(H= hot-drawn C= cold-drawn)

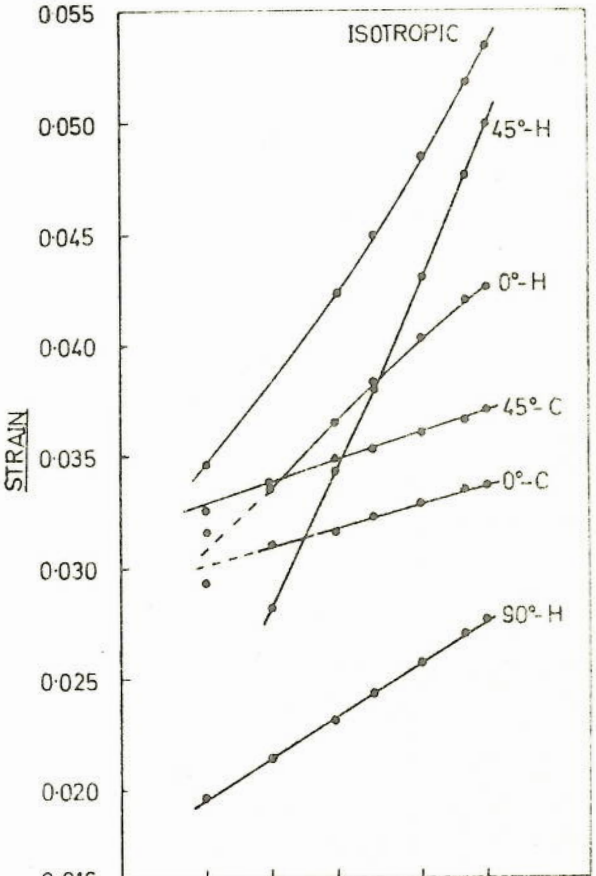

FIG 5. Variation of tensile strain with time for isotropi
and anisotropic polyethylene in the high strain reg
(H= hot-drawn C=cold-drawn).

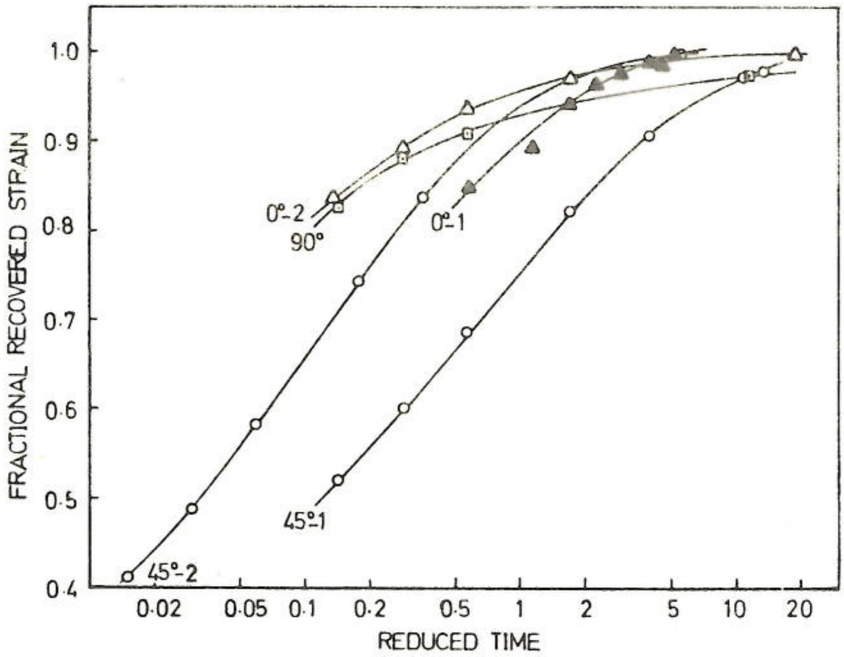

FIG 6. Recovery curves for hot-drawn polyethylene.
(See table 1 for the relevant experimental details).

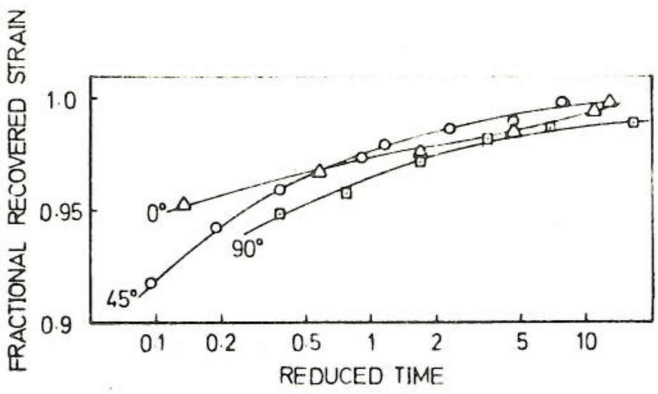

FIG. 7. Recovery curves for cold-drawn polyethylene.
(See table 1 for the relevant experimental details).