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The Mechanical Properties of Anisotropic Polymers

Progress Report No. 7

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A report of work carried out during the period 1st October, 1968 to 31st March, 1969.

Contents

Part I

General Developments

The major part of the period under review was devoted to a study of the tensile creep properties of isotropic and uniaxially oriented Perspex sheets (standard grade) using the three heavy-duty creep rigs mentioned in the previous Progress Report (No. 6. September, 1968). Measurements of lateral contraction were made simultaneously with the tensile strain measurements during most of the creep tests. The creep rupture behaviour and optical anisotropy of the oriented sheets were also studied in an attempt to present a more complete picture of the behaviour of the material. Some of the early results of this work have already been published and copies sent to the Ministry. (Darlington and Saunders, 1969). Details of the complete work will be found in part II of this report.

The two types of contraction extensometer described in Progress Report No. 5 were used during the Perspex studies and reasonable agreement was obtained between the results. The techniques required with the contraction devices were considerably improved during the period under review and the absolute validity of the contraction measurements is now more certain. Some comments on the general performance of the apparatus are given in section 2.8.4.

Part 2

Tensile Creep Properties of Isotropic and Uniaxially Oriented Polymethyl Methacrylate

2.1 Introduction

This study was undertaken to provide engineering data on polymethyl methacrylate (PMMA) in the isotropic and anisotropic states. Very little attention has previously been paid to the creep properties of oriented thermoplastics and this would appear to be the first systematic study on the tensile creep behaviour of uniaxially oriented PMMA.

Two grades of PMMA were provided by the Ministry of Technology for this project, but results on one of the grades only are available at present. These results are described and briefly discussed below. A detailed analysis of the results will be made when studies on the second grade have been completed.

The tensile creep data for the oriented material showed only a small degree of anisotropy. Creep rupture measurements were therefore carried out on the oriented material as marked anisotropy was detected during the machining of the test specimens.

Some of the early work on the oriented PMMA, including sample preparation and experimental details, has already been reported. (Darlington and Saunders, 1969). Parts of the paper are reproduced below for convenience. Details of some optical studies are also included.

2.2 Materials and Sample Preparation

The starting material for the preparation of the anisotropic sheets was I.C.I. 'Perspex' acrylic sheet with a nominal thickness of 0.25 inch. A sheet 23 cm. x 10 cm. was drawn at an extension rate of 6 cm./min. while totally enclosed in a hot air oven at 120°C. This will be referred to as sheet 'A'. The drawn sheet was allowed to cool to room temperature before being released from the grips. No contraction of the sheet was detected after the cold sheet had been released. A second sheet 21 cm. x 10 cm. was oriented using the same basic procedure but with an extension rate of 13 cm./min. and a temperature of 140°C. This will be referred to as sheet 'B'. Sheet 'A' had a draw ratio of 3.1 and a birefringence of 0.00094 while sheet 'B' had a draw ratio of 2.8 and a birefringence of 0.00056. (The draw ratio was measured by means of a grid drawn on the sample prior to stretching. The birefringence was measured using a Berek compensator).

Dumbell tensile creep specimens were machined from sheet A at angles of 0°, 45° and 90° to the draw direction. The overall length varied between 5 cm. and 6.6 cm. depending on the angle. (Smallest specimens at 90°). This gave parallel test sections of at least 2.3 cm.; gauge lengths of approximately 1.7 cm. being used on the smaller specimens.

The creep rupture specimens were machined from sheet B to the pattern shown in Progress Report No. 2 (figure 3.1). (Also given in figure 1 of above-mentioned paper).

2.3 Optical Properties of the Oriented Sheets

2.3.1 Distribution of Orientation

In the ideal case, the hot drawn sheet should possess a plane of optical isotropy perpendicular to the draw direction and have constant birefringence across its width and thickness. The purpose of this study was to look for deviations from the ideal case.

The apparatus consisted of a Babinet compensator mounted between crossed polarisers in the standard arrangement for the measurement of optical phase differences. White and sodium yellow light sources were used.

The transversely isotropic nature of the material was confirmed by examining a 90° specimen cut from the anisotropic sheet A, with the light beam incident at 90° to the specimen side (travelling through the specimen parallel to the sheet surface). In the Babinet system there was less than one-fifth of a fringe variation across the entire field of view with no significant edge effects. (The specimen occupied approximately one-half of the field of view).

The distribution of orientation across the specimen thickness was examined using a 0° specimen cut from sheet A, with the light beam incident at 90° to the specimen side and parallel to the sheet surface. Details of the field of view for white light are shown in figure 1. Only the zero order black fringe pattern is shown for simplicity. It will be seen that the birefringence is constant over the central part of the specimen thickness, the breadth of this region being approximately equal to two-thirds of the sheet thickness. On either side of this region the birefringence rises in a reasonably linear manner towards the sheet surfaces. However the maximum value of the birefringence, at the sheet surface, is only 18% above that in the central region. Thus, on average, there is one-third of the specimen thickness with a birefringence 9% higher than the remainder. As the birefringence was constant across the width of the specimen, the material is not exactly transversely isotropic. However in view of the small variation of modulus with draw ratio (birefringence) reported below the material may be regarded as transversely isotropic without introducing any significant error.

The variation of the degree of molecular orientation across the sheet thickness is probably due to the variation in cooling rate through the sheet after the hot-drawing process, as relaxation of the oriented molecules can occur reasonably quickly at temperatures near the drawing temperature. As the temperature is lowered the remaining orientation is 'frozen-in'. The relatively slow cooling rate at the centre of the sheet thickness thus allows more time for relaxation to occur there than at the sheet surface. Drawing the sheets at a lower temperature should reduce the magnitude of the variation across the sheet thickness, as at the lower temperature the relaxation time will be increased to a point where the time to reach the 'freezing temperature' will be too short for a significant loss of orientation to be produced anywhere through the sheet. Practical difficulties and material properties control the choice of a lower temperature.

2.3.2 Degree of Orientation

The birefringence of the drawn sheets was taken as an indication of the degree of induced molecular orientation. A Berek compensator mounted in a polarising microscope was used to measure the birefringence of six sheets, drawn at various temperatures. The variation of birefringence with draw ratio is shown in figure 2. For the sheets drawn at 140°C there would appear to be a linear relation between birefringence and draw ratio over the limited range investigated. By comparing the measurements made on the sheets drawn at different temperatures it will be seen that, for a given draw ratio, birefringence increases as drawing temperature decreases. This is almost certainly a consequence of the increased relaxation of the oriented molecules which can occur at the higher temperatures, both during the drawing process and immediately afterwards (i.e. before the specimen has cooled sufficiently to freeze the orientation).

2.4 Tensile Creep Apparatus

The tensile creep tests were carried out using the heavy-duty creep rigs and extensometers described in detail elsewhere. (Darlington and Saunders, 1969. Progress Report 4, 5, 6). Measurements of lateral contraction were made with either the single-transducer or the two-transducer contraction devices for comparison purposes. Vibrators were used on all the extensometers.

2.5 Experimental Procedures

All the creep and creep rupture measurements were made in a room with the temperature controlled at 20.2 ± 0.7°C and a relative humidity of (50 ± 5)%. The specimens were always stored in the room for at least several days prior to test.

2.5.1 Creep Measurements

The tensile creep behaviour of the anisotropic and isotropic specimens was initially examined in the strain range 0.1% to 3% using a procedure based on that described elsewhere for obtaining isochronous stress-strain curves. (Turner, 1963). The creep time varied between 100 seconds (extension measurements only) and 120 seconds (extension and contraction measurements). In most cases the recovery behaviour on removal of the creep load was also recorded and the next creep load was not applied until the recovery appeared to be virtually complete. The long-term creep tests were always carried out after several 100 second tests at lower stresses. A long-term creep test or a new isochronous stress-strain run was never started until stability of the initial 'zero' was achieved.

2.5.2 Creep Rupture Measurements.

Simple lever loading machines were used to apply the loads to the creep rupture specimens. (See Progress Report No. 3). Electronic timers operated by microswitches resting against the lever arms were used to determine the time to failure. No measurements of deformation were made. The nominal stress was calculated using the area of cross-section at the narrowest part of the specimen test section, prior to test.

2.6 Tensile Creep Results

2.6.1 Isochronous Tests.

The variation of the applied tensile stress with the tensile strain after 100 seconds of creep for isotropic and anisotropic PMMA is shown in figure 3. Each curve is based on the results obtained on a single specimen using the standard isochronous test procedure. A linear material would give a line of unit slope on such a log-log plot (dashed line in figure 3). If a selected stress value is divided by its associated 100 second strain, a 100 second tensile creep modulus is obtained. The variation of this modulus with the 100 second tensile strain, for all the specimens tested, is shown in figure 4. A linear material would give a line parallel to the strain axis on this type of plot. It will be seen from figures 3 and 4 that the isotropic and anisotropic specimens show deviations from linear behaviour above a tensile stress of approximately 0.2%; the non-linear behaviour being similar for all specimens. The modulus results of figure 4 also indicate that the degree of anisotropy of the creep modulus is relatively low, the variation of modulus with angle being only 20% at low strains.

The results given in figure 4 illustrate the magnitude of the scatter of results obtained at present. Thus at a tensile strain of 0.5% the total spreads in the results for the isotropic and the 0° and 90° anisotropic specimens are 4.5%, 5.7% and 3.5% respectively. As some of the early specimens were not prepared to the high standards achieved later in the programme the above scatters are considered to be very satisfactory. Recent improvements in the specimen preparation technique and refinements to the creep rigs (better alignment, improved specimen clamps and hooks) should reduce this scatter even more. However there will always be some scatter, especially with anisotropic specimens, due to inter-specimen (material) variability.

The variation of the 100 second creep contraction ratio, ν_t, with the 100 second tensile strain, for the isotropic and anisotropic PMMA is shown in figure 5. ν_t is defined as the ratio of the lateral strain in the thickness direction to the longitudinal strain at the same instant of time, during a tensile creep test. All of the results obtained so far are included in figure 5 although some may be suspect due to faulty specimens or poor alignment. Despite this the results are very promising, the largest spread in ν_t at a 100 second tensile strain of 0.01 being only 8% (i.e. ± 4% about a mean value). Within the limits of the experimental error, ν_t for the anisotropic material appears to be independent of angle and equal to the value for the isotropic material. At 1% tensile strain the present results suggest a value for ν_t at 100 seconds of 0.365 ± 0.015 for the materials. There appears to be a slight increase of ν_t with strain.

2.6.2 Long Term Tests.

For most of the long-term creep tests, stresses were chosen that would give 100 second tensile strains in the region of 0.5% or 1%. The lateral and longitudinal strains were usually measured during each creep test. The variation of tensile strain with time for the isotropic and anisotropic PMMA is shown in figure 6. At the lower strain level (i.e. approximately 0.5% at 100 seconds) the curve for a 0° anisotropic specimen was identical to that shown for the 90° specimen. Thus at low strains and creep times of at least 10^4 seconds, the shapes of the tensile creep curves of the isotropic and anisotropic (0° and 90°) specimens are identical. However, at the higher strains (i.e. approximately 1% at 100 seconds) significant differences are apparent between the three creep curves after a creep time of 10^3 seconds. Of particular interest is the fact that the 0° anisotropic specimen creeps faster than the isotropic specimen. After 10^3 seconds the 90° anisotropic specimen has the highest creep rate. Further measurements are obviously needed to confirm these observations.

Quantitative observations of crazing were not made during these creep tests. However it was noted that both the isotropic and 90° anisotropic specimens exhibited crazing by the end of the creep runs at the higher strains; the effect being greatest for the 90° specimen. The 0° specimens did not exhibit any noticeable crazing at any stress or time.

The variation of the lateral strain with time for the various specimens is shown in figure 7. The labels on each curve may be used to compare each lateral curve with its associated longitudinal curve given in figure 6. The lateral strain of a 0° anisotropic specimen at low strains has not yet been measured. The results at the lower strains show little significant difference between the isotropic and the 90° anisotropic specimens. However at higher strains the pattern of behaviour is similar to that found for the tensile strain.

The lateral and longitudinal results of figure 6 and 7 may be combined to give the variation of the lateral contraction ratio with time. The variation of the ratio, ν_t, with time at the higher strains is shown in figure 8. The lower strain data are omitted for the sake of clarity as scatter in the results tended to mask the true variation of ν_t with time. It will be seen from figure 8 that at the higher strains the curves exhibit the same shape within the limits of experimental error.

2.6.3 Recovery

Examples of the tensile recovery behaviour of the isotropic and anisotropic PMMA specimens are given in figure 9. The fractional recovered tensile strain is defined as

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

The creep time preceeding the recovery was 120 seconds for all the data illustrated. Several points emerge from these results.

(i) All the specimens recovered 99% of the final creep strain within a recovery time equal to 10 times the creep time, for final creep strains of up to 1.5%.

(ii) Recovery time increases with the final creep strain.

(iii) There is no significant difference between the recovery behaviour of the anisotropic and isotropic specimens when curves obtained after the same final creep strain are compared.

The recovery behaviour of the lateral strain after 120 second creep tests has also been studied. Details of these results and some recovery data obtained after the long term creep tests will be given in the next report.

2.7 Creep Rupture Results

Specimens machined from oriented sheet B at angles of 0°, 45° and 90° to the draw direction were used. The applied tensile stresses were chosen to give rupture times of up to 10^4 seconds. The variation of applied (nominal) stress with time-to-rupture for the anisotropic PMMA specimens is shown in figure 10. The horizontal lines at short times indicate the uncertainty in the time to rupture due to the time taken to apply the large loads. It is apparent from figure 10 that, for short times at least, the creep rupture behaviour is highly anisotropic. Thus for a life-time of 1000 seconds there is a spread of 60% in the applied stress values. The slopes exhibited by the three lines in figure 10 suggest that the anisotropy decreases at lower stresses (longer life-times).

When comparing the degrees of anisotropy of the modulus and creep rupture life it must be remembered that the modulus measurements were obtained for sheet A (birefringence = 0.00094) while the rupture specimens were machined from the less oriented sheet B (birefringence = 0.00056).

2.8 Discussion

2.8.1 Degree of Anisotropy

The results of the creep trials suggest that the mechanical behaviour of drawn Perspex is not particularly anisotropic at low stresses (100 second strains of 0.005) for a wide range of creep times. Furthermore the 100 second modulus results at higher stresses (3×10^8 dynes/cm.^{2}) also show a low anisotropy. However the creep curves at higher stresses show significant deviations in behaviour after 1000 seconds and the creep rupture behaviour (stresses of 5 to 12 x 10^8 dynes/cm^2) shows considerable anisotropy at short times. Thus although in the first instance it may appear safe to ignore anisotropy when producing or using creep data obtained on isotropic or uncharacterised samples of PMMA it must be remembered that extrapolation to very long times (i.e. 1 year) is uncertain and could easily lead to excessive strains or even premature failure. However it must also be remembered that the present samples were deliberately rendered anisotropic. If the degrees of orientation occurring in finished articles are low then it may well be safe to ignore the effects of anisotropy in PMMA. Examination of finished articles and long term creep data (> 3 months) at normal service stresses is obviously necessary.

It is tempting to regard the behaviour of PMMA as typical of glassy polymers. Cheatham and Dietz (1952) showed that uniaxial orientation in polystyrene increased the tensile modulus by only 25% while the tensile strength was more than double the isotropic value. (Oriented specimens tested in draw direction only). Studies on a range of polymers should prove interesting and useful. (See also Darlington and Saunders, 1969).

The data described here lead to the conclusion that uniaxial orientation in PMMA is not normally desirable as the poor performance of the material in the 90° direction more than outweighs the increase of stiffness in the 0° direction. It appears that biaxial orientation is considerably more beneficial although care must be exercised to prevent separation of the sheet into the layers. (See Nielsen, 1962, p. 244).

2.8.2 Creep Rates.

It is apparent from figure 6 that the creep rates of the 0° and 90° anisotropic specimens are higher than that for the isotropic material. For the 0° specimen at least, this is surprising at first sight. However it can be shown that if the material obeys Nutting's creep equation, an increase in creep rate with orientation would be expected if the mechanical damping also increased. (See Nielsen, 1962, p.208). This requires further investigation. It is of interest here to note that Cheatham and Dietz (1952) found that uniaxial orientation increases the rate of stress relaxation in polystyrene. (Specimens tested in the 0° direction only).

2.8.3 Volume Changes.

The creep data given in figures 6 and 7 may be combined to give the variations of volumetric strain with time during tensile creep for the isotropic and anisotropic (0°, 90°) PMMA specimens. The results given in figure 11 have been calculated from the higher strain (1%) creep data. The volumetric strain has been taken to be given by $\epsilon_\ell + 2\epsilon_t$ where ϵ_ℓ and ϵ_t are the longitudinal and lateral strains respectively. (ϵ_t is negative). For the purposes of determining curve shapes the error in the volumetric strains is probably ± 4%. The absolute error could of course be greater than this. For the isotropic and 0° anisotropic specimens, it is apparent from figure 11 that, to a first approximation, there is an instantaneous volume increase on application of the stress followed by creep at constant volume. For the 90° anisotropic specimen the same pattern is observed up to 10^4 seconds, but this is then followed by a further gradual increase of volume strain with time. This effect is almost certainly associated with the onset of crazing, and may prove to be a useful tool in further studies.

The variation of lateral strain with longitudinal strain during creep is shown in figure 12. The slopes of the lines for the isotropic and 0° anisotropic specimens are 0.50 ± 0.01, while the slope for the 90° specimen is only 0.46 ± 0.01.

2.8.4. Performance of Apparatus and Comparison with Other Work.

The tensile creep and lateral contraction behaviour of isotropic Perspex has recently been studied by McCammond (1968). He was able to use large samples which greatly reduced the problems of strain measurement. It is therefore useful to compare his data with our results on small isotropic Perspex specimens.

For 100 second tensile strains of 0.45% and 0.93% McCammond's data give 100 second creep moduli of 3.1 and 2.97 x 10^{10} dynes/cm^2 respectively. These values are within 2% of our mean values at the corresponding strains. (See figure 4). Even better agreement may be obtained if we use the true stress and true strain definitions used by McCammond.

McCammond gives a value of 0.39 for the 100 second creep contraction ratio, independent of strain. Our results give a value of 0.365 ± 0.005 at a tensile strain of 1%; with a slight increase in the ratio with increasing strain. The results of figure 5 show that there is no significant difference between the results obtained with the single-transducer and double-transducer contraction devices used during our creep tests.

In addition to the above isochronous comparisons, no significant differences appear to exist between our data on the variations of tensile and lateral strain with time and the corresponding data given by McCammond.

The above comparisons therefore provide a useful check on the reliability of the present creep apparatus.

References

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No. 2 - October, 1966. CoA Memo. No. 115.
No. 3 - March, 1967. CoA Memo. No. 123.
No. 4 - September, 1967. CoA Memo. No. 135.
No. 5 - March, 1968. CoA Memo. No. 151.
No. 6 - September, 1968. CoA Memo. No. 163.

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McCammond, D. (1968). Ph.D. Thesis. Queen's University, Belfast.

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Turner, S. (1963). Trans. and J. Plastics Inst. 31, 60.

Figure Captions

Figure 1.	Fringe pattern across the thickness of an oriented PMMA sheet. Babinet compensator, white light. (T = sheet thickness, x = fringe spacing).
Figure 2.	Variation of birefringence with draw ratio for hot-drawn PMMA.
Figure 3.	Variation of tensile stress with 100 second tensile strain for isotropic and hot-drawn PMMA. (--- gives slope of line for linear behaviour).
Figure 4.	Variation of tensile creep modulus with 100 second tensile strain for isotropic and hot drawn PMMA (I = isotropic).
Figure 5.	Variation of 100 second creep contraction ratio, ν_t, with 100 second tensile strain for PMMA
Figure 6.	Tensile strain-time curves for various specimens cut from isotropic (I) and hot-drawn PMMA sheets.
Figure 7.	Lateral strain-time curves for various specimens cut from isotropic (I) and hot-drawn PMMA sheets.
Figure 8.	Variation of contraction ratio, ν_t, with time for isotropic (I) and hot-drawn PMMA. (Tensile strains of 1% at 100 seconds).
Figure 9.	Tensile recovery data for isotropic and hot-drawn PMMA (Creep time, T = 120 seconds in all cases). (Numbers in brackets indicate approximate creep strain prior to recovery).
Figure 10.	Creep rupture behaviour of hot-drawn PMMA (Drawing temperature = 140°C. Draw ratio = 2.77).
Figure 11.	Variation of volumetric strain with time for isotropic and hot-drawn PMMA. (Derived from creep tests with 1% tensile strain at 100 seconds).
Figure 12.	Variation of lateral strain with longitudinal strain during creep for isotropic and hot-drawn PMMA.

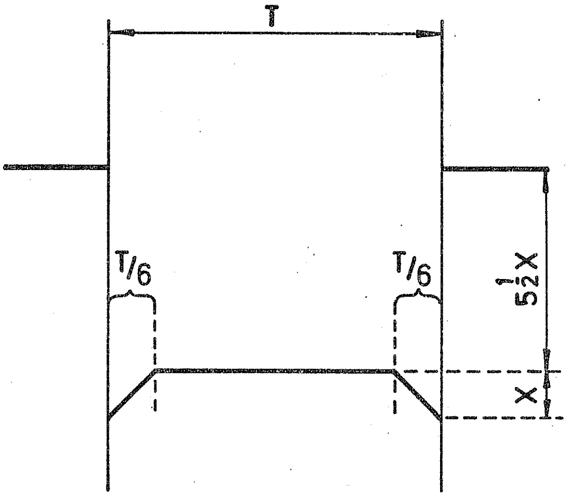

FIG. 1

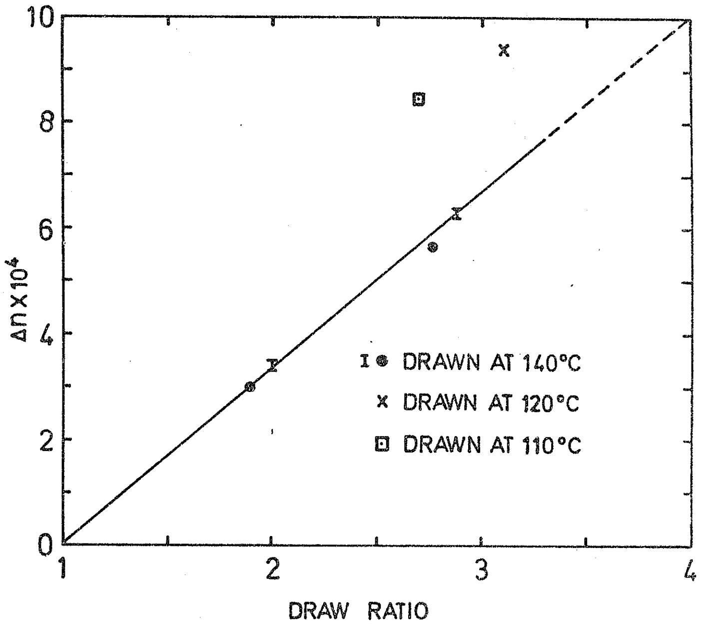

FIG. 2.

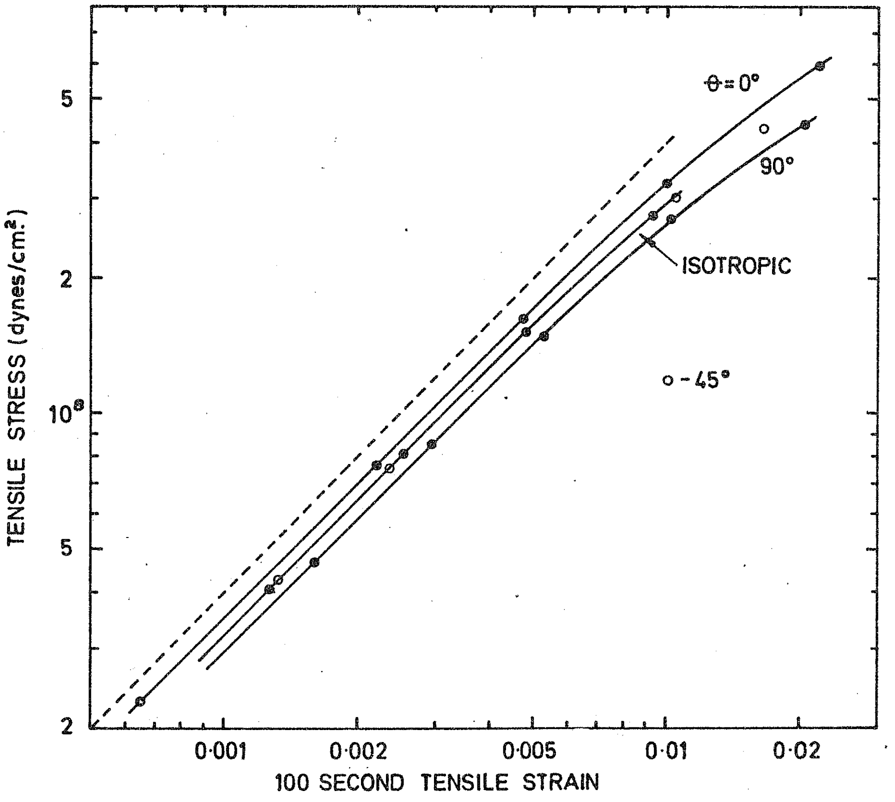

FIG. 3

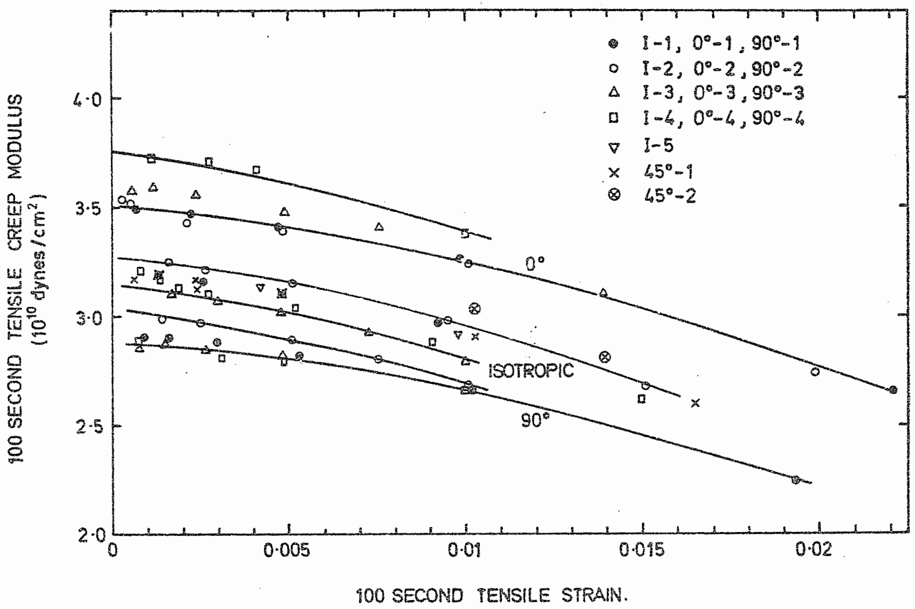

FIG 4

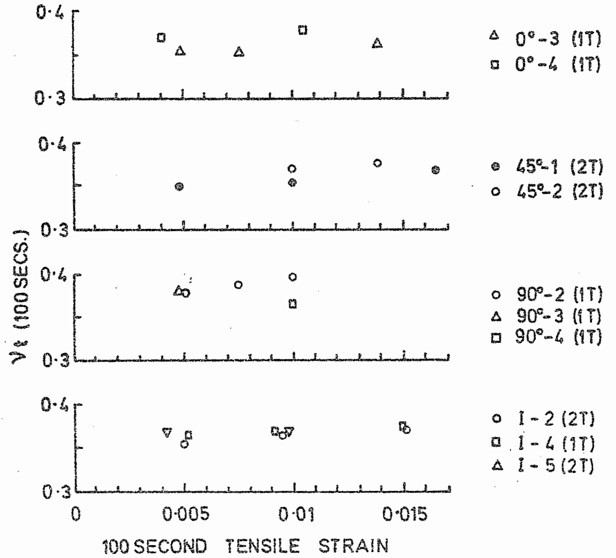

FIG.5

1T - SINGLE TRANSDUCER
2T - DOUBLE TRANSDUCER } CONTRACTION DEVICE

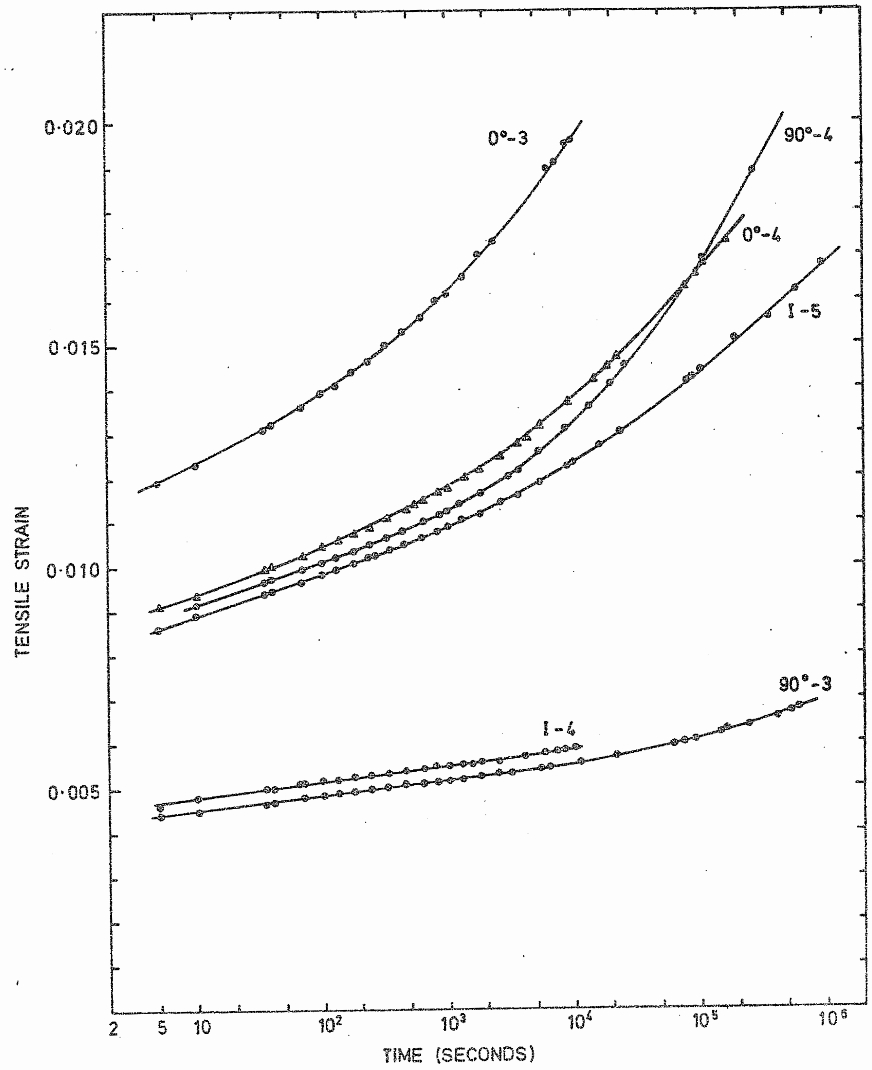

FIG. 6

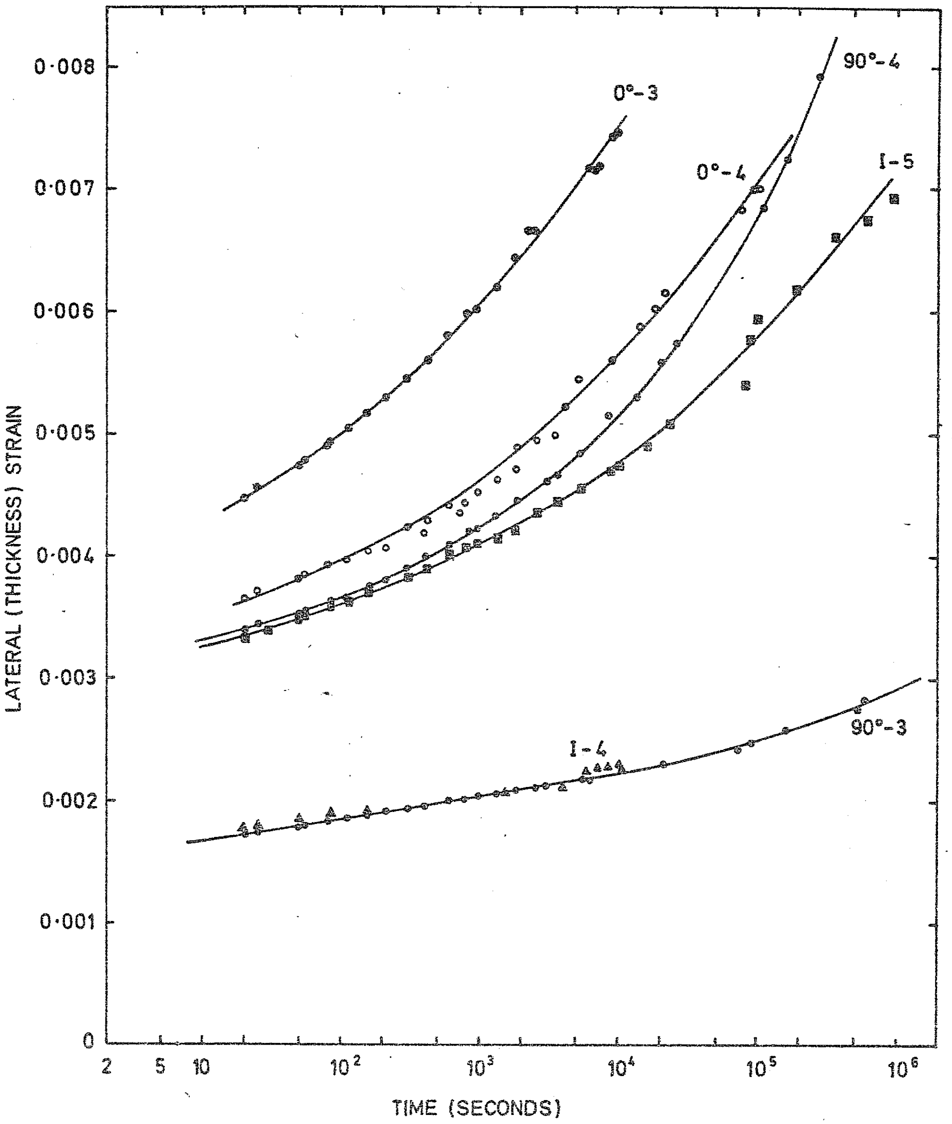

FIG.7

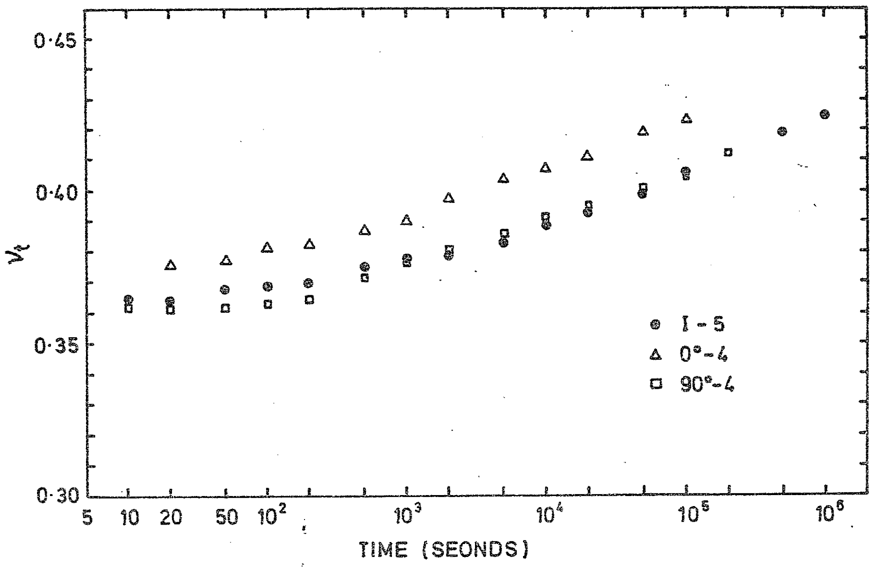

FIG. 8

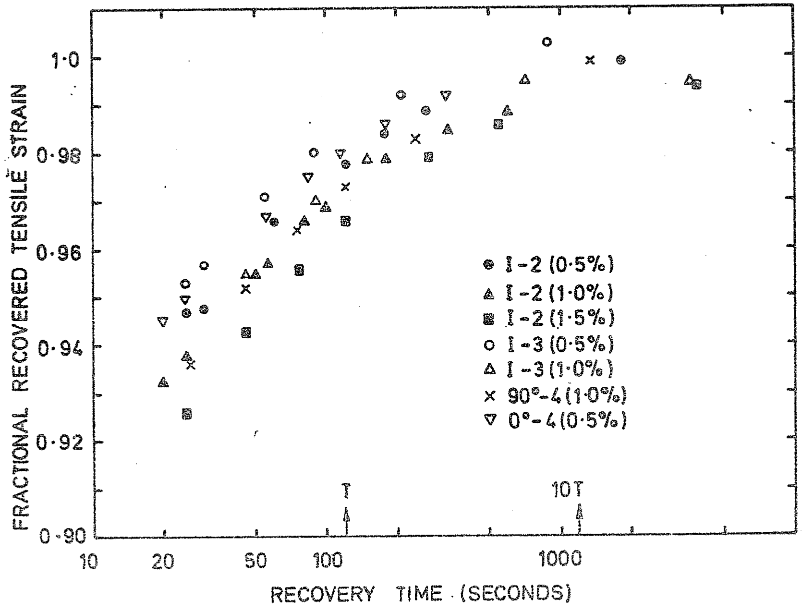

FIG. 9

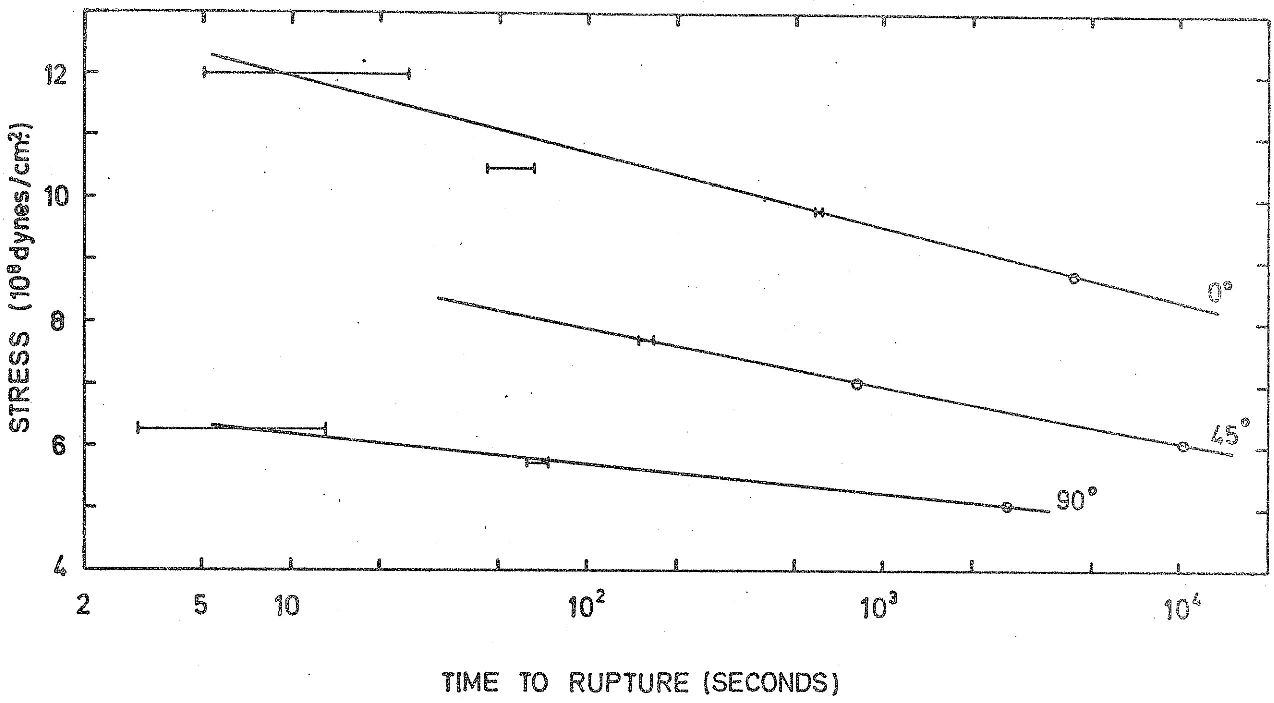

FIG. 10

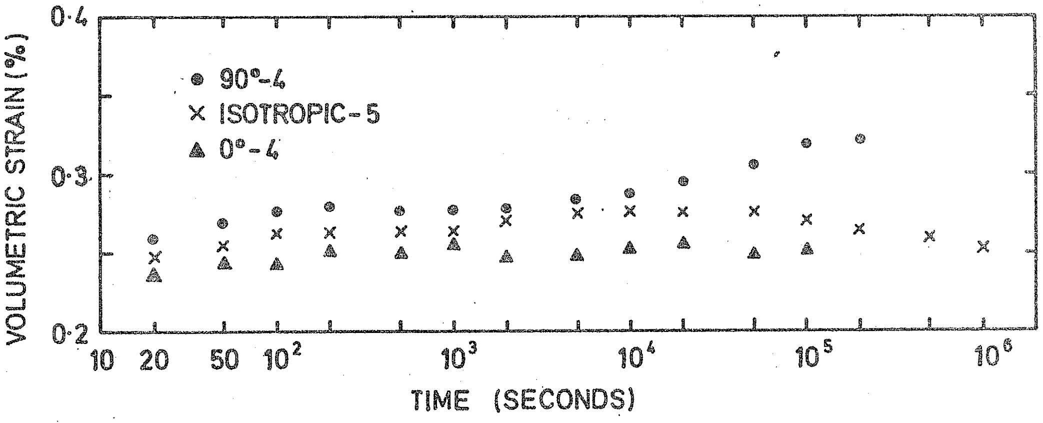

FIG.11

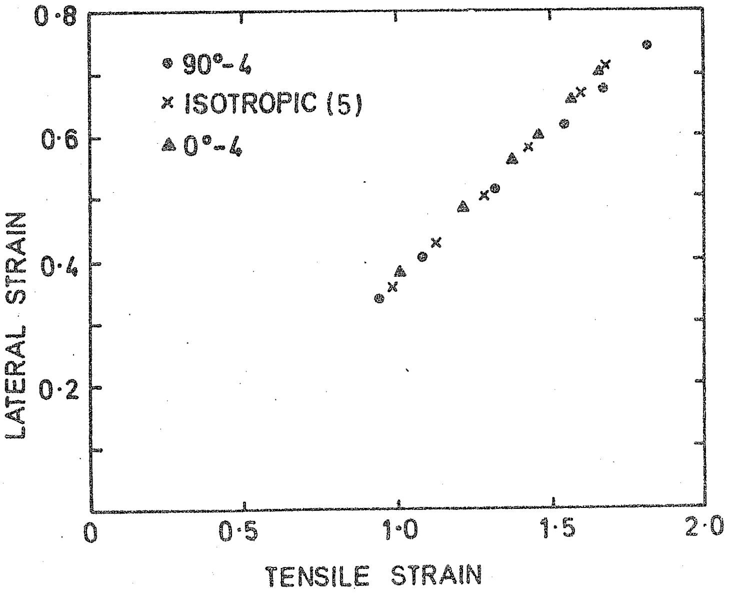

FIG. 12