

"The Time-Dependent Behaviour of Anisotropic Low Density Polyethylene"

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SYNOPSIS

Low density polyethylene has been oriented into a state of transverse isotropy by cold-drawing an originally isotropic blank in uniaxial tension, and the non-linear creep behaviour of the material has been completely characterised for the first time. The compliance matrix describing the deformation behaviour is characterised by five independent material parameters. Four of the parameters have been determined from uniaxial tensile creep experiments on specimens cut at 0° and 90° to the draw direction, and the fifth from torsional creep studies on a specimen cut parallel to the draw direction. The development and proof of experimental techniques for use with the respective apparatus have formed an important and necessary part of the work, and the accuracy and internal consistency of the results have been found to be excellent. Measurements of the compliances have been made at ten different degrees of anisotropy - measured by the draw ratio - over a range of strains from the pseudo-linear to the highly non-linear region.

The anisotropy of the deformation behaviour at a given draw ratio, and the trends of anisotropy with draw ratio, have been interpreted in terms of current structural knowledge. At low draw ratios the deformation is dominated by a c-axis shear mechanism and an inter-lamellar shear mechanism, and a relaxation mechanism has been discovered in specimens cut at 90° to the draw direction. At high draw ratios an inter-fibrillar shear mechanism is dominant in specimens cut at angles away from the 0° and 90° direction.

A simple engineering analysis of the results has examined the applicability of the formalisms of linear elasticity and visco-elasticity theory to the non-linear, anisotropic visco-elastic state. Also, the assumption of a constant volume deformation, which is commonly used in polymer science for the determination of the Poisson's ratio terms, has been investigated over the range of strains and compared with directly measured values. The measured values represent the first systematic study of Poisson's ratio in anisotropic polymers. The constant volume assumption is shown to be in error at all draw ratios.

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(ii) LIST OF PRINCIPAL SYMBOLS

a, b, c	Lengths of semi-axes of a rectangular cross-sectioned prism in the 1, 2, 3, directions respectively.
$\underline{a}, \underline{b}, \underline{c}$	crystallographic axes of the unit cell of polyethylene.
B	bulk compliance
D	torsional rigidity of a prism
E_{θ}	Young's modulus in the 3-2 plane of a sheet at an angle θ to the 3 direction.
$F(\xi_1, \xi_2)$	the equation to the boundary of the cross-section of a prism with respect to the $O\xi_i$ co-ordinate axes.
$f(x_1, x_2)$	the equation to the boundary of the cross-section of a prism with respect to the Ox_i co-ordinate axes.
G_{44}, G_{55}, G_{66}	the shear moduli governing laminar shear in the 2-3, 1-3, and 1-2 planes respectively.
$\bar{G}$	the effective shear modulus of an orthotropic rectangular prism.
$H(t)$	the Heaviside step function
i, j	dummy suffices taking the values 1, 2, 3, 4, 5, 6
I	moment of inertia of a cross-section.
K	Bulk modulus
l	measure of length
M	twisting moment
Ox_i	a right-hand set of mutually orthogonal reference axes
OX_i	a right-hand set of mutually orthogonal co-ordinate axes which define the symmetry directions of an orthotropic material.
S_{ij}	elastic compliances (contracted, two suffix).
t	time, and a measure of thickness

V_0, V_{90}	volume compliances of specimens cut at 0° and 90° to the symmetry direction of a transversely isotropic continuum.
w	a measure of width
α	angle of twist; also denotes a dominant transition in polyethylene.
$\gamma_{ij} (i \neq j)$	'engineering' shear strains
ϵ_{ij}	tensor strain components
e_i	'engineering' strain components
θ	angle of rotation
ν	Poisson's ratio
σ_{ij}	tensor stress components
σ_j	stress components (contracted)
$\tau_{ij} (i \neq j)$	shear stress components

SECTION 1. INTRODUCTION

In recent years there has been an increasing amount of systematic data collection in order to characterise the mechanical properties of many isotropic polymers for engineering design purposes. Also a substantial research effort has been expended in an attempt to interpret these properties in terms of deformation mechanisms involving basic polymer morphology. The work reported in this thesis is a contribution to these rapidly growing areas of interest, and is concerned with the complete characterisation of the non-linear anisotropic visco-elastic behaviour of low density polyethylene, and the interpretation of the anisotropy of properties in terms of current structural knowledge. An extensive analysis of the anisotropic state has not been reported previously.

Structural studies of crystalline polymers have identified the basic structural units and attempts have been made to describe their aggregation in the bulk crystallized polymer. The unit cell and the chain configuration in the crystalline region of many polymers has been determined by Bunn and co-workers, and Natta and co-workers. (See, for example, a review by Geil, 1963). Up to the early 1960's the so-called "fringed-micelle" model was used to describe the aggregation of crystalline units in the bulk polymer. However, advances in polymer chemistry and manufacturing techniques led to new stereo regular polymers which crystallized with high degrees of crystallinity. (See, for example, a review by Gee, 1960). Experimental investigations with these newer polymers highlighted the deficiencies in the fringed micelle concept of crystallinity, (Stein, 1966), and alternative models were necessary. The most significant observation was of thin platelets of single crystals of polyethylene deposited from a dilute solution of polyethylene in Xylene (e.g. Keller, 1957). From subsequent research, models of polymer crystallinity are evolving which describe the aggregation of lamellae in the bulk, and supersede the old "fringed-micelle" model. (Peterlin, 1969). Concurrent with these investigations attempts have been made to relate mechanical (and electrical) properties to the structure. The mechanical properties are usually measured at low strains, less than 0.1%, and are generally derived from oscillatory loading experiments designed to measure dynamic energy loss peaks. The loss peaks indicate the main transitions which are related to the structure and may be interpreted in molecular terms. The limitation of the work reported so far is that the deformation is studied at low strains and concentrates on the isotropic state. Polymers may be usefully employed at much higher strains (up to 5%) and are usually oriented and thus anisotropic in their mechanical properties. In the isotropic state the structure is not easily identifiable and since 1967, some workers have studied the anisotropic state in an attempt to simplify the morphology. The transitions in cold drawn and specially textured sheets of low density polyethylene have been reported by Ward and co-workers (see, e.g. Gupta

and Ward, 1967). However, these studies were also limited to the low strain region. The structural studies reported here have investigated cold drawn low density polyethylene (L.D.P.E.) at different degrees of anisotropy over a wide range of strains in the range 0.1% to 5.0% strain. The variation of the anisotropy of properties with degree of anisotropy have been interpreted in terms of current structural knowledge. A discussion of the whole field of polymer structure, mechanical loss transitions, and other mechanical properties is beyond the scope of the current text. However, a cross-section of the reported literature is reviewed in Sections 3 and 4, which adequately describes the aspects relevant to an understanding of the predominant morphological features in polyethylene, and the interpretation of the dominant transitions in terms of deformation mechanisms and their postulated molecular origins in both the isotropic and anisotropic states.

Concurrent with the above structural studies the field of engineering with polymers has grown rapidly in importance. Industrial organisations have attempted to systematically evaluate the stiffness behaviour of the high tonnage polymers and characterise the properties important for polymer engineering design. The stiffness behaviour has been determined over a range of strains up to 5% or more. A design for stiffness philosophy has emerged for isotropic polymers which has enabled successful designs in load bearing applications. Of necessity, standard methods of data collection and presentation have been developed which are based, in general, on deformation in uniaxial creep (see, for example B.S. 4613). These methods have evolved mainly from the efforts of Turner and co-workers (see, for example, Dunn, Mills, Turner, 1964). More recently the same workers have developed a uniaxial creep compression apparatus which works over the above strain range (Thomas, 1969), and a shear and flexure apparatus for the evaluation of Poisson's ratio at low strains (0.1%) (Bonnin, Dunn and Turner, 1969). The work has been concerned primarily with relatively large specimens in the isotropic state. However, many of the commercial applications of polymers involve the utilization of the anisotropy of the properties. By orienting the polymer parallel to the direction of greatest anticipated stress, the anisotropy is utilized in fibers and films. Also, in the majority of plastics moulding processes anisotropy of mechanical properties is accidentally introduced by orientation of the melt in injection mouldings or extrusions, or in the orientation inherent on vacuum forming a product. Often the orientation in these latter cases may have deleterious effects on properties and result in premature failure. No systematic studies have been reported on the anisotropic state in polymers and only recently has this topic received attention. In our laboratories a uniaxial tensile creep apparatus has been designed to work with non-rigid and rigid - anisotropic polymers. (Darlington and Saunders, 1970).

The extensometry simultaneously monitors the longitudinal and lateral strains, over a wide range of strains (exceeding 5%), and thus permits the calculation of the Poisson's ratios in these materials for the first time. (Since the start of this thesis in 1967 another apparatus has been reported which has been used to measure the Poisson's ratio in isotropic polymers over a wide range of strains, McCammond, 1967). One aim of the work reported here was to determine the range of application of the apparatus and develop techniques which gave consistent and reproducible values of the Poisson's ratio terms. (Section 5). The engineering features of the results were designed to:-

1. characterise, for the first time, the stiffness compliances describing a non-linear anisotropic visco-elastic polymer, and determine ways for suitable data presentation.

2. to examine a simple engineering approach to anisotropic visco-elasticity in the pseudo-linear and non-linear regions.

The formalisms of classical linear elasticity and visco-elasticity, which are used to describe anisotropy of stiffness behaviour, are presented and discussed in Section 2. However, the deformation behaviour is often non-linear and attempts are made to determine the cause of the non-linearities rather than examine the theoretical approaches currently in the literature. (Section 2.3). Low density polyethylene with transversely isotropic symmetry has been studied, and five compliance parameters are needed to characterise the stiffness matrix. Four of the five compliances are measured using the tensile creep apparatus and the fifth from torsional creep studies. The theory of torsion of anisotropic prisms is discussed in Section 2.4. A description of the apparatus and the techniques developed to improve accuracy and internal consistency are presented in Section 5. Details of specimen preparation may be found in Section 6.

The results presented in Section 7 give a complete characterisation of the non-linear anisotropic nature of drawn polyethylene at ten draw ratios, over a range of times and strains.

The analysis of results (Section 8) has enabled a discussion of the relationship between mechanical properties of drawn polyethylene in terms of current structural knowledge. In Section 9.1 four deformation mechanisms are postulated. A c-axis shear and inter-lamellar shear mechanism dominate the deformation at low draw ratios, and an anomalous contraction behaviour in 90° specimens also at low draw ratios has been observed. At high draw ratios inter-fibrillar shear is dominant. The non-linearities and volume changes occurring on deformation are analysed in Section 8.3 and 8.4 and are discussed in Section 9.1.

A simple engineering analysis has enabled the evaluation of the applicability of classical elasticity theory and the Boltzmann superposition integral to a non-linear anisotropic visco-elastic continuum and is discussed in Section 9.2. Often a constant volume deformation assumption is made in polymers to assign values to the Poisson's ratio parameters. The usefulness of this approach may now be examined by comparing measured values with constant volume data.

A summary of the findings is given in Section 10.

SECTION 2. THEORETICAL ASPECTS

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2.1 Linear Elasticity Theory

The constitutive equations relating stress, σ , and strain, ϵ , for linear elastic anisotropic continua are well documented (see, for example, Love, 1927, Nye, 1957, Hearmon, 1961, and Lekhnitski, 1963). Using matrix notation classical elasticity theory, (C.E.T.), relates stress and strain in the following way

$$\epsilon_i = S_{ij} \sigma_j \quad i, j = 1, 2, 3, 4, 5, 6 \quad 2.1$$

where the usual summation convention is denoted by the suffices i and j

and where ϵ_i is the strain matrix

σ_j is the stress matrix

and S_{ij} is the matrix of compliances

The form of the compliance matrix S_{ij} depends upon the degree of symmetry of the continuum. Typically, for orthotropic symmetry S_{ij} is of the form:-

$$S_{ij} = \begin{pmatrix} S_{11} & S_{12} & S_{13} & & & \\ S_{21} & S_{22} & S_{23} & & & \\ S_{31} & S_{32} & S_{33} & & & \\ & & & S_{44} & & \\ & & & & S_{55} & \\ & & & & & S_{66} \end{pmatrix} \quad 2.2$$

and the material is characterised (mechanically) by 9 independent elastic compliances, since:-

$$S_{ij} = S_{ji} \quad i \neq j \quad 2.3$$

A continuum with higher order mechanical symmetry, e.g. a transversely isotropic material, (so called fibre-symmetry), the S_{ij} are further reduced since the material has a plane of isotropy perpendicular to one of the principal directions. If the plane of isotropy is taken perpendicular to the 3-direction, (Figure 2.1) then 2.2 is reduced to:-

$$S_{ij} = \begin{pmatrix} S_{22} & S_{12} & S_{13} & & & \\ S_{12} & S_{22} & S_{13} & & & \\ S_{13} & S_{13} & S_{33} & & & \\ & & & S_{44} & & \\ & & & & S_{44} & \\ & & & & & S_{66} \end{pmatrix} \quad 2.4$$

$$\text{and } S_{66} = 2 (S_{11} - S_{12}) \quad 2.5$$

and the material is characterised by five independent elastic compliances.

The form of the constitutive equation given above (Equation 2.1), is investigated experimentally when the strain response, ϵ_i , to a given applied stress, σ_i , is determined and enables the evaluation of the compliances S_{ij} in 2.2 or 2.4. The compliance parameters for a transversely isotropic continuum are related to the more conventional moduli and Poisson's ratios as follows. (See Fig. 2.1).

$$S_{22} = S_{11} = \frac{\epsilon_{22}}{\sigma_2} = \frac{1}{E_{90}} \quad 2.6$$

$$S_{33} = \frac{\epsilon_{33}}{\sigma_3} = \frac{1}{E_0} \quad 2.7$$

$$S_{12} = S_{21} = \frac{\epsilon_{11}}{\sigma_2} = \frac{-\nu_{90}}{E_{90}} \quad 2.8$$

$$S_{13} = S_{32} = \frac{\epsilon_{11}}{\sigma_3} = \frac{-\nu_0}{E_0} \quad 2.9$$

$$S_{44} = S_{55} = \frac{2 \epsilon_{13}}{\tau_{13}} = \frac{\gamma_{13}}{\tau_{13}} = \frac{1}{G_{13}} \quad 2.10$$

$$S_{66} = \frac{2 \epsilon_{12}}{\tau_{12}} = \frac{\gamma_{12}}{\tau_{12}} = \frac{1}{G_{12}} \quad 2.11$$

where i ϵ_{22} and ϵ_{33} are axial strains of tensile samples subjected to axial stresses σ_2 and σ_3 .

ii ϵ_{11} is the lateral strain of tensile samples subjected to axial stresses σ_2 and σ_3 .

iii γ_{13} , γ_{12} are the shear strains in the 1,3 and 1,2 planes when subjected to shear stresses τ_{13} , τ_{12} respectively.

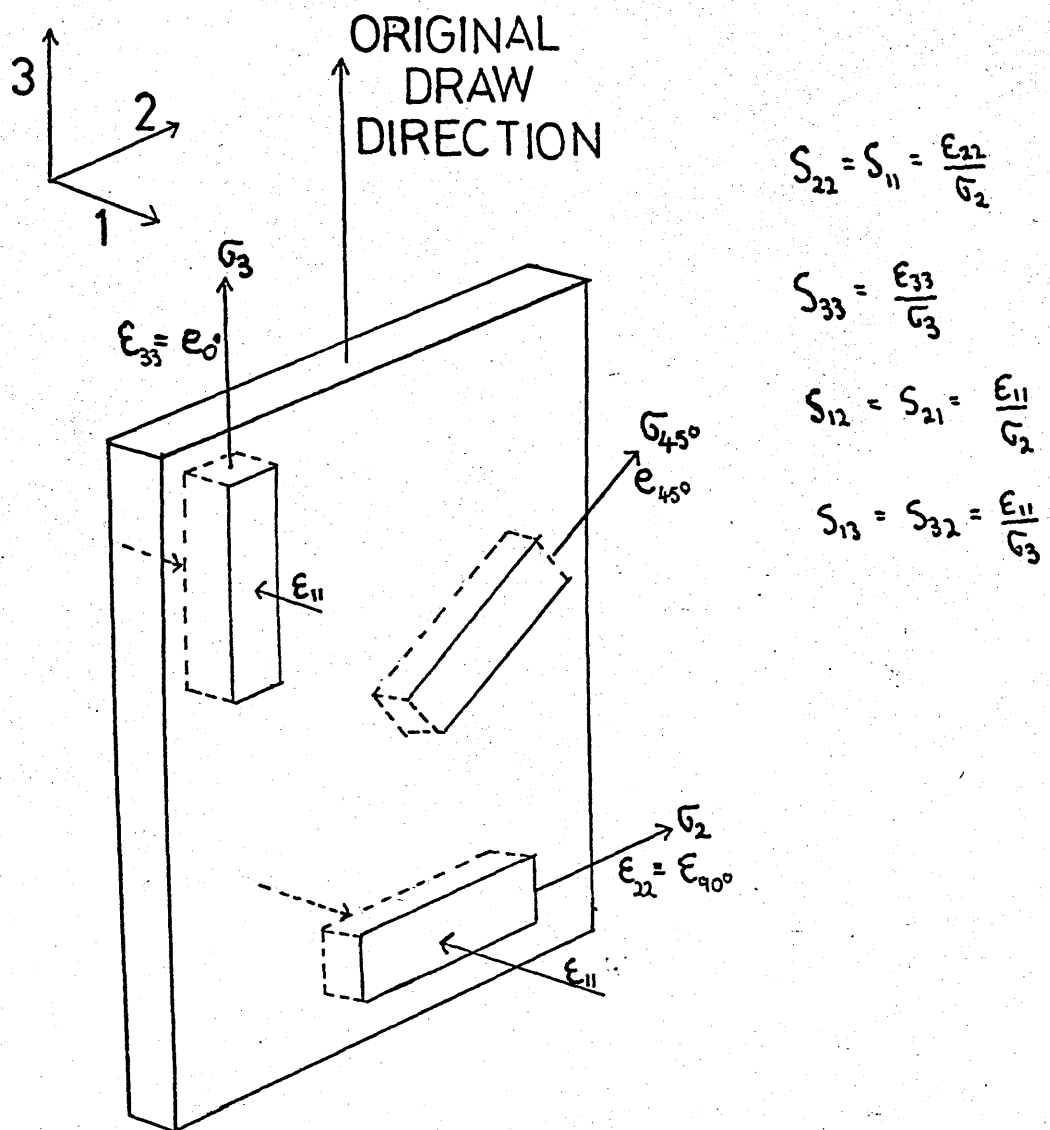


FIGURE 2.1 A Schematic representation of the components of the stress and strain matrices, and the compliance parameters from uniaxial tensile tests.

The longitudinal and contraction compliances S_{22} and S_{12} are obtained by taking specimens cut at 90° to the 3-direction, and the compliances, S_{33} and S_{13} from specimens cut parallel to the 3-direction (See Fig. 2.1). The shear compliances S_{44} and S_{66} are obtained from torsion experiments about the 3 direction and at 90° to the 3 direction respectively. In practice S_{44} is easy to determine since the laminar shear in the 1,3 and 2,3 planes is the same and is governed by the same shear compliance S_{44} . Thus S_{44} may be found directly. However, for 90° specimens laminar shear occurs in the 3,2 and 1,2 plane and the deformation is governed by S_{44} and S_{66} respectively. Hence the evaluation of S_{66} is more difficult. The subject of torsion of anisotropic prisms is dealt with and discussed in more detail in Section 2.4.

Volumetric compliances and the bulk modulus may also be defined. For a 0° specimen, the volume compliance, V_0 , is given by:-

$$V_0 = \frac{\text{volume strain for } 0^\circ \text{ specimen}}{\text{stress in the 3-direction}} = \frac{\epsilon_{33} + \epsilon_{11} + \epsilon_{22}}{\sigma_3} = S_{33} + 2S_{13} \quad 2.12$$

Similarly, for 90° specimens

$$V_{90} = \frac{\text{volume strain for } 90^\circ \text{ specimen}}{\text{stress in 2-direction}} = \frac{\epsilon_{22} + \epsilon_{11} + \epsilon_{33}}{\sigma_2} = S_{22} + S_{12} + S_{13} \quad 2.13$$

The bulk compliance, B , is given by:

$$B = (V_0 + 2 V_{90}) = S_{33} + 2S_{22} + 4S_{13} + 2S_{12} \quad 2.14$$

$$\text{and the bulk modulus, } K, = B^{-1} \quad 2.15$$

It may also be shown that in the elastic case the following inter-relationships between the parameters exist:-

$$S_{66} = 2 (S_{11} - S_{12}) \quad 2.16$$

$$S_{44} = \frac{4}{E_{45}} - S_{11} - S_{33} - 2S_{13} \quad 2.17$$

$$\text{and } \nu_{45} = -\frac{1}{2} E_{45} [S_{13} + S_{12}] \quad 2.18$$

where E_{45} ; and ν_{45} are the modulus and Poisson's ratio obtained from a tensile test on specimen cut in the 3,2 plane, the plane of the sheet, at 45° to the 3-direction (Fig. 2.1).

For the simplest anisotropic continuum, the case of transverse isotropy, five independent elastic compliances are necessary to define the compliance matrix. Such comprehensive data is not available in general and often simplifying assumptions are made to reduce the amount of evaluation work and simplify subsequent analysis. The most common assumption is that the deformation occurs at constant volume. For transversely isotropic media the following simplification is derived (see equation 2.12 and 2.13):-

$$S_{33} + 2S_{13} = 0 \quad 2.19$$

$$S_{22} + S_{12} + S_{13} = 0 \quad 2.20$$

which reduces the number of independent compliances to three, and gives the following "constant volume", c.v., values of the various parameters.

$$(S_{13})_{c.v.} = -\frac{1}{2} S_{33} \quad 2.21$$

$$(S_{12})_{c.v.} = -\left(S_{22} - \frac{S_{33}}{2}\right) \quad 2.22$$

$$(\mathcal{V}_0)_{c.v.} = 0.5 \quad 2.23$$

$$(\mathcal{V}_{90})_{c.v.} = \left(1 - \frac{S_{33}}{2S_{22}}\right) \quad 2.24$$

$$(S_{66})_{c.v.} = 4S_{22} - S_{33} \quad 2.25$$

$$(S_{44})_{c.v.} = \frac{4}{E_{45}} - S_{22} \quad 2.26$$

$$(\mathcal{V}_{45})_{c.v.} = +\frac{E_{45}}{2} (S_{11}) \quad 2.27$$

For the special case of an isotropic continuum which has an infinite number of degrees of symmetry, then the above relationships reduce to the more familiar form, viz:-

$$S_{11} = S_{22} = S_{33} = \frac{1}{E} \quad 2.28$$

$$\mathcal{V}_0 = \mathcal{V}_{90} = \mathcal{V}_{45} = \mathcal{V} \quad 2.29$$

$$S_{44} = S_{55} = S_{66} = 1/G \quad 2.30$$

and the constant volume assumption would yield $\mathcal{V} = 0.5$.

2.2 Linear Visco-elasticity Theory

In materials in general and polymers in particular time-effects are often significant and it is necessary to introduce time-dependence into the constitutive equation, 2.1. By assuming that the components of the stress and strain matrix are time-dependent, and that the material parameters S_{ij} are now time-dependent material functions, $S_{ij}(t)$, then the relationship between stress and strain involving time is of the form:-

$$\epsilon_i(t) = \int_{\tau=0}^{\tau=t} S_{ij}(t-\tau) \frac{d\sigma_j(\tau)}{d\tau} d\tau \quad 2.31$$

where $\epsilon_i(t)$ is the time dependent strain matrix

$\sigma_j(\tau)$ is the time dependent applied stress matrix

and the matrix of compliance parameters, $S_{ij}(t)$, are now time-dependent.

In this formulation of the constitutive equation it is assumed that the material is in its rest state at zero time. The components of the strain matrix at time t , are seen to be functions of the previous history of the stress matrix, and also of the time-dependent material parameters $S_{ij}(t)$. This integral representation of the constitutive equation is often derived from the Boltzmann Superposition Principle and named a Duhamel or Convolution integral equation. Expressed in its simplest form the equation states that the strain at time, t , $\epsilon(t)$, under an arbitrary stress history is a linear superposition of all stresses applied at previous times, τ , multiplied by a "weighting function", the compliance function, $S_{ij}(t)$, corresponding to time intervals $(t - \tau)$ which have elapsed since imposition of the respective stress, $\sigma(\tau)$.

The linear theory of visco-elasticity has received much attention in the literature and has been discussed many times. The more recent treatments which discuss the general anisotropic case have been given by Halpin, 1968, Schapery, 1968, Rogers and Pipkin, 1963, Halpin and Pagano, 1968, and Hayes and Morland, 1969.

The outstanding assumption in the above treatment concerns the symmetry of the compliance matrix. In the elastic case the tensor of compliances, S_{ijkl} , involves 81 independent compliance parameters which are reduced to 36 by considering the symmetry of the stress and strain tensors, and to a further 21 by assuming a positive strain energy function. Material symmetry is then invoked to reduce the

21 compliances even further. For the time-dependent case the compliances may be reduced to 36 again using the symmetry of the stress and strain tensors. However, further reduction is achieved by arguments involving irreversible thermodynamics using the Onsager reciprocity relations, and has been discussed by Biot, (1954), who deduced the symmetry of the compliance matrix. An alternative approach has been examined by Rogers and Pipkin, (1963), without introducing thermodynamic considerations, who showed that for the transversely isotropic case an asymmetric matrix results containing at least 6 independent coefficients compared to five if the matrix was symmetric. The thermodynamic theories of Biot predict 5 of these 6 terms, and the remaining symmetry requirement involves the equality of the compliances, S_{13} and S_{23} (See equation 2.2), which may only be resolved by experiment. Recently, Halpin and Pagano, (1968), and Darlington, (1970), have shown that the two contraction compliances are equal for materials in their linear viscoelastic region. The experimental results of both workers reconciles the two approaches and justifies the assumptions that the matrix of compliances has the same symmetry in the linear visco-elastic case as in the elastic case.

Using the constitutive equation, 2.31, the strain response to an arbitrary stress history may be predicted, or, alternatively, by defining the stress history and monitoring the strain response the time dependence of the compliance parameters may be determined. In the work reported here the strain response of several transversely isotropic continua has been examined for a simple stress history and the various $S_{ij}(t)$, have been determined. A step-function of stress has been applied to the body in its rest state at zero time and the strain response has been monitored (i.e. a simple creep test). At time $t = t_1$, the applied stress was removed and the material is allowed to recover under zero load. Figure 2.2 gives a schematic representation of the stress and strain cycle. For a step-function of stress

$$\sigma_j = \sigma_j^0 H(t) \quad 2.32$$

$$\text{where } \sigma_j^0 \text{ are constants and } H(t) = \begin{cases} 0 & t < 0 \\ 1 & t > 0 \end{cases} \quad 2.33$$

and thus substituting in 2.33 and noting $\frac{d}{dt} H(t)$ is the Dirac delta function yields

$$e_i = S_{ij}(t) \sigma_j^0 \quad 0 < t < t_1, \quad 2.34$$

$$e_i = S_{ij}(t) \sigma_j^0 - S_{ij}(t - t_1) \sigma_j^0 \quad 0 < t_1 < t < \infty \quad 2.35$$

where $S_{ij} \sigma_j^0$ is the creep strain

$S_{ij}(t - t_1) \sigma_j^0$ is the recovered strain

and e_i in equation 2.35 is the residual strain (See Fig. 2.2).

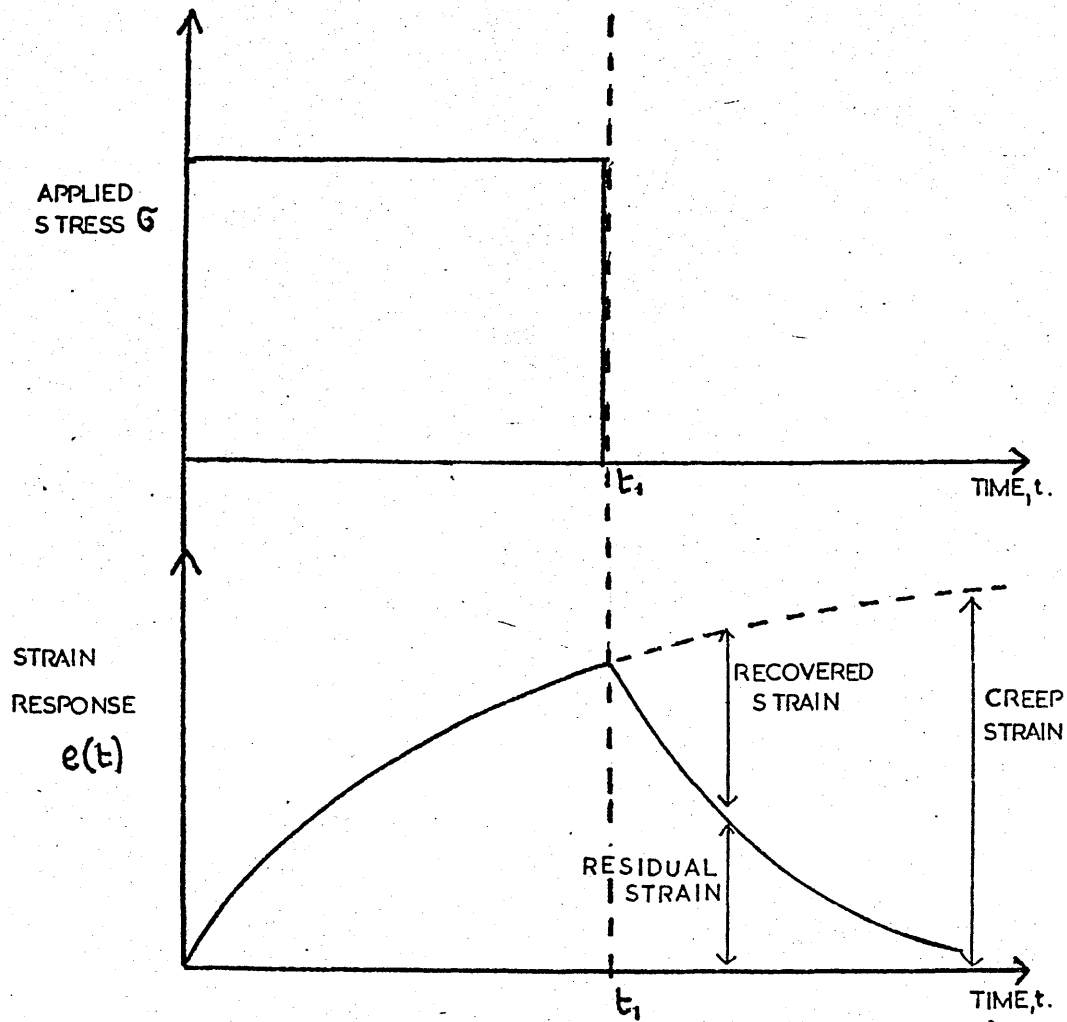


FIGURE 2.2 The Schematic Strain Response to a Step Function Stress History.

In the experiments reported here the creep and recovery strains have been monitored over a range of stress levels which give 100 second strains - (i.e. the strain recorded at $t = 100$) - in the range 0.1% to over 5%. Each material has been examined to establish the "region of linearity", and the applicability of the convolution or superposition integral in both the linear and non-linear regions. The results of experiments are discussed in Section 9.2.

As discussed previously, the compliance parameters for linear visco-elastic continua have the same symmetry as the corresponding elastic continua and have the same physical significance, except now the variables are time dependent quantities. Thus for a transversely isotropic material equation 2.2 may be re-written as

$$S_{ij}(t) = \begin{pmatrix} S_{22}(t) & S_{12}(t) & S_{13}(t) & & & \\ S_{12}(t) & S_{22}(t) & S_{13}(t) & & & \\ S_{13}(t) & S_{13}(t) & S_{33}(t) & & & \\ & & & S_{44}(t) & & \\ & & & & S_{44}(t) & \\ & & & & & S_{66}(t) \end{pmatrix} \quad 2.36$$

and equation 2.6 to 2.11 as:-

$$S_{22}(t) = S_{11}(t) = \frac{\epsilon_{22}(t)}{\sigma_2} = \frac{1}{E_{90}(t)} \quad 2.37$$

$$S_{33}(t) = \frac{\epsilon_{33}(t)}{\sigma_3} = \frac{1}{E_o(t)} \quad 2.38$$

$$S_{12}(t) = S_{21}(t) = \frac{\epsilon_{11}(t)}{\sigma_2} = \frac{-\nu_{90}(t)}{E_{90}(t)} \quad 2.39$$

$$S_{13}(t) = S_{32}(t) = \frac{\epsilon_{11}(t)}{\sigma_3} = \frac{-\nu_o(t)}{E_o(t)} \quad 2.40$$

$$S_{44}(t) = S_{55}(t) = 2 \frac{\epsilon_{13}(t)}{\tau_{13}} = \frac{\gamma_{13}(t)}{\tau_{13}} = \frac{1}{G_{13}(t)} \quad 2.41$$

$$S_{66}(t) = 2 \frac{\epsilon_{12}(t)}{\tau_{12}} = \frac{\gamma_{12}(t)}{\tau_{12}} = \frac{1}{G_{12}(t)} \quad 2.42$$

where i. $\epsilon_{22}(t)$ and $\epsilon_{33}(t)$ are the longitudinal creep strains of tensile samples subjected to axial stresses σ_2 and σ_3 .

ii. $\epsilon_{11}(t)$ is the lateral creep strain of tensile samples subjected to axial stresses σ_2 and σ_3 .

iii. $\gamma_{13}(t)$ and $\gamma_{12}(t)$ are the shear creep strains in the 1, 3 and 1, 2 planes when subjected to shear stresses τ_{13} and τ_{12} respectively.

iv. $\nu_0(t)$ and $\nu_{90}(t)$ are the creep contraction ratios of specimens cut at 0° and 90° to the 3-direction respectively.

It may be shown that the inter-relations between the time-dependent compliances, and their manipulation for the anisotropic linear visco-elastic case are similar to those for the anisotropic linear elastic case. This is achieved since the constitutive equations and inter-relations, of linear elasticity are related to the visco-elastic problem through the Laplace or Carson transform of equation 2.31, and is termed the elastic-viscoelastic correspondence principle. The visco-elastic relations are transformed from the real t -axis to the complex p -plane through the Laplace transform, and the resulting transforms in p may be manipulated algebraically and then inverted to regain the time-dependent form. The technique has been demonstrated by Lee, (1964), and has recently been developed and discussed by, for example, Schapery, 1965, and 1968, and investigated experimentally by Halpin and Pagano, (1968). Many other discussions may be found in the literature. For the transversely isotropic case the correspondence principle enables the elastic-inter-relations in equation 2.16 to 2.18 to be re-written as follows:-

$$S_{66}(t) = 2 (S_{11}(t) - S_{12}(t)) \quad 2.43$$

$$S_{44}(t) = \frac{4}{E_{45}(t)} - S_{11}(t) - S_{33}(t) - 2S_{13}(t) \quad 2.44$$

$$\text{and } \nu_{45}(t) = -\frac{1}{2} E_{45}(t) [S_{13}(t) + S_{12}(t)] \quad 2.45$$

The volume compliances, and bulk compliance will be given by (c.f. equations 2.12 to 2.15)

$$V_0(t) = S_{33}(t) + 2S_{13}(t) \quad 2.46$$

$$V_{90}(t) = S_{22}(t) + S_{12}(t) + S_{13}(t) \quad 2.47$$

$$B(t) = S_{33}(t) + 2S_{22}(t) + 4S_{13}(t) + 2S_{12}(t) \quad 2.48$$

$$\text{and } K(t) = B(t)^{-1} \quad 2.49$$

The above inter-relationships have been examined experimentally and the results of the manipulations both in the linear and non-linear visco-elastic regions are discussed in Section 9.

The creep contraction ratios $\nu_o(t)$, and $\nu_{90}(t)$, described above, equation 2.39 and 2.40, are not exactly analagous to the Poisson's ratio term in elasticity theory. The lateral contraction $\epsilon_i(t)$ is connected to the longitudinal extension $\epsilon_j(t)$ through the convolution integral as follows:-

$$\epsilon_i(t) = \int_0^t \nu_{ij}(t-\tau) \frac{d\epsilon_j(\tau)}{d\tau} \cdot d\tau \quad i \neq j \quad 2.50$$

$$= \nu_{ij}^o \epsilon_j(t) + \int_0^t \frac{d\nu_{ij}(t-\tau)}{d\tau} \cdot \epsilon_j(\tau) d\tau \quad 2.51$$

where $\epsilon_i(t)$ is the lateral creep contraction strain

$\epsilon_j(t)$ is the longitudinal creep strain

and ν_{ij} are the time-dependent Poisson's ratio

The creep contraction ratios $\nu_o(t)$ and $\nu_{90}(t)$ are defined as

$$\nu_o(t), \nu_{90}(t) = -\frac{\epsilon_i(t)}{\epsilon_j(t)} \quad i \neq j \quad 2.52$$

However, by considering stress-relaxation in linear extension a time-dependent Poisson's ratio, $\nu_{ij}(t)$, may be determined since in equation 2.50

$$\left. \begin{aligned} \epsilon_j(t) &= 0 \\ &= \epsilon_j^o H(t) \end{aligned} \right\} \begin{aligned} t &< 0 \\ t &> 0 \end{aligned} \quad 2.53$$

$$\text{and therefore } \epsilon_j(t) = \nu_{ij}(t) \epsilon_j^o \quad 2.54$$

where ϵ_j^o are constants equal to the instantaneous longitudinal strain. The difference between the creep contraction ratio and Poisson's ratio is small however in some isotropic materials (McCammond, 1967).

Clearly, for time-dependent materials the amount of experimental work needed for the complete characterisation of the compliance matrix is in many cases prohibitive, and it is often necessary to resort to simplifying assumptions as in the elastic case. By far the most difficult parameter to measure is the contraction compliance, and in many cases the most common assumption is that

the deformation occurs at constant volume. Other approximations may be made but these necessitate assigning arbitrary values to either the bulk modulus or the creep contraction ratio (Turner, 1966). Using constant volume assumptions equations 2.21 to 2.27 may be re-written as follows for the linear visco-elastic case:-

$$(S_{13})(t)_{c.v.} = -\frac{1}{2} S_{33}(t) \quad 2.55$$

$$(S_{12})(t)_{c.v.} = -\left[S_{22}(t) - \frac{S_{33}(t)}{2}\right] \quad 2.56$$

$$(\mathcal{V}_0)(t)_{c.v.} = 0.5 \quad 2.57$$

$$(\mathcal{V}_{90})(t)_{c.v.} = \left(1 - \frac{S_{33}(t)}{2S_{22}(t)}\right) \quad 2.58$$

$$(S_{66})(t)_{c.v.} = 4 S_{22}(t) - S_{33}(t) \quad 2.59$$

$$(S_{44})(t)_{c.v.} = \frac{4}{E_{45}(t)} - S_{22}(t) \quad 2.60$$

$$(\mathcal{V}_{45})(t)_{c.v.} = \frac{E_{45}(t)}{2} (S_{11}(t)) \quad 2.61$$

The usefulness of the constant volume assumption in both the linear and non-linear regions is fully discussed in Section 9.

2.3 Non-Linear Visco-Elasticity Theory

In the preceding discussion arguments have been presented which allow the extension of the formalism of C.E.T. to materials with more complex rheological characteristics. However, the correspondence is only justified theoretically when the time-dependent materials are deformed in their linear visco-elastic region. Also the theory restricts the deformation to "infinitesimal" strains, where the strain is defined by the **Cauchy** strain tensor, and neglects the squares and products of the displacement gradients. However, in practice, the useful working strain range of thermoplastics may cover strains from 0.1% to 5% or more, and thus approach finite displacement gradients. At these strain levels the "infinitesimal" strain premise is violated and most thermoplastics exhibit a marked non-linear deformation behaviour. Various attempts have been made to modify the equations formulated for linear materials, usually the constitutive equation, but, primarily these have been attempts to account for particular results and no universally acceptable general theory has been developed. The non-linearity may take many forms and, for example, the time-dependent compliances may be a function of the

applied stress, or the strain level, and the constitutive equation may be modified to account for this special form of non-linearity as follows:-

$$\epsilon_i(t) = \int_0^t s_{ij}(\sigma_j, t - \tau) \frac{d\sigma_j}{d\tau} \cdot d\tau \quad 2.62$$

$$\text{or } \epsilon_i(t) = \int_0^t s_{ij}(\epsilon_i, t - \tau) \frac{d\epsilon_j}{d\tau} \cdot d\tau \quad 2.63$$

An alternative approach is to express the constitutive equation in the form of a sum of multiple integrals. This type of representation was developed by Green and Rivlin, 1957, and Green, Rivlin, and Spencer, 1959, and has been investigated by several workers. An early investigation of the multiple integral theory by Nakada, 1961, was followed by work, for example, by Ward and Onat, 1963, and more recently by Findley and co-workers, (see, for example, Onaran and Findley, 1965 and 1968, and Lai and Findley, 1968 a, and b). This representation is advantageous since it is not limited to a particular material, or class of materials, and allows a material description with any order of non-linearity desired. However, the multiple integral theory becomes impractical with strong non-linearities since the kernels of many integrals have to be characterised experimentally. Lockett, 1965, has examined the general theory and has shown that around 100 tests would be needed to characterise all the material functions. Another disadvantage of the multiple integral representation is that if the material parameters are determined from creep experiments another set of parameters must be generated for stress-relaxation, since there is no way of inverting the multiple integral inter-relationships. Clearly, the complexity of the problem is greatly increased when considering anisotropic materials. Other workers, Findley and Khosla, 1956, and Sharma and Wen, 1964, have tried fitting "creep" equations to describe non-linear behaviour, but often the equations have no theoretical justification and are purely empirical. Various approaches to non-linearity in visco-elastic continua have been reviewed by Turner, 1966, Halpin, 1968 and Schapery, 1969, and other workers have discussed individual approaches which endeavour to simplify the multiple integral representation, (see, for example, Lockett, 1965, Rogers and Pipkin, 1968, Hall, 1968, and Stafford, 1969).

The approach to non-linearity in the anisotropic visco-elastic continua studied here has been firstly, to determine the physical differences of the origin of the non-linearities for the different materials and determine how they arise. Secondly, the linear constitutive equation 2.31 has been applied to the creep and recovery data, to determine the errors involved in assuming linearity and small strain deformation in the non-linear region. The philosophy has been to examine the various continua over their possible working strain range, use a simple theory which allows easy manipulation of the data and find the errors involved. A discussion of the results of this approach may be found in Section 9.2.

2.4 The Torsion Problem

The torsion problem involving isotropic prisms is well documented and has been presented many times in the literature, (see, for example, Love, 1927, Sokolnikov, 1956, and Timoshenko and Goodier, 1951). However, this is not the case for anisotropic prisms and only a limited number of discussions may be found. (Trayer and March, 1929, Sokolnikov, 1956, Hearmon, 1961, and Lekhnitski, 1963). A synopsis of the theory is presented below, with particular reference to rectangular cross-sectional prisms, and is collated from the above treatises but in a consistent nomenclature. The theory is then applied to a material with transversely isotropic symmetry in order to evaluate the shear compliances, S_{44} and S_{66} . The evaluation of the latter compliance, S_{66} , is determined from a study of torsion of an orthotropic prism.

2.4.1 Torsion of an Isotropic Rectangular Prism

Figure 2.3 is a schematic diagram of a rectangular cross-section prism of side $2a$, parallel to the x_1 -axis, and side $2b$, parallel to the x_2 -axis. The x_3 axis passes through the centre of the cross section. The axes Ox_i , $i = 1, 2, 3$, are a right-hand set of mutually orthogonal reference axes. Torsion about the Ox_3 -axis is governed by the following equation:-

$$M = \alpha D \quad 2.64$$

where M is the applied twisting moment

α is the angle of twist per unit length

and D is the torsional rigidity

The torsional rigidity, D , for an isotropic rectangular prism, of side $2a$, $2b$, is given by:-

either $D = G a b^3 \left[\frac{16}{3} - \frac{b}{a} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh \frac{(2n+1)\pi a}{2b} \right] \quad a > b \quad (2.65)$

or $D = G b a^3 \left[\frac{16}{3} - \frac{a}{b} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh \frac{(2n+1)\pi b}{2a} \right] \quad b > a \quad (2.66)$

or alternatively $D = G \frac{w t^3}{16} \left[\frac{16}{3} - \frac{t}{w} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh \frac{(2n+1)\pi w}{2t} \right] \quad w > t \quad (2.67)$

where G is the shear modulus

and w = width of the section

t = thickness of the section

The maximum shear stress and strain are found to be at the middle of the largest side (width) and are given by:-

$$\text{maximum shear stress } \tau_{mx} = G \cdot \alpha \cdot t \left[1 - \frac{8}{\pi^2} \operatorname{sech} \left(\frac{\pi w}{2t} \right) \right] \quad (2.68)$$

$$\text{maximum shear strain } \gamma_{mx} = \alpha t \left[1 - \frac{8}{\pi^2} \operatorname{sech} \left(\frac{\pi w}{2t} \right) \right] \quad (2.69)$$

$$\approx \alpha t \quad w > 3t$$

Note that in the isotropic case:

$$G = G_{12} = \frac{1}{S_{66}} = G_{13} = \frac{1}{S_{55}} = G_{23} = \frac{1}{S_{44}} \quad (2.70)$$

2.4.2 Torsion of an Anisotropic Rectangular Prism

The solution of the torsion problem of anisotropic prisms has only been solved for the orthotropic case and materials with higher symmetries. Moreover, the solution is only resolved for the case where the twisting moment, M , is applied about one of the principal axes.

Consider the orthotropic prism shown in Figure 2.4 where the prism has three planes of elastic symmetry, one of which is perpendicular to the direction of the length of the prism, Ox_3 . The boundary of the cross-section is defined by a function $f(x_1, x_2) = 0$, where axes Ox_i are reference co-ordinate axes. The

co-ordinate axes Ox_i , $i = 1, 2, 3$, define the symmetry directions of the material. The co-ordinate axis x_3 is coincident with the symmetry direction, X_3 , and the angle between the x_1 , X_1 and x_2 , X_2 , directions is in general, θ . The laminar shear in the X_1 , X_3 plane is governed by $G_{13} = \frac{1}{S_{55}}$, in the X_2 , X_3 , plane by $G_{23} = \frac{1}{S_{44}}$, and in the X_1 , X_2 , plane by $G_{12} = 1/S_{66}$. For

torsion about the x_3 axis the deformation is governed by G_{13} , and G_{23} only. It may be shown that the solution of the torsion problem for such a prism can be reduced to the solution of the same problem for an isotropic prism whose section is obtained by transforming the boundaries of the original section through a linear transformation and whose modulus of rigidity is expressed in terms of the original moduli. The transformed cross-section is determined by $F(\xi_1, \xi_2) = 0$ where,

$$\xi_1 = \frac{(G_{13} G_{23})^{\frac{1}{2}}}{A} x_1 \quad (2.71)$$

$$\xi_2 = x_2 - \left(\frac{B}{A}\right) x_1 \quad (2.72)$$

$$\left. \begin{array}{l} \text{where } A = G_{23} \sin^2 \theta + G_{13} \cos^2 \theta \\ \text{and } B = (G_{23} - G_{13}) \sin \theta \cos \theta \end{array} \right\} \quad (2.73)$$

and the effective modulus of rigidity is

$$\bar{G} = \frac{(G_{23} \sin^2 \theta + G_{13} \cos^2 \theta)^2}{(G_{13} G_{23})^{\frac{1}{2}}} \quad (2.74)$$

Torsion about the Ox_3 -axis would be governed by equation 2.64, but where the torsional rigidity, D , is now a product of the effective shear modulus, $\bar{G}$, and a function of the geometry of the transformed cross section.

Consider now a rectangular cross-sectioned specimen whose principal axes X_1 , X_2 are parallel to the co-ordinate axes x_1 , x_2 respectively (Figure 2.5.) The orthotropic prism is transformed to an equivalent isotropic prism by substituting $\theta = 0^\circ$ in equations 2.71 to 2.74. Using 2.71 and 2.72 the sides $2a$, $2b$ are transformed to

$$2a > 2a \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}} \quad (2.75)$$

$$2b > 2b \quad (2.76)$$

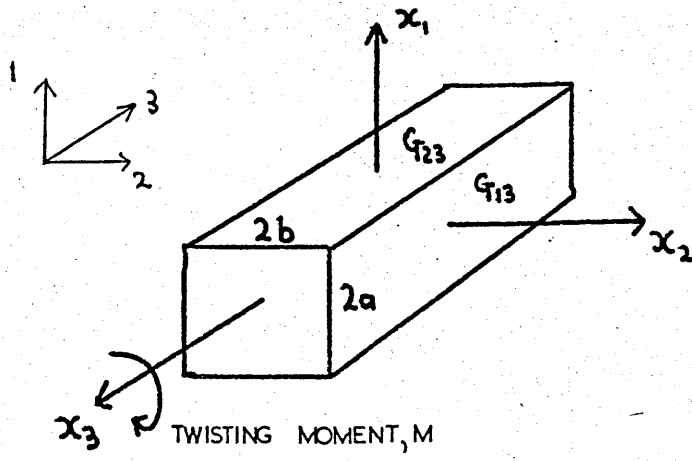


FIGURE 2.3 Torsion of an Isotropic Rectangular Prism

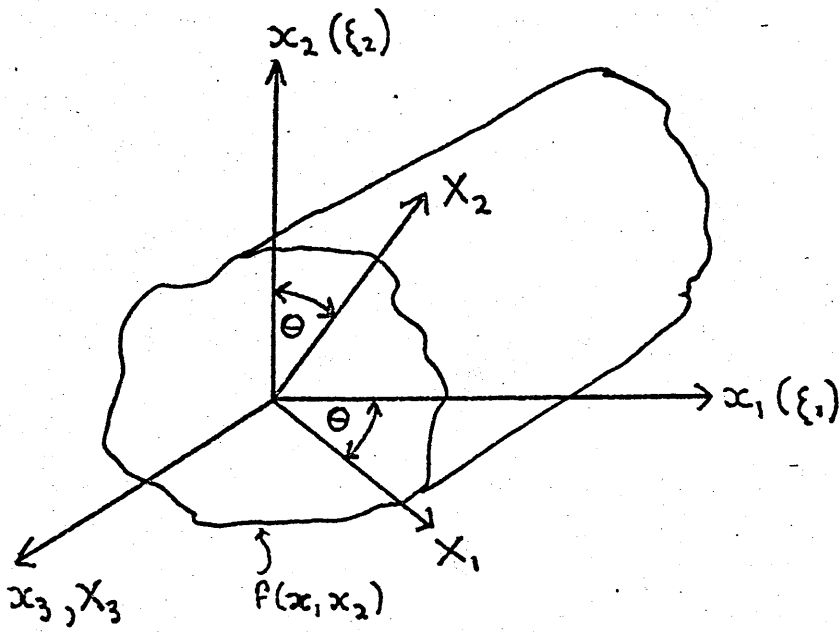


FIGURE 2.4 Torsion of an Anisotropic Prism

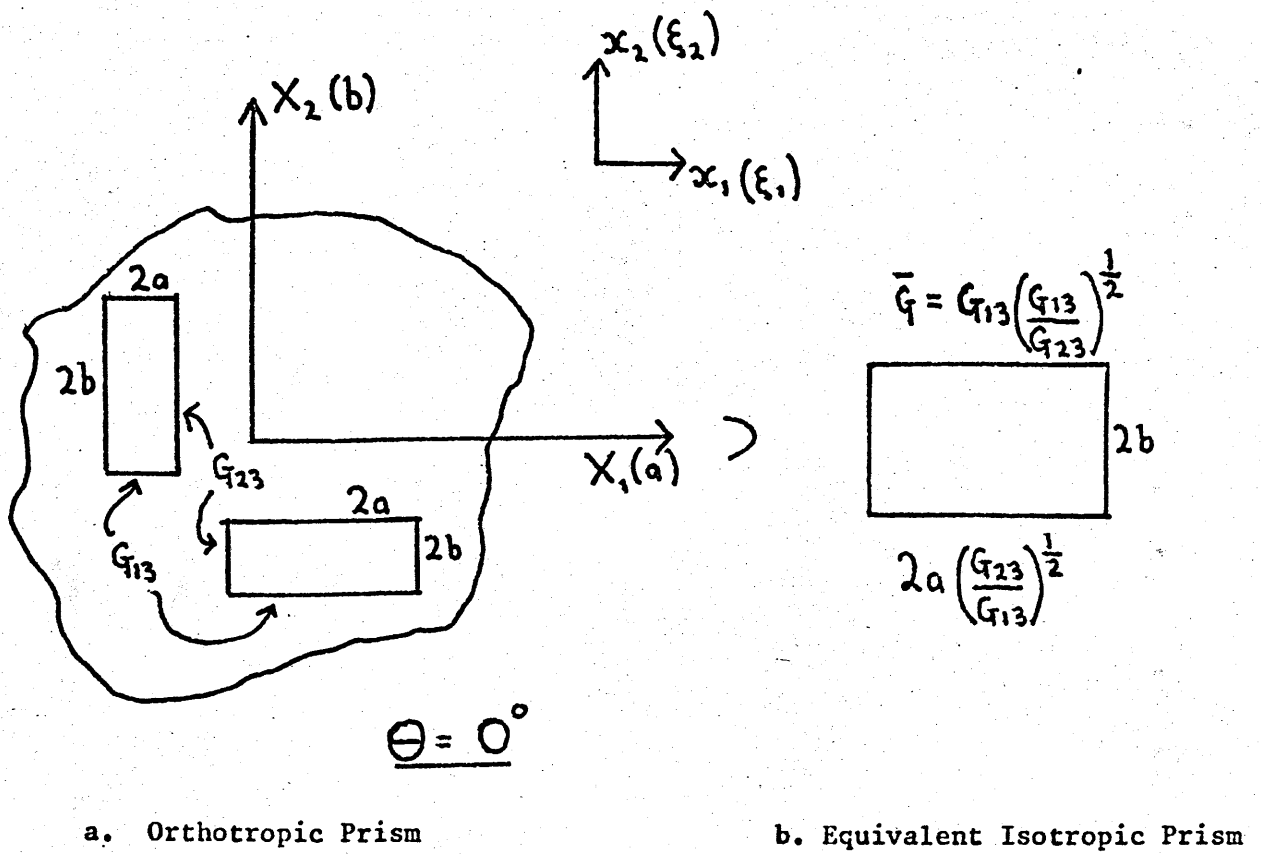


FIGURE 2.5 Torsion of an Orthotropic Rectangular Prism ($\theta = 0^\circ$)

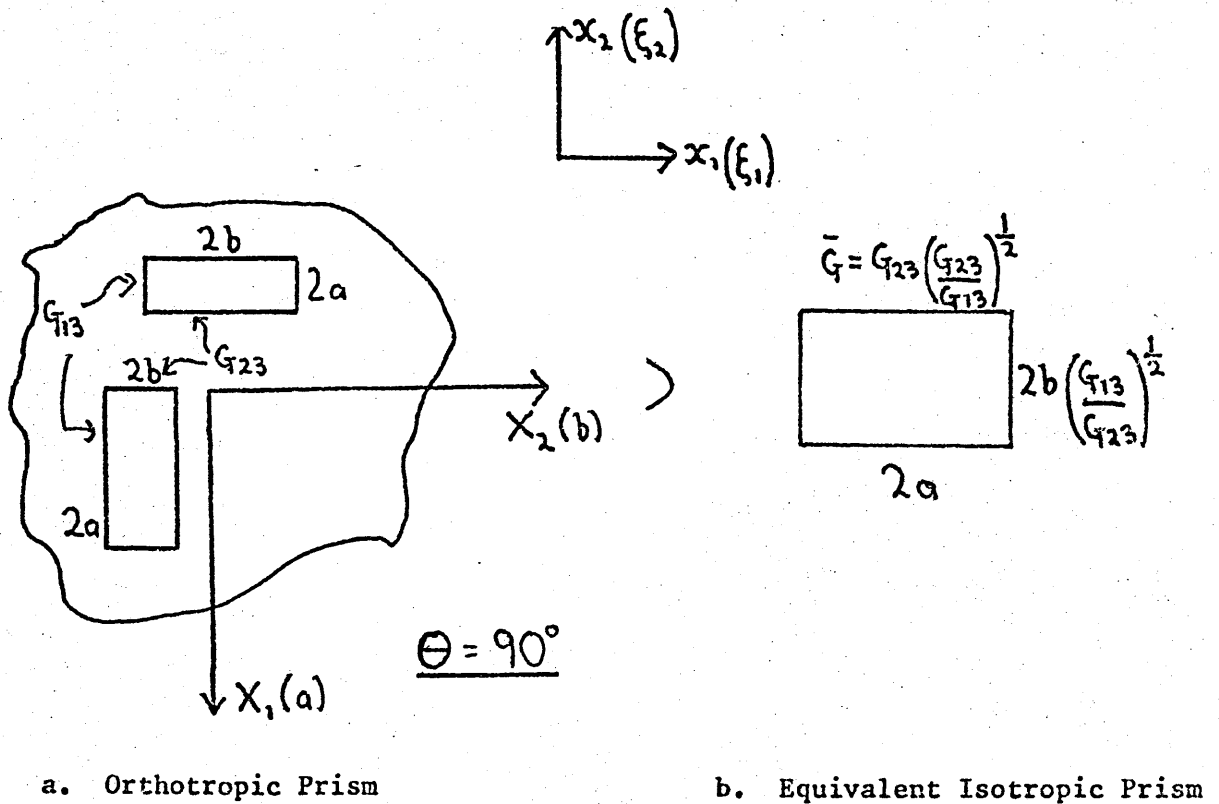


FIGURE 2.6 Torsion of an Orthotropic Rectangular Prism ($\theta = 90^\circ$)

and the effective modulus $\bar{G}$ is given by

$$\bar{G} = \left(\frac{G_{13}}{G_{23}} \right)^{\frac{1}{2}} G_{13} \quad (2.77)$$

This is shown schematically in Figure 2.5a and 2.5b. The torsional rigidity, D , is now found by substituting in equation 2.65 or 2.66. Thus, for

$$a \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}} > b$$

$$D = G_{13} a b^3 \left[\frac{16}{3} - \frac{b}{a} \left(\frac{G_{13}}{G_{23}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \frac{\tanh \frac{(2n+1)\pi a}{2} \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}}}{b \left(\frac{G_{13}}{G_{23}} \right)^{\frac{1}{2}}} \right] \quad (2.78)$$

or if $b > a \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}}$

$$D = G_{23} a^3 b \left[\frac{16}{3} - \frac{a}{b} \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \frac{\tanh \frac{(2n+1)\pi b}{2} \left(\frac{G_{13}}{G_{23}} \right)^{\frac{1}{2}}}{a \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}}} \right] \quad (2.79)$$

where $2a$, $2b$, are the original specimen dimensions. Note, that if from the general case the principal axes X_1 , X_2 , were now parallel to the x_2 , x_1 axes respectively, i.e. $\theta = 90^\circ$, the above equations are still valid, since in this case (see Figure 2.6):

$$2b > 2b \left(\frac{G_{13}}{G_{23}} \right)^{\frac{1}{2}}$$

$$2a > 2a$$

$$\text{and } \bar{G} = G_{23} \times \left(\frac{G_{23}}{G_{13}} \right)^{\frac{1}{2}}$$

which yield equation 2.78 and 2.79 on substituting in equation 2.65 or 2.66. The difference in the two cases constitutes a rigid body rotation through 90° about the x_3 -axis.

For a transversely isotropic material, for torsion about the axis perpendicular to the plane of isotropy, i.e. the 3 direction, the deformation is governed by $G_{13} = \frac{1}{S_{55}}$ in the 1,3 plane, and

$G_{23} = \frac{1}{S_{44}}$ in the 2,3 plane. (Figure 2.7 a. and b). However,

in this case $S_{44} = S_{55}$, and the problem reverts to that of an isotropic prism with torsional rigidity given by equation 2.67. For torsion about the 2-direction, i.e. a specimen cut at 90° to the 3-axis, the deformation is governed by $G_{23} = \frac{1}{S_{44}}$ in the 2,3 plane, and by $G_{13} = \frac{1}{S_{66}}$ in the 1,2 plane.

Figure 2.7 b). The expressions for the torsional rigidity, D, are then given by:

$$D = \frac{ac^3}{S_{66}} \left[\frac{16}{3} - \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh \frac{(2n+1)\pi a}{2} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \right] \quad 2.80$$

for $\frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \gg 1$

$$\text{or } D = \frac{ca^3}{S_{44}} \left[\frac{16}{3} - \frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh \frac{(2n+1)\pi c}{2} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \right] \quad 2.81$$

for $\frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \gg 1$

where $2c$ is the length of the cross-section measured in the 3-direction. By considering the convergence of the series in 2.65, i.e. for the isotropic case, and in equations, 2.80, 2.81, in the orthotropic case, it can be shown, (Appendix A.1), that the equations may be reduced to the following:-

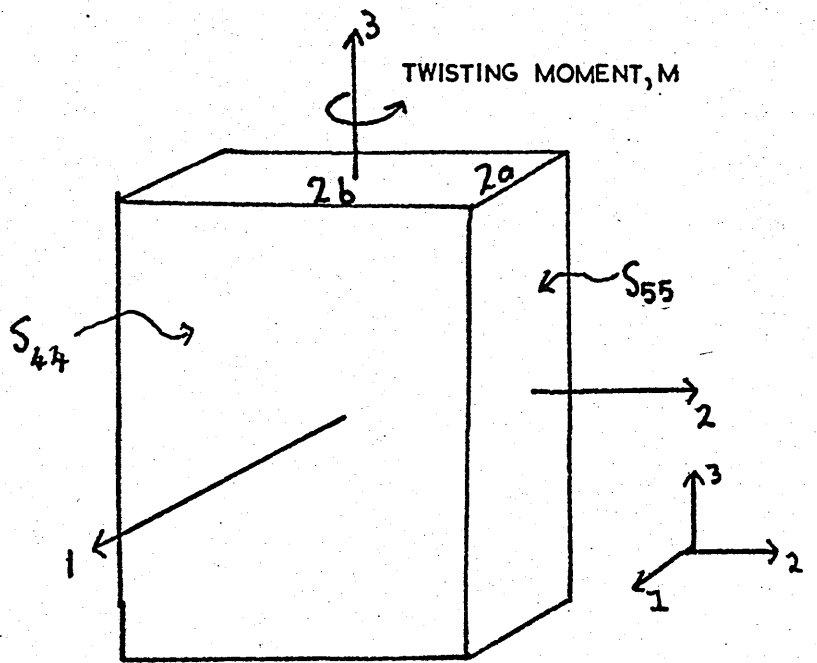
$$D = \frac{ac^3}{S_{66}} \left[\frac{16}{3} - \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \tanh \frac{\pi}{2} \cdot \frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \right] \quad \frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \gg 1 \quad 2.82$$

$$D = \frac{ca^3}{S_{44}} \left[\frac{16}{3} - \frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \tanh \frac{\pi}{2} \cdot \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \right] \quad \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \gg 1 \quad 2.83$$

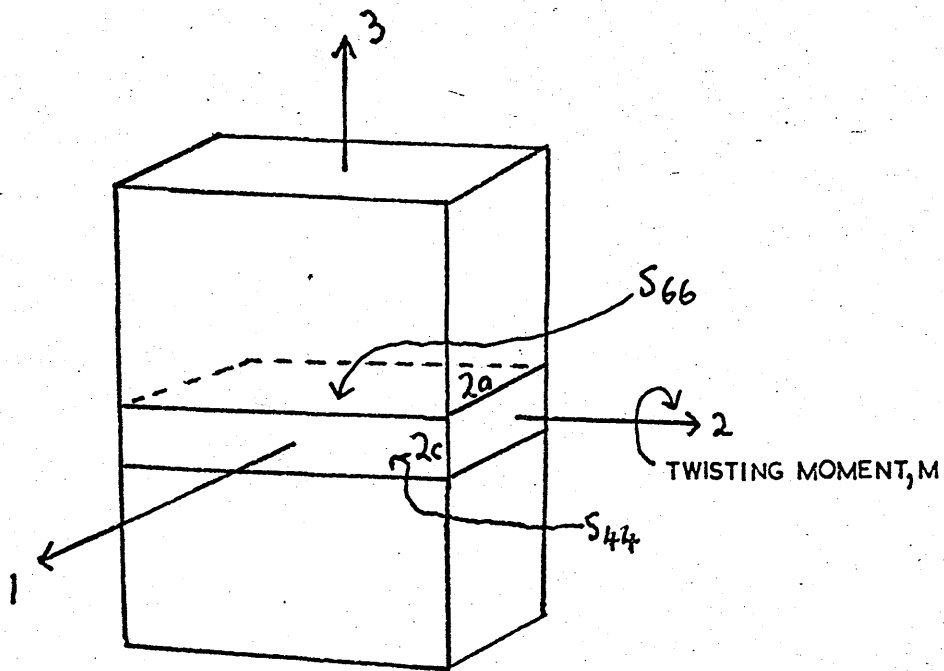
The maximum shear stresses for a prism sides $2a$, $2b$, are

$$(\tau_{12})_{\max} = \frac{16 M}{a c^2} k_1 \quad \text{at the mid-point of the side, } 2a \quad 2.84$$

$$\text{and } (\tau_{23})_{\max} = \frac{16 M}{a c^2} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} k_2 \quad \text{at the mid-point of the side, } 2c. \quad 2.85$$



a. ABOUT THE 3-AXIS



b. ABOUT THE 2-AXIS

FIGURE 2.7 Torsion of a Transversely Isotropic Prism

where k_1 and k_2 are functions of the aspect ratio, a/c , and the shear moduli, $\left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}}$, and are given in Table 2.1, below,

for $\frac{a}{c} \left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}} \gg 1$. (This table is reproduced from Hearmon, 1961, p.52, who corrected a previous table by Lekhnitski, 1950, table 3, p.152, for certain values of k_2).

Table 2.1 Values of k_1 and k_2

$\frac{a}{c} \left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}}$	k_1	k_2
1	4.80	4.80
1.25	4.52	4.14
1.50	4.33	3.72
1.75	4.19	3.43
2.00	4.07	3.23
2.50	3.88	2.98
3.00	3.74	2.82
4.00	3.55	2.64
5.00	3.43	2.55
10.00	3.20	2.38
20.00	3.10	2.27
∞	3.00	0

The maximum shear strains may be calculated since

$$M = \alpha D, \text{ where } D \text{ is given by equation 2.80 for } \frac{a}{c} \left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}} > 1$$

$$\text{and, therefore, } (\gamma_{12})_{\max} = \frac{16 k_1}{a c^2} \propto D S_{66} \text{ at the mid-point of side } 2a.$$

2.86

$$\text{for } \frac{a}{c} \left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}} > 1$$

$$\text{and } (\gamma_{23})_{\max} = \frac{16 k_2}{a c^2} \left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}} \propto D.S_{44} \text{ at the mid-point of the side } 2b \quad 2.87$$

$$\text{for } \frac{a}{c} \left(\frac{S_{66}}{S_{44}}\right)^{\frac{1}{2}} > 1$$

2.4.3 The Increase in Torsional Rigidity of a Prism due to Axial Tension

Biot (1939), has calculated the increase in torsional stiffness of an isotropic prism when subjected to an axial tensile loading. It was found that the classical shear stress distribution was not affected by the applied stress. However, an increase in torsional rigidity is produced due to the fact that the boundary condition over the cross-section contains not only the shear stresses but also the axial stress system. The increase in torsional stiffness is found to be proportional to the polar moment of inertia of the cross-section with respect to its centre of gravity.

Biot's analysis for an isotropic prism of cross-section given by an arbitrary contour $f(x_1, x_2)$, yields an equation for the twisting moment, M , of the form:-

$$M = \left(1 - \frac{\sigma}{2G}\right) \iint_{\text{AREA}} (-\tau_{13} x_2 + \tau_{23} x_1) dx_1 dx_2 + \sigma \alpha \iint_{\text{AREA}} (x_1^2 + x_2^2) dx_1 dx_2 \quad (2.88)$$

where σ is the axial stress

G is the shear modulus

and α is the angle or twist per unit length.

Now, $\iint_{\text{AREA}} (-\tau_{13} x_2 + \tau_{23} x_1) dx_1 dx_2$ is the couple calculated assuming the bar is initially in an unstressed state, and $\iint_{\text{AREA}} (x_1^2 + x_2^2) dx_1 dx_2$, is the moment of inertia of the cross-section with respect to the origin of co-ordinates. However, it may be shown, (Biot, 1939), that the origin must be at the centre of gravity of the cross-section, i.e.

$$\iint_{\text{area}} (x_1^2 + x_2^2) dx_1 dx_2 = I_G \quad 2.89$$

where I_G is the polar moment of inertia of the cross-section with respect to its centre of gravity. Hence, equation 2.88 may be re-written

$$M = \left(1 - \frac{\sigma}{2G}\right) M_0 + I_G \alpha \sigma \quad 2.90$$

where M is the applied twisting moment

and M_0 is the twisting moment required for deformation with axial loading.

The theory has only been developed for isotropic materials and is not applicable to anisotropic prisms. However, for a transversely isotropic prism twisted about the axis perpendicular to the plane of isotropy, the problem reverts to the isotropic case and the above inter-relation may be investigated experimentally. To overcome these experimental difficulties an apparatus was designed which allowed torsion of the specimen in the absence of applied axial loads, or with well defined axial loads. (See Section 5).

2.4.4 The Effect of Clamping on the Torsion Problem

In the discussion of the torsion problem it has always been assumed that the torque is applied by means of shearing stresses distributed over the ends of the prism in a definite manner. If the distribution of the stresses at the end is different from this, a local irregularity in stress distribution results and the solution can only be applied in regions some distance from the ends of the prism. This is the St.Venant's principle. For isotropic prisms which are clamped at their ends, the irregularities are smoothed out a distance from the clamp which is approximately equal to the clamp width. However, anisotropy may cause significant changes in the smoothing distance of a disturbance, e.g. a specimen clamp, but at present this problem has not been solved theoretically. An analogous problem of heat conduction in anisotropic media has been considered by Noyes, 1965, who concluded that anisotropy may significantly increase or decrease the smoothing distance. In the experimental work reported here, concerning the torsion problem, care has been taken to investigate the St.Venant clamping effect by determining the shear moduli from specimens with different length to width ratios. (Section 5).

A second irregularity in stress distribution occurs in rectangular specimens which are twisted by clamps at their ends. This problem has been discussed by Timoshenko and Goodier, 1951, who showed that the middle cross-section of the prism remains plane during torsion, and that by preventing warping the torsional rigidity of the prism is increased. The effect of this irregularity in stress distribution is to cause an effective reduction in length of the prism. The effective length, ℓ' , is given by the equation:-

$$\ell' = \ell \left[1 - \frac{a \sqrt{5(1+\nu)}}{6\ell} \right] \quad (2.93)$$

where ℓ' is the effective length

ℓ is the true length between clamps

and $2a$ is the width of the cross-section

This correction has been investigated experimentally by taking different specimens with different width to length ratios.

SECTION 3. BACKGROUND STUDIES ON THE STRUCTURE AND
MORPHOLOGY OF POLYETHYLENE

3.1 MORPHOLOGICAL STUDIES ON SINGLE CRYSTALS AND ISOTROPIC
POLYETHYLENE.

3.1.1 The Unit Cell of Polyethylene

3.1.2 Polyethylene Crystal Studies

3.1.3 Spherulitic Studies on Thin Films of Polyethylene

3.1.4 The Morphology of Isotropic Bulk Crystallized Polyethylene

3.1.5 Current Models for Isotropic Polyethylene (and other
Crystalline Polymers).

3.2 MORPHOLOGICAL STUDIES ON ORIENTED POLYETHYLENE

3.2.1 Low Draw Ratio Materials

3.2.2 Intermediate Draw Ratio Materials

3.2.3 The Highly Drawn State

3.3 SPECIAL TEXTURES IN ORIENTED POLYETHYLENE

In recent years some of the basic structural units which aggregate in bulk crystallized polyethylene have been identified, but to date the complex morphology has not been elucidated and is the topic of current research. The unit cell of polyethylene was determined by Bunn and co-workers, (see, for example, Bunn, 1953), and a further major advance in the understanding of the basic crystalline structural units of polyethylene, and other crystalline polymers, was made when Keller and other workers, (Keller, 1957, Till, 1957 and Fischer, 1957), made the first observations of crystalline lamellae which were precipitated from dilute solutions of polyethylene in Xylene. (See Section 3.1.2). Concurrent investigations, notably by Keith and Padden, 1964 a and b, on the morphology and structure of spherulites formed in solution and melt cast thin films showed that the spherulites were complicated aggregates of lamellar fibrils which had the same intra-crystallographic orientations as the lamellae obtained from dilute solutions. (Section 3.1.3). Later work by Palmer and Cobbold, 1964, and Keller and Samada, 1964, demonstrated that the same crystalline lamellae unit was predominant in the bulk crystallized polymer, (Section 3.1.4). The discovery of these new structural features necessitated a revision of the old fringed micelle model of polymer crystallinity. The two models which are currently advocated in the literature are discussed in Section 3.1.5.

The anisotropic state in crystalline polymers is important commercially and has received much attention. Early investigations on fibres and drawn film and sheet identified the orientation of the crystallographic axes with respect to the draw direction, and results on polyethylene have been reported by Keller, 1955, Aggarwal and Sweeting, 1957, and Stein and Norris, 1956. Further studies on drawn polyethylene identified the orientation of the lamellar fibrils and the spherulites at low draw ratios, and their gradual fragmentation with increasing draw ratio. The results of these studies are reviewed and discussed in Section 3.2, and current models for the highly oriented polymer are also presented.

Recent advances on the preparation of specially textured oriented sheets are noted in Section 3.3.

3.1 MORPHOLOGICAL STUDIES ON SINGLE CRYSTALS AND ISOTROPIC POLYETHYLENE

The investigation of the morphology of polymers may be divided into two classes and different techniques are used in each category.

The crystal structure and its orientation are explored using wide-angle X-ray and electron diffraction patterns by the use of established methods of structural crystallography, (see, for example, Cullity, 1956, and Kaelble, 1967).

The texture of the crystalline material, i.e. the size and shape of the crystalline entities, their forms of aggregation, and their arrangement in the bulk sample are investigated using low angle X-ray diffraction and electron microscopy techniques.

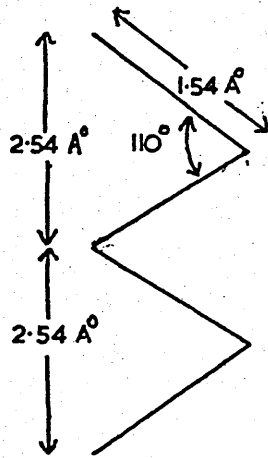
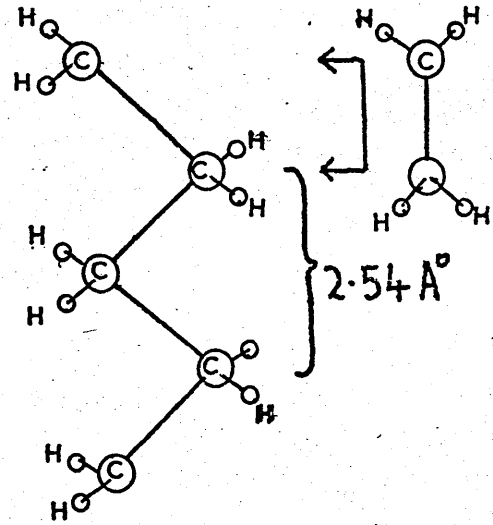
The overall measurement of the degree of crystallinity is determined by X-ray analysis, density measurements, nuclear magnetic resonance, and infra-red techniques. Optical studies yield information on the orientation of the crystallographic axes, and the form and rates of growth of the spherulitic entities.

The results of the above investigation, reported in the literature, will be described and discussed for the special case of polyethylene.

A general discussion of X-ray and electron diffraction techniques, and investigations on many polymers has been given by Geil, 1963, and a review of X-diffraction in polymers has been presented by Statton, 1967, b.

3.1.1 The Unit Cell of Polyethylene

The crystal structure of polyethylene has been determined from the fibre diagrams of cold drawn polyethylene threads; the repeat distance of the molecule was deduced from the layer line spacing and is that of a fully extended zig-zag chain of carbon atoms of inter atomic distance, $c - c$, of $1.54\text{\AA}$, with a bond angle of approximately 110° . It was deduced that the chain in polyethylene has the conformation shown in Figure 3.1, and that the unit cell of polyethylene had the form shown in Figure 3.2. (Bunn, 1953).



Line Diagram of C - C Chain

Structure of P.E.

FIGURE 3.1 Configuration of the Polyethylene (P.E.) Chain

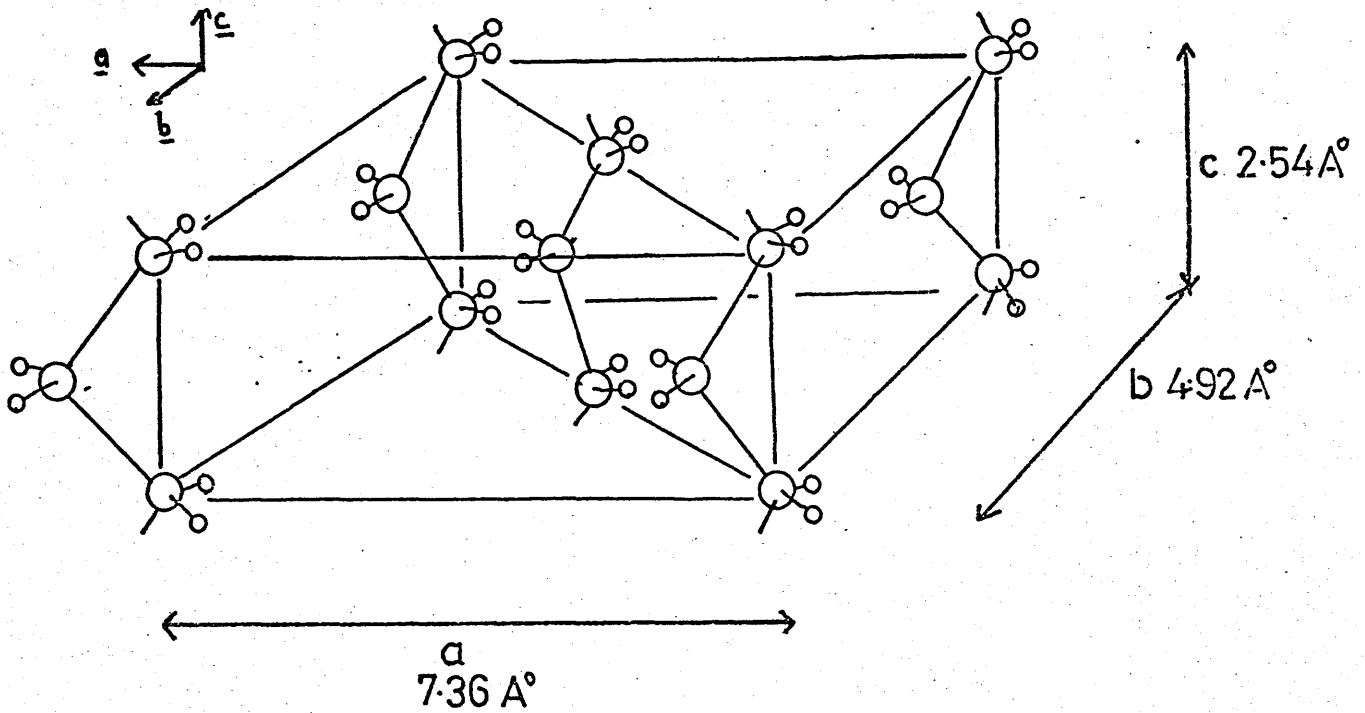


FIGURE 3.2 Unit Cell of Polyethylene

3.1.2 Polyethylene Crystal Studies

Initial studies on monolayer single crystals defined the orientation of the crystallographic axes within the lamellae and proved the existence of folded polymer chains in lamellar crystals. Further work on single crystals and multilayer lamellar aggregates identified between a 10% and 20% amorphous component within the crystalline lamellae, which is now considered intrinsic to the crystalline habit of polymers, but the nature and location of the amorphous regions is unresolved, and is a topic of current research and discussion. It is generally believed that the amorphous component is associated with the fold surface, but there is evidence of both a regular and a 'loose' chain fold. The results of crystal investigations have important implications on the deformation studies of the bulk crystallized material and the understanding of the molecular nature of the deformation mechanisms.

The observations of single crystals was reported almost simultaneously by three workers, Keller, 1957, Fischer, 1957, and Till, 1957. It was found that on slow deposition from a dilute solution of polyethylene in Xylene (0.1%) that orthorhombic single crystals grew in the form of diamond shaped flakes bounded by (110 planes). The top and bottom of each flake, (lamella), are (001) planes and the molecules lie in the 001 direction normal to the plane. Electron diffraction studies showed that the a and b axis of the unit cell lie respectively along the long and short axes of the crystal. The molecules which lie parallel to the c axis are normal to the crystal plane, and since the thickness of the lamellae are of the order of $100\text{\AA}$ the chain must be folded. On average the chain must fold about every 100 CH_2 groups, a molecule of average molecular weight 10^5 would fold about 70 times. A schematic diagram is given in Figure 3.3.

Models and thermodynamic theories were derived on the basis of these first discoveries which argued in favour of a regular crystalline structure with a regular fold surface. However, since these early studies many other investigations and measurements on multilayer aggregates cast doubt on the perfection of the chain folded crystals, and in general it was suggested that a 10% to 20% amorphous component existed. Details of this work is collated and discussed in two recent reviews, (Keller, 1968, and 1969). Moire patterns produced by overlapping crystal layers indicate that there are no sizeable amorphous regions within the crystal lattice and it was deduced that the amorphous material should lie outside the lattice, and hence in the fold surface of the crystal. However, density measurements, (Kawai and Keller, 1963), electron diffraction studies, (Tanaka, et al, 1963), crystal growth features, (Keller, 1962), and fracture studies on single crystals, (Geil, 1963), all provide evidence for the existence of a more or less regular adjacent

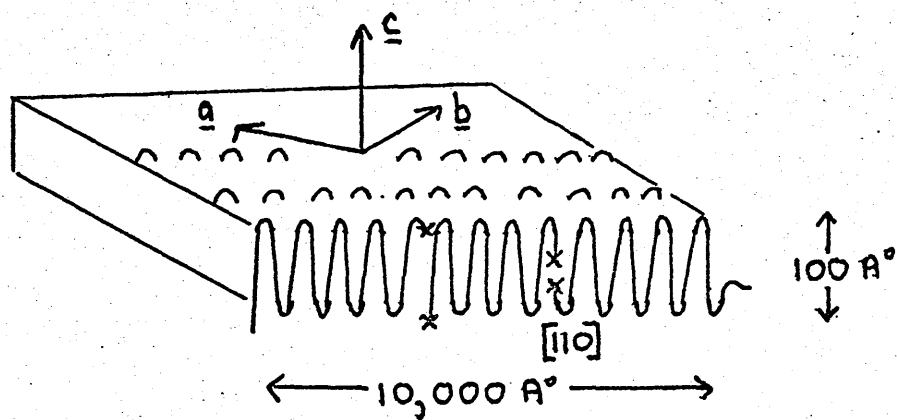


FIGURE 3.3 Polyethylene Lamellae Crystal

re-entry type chain folding of the type depicted in Figure 3.3. Thermodynamic theories, (Hoffman, 1964), demonstrate the high probability of such a regular, adjacent re-entry folded crystal. Direct evidence for regularity is the interfacial dislocation phenomenon reported by Holland, 1964, and Holland and Lindenmeyer, 1965. A more detailed account and informative discussion of the importance of the fold surface may be found in Hoffman, 1964, and two more recent reviews by Keller, (Keller, 1968 and 1969). As a working model, Keller, 1969, suggests a compromise fold surface consisting of adjacently re-entering folds and various elements of surface looseness.

Lindenmeyer, 1966, assumes a regular surface layer and on the basis of the studies reported above proposes the crystal-defect model of polymer structure. Lindenmeyer postulates that in the bulk the crystallites are not separated by amorphous regions, but are separated by dislocation arrays, and demonstrates that an interaction of inter- and intra-lamellar dislocations may be used to explain inter-lamellar slip. However, other workers believe that the amorphous regions may play an important part in the deformation behaviour of the bulk material. The above postulates are still topics of current research work, and extrapolations of the work on single crystals to the bulk crystallized polymer is at present dubious, but clearly, if the basic crystalline unit has amorphous regions this will be an important feature in the understanding of the deformation mechanisms in the bulk material and their molecular origin.

A crystalline feature which has only recently been reported, (Pennings, 1967), is the fibrous crystal which is produced when a rotary stirrer is immersed in a super-cooled solution. A fibrous crystal deposits on the stirrer which consists of so-called "shish-kebabs". A fibrous backbone first forms and large platelets develop when the solution is cooled to room temperature. The fibres act as nuclei for the still uncrystallized molecules which precipitate out forming the usual chain folded lamellae. The morphology of the fibrous backbone and the platelets has been investigated by several workers and has been included in the review by Keller, 1969. The fibrous backbone, free from platelets, was investigated and shown to comprise of micro-shish-kebabs with a periodicity of $200 \text{ \AA}$ to $300 \text{ \AA}$ along the length of the fibre, which was due to an alternation in material density within the fibres. It is postulated that the fibrous backbone consists of a central core of extended chain crystals with the addition of a mixture of folded and extended, or partially extended, chains within the fibre which were responsible for the observed striations. The platelets which attach to the fibrous backbone on cooling are the conventional chain folded material. A model for the formation of the fibrous crystals is discussed by Yamaura, 1970.

The implications of the fibrous crystal are manifold and may be a feature common to all oriented materials. Shish-kebabs have been identified in highly strained rubber, (Andrews, 1966), and have similar morphological features to the fibrillar models proposed by many workers for highly oriented polyethylene. (Section 3.2.3).

3.1.3 Spherulite Studies in Thin Films of Polyethylene

Optical and electron microscopy studies of spherulites in thin films of polyethylene have been used to determine the orientation of the crystallographic axes, the morphology of the spherulite, and the overall growth pattern and other general features. On the basis of these observations a model for spherulite growth was postulated, and two contrary models were presented which attempt to describe the manner in which space-filling takes place during spherulite growth.

Observations on thin films of polymers showed that polyethylene crystallized in a spherulitic habit. When a thin film of supercooled polymer melt is observed between crossed polars, in a polarizing microscope, the first sign of crystallization is the appearance of small birefringent areas which steadily grow from the sites of the primary nuclei.

In the early stages they appear as sheaves of fibrous crystallites, which, on further growth assume circular symmetry. The circular disc-like bodies continue to grow at constant radial rate (under isothermal conditions) into an array of polygonal boundaries. Centred on each primary nucleus is an extinction cross (Maltese Cross) whose arms are oriented parallel to the pass direction of the analyzer and polarizer. On rotation of the microscope the orientation remains unchanged. Superposed on the extinction cross are a series of concentric rings whose centres are at the spherulite nucleus.

The following model has been proposed, (Keith and Padden, 1964 a, b), as a result of detailed observations on spherulite growth. The spherulite consists basically of an array of crystalline fibrils which grow radially outwards from a common centre. The fibril axis corresponds to a particular crystallographic axis which, for polyethylene, is the b axis. The a and c axes are perpendicular to the radius, i.e. tangential to the spherulite growth face. A constant radial flux of fibres is maintained by a process of small-angle branching; the branching bears no fixed relation to the crystallographic axes present. The ring pattern superposed on the Maltese cross is indicative of some periodic variation in crystallographic orientation about the radius.

It is proposed that the fibrils in these spherulites twist spontaneously as they grow, and the crystallographic axes therefore rotate uniformly about a radius. Moreover, the orientation of neighbouring fibrils twist in the same sense with the same pitch and phase. It is postulated that the fibrils take the form of inter-leaved ribbon like crystals (lamellae) so that groups of them are constrained to move in concert. The growing fibril is of parent material and will reject all impurities preferentially. The impurities may include low molecular weight fractions, additives and different molecular species. The resulting lamellae are thus separated by amorphous or low crystalline material of high impurity content. These early postulates were demonstrated later by Keith, et al, 1965, by the rejection of uncrystallizable atactic poly propylene in mixtures of atactic and syndiotactic poly propylene (different molecular species), and also rejection of paraffins in polyethylene (different molecular weights). The other important observation in the latter experiment revealed the existence of inter-lamellar ties in the form of fibrous crystals. Electron diffraction studies showed the chains to lie along the fibril axis.

Contrary to the above model, Lindenmeyer, 1966, in discussing the 'crystal-defect' model of crystallinity, suggests that lamellae are separated into crystalline domains by dislocation arrays. These cause the lattice to twist and branch in a more or less coherent (but not crystallographic) manner along the direction of growth. Crystallization proceeds by a fractionation process and growth faces propagate using molecules of similar molecular weight. The low molecular weight material is fractionated and on solidification may crystallize in the interstices between the folded chain crystals in the form of extended chain crystals.

The crystal defect model and the two-phase model of crystallinity are discussed in Section 3.1.5.

Direct study of morphological detail may be achieved by electron microscopy. In crystalline polymers, in which the molecular orientation is known from optical studies to twist co-operatively, the crystalline fibrils appear as lamellae. It has been shown, (Fischer, 1963, that the lamellae twist through 180° about a spherulite radius within each band, and that the molecules are perpendicular to the planes of the lamellar fibrils with a long spacing of around $150 \text{ \AA}$, (Fuijwara, 1960).

3.1.4 The Morphology of Bulk Crystallized Polyethylene

The detailed morphology of bulk crystallized polyethylene is extremely complex and unknown. However, some features of the fine structure have been identified which are similar to those observed in dilute solution.

Using an oxidation dispersion technique Palmer and Cobbold, (1964), isolated lamellae blocks from bulk crystallized polyethylene. The technique was also used by Keller & Sawada, (1964), who critically examined the crystalline debris. The following conclusions emerged. For polyethylene the crystalline units are of lamellae origin. The lamellae are elongated and lath-shaped bounded by (110) and (100) faces, with the direction of elongation along the b axis. By analogy with dilute solution studies it was inferred that the lamellae were in folded chain conformation. Fragments of twisting aggregates were observed which could be identified with the constituents forming the bonded spherulite. The long dimension, the crystallographic b axis, lies along the spherulite radius, and the twist period corresponds to the banding seen with the polarizing microscope prior to dispersion. Thus the morphology of the spherulite formed from bulk crystallized material can be linked with the simplest crystal formed from dilute solution. However, many additional morphological features remain unexplained. These include the nature of the amorphous material in the spherulite, the origin of the twist in the spherulite, and the possibility of superstructures.

3.1.5 Current Models for Isotropic Polyethylene and Other Crystalline Polymers

The preceding sections have presented the major morphological and textural features of polyethylene, P.E. Complications arising from variations in temperature and heat treatments, molecular weight, pressure, concentration of solution, and degree of supercooling, have not been presented. Such a discourse is beyond the scope of the present text. However, an attempt has been made to establish the crystalline nature of P.E., and the basic crystalline units which aggregate to form the bulk crystallized P.E. polymer. The variation of morphology with the many variables listed above for P.E. and other polymers have been discussed elsewhere, (Geil, 1963). The two models of crystalline polymers currently advocated in the literature will now be discussed.

Two models of crystalline polymers have been proposed to explain the properties and deformation behaviour of bulk material. Firstly, a "two-phase" model which has crystalline and amorphous regions, (Keith and Padden, 1964 a, b), and secondly, a "crystal-defect model of polymer structure", which envisages the bulk material

has an assemblage of crystalline units and crystalline imperfections in the form of a network of dislocations, (Holland, 1964), Holland and Lindenmeyer, 1965, Lindenmeyer, 1966). The basic difference between the models is in the interpretation of the regions which do not have long range three-dimensional order. The first model admits to the existence of disorder, and polymer chains in random, but not necessarily maximum entropy, configuration. The second model, also subscribed to by Statton, 1967, Stuart, 1959, and Geil, 1960 and 1965, considers the amorphous phase as a network of crystal defects in the form of dislocations. This model can be shown on theoretical grounds to explain the 'amorphous' halo on X-ray diffraction patterns, (Statton, 1967), and account for the observed density being less than that for the ideal crystalline structure. The model also explains inter- and intra-lamellar slip as possible deformation mechanisms in the bulk polymer, (Lindenmeyer, 1966).

Various morphological features will now be summarized and the imperfections, both inter- and intra-crystalline, will be discussed in terms of the two models.

Intra-crystalline imperfections may arise due to chain ends, or from chain configuration and conformation irregularities, for example, branches or spurious bulky side groups or kinking, (Reneker, 1962). Both models can accommodate these type of imperfections which give rise to intra-crystalline dislocations. However, Keith and Passaglia, 1964,, have described various types of dislocation which might be expected in P.E. crystals and conclude, that "deformations of appreciable magnitude in chain-folded polymer crystals cannot be attributed solely to dislocation mechanisms". Lindenmeyer and co-workers, (see, for example, Lindenmeyer, 1966), are at variance with this conclusion and argue that the dislocation types of Keith, et al, are improbable, and that the deformation behaviour of P.E. may be successfully described using dislocation mechanisms.

It is apparent from Section 3.1.2 that the fold surface of an isolated polyethylene crystal presents many problems, and theoretical arguments and experimental evidence exists for either an amorphous, or a regular adjacently re-entering fold surface. The dilemma of the form of the fold surface is unresolved. The crystal defect model envisages a regular, adjacently re-entering fold surface, whereas the two-phase model requires a loose fold surface to promote inter-lamellar cohesion, since forces are necessarily transmitted directly from one crystal to another by means of inter-lamellar contact. Major differences of opinion between the two models are

in the nature of the inter-lamellar cohesion and the segregated or fractionated materials arising during spherulite growth. In the isotropic state the polymer has crystallised into a polygonal spherulitic structure and segregated impurities and fractionated polymer abounds at the spherulite boundaries. The spherulitic inter-face may be amorphous or slightly crystalline and many imperfection types may exist. (Keller, 1969, Keith, et al, 1966). The inter-spherulite cohesion is maintained by the molecules which traverse from spherulite to spherulite. The intra-spherulite regions consist of radiating lamellar-like fibrils separated by segregated materials which are in a less well-ordered state. In the model of spherulite growth according to Keith and Padden, 1964, the inter-lamellar regions will consist of amorphous material with low molecular weight, and high impurity content, and more important, tie molecules or tie crystals which facilitate inter-lamellar cohesion.

Contradictory models, (Holland, 1964, Holland and Lindenmeyer, 1965, and Lindenmeyer, 1966), suggest that the "amorphous" entity is a network of crystalline dislocations, and the segregated material is low molecular weight polymer which crystallizes into a more thermodynamically stable, extended chain crystal. Cohesion is maintained by the normal crystal lattice forces and tie molecules. However, with this model whenever polymer chains pass from one crystallite to another, they do so in an orderly way. Thus stress which has been concentrated on a given crystallographic plane in one crystal may be transmitted to the corresponding plane in the next crystal.

Further imperfections may arise as the lamellae twist, but imperfections associated with twisting are unknown. Other imperfections of spherulite geometry occur at the nucleus due to the sheaf-like structure, and also discontinuities may arise associated with space filling of the radiating twisting ribbons. Thirdly, the spherulite boundary presents a macroscopic discontinuity and also a site for the accumulation of segregated material.

It is the author's contention that the crystal defect model cannot satisfactorily explain some observations made in this laboratory and reported in the literature. The observations of Hay and Keller, 1965, on spherulite deformation in elongated films showed, in many cases, that large deformations were reversible and that this requires a large elastic deformation of the type associated with a low modulus rubber. It was speculated that this behaviour was symptomatic of an amorphous matrix in which the crystals are embedded and cohered via tie molecules connecting the lamellae. On deformation the crystals are displaced relative to one another with strained material between in which stored energy is accumulated.

The stored energy is the origin of the restoring force on removal of applied stress. Similar observations were made during the study reported here at all draw ratios, from isotropic to D.R.5, on uniaxially cold drawn low density polyethylene sheets. Whilst dislocation theory can readily explain high elongations under applied stress, it cannot explain the large recoverable strains observed on removal of stress. Thus the crystal-defect model and the dislocation mechanisms, proposed by Holland and Lindenmeyer, cannot fully explain the deformation behaviour of polyethylene. Stein and Norris, 1956, have measured the infra-red absorption spectra of isotropic polyethylene and have reported an absorbancy band associated with an amorphous phase, also, from selective oxidation, (Meinel and Peterlin, 1967), and sorption studies, (Peterlin and Olf, 1966,) it is postulated that an amorphous phase is present which is attacked preferentially to the crystalline regions. This is collaborative evidence for a two-phase model of crystalline polymer structure. More recently, Kavesh and Schultz, 1970, have reported an X-ray diffraction method of analysis which can differentiate between a one phase, homogeneously dis-ordered structure - as invoked by the crystal-defect model - and a two-phase structure consisting of ordered and disordered regions - as described by the two phase model of crystallinity. The authors conclude that a two-phase structure must exist in bulk crystallized polyethylene, and amorphous regions must be present. Furthermore, their study suggests that the lamellae in bulk polyethylene are composed of mosaic blocks within which the molecules are in regular lattice array and with boundaries defined by dislocations.. The disorder within the mosaic blocks arises primarily from thermal vibrations and possibly point dislocations such as have been proposed by Reneker, 1962. The mosaic block composition of the lamellae crystals has been proposed earlier by other workers, (Hosemann, 1967, Hosemann, 1963, Lindenmeyer, 1964, and Statton, 1967 a).

It is concluded that the two-phase model of crystallinity in polymers, which invokes an amorphous component, is a more appropriate model for bulk crystallised polyethylene, but that the crystal-defect model is consistent with the intra-crystalline regions.

3.2 MORPHOLOGICAL STUDIES ON ORIENTED POLYETHYLENE

A hypothesis of the morphology, and the morphological changes occurring during the orientation of cold-drawn polyethylene will now be given based on information currently available. An attempt has been made to correlate and discuss the observations which have been presented over the last few years. The discussion has been divided into three sections, each section concentrating upon the morphology of cold drawn P.E. within a particular draw-ratio range. The current models proposed for the highly oriented state are also discussed.

3.2.1. Low Draw Ratio Materials

At low draw ratios, (D.R. 1.05 to D.R. 1.40), the original crystalline structure has been permanently deformed, and it is argued that this may arise due to irreversible crystalline deformation processes and/or inhomogeneous deformation of the spherulities. The orientation of the crystallographic axes on deformation of single crystals and bulk crystallized polyethylene are similar, and indicate that the crystalline units aggregated in the bulk material may be irreversibly deformed. Also optical and electron microscopy studies on thin films and bulk crystallized polyethylene demonstrate that, at constant temperature, the spherulites may be irreparably deformed, and the lamellae within the spherulites become oriented about the draw direction. A review of the observations on cold drawn polyethylene at low draw ratios is presented below.

Investigations of the deformation behaviour of P.E. single crystals have shown that twinning, and chain tilt and slip, can give rise to 5% to 15% permanent deformation, (Peterlin, 1966, Ingram, et al, 1967). This deformation corresponds to a draw ratio range 1.05 to 1.15. Further deformation can occur due to chain slip. In the early stages of deformation, for a favourable crystal orientation, first twinning, and then phase transformation and chain tilting are observed. When the draw direction is parallel to the a axis then twinning occurs on the (110) diagonals and the a axis becomes nearly perpendicular to the draw direction, (Figure 3.4a). If the draw direction is closer to the b axis, the orthorhombic lattice transforms into a monoclinic phase. This phase transformation does not appreciably rotate either the a or b axes. Thus for a random assemblage of crystals the main effect is the shift of the a axis into a plane perpendicular to the draw direction as a consequence of twinning. An important deformation mechanism is chain tilting about the (310) direction which proceeds by successive chain slip, (Figure 3.4.b), and hence chains are progressively shifted towards the draw direction.

An anomalous orientation of the a axes perpendicular to the draw direction in the early stages of drawing of bulk crystallized P.E. has been observed, (Keller, 1955, and Aggarwal and Sweeting, 1957), and other wide angle X-ray diffraction studies have been reported, (Stein and Norris, 1956, Aggarwal, Tilley, and Sweeting, 1961). The orientation of the crystallographic axes was shown to proceed as follows. The a axes first become oriented perpendicular to the direction of draw, and the planes containing the b and c axes are randomly distributed in the plane perpendicular to a. Further deformation rapidly rotates the c axes towards the draw direction with a and b axes randomly oriented, the direction (OIL) becoming aligned parallel to the draw direction. The mean orientation of the c axes is at 35° to the draw direction at D.R. 1.4. (Keller, 1955, Stein and Norris, 1956, Gupta, Keller, Ward, 1968). A recent

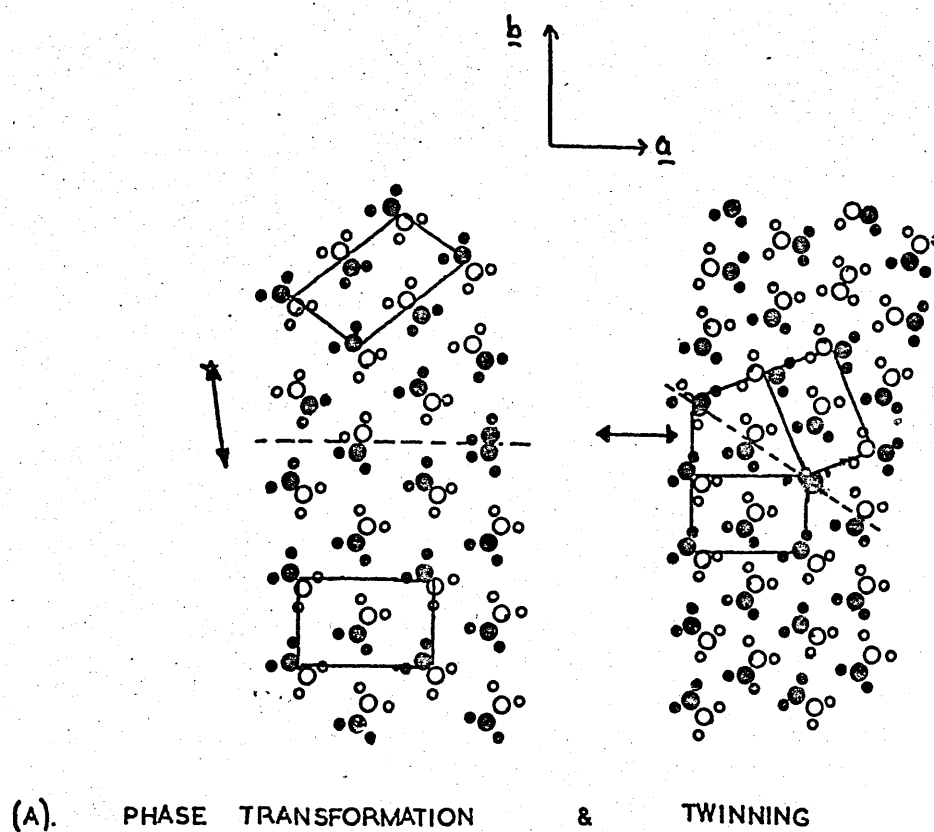
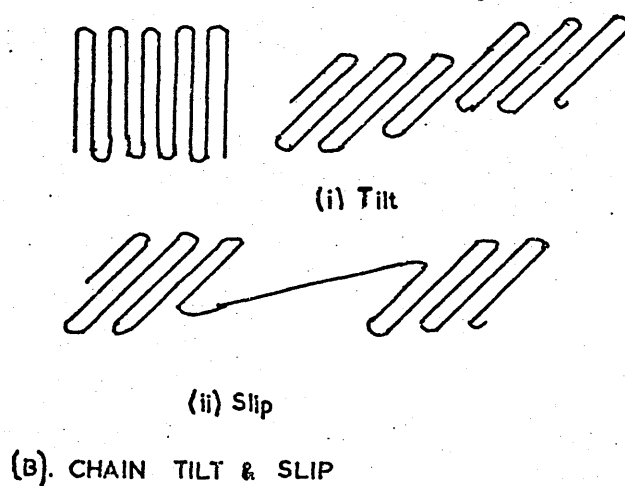


FIGURE 3.4 Deformation of Polyethylene Crystals
(after Peterlin, 1966)

study, using wide angle X-ray diffraction techniques, (Gupta, et al, 1968), has determined the orientation distribution of the c-axes in uniaxially drawn L.D.P.E. films over a range of draw ratios. For low draw ratio films (D.R. = 1.4) four intensity maxima were observed at 35° to the draw direction. As the draw ratio increases these maxima merge, and the average orientation of the c-axes about the draw direction is greatly reduced. Similar observations were reported earlier, (Stein and Norris, 1956), which showed that the spread of c-axes about the mean is also decreased with increasing draw ratio at low draw ratios.

The orientation of the crystallographic axes in single crystals and bulk crystallized P.E. are clearly similar. It has been postulated, (Peterlin, 1966), that the observations in the bulk are a manifestation of the deformation behaviour of the lamellae crystalline units. Peterlin suggested that twinning occurs in the early stages of deformation, and further orientation develops by a chain tilt and slipping mechanism. However, other mechanisms may contribute to the overall permanent deformation at low draw ratios and may derive from an inter-lamellar slip mechanism, and homogeneous and inhomogeneous deformation of the spherulites.

Investigations of spherulite deformation in films of melt cast P.E. have been made by Hay and Keller, 1965, who reported the effects of orientation over a wide range of draw ratios, and supplemented optical measurements with X-ray diffraction and electron microscopy studies. Two modes of spherulite deformation were observed:

(i) Homogeneous deformation where the whole spherulite deformed, but had no simple relation between the change of shape and the applied forces, or the macro-deformation of the films. (In some cases homogeneously deformed spherulites were observed up to D.R.10, and up to D.R.5, the original spherulitic form was reconstituted).

(ii) Inhomogeneous deformations were observed where regions of weakness yield - both intra- and inter-spherulite - and draw out leaving areas of apparently undeformed spherulites. Such deformations were not recoverable on the removal of stress.

Hay and Keller suggest that the reversibility in spherulite shape and crystal orientation requires large elastic deformations which are entropic in character. This suggests that the crystals are either in an amorphous matrix, or have tie molecules connecting the lamellae. The tie molecules may be present in the undeformed

material or created during cold-drawing. Reversibility then implies that the crystals are displaced relative to one another with strained tie molecules in which elastic energy is stored. The existence of inter-lamellar tie crystals in isotropic P.E. has been demonstrated, (Keith, et al, 1966), and the existence of an inter-lamellar amorphous region may be argued from the results of the studies of Palmer and Cobbold, 1964, and Keller and Savada, 1964. Other workers, (Zubov, Kargin and others, 1967), found that on cold drawing sheets of L.D.P.E. to a D.R. 2.00 there was a homogeneous deformation of the spherulites. Further elongation induced necking, and in films with a D.R. 5.5 highly elongated spherulitic regions were observed. On heating the films retracted and the normal spherulitic nature was restored. The authors concluded that at high draw ratios the spherulites are destroyed, but elements of the lamellae remain intact. It was proposed that the stretching proceeded as follows:-

(i) up to D.R. 2.00 uniform elongation of the spherulites occurs which proceeds mainly through slipping and rotation of the lamellae.

(ii) further drawing in the necking zone destroys the spherulitic structure, but retains the simpler lamellar units and the inter-lamellar ties.

This has been confirmed by light scattering observations, (Stein and Rhodes, 1960), which showed that elongations up to 50% (D.R. 1.50) represent the deformation of the spherulites, and only at greater elongation are the spherulites converted to a fibrillar structure.

Further evidence suggests that the spherulitic nature of P.E. is maintained and the lamellae are oriented about the draw direction at low draw ratios. Electron micrographs, (Peck and Kaye, 1954), show that in L.D.P.E. drawn 50% groups of lamellae have swung as units towards the draw direction; the lamellae retaining the basic spherulitic structure. Low angle X-ray diffraction studies, (Hendus, 1963), also show an orientation of lamellae towards the draw direction, and the existence of a four-point diffraction pattern indicates that large crystalline regions are still present inclined at an angle to the draw direction, but with a distribution about some mean orientation. The lamellar texture is still retained when L.D.P.E., at D.R. 1.5, is redrawn at 90° to the original draw direction, (Peck and Kaye, 1954). However, in this case deformation occurs by an inter-lamellar slip mechanism; there is also evidence that fibrillation occurs. Hendus, 1963, investigated the changes in the diffraction pattern that occur when a drawn sample of L.D.P.E. (elongated 200%, D.R. 3.00) is redrawn at 90° to the original draw direction and also found that the lamellae reflections are retained.

The observations on spherulite deformation and lamellae orientation suggest that during the early stages of drawing (up to D.R. 2.00) the deformation is dominated by an inter-lamellar slip mechanism, which leads to the orientation of the spherulite. However, no reference is made to the possibilities of intra-lamellar (crystalline) deformation, which is at variance with the mechanisms proposed by Peterlin, 1966. Peterlin suggests that up to D.R. 1.15 plastic deformation of the crystalline regions dominate and is the cause of the permanent deformation. However, one postulate does not necessarily preclude the existence of the other, and it is possible that the residual orientation at low draw ratios arises from a combination of all deformation mechanisms.

Clearly, the amorphous regions in the oriented polymer make a significant contribution to the deformation behaviour. However, only a limited amount of information is available about these regions as it is difficult to separate the contributions of the crystalline and amorphous regions in the methods of investigation currently available. It has been shown, (Stein and Norris, 1956), that the amorphous regions in the drawn polymer become highly strained and are anisotropic to infra-red dichroic and sorption measurements. The infra-red absorption spectra of L.D.P.E. exhibits a doublet due to CH₂ rocking at 720 - 730 cm⁻¹. Stein and Norris resolved this doublet into its two component peaks, labelled A at 720 cm⁻¹ and B at 730 cm⁻¹. Component A (720 cm⁻¹) has contributions from both the crystalline and amorphous regions and absorbs only when radiation is polarized along the b crystallographic axis. Component B (730 cm⁻¹) has contributions solely from the crystalline regions, and absorbs only when radiation is polarized along the a crystallographic axis. (Measurements at temperatures above the melting point confirm that band B disappears and band A intensifies). Neither component absorbs radiation which is polarized parallel to the c-axis. Using radiation polarized parallel to the draw direction the absorbancy for the B band decreased rapidly up to D.R. 2.00, with a similar, but less pronounced, decrease in the A band. This indicates that the c-axes in the crystalline regions orient rapidly towards the draw direction, but the c-axis orientation in the amorphous regions is much less spontaneous. For radiation polarized perpendicular to the draw direction, up to D.R. 2.0, the B band (crystalline absorption only) shows an increased absorbancy with an even more pronounced increase in the A band. This indicates that the a crystallographic axes in the crystalline region are oriented perpendicular to the draw direction, and also the b axes in both the amorphous and crystalline regions is gradually oriented perpendicular to the draw direction. The anisotropy

of the absorbancy up to D.R. 2.00 is greater for band B than band A, which suggests that orientation of the crystalline regions occurs more rapidly than the amorphous regions with a preponderance of a axes oriented perpendicular to the draw direction. Gupta and Ward, 1968, also attempted to measure the orientation of the non-crystalline regions using infra-red and N.M.R. techniques; their measurements were only reported for the highly drawn state and no further useful information may be deduced.

Current knowledge of the morphology and morphological changes occurring on orientation of L.D.P.E. by cold-drawing at low draw ratios can be summarised as follows:

1. Wide angle X-ray diffraction studies show that in the initial stages of drawing the a axis is preferentially oriented perpendicular to the draw direction, but as drawing proceeds the a and b axes are randomly distributed about the c axes. At low draw ratios (up to D.R. 1.4) the c-axes orient rapidly into a cone distribution about the draw direction with the average c-axis orientation of 35° . The spread of c-axes about this mean orientation decreases with increasing draw ratio at low draw ratios.
2. Observations reported from studies using low angle X-ray diffraction, light scattering, and electron microscopy indicate that the lamellae are intact and inclined at an angle to, and oriented about, the draw direction.
3. The amorphous regions are strained with the c-axes oriented towards the draw direction.
4. The spherulites may be homogeneously and/or inhomogeneously deformed, but the available evidence suggests that the deformations are mostly of the homogeneous type.

3.2.2 Intermediate Draw Ratio Material

To achieve intermediate draw ratios (D.R. 2.00 and D.R. 2.65), the original isotropic blank is first drawn, with necking, to draw ratios in the range D.R. 3.00 to D.R. 3.7. When the drawn material is then left in the stress free state at room temperature it recovers to an equilibrium state of D.R. 2.00 and D.R. 2.65 respectively. The mechanisms which control this behaviour on drawing will be dominated by chain tilting and slipping in the crystalline regions together with an eventual breaking off of lamellae blocks. These blocks cohere to one another by tie molecules which were there in the original structure or are produced on rupture. The spherulitic superstructure is destroyed and fibrillation proceeds. The high retractive forces which give rise to a recovery of around 100% arises from the strained amorphous regions. On necking the c axes

are further oriented towards the draw direction, but still maintain a mean angular distribution about the draw direction of 15° at D.R. 2.00, and 10° at D.R. 2.65, (Stein and Norris, 1956, and Gupta, Keller and Ward, 1968). However, the spread of c-axes orientation about the mean decreases with increasing draw ratio. Low angle diffraction patterns (Hendus, 1963), approach a line diagram, but with diffuse scattering. This indicates a breakdown of the large lamellae blocks into smaller crystalline entities which are aligned approximately perpendicular to the draw direction.

The amorphous regions become more oriented than at low draw ratios with a further orientation of the amorphous c axes in the draw direction, and the a and b axes in the crystalline and amorphous regions are randomly oriented approximately perpendicular to the draw direction, (Stein and Norris, 1956). The amorphous regions will now have a different origin. A proportion of this phase will be the original amorphous material segregated at the spherulite boundaries and the inter-lamellar regions, and a further portion will arise from the breakdown of the crystalline structure and may be present in the form of tie-molecules. After necking the remains of the spherulitic structure is only fragmentary. Substantial amounts of inhomogeneous deformation of the spherulites has occurred and only the tip of the spherulite - which has been maintained in the direction of draw - and the nucleus, may be intact, (Hay and Keller, 1965). Optical (Zubov, et al, 1967) and electron (Geil, 1963), micrographs show that striations which have spherulitic features can occur even at elongations of 500%.

The morphology of intermediate draw ratio L.D.P.E. can be summarised as follows:-

1. Wide angle X-ray diffraction patterns show that the c-axes are further aligned towards the draw direction, and a and b axes are randomly oriented in the plane perpendicular to the c axes.
2. Low angle diffraction patterns indicate that the crystalline structures are oriented approximately perpendicular to the draw direction and the diffuse scattering suggests these are smaller entities than the original lamellae.
3. The c axes in the amorphous regions become more aligned towards the draw direction.
4. Only fragments of the spherulite structure persist.

3.2.3 The Highly Drawn State

Material which is cold drawn to draw ratios of about 5 recovers to draw ratios of about D.R. 3.8 to D.R. 4.2 in the stress free state. At these higher draw ratios the average c-axis orientation is 4° to the draw direction, (Stein and Norris, 1956, Gupta, et al, 1968). The low angle X-ray diffraction patterns become less diffuse and the two line pattern is more evident. The diffuse scattering may be due to the small crystalline size or poor orientation of the crystalline units or both, (Peterlin, 1969, and Hosemann, 1963).

In the neck region electron micrographs of the deformed spherulites show a gradual transition from the lamellar to the fibrillar structure, although there is some evidence that the ring structure parallel to the draw direction persists in the highly drawn material, (Geil, 1963, Hay and Keller, 1965, Yeh and Geil, 1968). It is postulated that in the highly drawn state the material has a fibrillar texture with strained amorphous and crystalline regions. However, little is known about the morphology of the bulk crystallized cold drawn polyethylene, but some of the studies on thin films in the highly drawn state are discussed below along with the models proposed by some workers.

It has been shown, (Zubov, et al, 1967), that on annealing cold drawn highly oriented polyethylene, a proportion of the original lamellae were incorporated into a coarser new spherulite structure. It was suggested that the broken lamellar blocks were joined by tie molecules, and on annealing the blocks were reorganised in the spherulitic form, but not necessarily with the same nuclei. It was deduced that further elongations of the highly drawn material occurred by straining the amorphous regions without affecting the crystalline blocks. Supporting evidence, (Stein and Norris, 1956), shows that the intensity of the A band infra-red absorption parallel to the draw direction continues to decrease with increasing draw ratio at high draw ratios, indicating a better alignment of the c axes parallel to the draw direction, whilst the intensity of the B band absorption parallel to the draw direction is constant; this suggests that the crystalline regions are fully oriented. If increased elongation further destroyed the crystalline regions the B band would disappear. Also, Hendus, 1963, shows that re-drawing the highly oriented material at 90° to the original draw direction does not destroy the structure, but re-orientes the crystalline regions. The deformation may be facilitated by the amorphous regions. Similar findings have been reported by Clayton, 1968, who found that on rolling highly oriented, cold-drawn polyethylene, (i.e. compression transverse to the plane of the sheet and perpendicular to the draw direction), the crystalline regions were undamaged. The investigations

showed that the crystalline regions were re-oriented by a twinning mechanism and by deformation of the strained amorphous regions. On annealing these cold drawn and rolled materials the presence of regions of amorphous material was observed, (Cowking, et al, 1968, see also Section 3.2.4). Assuming that rolling or annealing does not produce amorphous material it may be concluded that the original cold drawn sheet also has the same amorphous regions but in the strained state. Concurrent work, (Yeh and Geil, 1968), using X-ray, and electron diffraction and microscopy techniques support these ideas. Yeh and Geil demonstrate the presence of alternating fibrils of an essentially disordered (amorphous) region, and fibrils with intra-fibrillar lamellae regions. The latter fibrils were reported to have alternating crystalline and amorphous regions with a periodicity of $100 \text{ \AA}$ to $150 \text{ \AA}$, with an amorphous thickness of 60 to $70 \text{ \AA}$, and are similar to the micro-fibrils proposed by other workers, (Hosemann, 1963, and Peterlin, 1969).

Models for the highly drawn state proposed by Hess, Mahl and Gutter, 1957, and later by Statton, 1959, were discounted by Hosemann, as theoretical calculations showed that these models gave rise to strong, small-angle meridional scattering far in excess of that observed in practice. Based on an original idea by Bonart, 1959, Bonart and Hosemann, 1960, and Hosemann, 1963, proposed a paracrystalline model for highly oriented polyethylene, which introduces the concept of folded chain lamellae blocks, with both regular and looped folds, and with tie-chains which arise in an amorphous region. This model satisfactorily explains the observed X-ray diffraction patterns. Based on observations of small angle X-ray diffraction patterns, and the changes in the patterns on shear deformation, Hosemann, proposed that micro-fibrils combine together and were displaced relative to each other without correlation to form macro-fibrils: in cold-drawn L.D.P.E. the fibrils, combinations of single, double, and triple micro fibrils would be separated by voids, (Figure 3.5). Hosemann suggests that the crystalline regions are small three-dimensionally ordered units with lateral dimensions of a few hundred Angstroms, and have no lateral register. However, Peterlin, 1966, argues that "the narrowness of wide-angle X-ray diffraction spots demands a much wider lateral extension of coherent crystal lattice than a few hundred Angstrom units, so that the latter dimensions characteristic of the intensity distribution in the small-angle diagram must be a consequence of surface waviness of the lamellae". Peterlin reconciles the disparity by postulating that "blocks of folded chains with such lateral dimensions (a few $100 \text{ \AA}$), but of widely varying surface orientation are put together with a nearly

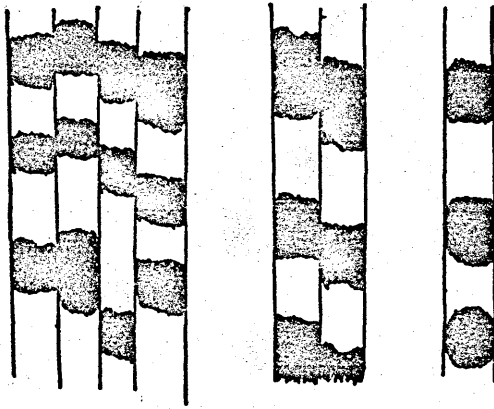


FIGURE 3.5 Model for Highly Drawn Polyethylene

crystallographic fit on the lateral faces, so that the lateral coherence of the lattice, as manifest by the width of wide angle reflections, extends over much wider areas as one single block". Other workers, (Yeh and Geil, 1968), have reported experimental evidence which showed that, at the draw ratios associated with the initially necked specimens, there is a lateral order of the crystalline units which gives rise to a "wavy lamellae". Electron micrographs of nitric acid etched highly drawn bulk P.E. demonstrate the existence of a few thousand Angstrom thick fibrils containing stacks of more or less regular lamellae with widely varying orientation of the surface, (Peterlin, 1969). It was concluded that the fibril of bulk oriented P.E. was composed of many micro-fibrils, and that the lattice mis-match and orientational variation of the crystal blocks in adjacent micro fibrils are a nearly ideal model of a paracrystalline order.

There is evidence for an inter-fibrillar amorphous region which is not invoked in the models described in the literature referred to above, (Hay and Keller, 1966, 1967, and Cowking, et al, 1968). The model of Hosemann, Figure 3.5., suggests that the fibrils are separated by voids. The formation of such voids has been reported by Hay and Keller, 1965, and Yeh and Geil, 1968, but in both cases the conditions have been extreme. The deformation has been grossly inhomogeneous and local elongations of 1000% were reported in the areas where voids were observed. Otherwise, inter-fibrillar amorphous material is observed which is contrary to the Hosemann model. Peterlin, 1969, discounts the presence of voids in necked P.E. and invokes the existence of a strained amorphous phase based on experimental studies reported by himself and co-workers.

Summarising, for the highly drawn state there is general agreement about the existence of macro fibrils composed of micro fibrils, which have alternating crystalline and amorphous regions. The lateral register of the fibrils explain the discrete maxima observed on wide-angle X-ray diffraction patterns, and the intense diffuse equatorial scattering in low angle X-ray patterns. The model proposed by Hosemann is the one most generally accepted. However, it does not account for the inter-fibrillar amorphous regions which dominate the deformation behaviour, and are apparent from X-ray and electron microscopy studies. A modified Hosemann model is proposed with an inter-fibrillar strained amorphous region, and where the micro-fibrils have some lateral register and combine to give macro-fibrils of $1000 \text{ \AA}$. This model will be adopted in a later Section, Section 9., to explain the mechanical properties of highly drawn L.D.P.E. If voids are induced by drawing they will result from the inhomogeneous deformation of the spherulitic structures and will be a localised phenomena, and it is unlikely that they will extend the length of the fibrils.

3.2.4 Special Textures in Oriented Polyethylenes

After some early work by Point, 1956, Keller and co-workers devised a method involving drawing, rolling and annealing whereby it was possible to design specially textured structures, (Hay and Keller, 1966, 1967, Cowking, et al, 1968, Point, et al, 1969). These structures had well defined principal crystallographic axes orthogonal to the draw direction and the plane of the sheet and, by various annealing treatments, it was found possible to orient the crystallites (lamellae) at well defined angles to the crystallographic axes. By concurrently determining small and wide angle X-ray diffraction patterns with annealing treatment it was found that:-

1. The amorphous material in the originally cold drawn sheet was highly strained which, when the sample was annealed, gave rise to a high retractive force. However, the nature and orientation of the amorphous regions was unknown, but tie molecules or crystals were thought to be present.

2. Two types of amorphous material were postulated, both inter-crystalline and an amorphous superstructure, but the whole is an integral system with a well defined amorphous-crystalline inter-action.

3. The material deforms by two mechanisms. Firstly, inter-lamellar shear, which is most easily activated, and secondly, intra-lamellar shear on planes containing c-axes.

Cowking, et al, (1968), observed results of macro-deformation on selected samples and found with these samples that inter-lamellar slip was the most probable deformation mechanism. However, they calculated that only about 25% of the deformation could readily be accounted for by this process; the remainder was due to a more extensible amorphous phase. Also it was found that the crystallite size remained constant in their studies which suggested that there was an extra lamellar amorphous region that is in intimate and well defined relation to the crystal, which combines to give a super-lamellar texture. This extra amorphous packet gives rise to a high reversible elastic effect.

SECTION 4. THE MECHANICAL PROPERTIES OF ISOTROPIC AND
ANISOTROPIC POLYETHYLENE

4.1 Transitions in Isotropic Polyethylene

4.1.1 The α' transition

4.1.2 The α transition

4.1.3 The β transition

4.1.4 The γ transition

4.2 Creep Studies of Isotropic Polyethylene

4.3 Transitions in Oriented Polyethylene

4.4 Creep Studies of Oriented Polyethylene

4.5 The Relation between Structure and Mechanical Properties

In this section the dynamic and quasi-static (creep) mechanical properties of polyethylene (P.E.), both in the isotropic and anisotropic state, will be discussed. The dynamic properties, particularly the dynamic mechanical loss peaks, have been extensively studied, but little has been reported on the creep behaviour of P.E. (The dielectric loss transitions will also be referred to to aid the discussion).

The prominent mechanical and dielectric loss transitions in isotropic high density polyethylene, H.D.P.E., and low density polyethylene, L.D.P.E., have been recorded for many years. The mechanical loss peaks for L.D.P.E. were studied by Schmeider and Wolf (1953), and later investigations by Flocke, 1962, included H.D.P.E. Three main transitions are apparent in both H.D.P.E. and L.D.P.E. A schematic diagram of the transitions is shown in Figure 4.1 indicating their relative magnitudes and positions on the temperature axis at constant frequency. In the usual manner the L.D.P.E. peaks are labelled α , β , γ , and the H.D.P.E. peaks α' , α , γ . Dielectric loss studies by Oakes and Robinson (1954), Tsuge et al (1962), and Mikhailov et al (1957), indicated corresponding dielectric loss transitions.

An analogy between dielectric and mechanical transitions has been made and the activation energies from both sets of data calculated. The α and γ values are in good agreement, but there is a large discrepancy in the values for the β relaxation. The α process has an activation energy at 28 k cal/mol from dielectric studies, and 25 k cal/mol from mechanical measurements, whereas that for the γ is of the order of 11 k cal/mol by both methods (Willbourn & Sandiford, 1960). The β process, however, has been attributed with activation energies varying through 38 k cal/mol, 25, 20 and 16 k cal/mol from both mechanical and dielectric experiments.

The nature of the mechanisms manifest in the loss transitions in P.E. were unknown prior to the start of the work reported in this thesis, and have only recently been postulated. The molecular origin of the transitions has been suggested by many workers, but is still in dispute. Attempts to clarify this latter point have been made using mats of single crystals, but an unequivocal designation of the molecular origins of the transitions is still not available.

The results of dynamic loss studies on isotropic and single crystal mats of linear P.E., and the postulated molecular origins of the transitions are discussed in Section 4.1. The information currently available in the literature will be presented, not only for L.D.P.E., but also for linear P.E., where the work and information

is relevant to the discussion and interpretation of the transitions in L.D.P.E. The stiffness properties of L.D.P.E. at larger strains (up to about 5%) are discussed in Section 4.2. The information is derived mainly from the manufacturers literature as few, if any, systematic studies of the deformation behaviour of L.D.P.E. have been reported.

Dynamic mechanical loss studies on cold drawn L.D.P.E. and H.D.P.E. have been reported by Stachurski and Ward, (1968, a), and are discussed in Section 4.3. Further work by Stachurski and Ward, (1968, b), documented the anisotropy of the mechanical loss peaks in textured materials: it was shown that two transitions occur, an inter-lamellar shear process at low temperatures, and an intra-lamellar shear process at high temperatures (Section 4.3). Other deformation studies on oriented P.E. are discussed in Section 4.4., and the state of knowledge, which existed at the start of this thesis, relating structure to mechanical properties is discussed in Section 4.5.

4.1 TRANSITIONS IN ISOTROPIC POLYETHYLENE

The prominent transitions in P.E. will now be treated separately, and their postulated molecular origins will be discussed.

4.1.1 The α' Transition

The α' transition has only been reported in dynamic mechanical loss studies on H.D.P.E., and does not occur in L.D.P.E., or single crystal mats of linear P.E.. Dielectric loss measurements do not detect this transition.

Iwayanagi, (1962), proposed that the α' relaxation is a boundary phenomena analagous to grain boundary slip observed in metals. However Takayanagi, (1963), suggested a contrary relaxation due to the translational motion of the molecule in the direction of the molecular axis in the crystalline regions. A later investigation by McCrum and Morris, (1966), on both the α and α' transitions associated the former with the crystalline regions, and the latter to slip at the lamellae boundaries. The proposals by McCrum et al and Iwayanagi indicate a relaxation associated with amorphous regions, whereas Takayanagi postulates an intra-crystalline relaxation. However, as the transition is not observed in single crystal mats, it is reasonable to assume that the α' peak would be related to the amorphous regions in the bulk crystallised P.E. The experiments of Flocke (1962) are consistent with the latter explanation. Flocke showed that the α' relaxation occurred at lower temperatures in a quenched specimen than in a slow cooled sample. The slow cooled specimens have a coarse spherulitic structure with well formed lamallae with a thickness around $290\text{\AA}$, in contrast to the quenched specimens which have a fine spherulitic

structure with lamellae thicknesses about 190Å, (Corneliussen and Peterlin, 1967). Consequently, in the latter case, there is more amorphous component and the transition is more easily activated and appears at a lower temperature.

Although the α' peak in H.D.P.E. is associated with the amorphous regions, it does not bear the same relationship to the α peak as the amorphous transitions in L.D.P.E. The amorphous transition in L.D.P.E. is manifest in the β loss peak, which is approximately 40°C below the α transition, and has been interpreted as inter-lamellar shear (Section 9.1). The α' peak in H.D.P.E. has also been attributed to an inter-lamellar shear mechanism. (McCrum and Morris, 1966). However, it is unlikely that as the density of the P.E. is decreased the amorphous transition, of evidently the same origin, would change position relative to the α peak on the temperature scale. No explanation of this apparently anomalous behaviour has appeared in the literature.

4.1.2 The α Transition

The first informative investigations on the nature of the α relaxation were by Schneider & Wolf, (1953), who studied the magnitude and position of the loss peak as a function of chlorine content in chlorinated P.E., using the torsion pendulum technique. The principal effect of the chlorine atoms is to lower crystallinity: at high chlorine content, when the crystalline content is very low, no α peak was discernible. An increase in chlorine content decreases the magnitude of the peak and moves it to lower temperatures until at high chlorine content the α peak is absent. As the α peak diminishes and disappears the crystalline reflections of X-rays also diminishes and disappears. These results indicate that the α peak is associated with the crystalline regions.

The dielectric α peak was also assigned to the crystalline region by Mikhailov and co-workers, (1957). Further work by Tuijman, (1963), and Booij, (1965), also supports this hypothesis, and these workers proposed that the dielectric relaxation was due to the re-orientation of the molecules within the crystals.

Other workers have attributed the relaxation to the crystalline regions but have proposed different molecular origins. Rempel, (1957), attributed it to "vibrational and re-orientational motion within the crystal" whereas Pechold et al, (1963), described it as a "motion of lattice defects, where the defects take the form of kinks in a predominantly planar zig-zag chain".

Work on single crystal mats also suggests that the α loss peak is a manifestation of a crystalline transition. (Thurn, 1960, Takayanagi, 1963, Sinnott, 1966). Sinnott demonstrated that the mechanism is associated with the chain folds. On annealing, the single crystals irreversibly thicken, with a corresponding decrease in the number of folds and, at the same time, the intensity of the relaxation falls.

Clearly, an accurate designation of the molecular origin of the α process is difficult. Hoffman et al (1966) present a model which attempts to reconcile the findings in bulk crystallized material and crystal mats. They suggest that the α process consists of two overlapping mechanisms and is a result of "motion of chain folds and re-orientation (with translation) of chains in the interior". Using their model they have calculated activation energies for the α and γ process which compare favourably with experimental data.

The conclusions reached thus far have been based on idealised molecular models and no account has been taken of the presence in the bulk crystallized material of the many possible crystalline imperfections which may arise during crystal growth (Section 3). In the case of L.D.P.E., where the crystallinity is typically of the order of 50%, the amorphous-crystalline interaction may have a dominant effect, and the proposed models do not consider the many other complex molecular mechanisms which may also be available. A large number of relaxation types should be invoked, with a wide distribution of relaxation times, to account for the possible crystal-crystal and crystal-amorphous interactions, but with a predominance of the re-orientation types suggested above. Stein, 1966, infers that the higher activation energy of the α process in H.D.P.E. is due to the different size and environment of the crystalline regions, in agreement with the discourse above. Using a dynamic birefringence technique he indicated that the α mechanism in L.D.P.E. was due to two overlapping mechanisms involving the crystalline regions, and proposed that on deformation the spherulites deform instantaneously, followed by a crystal re-orientation mechanism involving inter-lamellar slip. Similar observations were made at higher temperatures with H.D.P.E.; Stein concluded that the inter-lamellar shear process is shifted to higher temperatures since the process has a higher activation energy in the more crystalline material. This interpretation of the α mechanism for L.D.P.E. is contrary to the findings discussed previously, and those reported in this thesis. Observations by Moore and Geiniewski, (1966), of the change of light scattering diffraction patterns during uniaxial tensile creep of L.D.P.E. confirm an instantaneous super structure (spherulitic) deformation, but invoke re-orientation of the lamellae due to an intra-lamellar slip mechanism. If one postulates that the intra-lamellar shear is made easier as the

number of defects in the crystalline regions is increased, and that the energy barriers opposing the various vibrational and re-orientational modes are decreased as imperfections in the crystalline regions increase, then the observed shift in the α peak to lower temperatures with decreasing crystallinity is explained. The intra-lamellar shear process seems more feasible than that proposed by Stein, and also reconciles the proposals of other workers.

4.1.3 The β Transition

The β transition is not apparent in H.D.P.E. and is only observed in L.D.P.E., and it is generally accepted that the β transition is due to the motion of branch points on the polymer chain. A relationship between the β relaxation and the amount of side-branching has been demonstrated, (Kline et al, 1956). It was found that as the density was increased, i.e. the number of methyl groups per 1000 C-atoms decreased, the magnitude of the β peak diminished until, at a level of one methyl group per 1000 C-atoms, the β peak was almost absent. It was concluded that the β peak in L.D.P.E. was due to the relaxation of branch points associated with the amorphous regions within the polymer. Studies on single crystal mats show no evidence of a β transition, which further confirms that the β peak is associated with the amorphous regions. Mikhailov et al, (1957), showed that the dielectric loss factor for the β relaxation increased in magnitude and moved to lower temperatures if the material was quenched rather than annealed. The quenched material has less well defined crystalline regions and a bigger amorphous component. (The crystalline α transition was absent in the quenched material).

4.2.3 The γ Transition

The γ relaxation has been investigated by many workers but the interpretation and assignment of a deformation mechanism and its molecular origin are widely varying.

Many workers believe that this transition is due to the crankshaft motion of $-(CH_2)-$ segments in the P.E. chains, but does not involve more than 10% of the amorphous material. (See, for example, Boyer, 1963). However, Cole and Holmes (1960) suggest a mechanism which involves both the crystalline and amorphous regions. Measurements of the dynamic loss transitions in $C_{20} - C_{22}$ paraffins show three prominent peaks corresponding to the α , β , γ peaks in the bulk crystallized polymer. (Pechold et al 1963). Pechold attributed the γ peak to re-orientation of lattice imperfections within the crystal and extrapolated the result to the bulk crystallized polymer. Sinnott, (1966), using single crystal mats of linear P.E., determined that the γ transition was associated with the crystalline regions and was due to the re-orientation of dislocation points within the crystal lattice. It was argued that the γ transition in single

crystal mats, paraffins and bulk crystallized material had the same molecular origin. However, the latter conclusions seem highly unlikely, as demonstrated by the experiments of Willbourn (1958). Willbourn studied a series of polymethylenes with a known number and type of alkyl side-branches. Results for methyl branched polymethylenes containing 10 and 140 methyl groups per 1000 C-atoms showed that the γ peak was only slightly affected, although the latter material did not exhibit the crystalline, α transition. Similar conclusions may be drawn from the dielectric loss studies of Mikhailov et al, (1957) who also found that in a material without a crystalline transition the γ peak was still prominent, but moved to slightly higher temperatures with a small decrease in magnitude. Therefore, the γ peak in bulk crystallized material is not directly attributable to the crystalline regions; however there is evidence of an amorphous crystalline interaction. With increased crystallinity there is a tendency for a narrowing of the loss peak and a small increase in the magnitude of the peak. As in the case of the α transition, the molecular processes which control the transitions is still unresolved, and extrapolations of the mechanisms from one material form to another is suspect.

4.2 CREEP STUDIES ON ISOTROPIC POLYETHYLENE

The most informative study on the uniaxial creep and recovery behaviour of high and low density P.E. was reported by Turner (1964). Turner investigated the variation of stiffness behaviour with density and heat treatment over a range of strains and experimental times. Both high and low density P.E. were shown to be non-linear and the creep rates were sensitive to the stress level. There are no other systematic studies of the stiffness behaviour of isotropic P.E., although examples of the time-dependence may be obtained from the manufacturer's technical service notes and other publications. (See, for example, *Plastics Materials Guide*, (1970), *Design Engineering handbook*, 1969).

4.3 TRANSITIONS IN ORIENTED POLYETHYLENES

Studies of the transitions in oriented polyethylenes have only recently been reported. As part of an extensive study on oriented polymers Stachurski and Ward, (1968 a,b), have investigated the anisotropy of the transitions in highly oriented cold drawn L.D.P.E. and H.D.P.E., and in a series of specially textured sheets with a well defined morphology.

For the uniaxially cold-drawn polyethylenes only the highly drawn state was investigated. In highly oriented cold drawn L.D.P.E. only a single peak is apparent at temperatures above the γ transition. Ward labelled this peak β^* and showed that it had an anisotropy of mechanical loss factor $\tan \delta_{45} > \tan \delta_0 > \tan \delta_{90}$. (Figure 4.2 and 8.8).

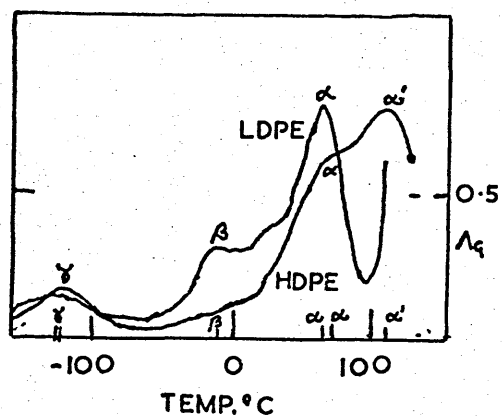


FIGURE 4.1 A Schematic Diagram of the Main Transitions in L.D.P.E. and H.D.P.E.

(After Flocke, 1962)

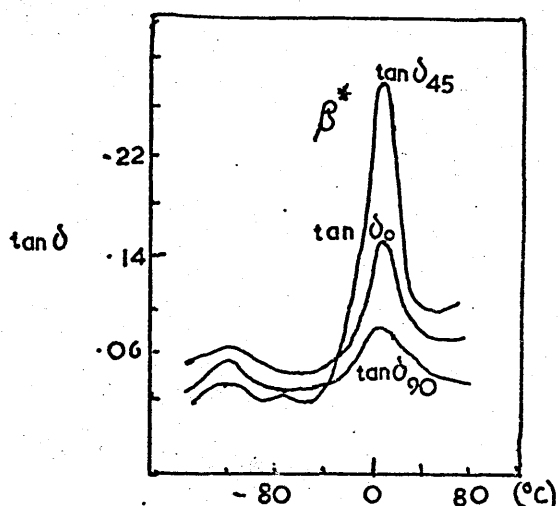


FIGURE 4.2 The Mechanical Loss Transitions in Cold Drawn L.D.P.E.

(After Stachurski and Ward, 1968, a.)

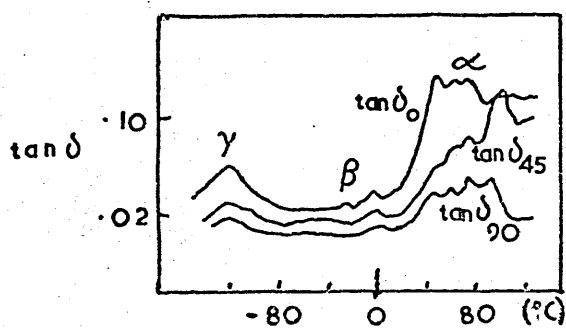


FIGURE 4.3 The Mechanical Loss Transitions in Cold Drawn H.D.P.E.

(After Stachurski and Ward, 1968, a.)

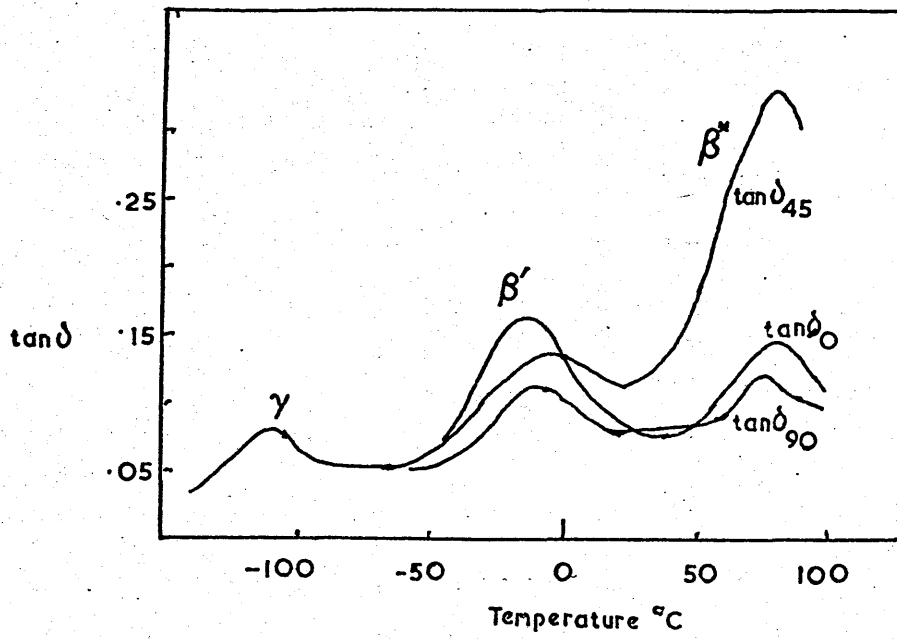


FIGURE 4.4 The Mechanical Loss Transitions in Cold Drawn and Annealed L.D.P.E.

(After Stachurski and Ward, 1968, b.)

It was suggested that this transition was dependent on the orientation of the crystallites and did not depend on the morphology of the drawn polymer. Further, it was "associated with a specific deformation which appears to be shear on planes containing the axis of drawing in the draw direction (which is the preferred direction of c-axes orientation as shown by X-ray diffraction), or on planes perpendicular to this axis". Other work on highly oriented cold drawn polyethylene, reported at the same time, has shown that at low strains (Darlington and Saunders, 1968, 1970), and near yield (Hinton and Rider, 1968), that the dominant deformation mechanism is an "easy-shear mechanism on planes containing the c-axis". It seems reasonable, therefore, that the mechanism observed by Ward, is in fact this same easy shear mechanism, and that this mechanism dominates the deformation behaviour from infinitesimal to finite strain.

In the case of cold drawn H.D.P.E., two prominent peaks, labelled α and γ , and a residual β peak remain, each with an anisotropy of mechanical loss factor $\tan \delta_0 > \tan \delta_{45} > \tan \delta_{90}$, Figure 4.3. This investigation, (Stachurski and Ward, 1968, a), did not elucidate the deformation mechanisms responsible for the transitions.

Specially textured sheets of L.D.P.E. have been prepared by Hay and Keller, (1966). Using these sheets, Stachurski and Ward, 1968, b), found that, on annealing, the single peak of the cold drawn low density polymer resolved into two prominent peaks, one at -10°C and the other at $+75^\circ\text{C}$. (Figure 4.4). Dynamic measurements showed that the lower temperature peak, labelled β' , had an anisotropy $\tan \delta_0 > \tan \delta_{45} > \tan \delta_{90}$, and was determined by the configuration of the lamellae and did not depend on the molecular orientation within the lamellae. This transition was attributed to an inter-lamellar shear process. The high temperature peak, at $+75^\circ\text{C}$, had similar anisotropy to the cold drawn L.D.P.E. (viz. $\tan \delta_{45} > \tan \delta_0 > \tan \delta_{90}$), and by analogy it was postulated that the transition in the textured sheet derived from the same relaxation process, and was labelled β^* .

It was noted that "the anisotropy of the α process in cold drawn H.D.P.E. is equivalent to that of the β' process in the annealed sheets. This suggests that the α process in the cold drawn high density polymer could be due to an inter-lamellar shear process". This analogy seems rather dubious. In H.D.P.E. of sufficiently low density for the β peak to be prominent, the α peak is due to a crystalline relaxation and the β peak to an amorphous relaxation. It would be equally reasonable to assume that if the peaks still appear after drawing that the anisotropy of the β peak was still due to the amorphous content, but had an anisotropy dependent on the orientation of the amorphous regions. However, Ward et al postulate

that the α peak is now due to an inter-lamellar shear process associated with the relaxation of inter-lamellar amorphous material. This seems unlikely and a direct analogy appears hazardous. A more reasonable postulate would be that the low temperature β peak in the cold drawn H.D.P.E. with anisotropy $\tan \delta_0 > \tan \delta_{45} > \tan \delta_{90}$ was due to inter-lamellar shear. Similarly, the analogy between the peak labelled β^* in the cold drawn material and the annealed material is dubious. Whilst admitting the peaks are associated with the orientation of the crystallites the morphology in the two cases is markedly different and care must be taken in making such analogies. In the cold drawn material the crystallites are arranged in fibrils (Section 3), and it is difficult to distinguish between inter-fibrillar and intra-crystalline shear. An inter-fibrillar shear mechanism is proposed in this thesis (Chapter 9), and has also been referred to by Gupta et al, (1968), and Hosemann, (1963). However, in the annealed sheets the existence of an intra-lamellar C-axis shear process seems highly likely. Hay and Keller, (1966, 1967), and Cowking et al, (1968), in detailed studies of these textured materials, demonstrated that the dominant deformation mechanisms were an inter- and intra-lamellar shear deformation.

Work described in this thesis (Section 8) demonstrates the anisotropy of the mechanical loss peaks in L.D.P.E. with different draw ratios, and is discussed in Section 9.1.

4.4 CREEP STUDIES ON ORIENTED POLYETHYLENE

The experimental results discussed in Section 4.3 were at infinitesimal strains using oscillatory vibration techniques to investigate mechanical loss peaks; relatively few systematic deformation studies at finite strains (up to 5% say) have been reported. Raumann and Saunders, (1961), and Raumann, (1962), first measured four isochronous compliance parameters for uniaxially drawn L.D.P.E., over a range of draw ratios, and emphasised the anomalous behaviour of the stiffness parameters. The tensile moduli at 0° , E_0 , and 90° , E_{90} , to the draw direction first decrease with increasing draw ratio, with $E_{90} > E_0$, and then at intermediate draw ratios a cross-over point occurs in the modulus v draw ratio curves and E_0 becomes greater than E_{90} . At high draw ratios E_0 is much greater than E_{90} which is greater than E_{45} . The low E_{45} is associated with a high shear compliance governing laminar shear in the plane containing the draw direction and the mutually orthogonal co-ordinate axis perpendicular to the draw direction. Gupta and Ward, (1967), have also examined the anisotropy of the tensile moduli on a limited number of draw ratios but over a range of temperatures. However, the experiments were designed to examine an aggregate theory for oriented polymers and no structural interpretations were attempted. Similar experiments were reported for the textured materials (Gupta et al, 1968). A detailed study of the tensile moduli

of highly drawn L.D.P.E. has been made by Darlington & Saunders, (1970), over a range of strains on specimens cut at different angles to the draw direction in the plane of the sheet. Creep compliances were recorded up to 100 seconds at each angle and it was deduced that an easy shear mechanism parallel to the C-axis was the dominant process in the highly drawn state.

The anisotropic state is important technologically, but the information available on drawn polymers is minimal. The transitions have been well documented, but the stiffness parameters have had only slight attention. The work reported in this thesis attempts such a systematic study for cold drawn L.D.P.E. over a range of times, strains, and draw ratios, at constant temperature.

4.5 THE RELATION BETWEEN STRUCTURE AND MECHANICAL PROPERTIES

Crystalline lamellae were identified as the basic structural unit in bulk crystallized polyethylene in 1964. (Palmer and Cobbold, 1964, and Keller and Sawada, 1964). Previously reported work which had involved X-ray, infra-red, and electron microscopy techniques, and deformation studies could then be explained more fully, but in 1965 the relationship between structure and mechanical properties was not well understood. During 1964 and 1965 several morphological studies on the oriented state were reported (for example, Hay and Keller 1964 and 1965). Hay and Keller investigated the effect of orientation on spherulite deformation in thin films, and identified crystalline lamellae units in bulk oriented polyethylene. Deformation studies, (Stein, 1966, Moore and Geinewski, 1966, and McCrum and Morris, 1966), indicated possible deformation mechanisms in H.D.P.E. and L.D.P.E., but the interpretation of the data was of a contrary nature. At the same time, the effect of deformation on the morphology of single crystals and bulk crystallized P.E. was investigated to try to elucidate the morphology of the highly drawn polymer (See, for example, Peterlin, 1966, Corneliussen & Peterlin, 1967). This thesis represents the first systematic study which attempts to interpret the anisotropic quasi-static (creep) properties of oriented L.D.P.E. in terms of current structural knowledge. Recent work, (Stachurski and Ward, 1968 a and b, and Gupta and Ward, 1968) has examined the anisotropy of the mechanical loss transitions in highly drawn and specially textured P.E., and these workers have postulated an inter-lamellar shear and an intra-lamellar shear mechanism dominate the deformation behaviour. Several informative morphological studies on the oriented state have also been completed, (Yeh and Geil, 1968, Cowking, Rider, Hay and Keller, 1968, and Peterlin, 1969). Cowking et al also postulated the inter- and intra-lamellar shear mechanisms in the same specially textured sheets used by Ward and co-workers. These recent investigations have been discussed in Section 3 and 4.3.

SECTION 5. APPARATUS

The five principal independent compliance parameters of uniaxially oriented polyethylene were determined using tensile and torsional creep apparatus which have been developed in this laboratory. The tensile creep apparatus allows the simultaneous measurement of the longitudinal and contraction creep strains, and these measurements are used to determine four of the five principal compliance parameters. The fifth independent compliance parameter is determined from torsional creep measurements. A torsion pendulum apparatus has been designed and built as part of this work and used primarily to calibrate the torsional creep rig. No results on L.D.P.E. are reported using this technique. Each apparatus has been specially designed to accommodate the necessarily small, and extremely flexible, samples afforded by the drawn L.D.P.E., and in each case novel design features have been incorporated to overcome the experimental difficulties associated with testing these materials. The individual apparatus are described separately below.

5.1 The Tensile Creep Apparatus

The apparatus has been described in detail elsewhere (Darlington and Saunders, 1970), and only a brief description will be presented here. A schematic diagram of the apparatus is shown in Figure 5.1. The specimen is loaded axially via the lever loading system and the slide guide, which ensures that the specimen is free from any torsional or transverse loading. The loads are applied in a steady manner in about 0.5 to 1.0 seconds.

The extensometry has been fully described by Darlington and Saunders, (1970), and enables the simultaneous measurement of the longitudinal and through thickness creep deflection (Extensometers 1 and 2). The extensometers are mounted using a system which ensures that load perturbations of less than 1 gm are superposed upon the uniaxially applied creep loads which are in the range 50 to 3000 gms. The transducers and associated recording equipment have a limit of resolution corresponding to a shaft movement of 2.5×10^{-6} cm. However, in practice, the smallest accurate measurable deflection is 1.2×10^{-5} cm. Thus on a typical gauge length of 1.2 cms a limit of accuracy of 1% at 0.1% strain is realizable, and this latter strain was, in general, the smallest longitudinal strain measured. The limit of accuracy on the contraction strain varies with sample thickness and draw ratio and typical values are shown in Table 5.1.

DRAW RATIO	LONGITUDINAL STRAIN (%)				
	0.1	0.3	0.5	1.0	2.0
ISOTROPIC	12.5%	6.25%	3.75%	1.96%	1.0%
D.R. 0° 1.40 90°	14.5% -	7.2% 18.5%	3.1% 10.5%	1.56% 5.60%	0.7% 2.5%
D.R. 0° 2.65 90°	- 50%	12.0% 20%	5.2% 10.5%	2.9% 3.9%	1.4% 1.2%
D.R. 0° 400 90°	- 31%	14.0% 11.0%	8.6% 6.95%	4.4% 2.9%	1.8% -

Table 5.1 The Variation of the Limit of Accuracy of the Contraction Strain with Strain and Draw Ratio.

The recommended procedure for creep testing is given elsewhere (Turner, 1963 and B.S. 4613). However, whilst this procedure was adopted in principle, minor modifications were made to determine the recovery behaviour in full. The isochronous curve is obtained by loading the specimen and noting the creep strain after 100 seconds. The load is subsequently removed and the recovery strain is monitored. In the standard procedure a recovery period of four times the creep period is recommended, however, in these studies the recovery period was at all times greater than ten times the creep time, or until such time when complete recovery occurred. At the 0.5% and 1.0% 100 second strain levels the creep time was 1000 seconds and the recovery period was again ten times the creep time, but often the sample was left to recover overnight. After the long term tests a 100 second test at a lower strain level was repeated to ensure no permanent damage had occurred in the material.

The contraction results reported here represent the first systematic study of creep contraction data over a range of strains and draw ratios for an anisotropic continuum. In the original design of the contraction extensometer brass contact pads were fitted to the ends of the extensometer arms. The pads made direct contact with the specimen surface and contact was maintained by a small but positive pressure provided by the spring on the transducer shaft.

However, during the course of the experimental work reported here, it was thought probable that over a period of time that the pads would sink into the specimen surface and thus produce erroneous instantaneous results and exhibit incorrect time dependent behaviour, especially on specimens of low modulus material that remained mounted in the rig over a period of days and/or during a long term creep and recovery run. In order to investigate this possibility small glass optical flats were introduced between the glass pads and the specimen to reduce the localised pressure and exhaustive tests were made using both techniques to investigate the following points.

1. To determine the difference, if any, between the experimental techniques using direct contact of the specimen with the pads - to be referred to as 'pads' techniques - or by introducing the optical flats - to be referred to as the 'plates' technique. A range of materials with widely varying creep rates and moduli were tested over times up to several hours, many of which had been mounted over a period of days.

2. To ensure that neither technique for the determination of the contraction strain affected the longitudinal strain measurement.

This point was investigated previously by Darlington and Saunders (1970), but only for the case of the 'pads' alone. Also the experiments were conducted over a limited time scale with a high draw ratio material which has a high modulus and exhibits little time-dependence. Under those conditions 'sinking', if it occurred, would be negligible and not vary appreciably with time.

3. The recovery behaviour was monitored using both 'pads' and 'plates' techniques to ensure that the apparatus operated in a friction-free manner with the contraction extensometer mounted.

4. To determine the repeatability and reproducibility of the longitudinal and contraction results in creep and recovery over a range of draw ratios at different strain levels. Some of the results on the isotropic material have been reported elsewhere (Darlington and Saunders, 1970).

Detailed tests were made at nearly all draw ratios and typical results for isotropic, D.R. 1.4, and D.R. 3.8, specimens are discussed below. The isotropic state was chosen to examine the creep and recovery behaviour at relatively high creep rates in a low modulus material, and Figures 5.2 to 5.4 show the isotropic contraction data on a series of specimens. The variation of the isochronous contraction compliance with strain for three samples is shown in Figure 5.2. The largest difference between the 'pads' and 'plates' results is in Sample C, which shows a difference of 13% at 0.3%, 100 second-strain and 5% at 0.5% 100 second strain. However, the limit of accuracy at these strain levels is 6.25% and 3.75% respectively (Table 5.1) and the results are thought to be extremely good. The variation of the contraction compliance with strain is similar for all three specimens in both 'pads' and 'plates' experiments. The time dependent behaviour of the contraction strain at 0.5% and 1.0% 100 second longitudinal strain is shown in Figure 5.3 and 5.4 respectively, and in no case is the difference in time dependence between 'pads' and 'plates' experiments greater than 5%. The marked similarity of the recovery strain in all cases is particularly encouraging, as this shows a lack of friction in the rig, that no sinking occurs and that the repeatability is excellent even at low strain levels.

The specimen to specimen comparison shows a similarity of both creep and recovery behaviour and emphasises the reproducibility of the results at both strain levels in a material which is markedly time dependent with a low modulus in which the effects of 'sinking' of the contraction pads might be anticipated. The overall reproducibility may be deduced from Figure 5.5 and 5.6 which shows the variation of the isochronous creep modulus and contraction compliance with strain for 5 different specimens repeated without a contraction extensometer, with pads alone, and with glass plates. For specimens which were tested in the temperature range 20.1°C to 20.9°C the spread of contraction compliance was no greater than 10% at 1% 100 second strain, but the overall spread in the temperature range 20.1°C to 21.8°C is 14%. However, this is considered good as a change in temperature of 1°C may change the compliance by 3%, and also the limit of accuracy is only 2.0% at 1% 100 second strain. Similarly, the modulus shows an 8% spread overall, but excluding the results at temperatures greater than 21°C the spread of results is less than 6% at 1% 100 second strain. Tests were also carried out on two specimens to determine the effect of the two contraction techniques on the longitudinal deformation and the differences in time dependent behaviour were well within experimental error, but a discrepancy of 10% in modulus values was detected at 0.15% strain. However, at high strains the difference was negligible. (Figure 5.7 - 5.9).

The results of a study on a 90° specimen at D.R. 1.4 are shown in Fig. 5.10 to Fig. 5.13. This specimen was of particular interest as it exhibited anomalous contraction behaviour and also high creep rates and had a low modulus, so sinking in would be emphasized. The instantaneous contraction is followed by a time-dependent thickness increase and on removal of the applied load, the sample instantaneously recovered to a thickness greater than the original thickness and progressively recovered to the original dimensions. The creep and recovery behaviour of both the longitudinal and contraction strain at 0.5% and 1.0% 100 second strain are shown in Figure 5.11 to 5.12. The longitudinal strain shows no noticeable difference in time dependence and the discrepancy in the contraction behaviour is within the limit of accuracy of the experiment (Table 5.1). Clearly, there is no difference between the two contraction techniques and even though the contraction was left set up greater than 3 days and no evidence of 'sinking' was observed. The apparent discrepancy between the sets of recovery curves arises since the creep experiments were of different duration. Tests run for the same time at the same strain level show good repeatability, viz Run 2 and 4 at 0.5% strain and Run 3 and 4 at 1% strain. The isochronous contraction compliance/strain curve shows an overall spread of 7% at 1% strain; however, the limit of accuracy is only 5% at this strain level

for this DR and angle (Table 5.1) and the agreement is considered to be good. This set of results supports the conclusion deduced above about the effects of 'sinking in'. The isochronous modulus/strain curves show a spread of 7% at 1% strain; however, Run 4 was conducted at 21.7°C, which was approximately 1.0°C higher than Run 1-3. Thus excluding Run 4, the repeatability of the isochronous modulus/strain curve is better than 3% for the two contraction techniques.

The different effects of 'sinking in' between the two contraction techniques would be exaggerated in a long term test in a 0° specimen at D.R. 3.8. The time-dependent contraction is relatively small and thus a small amount of 'sinking' would make an appreciable contribution to the apparent contraction strain. However, there was no noticeable difference between the two techniques and neither technique affected the tensile behaviour (Figure 5.14 and 5.15).

As a result of the above tests, and others carried out during the course of the experimental work the following conclusions were made.

1. The contraction deformation behaviour is the same for the pads and plates techniques within the limit of accuracy of the measurements. The use of glass plates between the contraction arm and specimen is now standard procedure in these laboratories.
2. Neither technique affects the tensile deformation behaviour
3. The apparatus functions in a friction-free and 'stick-slip' free manner, and consequently the creep and recovery data has a high limit of reliability.
4. The repeatability of the isochronous compliances is excellent for both the contraction and longitudinal compliances at all draw ratios. The time dependent behaviour is highly repeatable.
5. The overall reproducibility is $\pm 3\%$ on the longitudinal modulus and $\pm 5\%$ on the contraction compliance at 1% 100 second longitudinal strain.

The extensive examination of results in the above manner enabled the development of techniques which give a high standard of repeatability and reproducibility, and give an increased accuracy over the results obtained prior to this study.

5.2 THE TORSIONAL CREEP APPARATUS

The torsional creep apparatus is based on an original design by Morrison, et al, (1955), and is shown schematically in Figure 5.16. The coil consists of 1300 turns of 40 SWG enamelled copper wire suspended in the field of a Magnetron permanent magnet by a 0.015" suspension wire. The upper sample clamp is attached to the coil and by applying a voltage across the coil torques up to 100 gm.cms. may be applied to a sample. The pole pieces have been machined so that the torque is directly proportional to the applied voltage and independent of the angular deflection over the range of deflections encountered. Thus the torque applied to a sample remains constant during a creep experiment. To test the linearity of the field the deflection of a metal shim was noted for a given applied voltage. The magnetic field was then rotated and the test repeated and for the same applied voltage the deflection remained constant.

The bottom clamp is firmly attached to, and supported by, a specially designed linear bearing which enables specimens to be mounted in the apparatus free from axial loads. This is particularly important with the thin, low rigidity specimens used in this study as axial loads increase the torsional rigidity of the specimen. The linear bearing restricts all rotational movement of the clamp but allows almost free axial movement. Thus specimens of varying length may be used and also thermal expansion and contraction may occur freely without applying thermal loading to the specimen. Another feature of the bearing is that selected axial loads may be applied to the specimen, thus enabling combined tensile and torsional creep experiments.

The suspension wire, the axis of the coil and sample, and the line of action of the linear bearing, are all aligned in the same vertical axis, the torsion axis.

The torsional creep apparatus was calibrated using a torsion pendulum apparatus (Section 5.3) and two metal shims. The torsional rigidity of the metal shims was determined from free damped vibrations in the pendulum apparatus, and the same metal shims were then used in the torsional creep apparatus to determine the voltage-deflection torque-voltage constant as 13,390 dyne.cm./volt. The repeatability and reproducibility of the characteristics at both stages of the calibration were excellent and were found to be independent of small errors in sample misalignment, and the relative positions of the coil and magnets. The applied voltages correspond to a range of torques between 0.4 gm. cms. for the highly drawn specimens, to 12 gm.cms. for the isotropic material. The applied voltage is continuously displayed on a digital

voltmeter and over the range of experimental times used the voltage fluctuations are no more than 0.1% of the applied voltage. The angular deflections are measured using an optical lever system and the reflected light spot is automatically followed by the photocell in a Graphispot recorder. The deflections are read to 1 mm, which, with the present optical lever, is equivalent to an angular deflection of approximately 2 minutes of arc. Surface shear strains were in the range 0.05% to 0.5% and changes in surface shear strains of less than 0.002% can be accurately determined.

The instrumentation used for load application is shown in Figure 5.17. The Farnell stabilized voltage supply, (S.V.S. 1), drives a linear potentiometer via a motor and gear box. The potentiometer replaces the control knob on the second stabilised voltage supply, (S.V.S. 2), and the two cams, C₁ and C₂, and associated micro switches, M_{s1} and M_{s2}, control the extent of the rotation of the potentiometer and thus the voltage supplied to the coil. The time of application of the load can be varied from a fraction of a second to several seconds, and this facility will be used in future work to apply ramp function inputs, which with suitable analysis can yield the shear compliance at times less than 5 seconds. In another arrangement (dotted lines) the motor and gear box can drive a sine-cosine potentiometer (s/c pot). A constant voltage is supplied to the input terminals of the sine-cosine potentiometer and a sinusoidal voltage output is fed to the coil. The peak to peak voltage is determined by the input voltage, and the frequency by the speed of the motor. Frequencies usually encountered are in the region of 0.003 Hz to 2 Hz.

Many experiments were performed on samples, at selected draw ratios, through the range of draw ratios, to determine the affect of end effects, and the reproducibility of the results. The end effects are of two types. Firstly, the torsional rigidity of the rectangular cross-section prism is increased since the clamp prevents warping of the cross-section on deformation. However, end effects of this type were overcome by applying a simple theoretical length correction to the specimens (See Section 2.4). The second end effect is due to local irregularities in stress distribution in the area of the clamps, the St. Venant effect. No simple correction may be applied in this case, and it is usual to work with long specimens with high length to width ratios to negate the effect. However, in this work, the drawn blank size made severe limitations on specimen size and dimensions and it was not always a practical proposition to work with long specimens. End effects were investigated by keeping a nominally constant sample length of 5.2 cms and varying the length to width, and width to thickness ratios and detecting trends with ratio, if any existed, and examining the reproducibility of the results. Typical isochronous modulus-strain curves are shown

in Figure 7.33 to 7.35. Figure 7.33 shows the variation of the shear compliance with strain over a range of draw ratios, with two samples at each draw ratio and a full investigation at typical draw ratios is shown in Figure 7.34. to 7.36. No systematic variation of the shear compliance with length to width and width to thickness ratio may be detected over a wide range of ratios, and the reproducibility of results is considered to be good. At low strains (0.01%) the spread of results is no greater than 5% and is reduced to 3% at 0.5% 100 second strain. It was concluded that no errors were inherent in the results due to St.Venant's type end effects.

The reproducibility of the time dependence is shown in Figure 7.25 for some typical draw ratios. At low draw ratios, and D.R. 38, the difference in time dependence is less than 2% and the largest discrepancy arose at D.R. 3.00 when a difference of 5% in time dependence was recorded. The large difference at D.R. 3.00 may arise from differences in specimens due to the difficulty of sample preparation at this draw ratio.

In the normal working position the specimens are free from axial loads; however, the results of experiments designed to determine the effect of applied axial loads on the torsional rigidity are shown in Fig. 7.37 to 7.38 and, as expected, the apparent shear compliance decreases with increasing load.

5.3 The Torsion Pendulum

The apparatus is an inverted torsion pendulum designed to investigate the dynamic mechanical properties of polymers using free-damped oscillations. A schematic representation of the apparatus is given in Fig. 5.18.

The bottom specimen clamp is rigidly fixed to a linear bearing of the type used in the torsional creep apparatus. The upper clamp forms part of the inertia system, the remainder of which consists of an aluminium boss, two horizontal inertia bars and two inertia bobs when necessary. The inertia bars have been machined with a micro-thread so that the inertia bobs may be screwed to the same radial distance from the axis of rotation to better than 0.001". The inertia of the system is varied either using bars of different materials and addition of inertia bobs or by varying the position of the bobs on the bars.

The inertia system is suspended from a phosphor bronze suspension element attached to the upper fixed plate by a ground and polished slide guide and mating bush. Preliminary experiments had shown that the use of relatively flexible samples such as low density polyethylene in conjunction with a wire suspension had led to unwanted ancillary vibrations in the system which appeared as perturbations in the desired torsional vibrations. A special suspension system with a cruciform cross-section was designed to be weak in torsion but stiff in flexure and thus stray vibrations were eliminated.

The system has been carefully machined and constructed so that the axis of symmetry of the system and sample is coincident with the axis of rotation. Thus only a pure torsional vibration is imparted to the system.

Different length samples can be accommodated by adjusting the position of the slide guide in the bush.

A mirror attached to the suspension element reflects a beam of light on to the photo-cell of a Graphis pot chart recorder. The photo-cell is seated on the pen carriage of the instrument and automatically follows the light spot so that a trace of the oscillations is recorded on the chart. The chart speeds are from 0.6 mm/min. to 600 mm/min. The frequency and the logarithmic decrement of the oscillations are determined from the chart knowing the chart speed. The frequency is determined to 0.1% and logarithmic decrement to about 1%.

The system is set in oscillation by two electro-magnets set symmetrically about the torsion axis.

The results of the above experimental investigations are presented on the following pages preceded by a list of figure captions.

- Figure 5.1 A schematic representation of the tensile creep and transverse contraction apparatus.
- Figure 5.2 The variation of the 100 second contraction compliance with 100 second strain for different isotropic specimens.
- Figure 5.3 The variation of the contraction creep and recovery strain with time at 0.5% 100 second strain for isotropic specimens.
- Figure 5.4 The variation of the contraction creep and recovery strain with time at 1.0% 100 second strain for isotropic specimens.
- Figure 5.5 The variation of the 100 second modulus with 100 second longitudinal strain for isotropic specimens.
- Figure 5.6 The variation of the 100 second creep contraction compliance with 100 second longitudinal strain.
- Figure 5.7 The variation of the 100 second creep modulus with 100 second strain for different isotropic specimens.
- Figure 5.8. The variation of the longitudinal creep and recovery strain for isotropic samples at 0.5% 100 second strain.
- Figure 5.9 The variation of the longitudinal creep and recovery strain for isotropic samples at 1% 100 second strain.
- Figure 5.10 The variation of the 100 second creep modulus, E_{90} , and the contraction compliance, S_{12} , with 100 second strain for a D.R. 1.4. 90° specimen.
- Figure 5.11 The variation of the longitudinal creep compliance, $S_{22}(t)$, and the contraction creep compliance, $S_{12}(t)$, with time, for a D.R. 1.4 90° specimen, at different 100 second strain.
- Figure 5.12 The variation of the contraction recovery strain with time, at 0.5% and 1.0% 100 second strain levels for D.R. 1.4 90° specimens.
- Figure 5.13 The variation of the longitudinal recovery strain with time, at 0.5% and 1.0% 100 second strain levels for D.R. 1.4 90° specimens.
- Figure 5.14 The variation of the longitudinal and contraction creep compliance, S_{33} , and S_{13} , with time, at different strain levels, for a D.R. 3.8 0° specimen.

- Figure 5.15 The variation of the 100 second creep modulus, E_0 , and the contraction compliance, S_{13} , with 100 second strain, for a D.R. 3.8 00 specimen.
- Figure 5.16 The torsional creep apparatus
- Figure 5.17 The instrumentation used for load application for the torsional creep and forced oscillation apparatus.
- Figure 5.18 The torsion pendulum apparatus

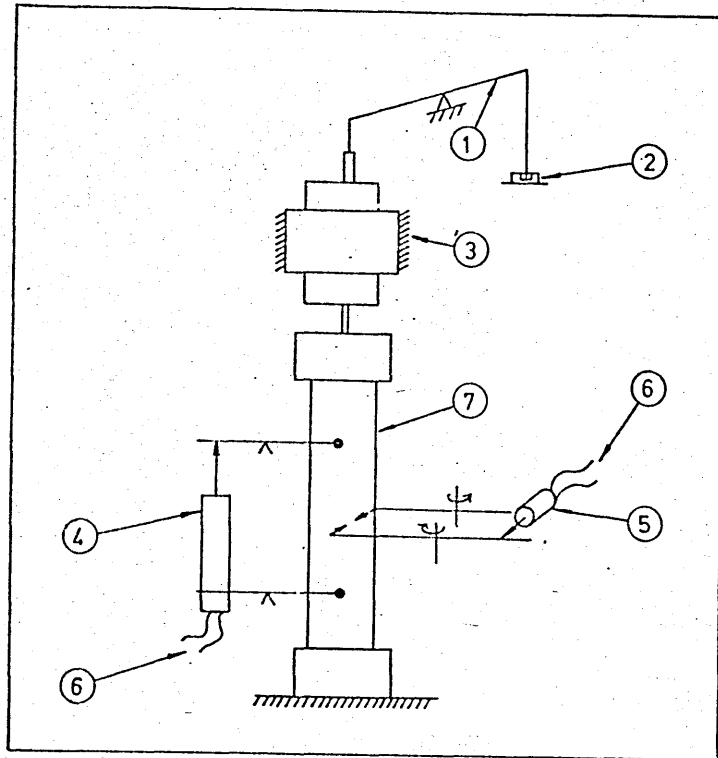


FIGURE 5.1 A SCHEMATIC REPRESENTATION OF THE TENSILE CREEP AND TRANSVERSE CONTRACTION APPARATUS (DARLINGTON 1968)

- ① THE LEVER LOADING SYSTEM ② APPLIED LOAD
 ③ SLIDE GUIDE ④ UNIAXIAL CREEP EXTENSOMETER 1.
 ⑤ CONTRACTION CREEP EXTENSOMETER 2.
 ⑥ LEADS TO RECORDING APPARATUS. ⑦ SAMPLE

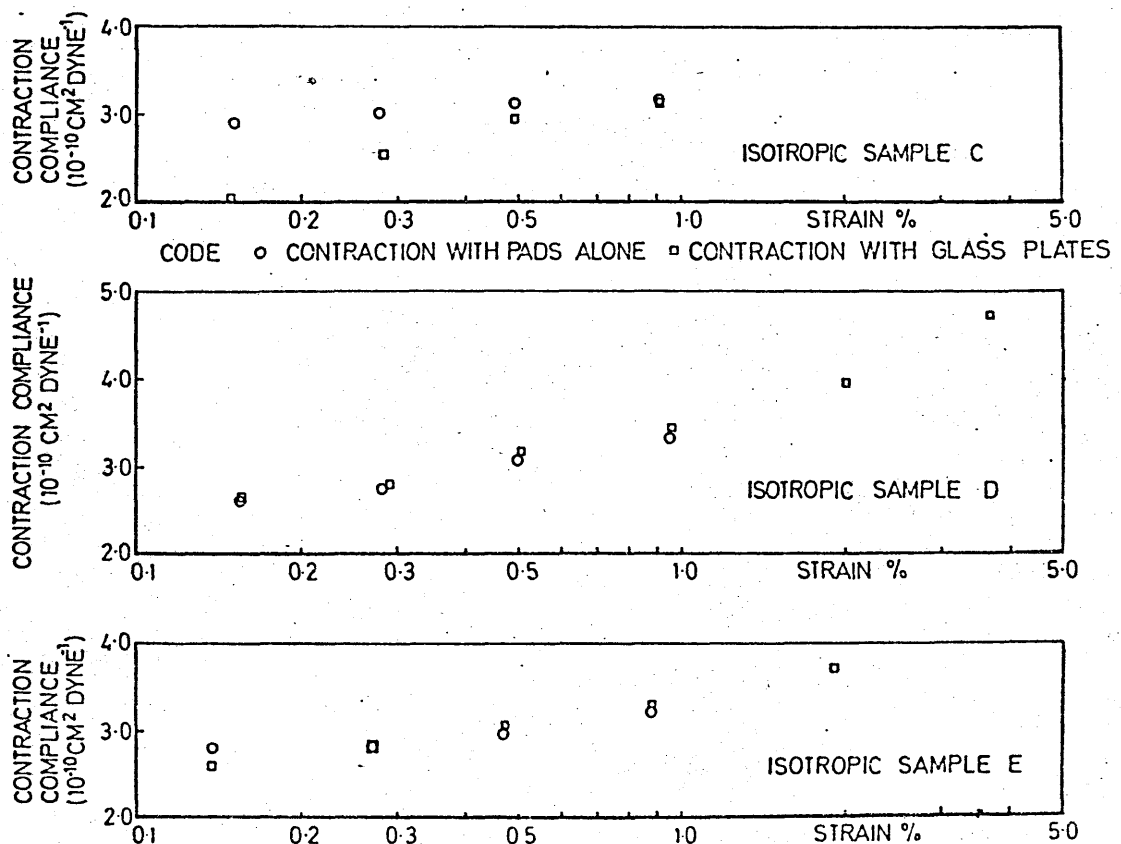


FIG 5.2 THE VARIATION OF THE 100 SECOND CONTRACTION COMPLIANCE WITH 100 SECOND STRAIN, FOR DIFFERENT ISOTROPIC SPECIMENS.

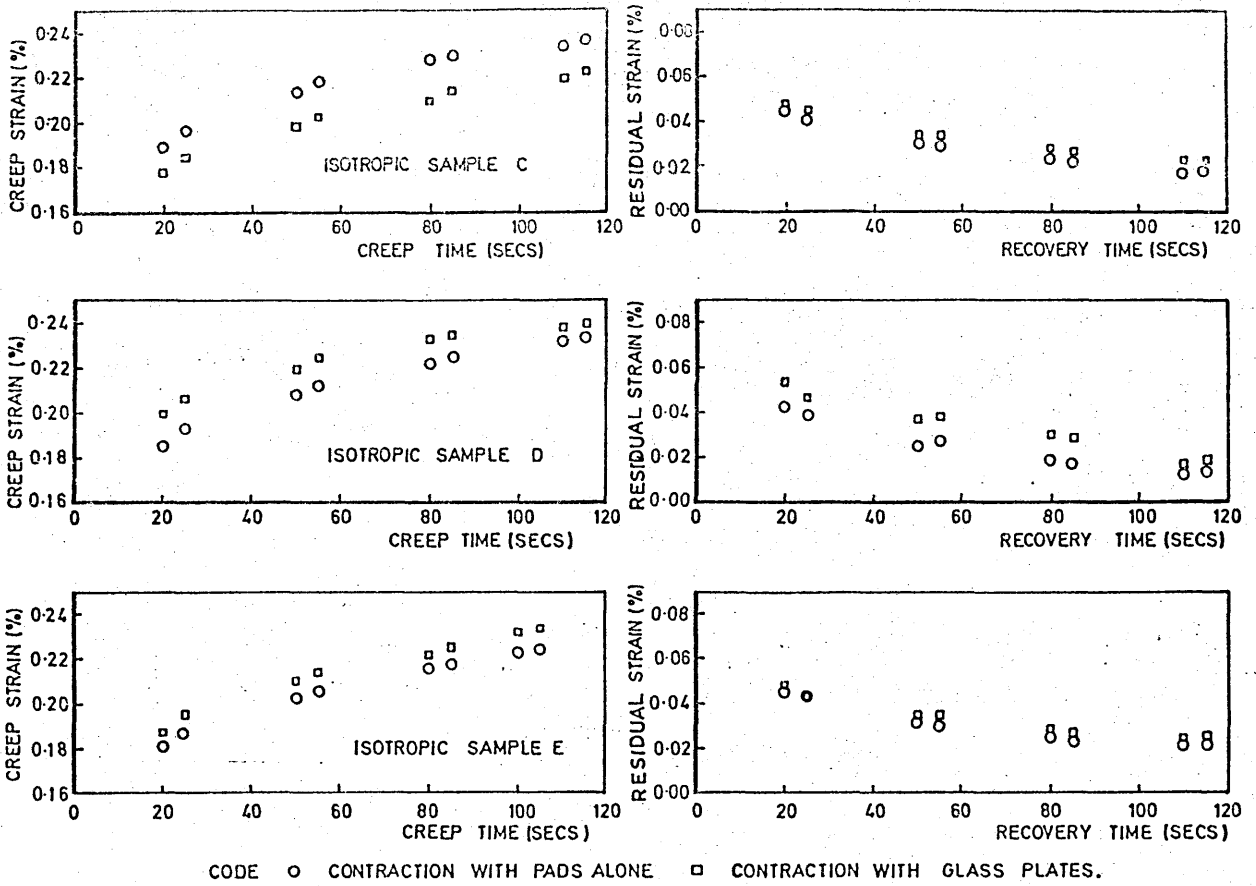


FIG.5.3 THE VARIATION OF THE CONTRACTION CREEP AND RESIDUAL STRAIN WITH TIME AT 0.5% 100 SECOND STRAIN FOR ISOTROPIC SAMPLES.

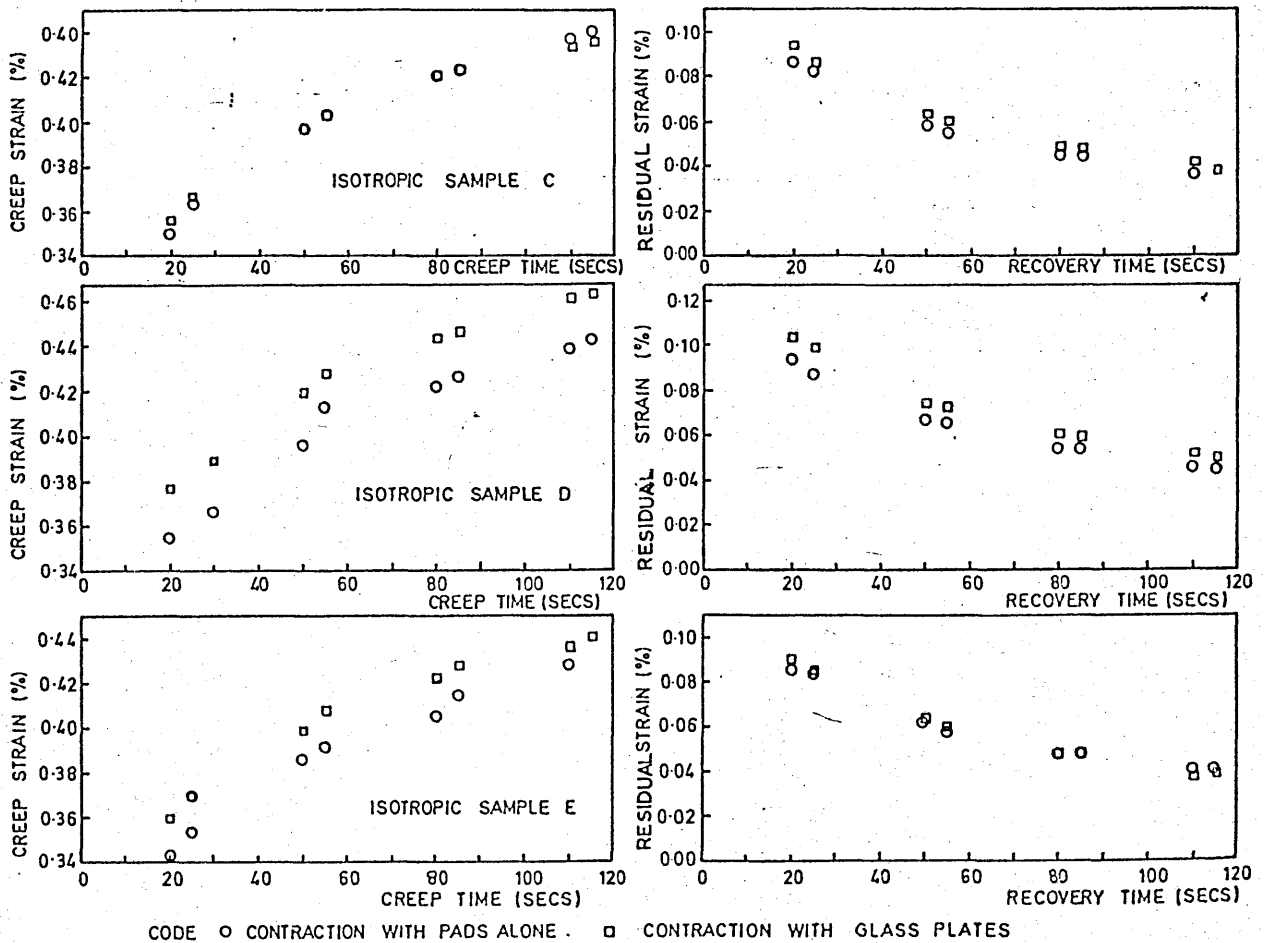


FIG.5.4 THE VARIATION OF THE CONTRACTION CREEP AND RESIDUAL STRAIN WITH TIME AT 1% 100 SECOND STRAIN FOR ISOTROPIC SAMPLES.

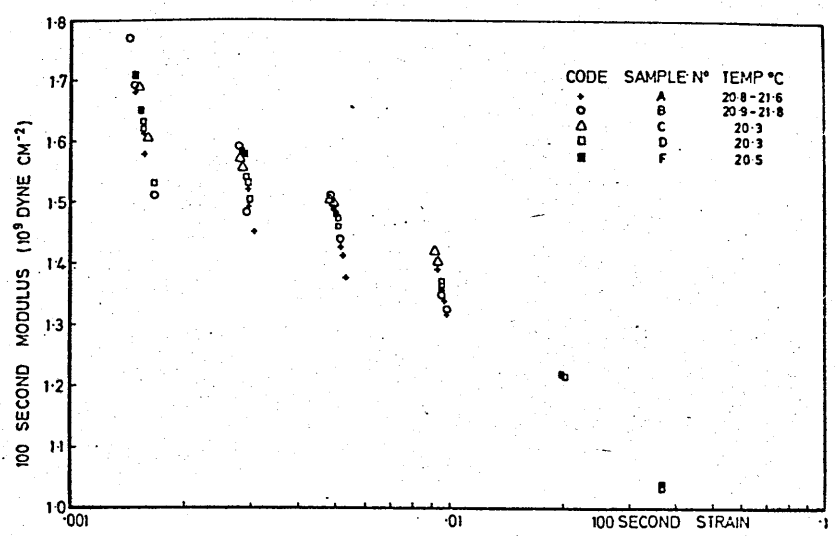


FIG5.5 THE VARIATION OF THE 100 SECOND MODULUS WITH 100 SECOND LONGITUDINAL STRAIN FOR ISOTROPIC SAMPLES. (DATA INCLUDES SPECIMENS WITHOUT CONTRACTION, WITH PADS ALONE, AND WITH GLASS PLATES.)

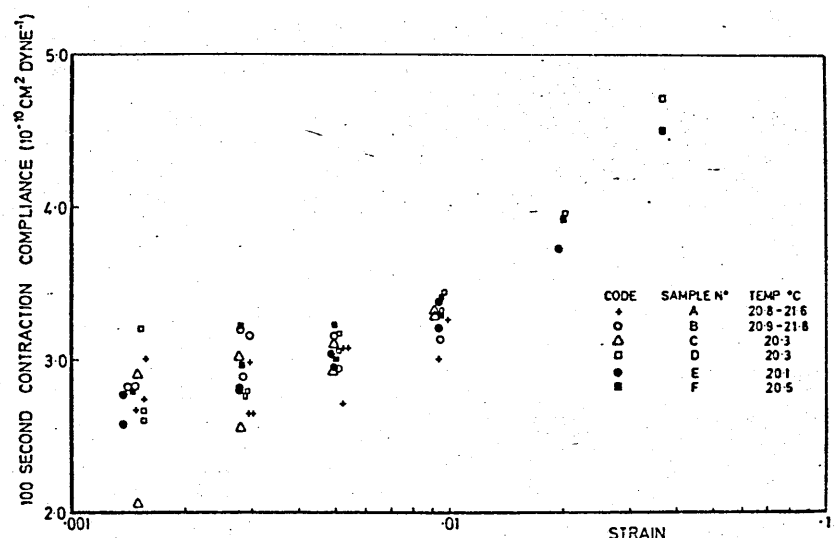


FIG5.6 THE VARIATION OF THE 100 SECOND CREEP CONTRACTION COMPLIANCE WITH 100 SECOND LONGITUDINAL STRAIN. (DATA INCLUDES SPECIMENS WITH PADS ALONE, AND WITH GLASS PLATES.)

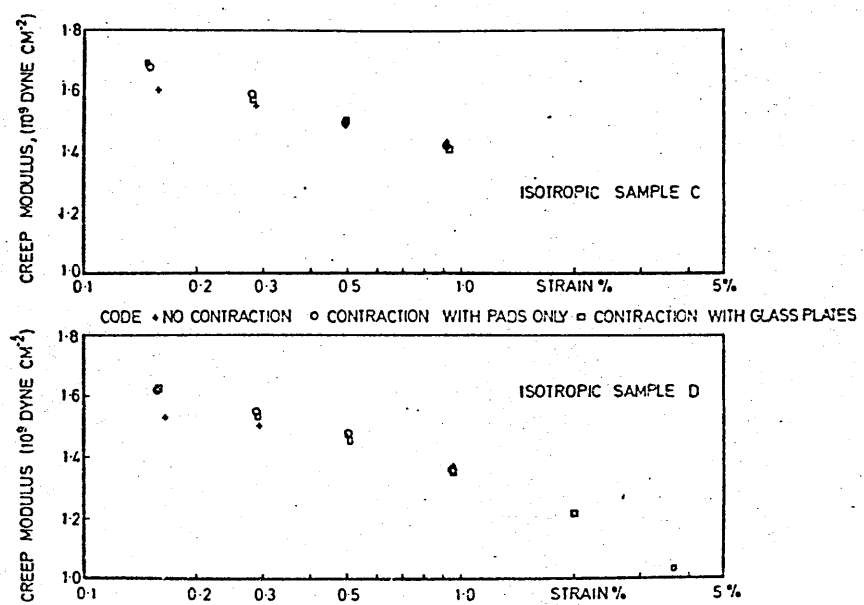


FIG5.7 THE VARIATION OF THE 100 SECOND CREEP MODULUS WITH 100 SECOND STRAIN FOR DIFFERENT ISOTROPIC SAMPLES.

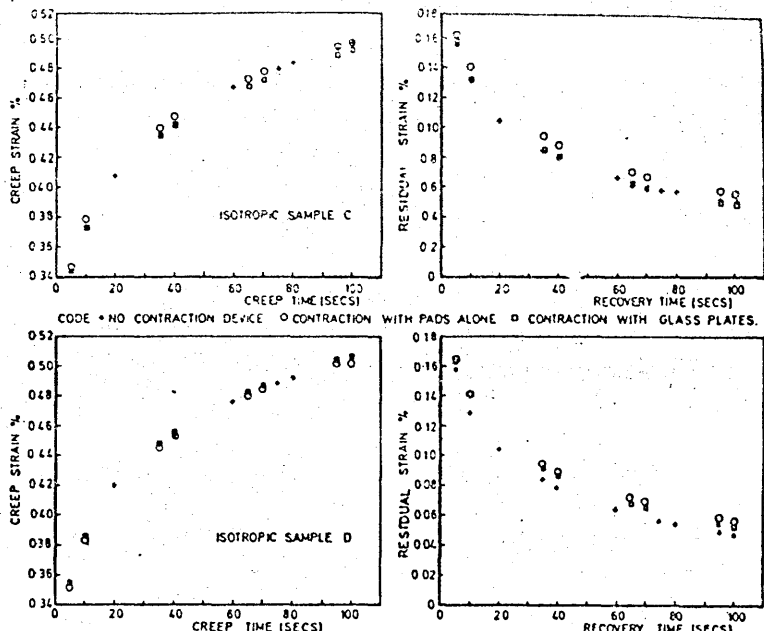


FIG. 5.8 THE VARIATION OF THE LONGITUDINAL CREEP AND RESIDUAL STRAIN FOR ISOTROPIC SAMPLES AT 0.5% 100 SECOND STRAIN.

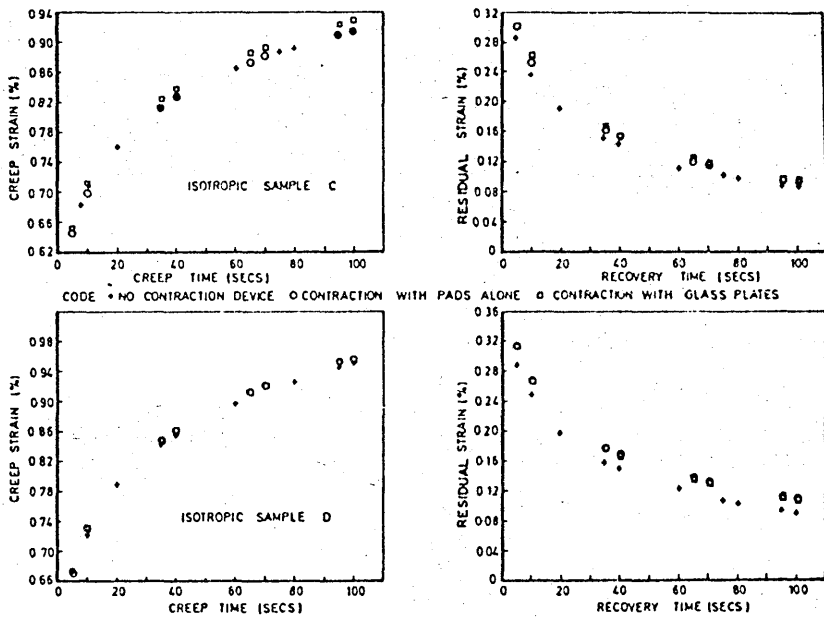


FIG. 5.9 THE VARIATION OF THE LONGITUDINAL CREEP AND RESIDUAL STRAIN FOR ISOTROPIC SAMPLES, AT 1% 100 SECOND STRAIN.

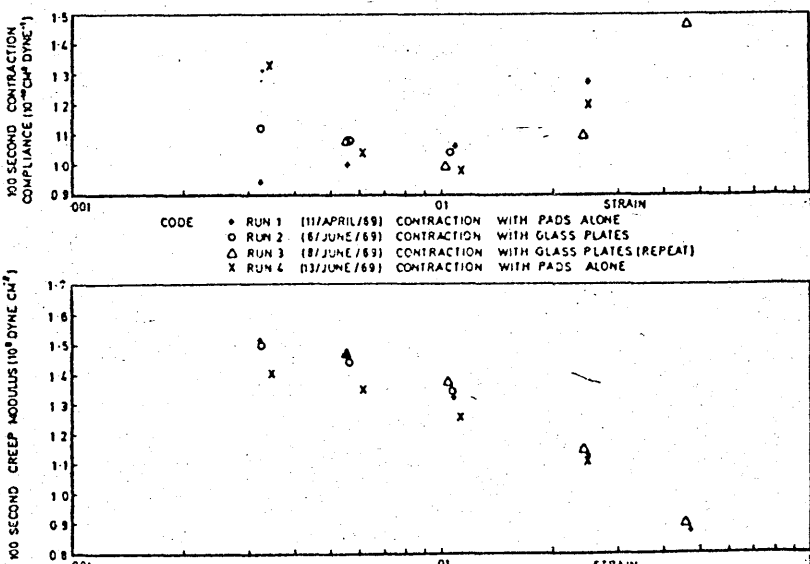


FIG. 5.10 THE VARIATION OF THE 100 SECOND CREEP MODULUS, E_{90} , AND THE CONTRACTION COMPLIANCE, S_{12} , WITH 100 SECOND STRAIN, FOR A DR 14, 90° SPECIMEN

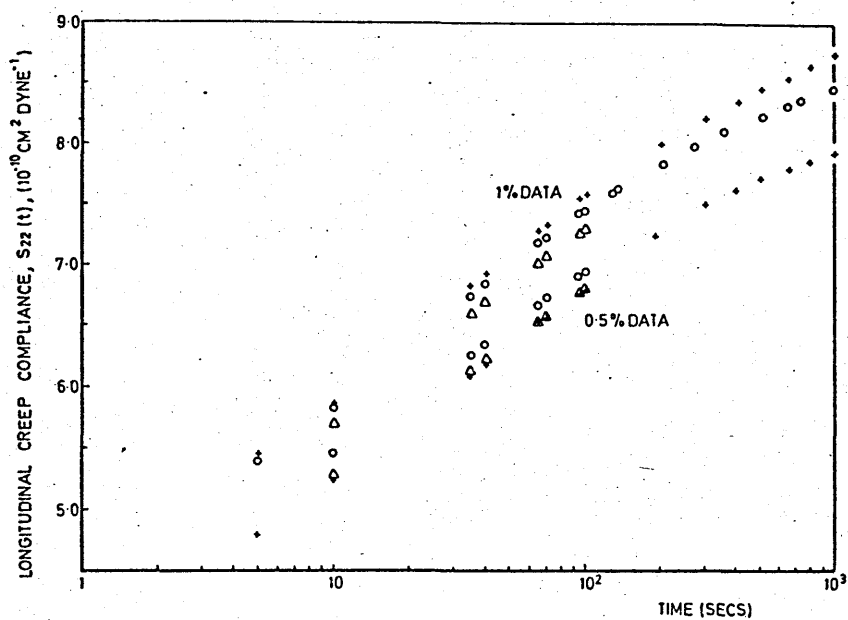
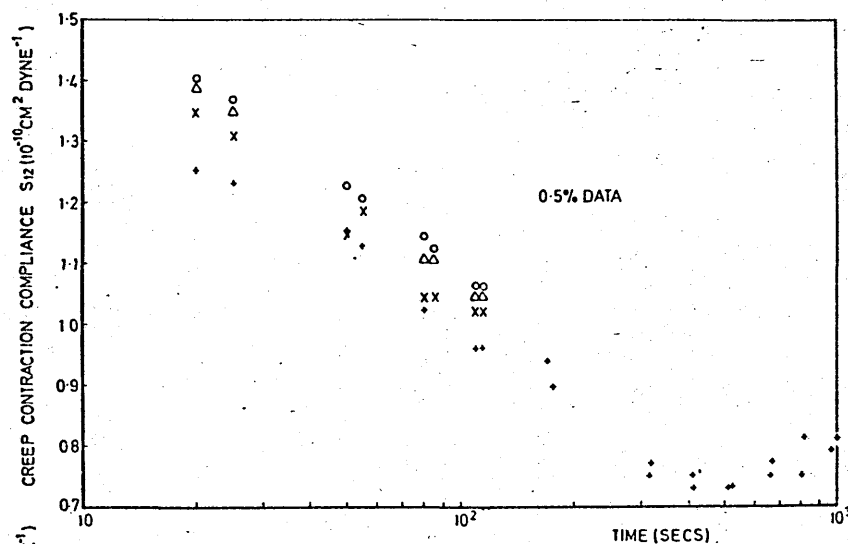
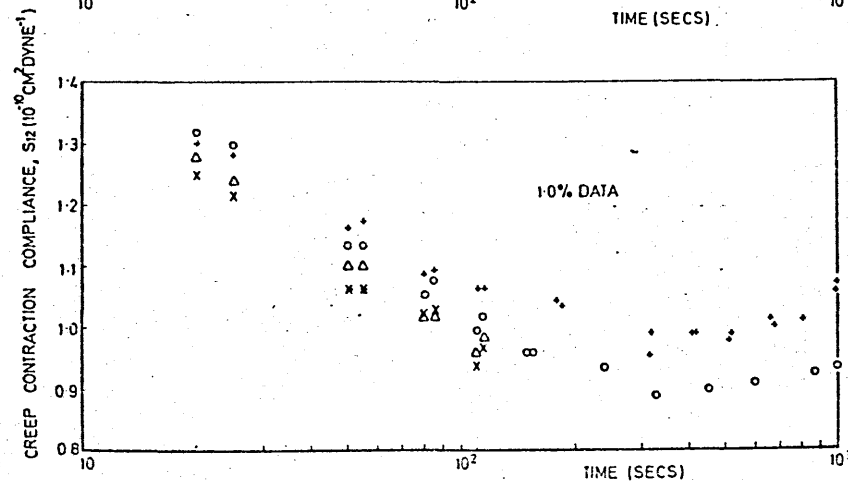


FIG 5.11 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE $S_{22}(t)$ AND THE CONTRACTION CREEP COMPLIANCE, $S_{12}(t)$ WITH TIME, FOR A D.R.14, 90° SPECIMEN, AT DIFFERENT 100 SECOND STRAINS

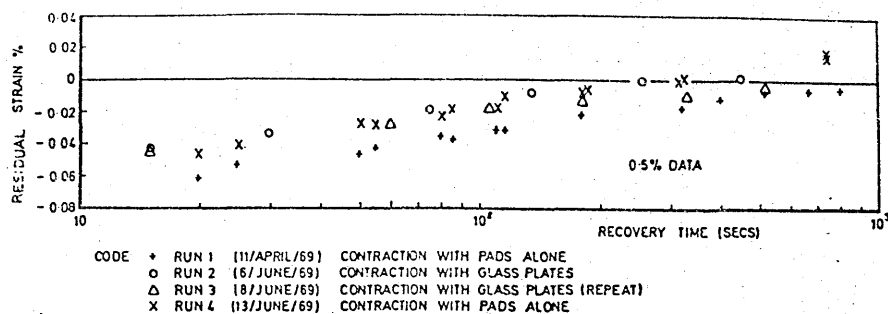
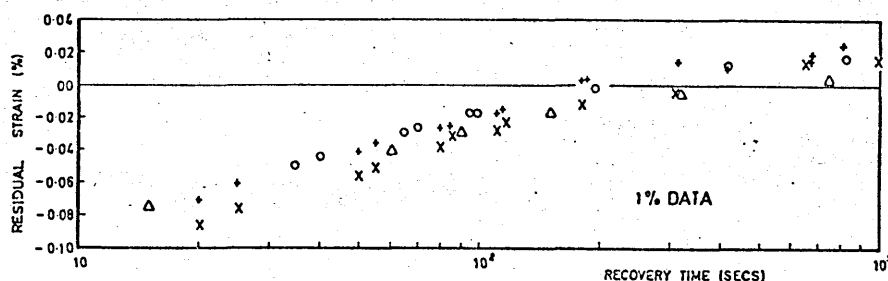


FIG 5.12 THE VARIATION OF THE CONTRACTION RESIDUAL STRAIN WITH TIME, AT 0.5% AND 1.0% 100 SECOND STRAIN LEVELS FOR D.R.1:4 90° SPECIMENS.

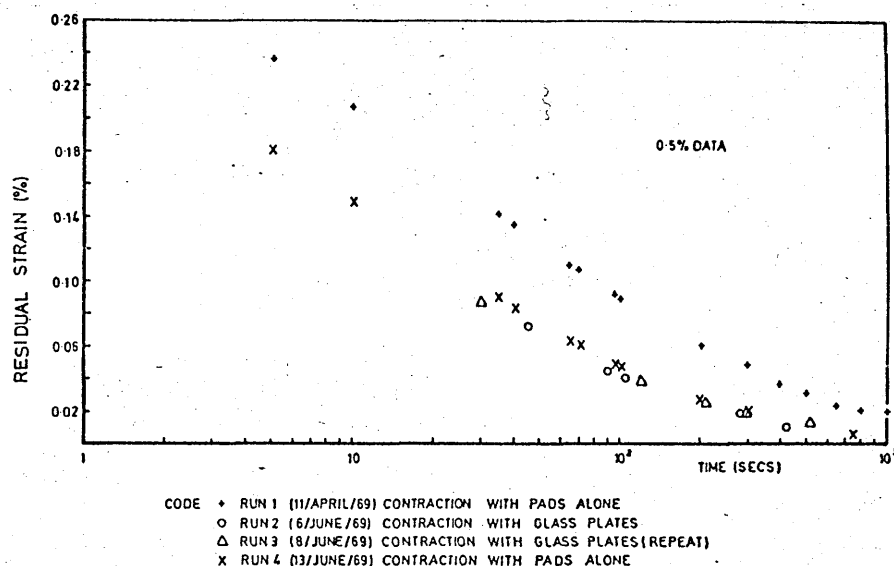
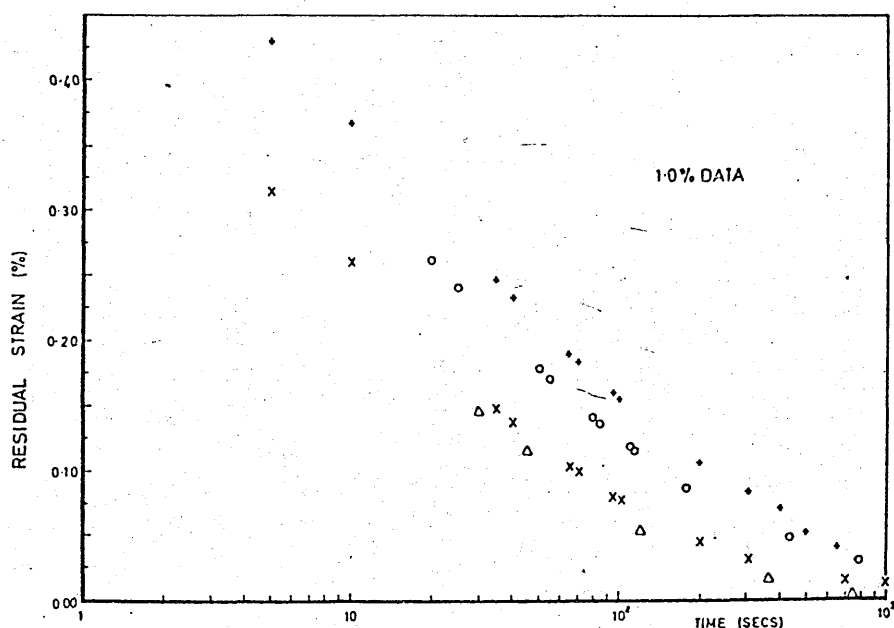


FIG 5.13 THE VARIATION OF THE LONGITUDINAL RESIDUAL STRAIN WITH TIME, AT 0.5% AND 1.0% 100 SECOND STRAIN LEVELS FOR D.R.1:4 90° SPECIMENS.

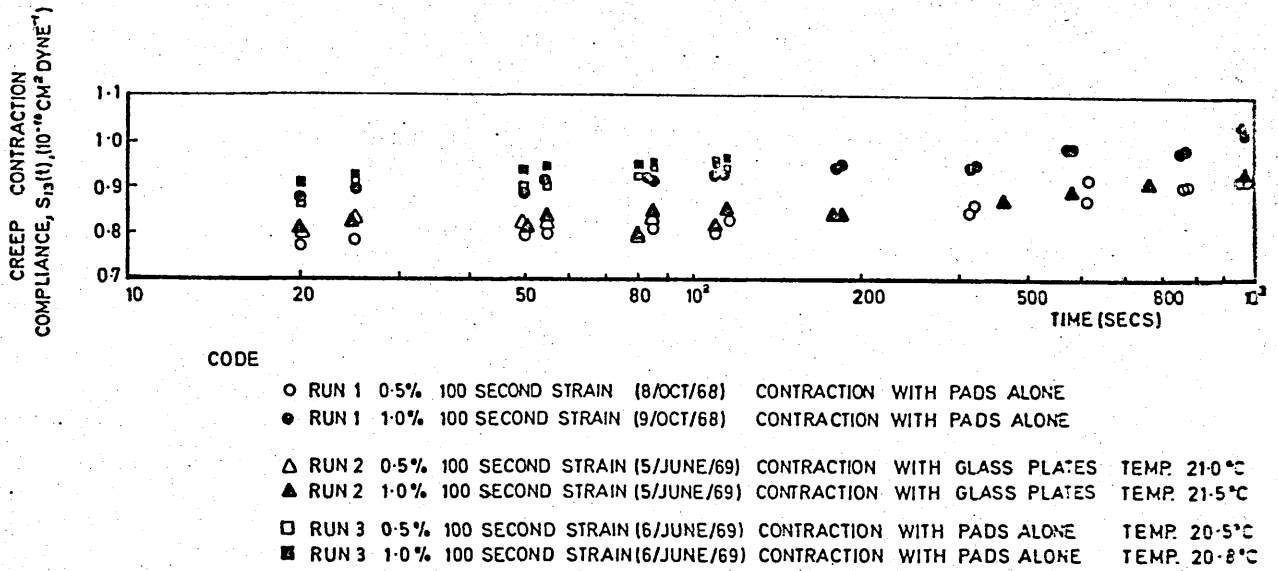
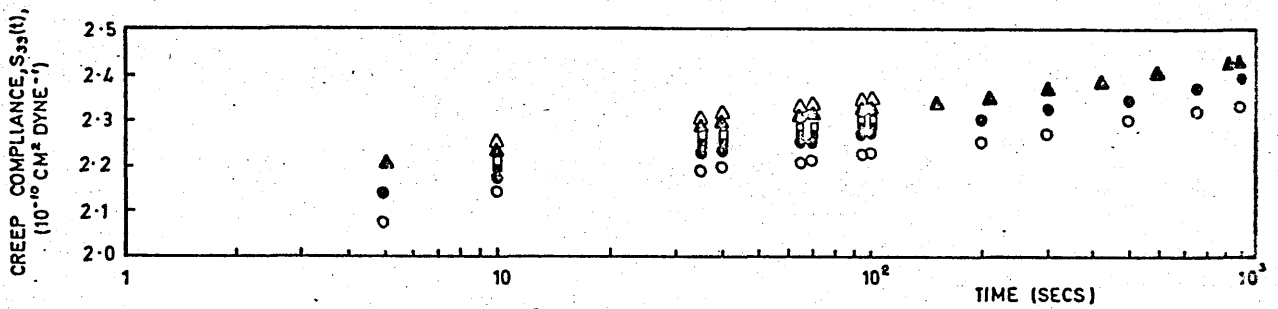


FIG5.14 THE VARIATION OF THE LONGITUDINAL AND CONTRACTION CREEP COMPLIANCE, S_{33} AND S_{13} , WITH TIME AT DIFFERENT STRAIN LEVELS, FOR A D.R. 3-8, 0° SPECIMEN.

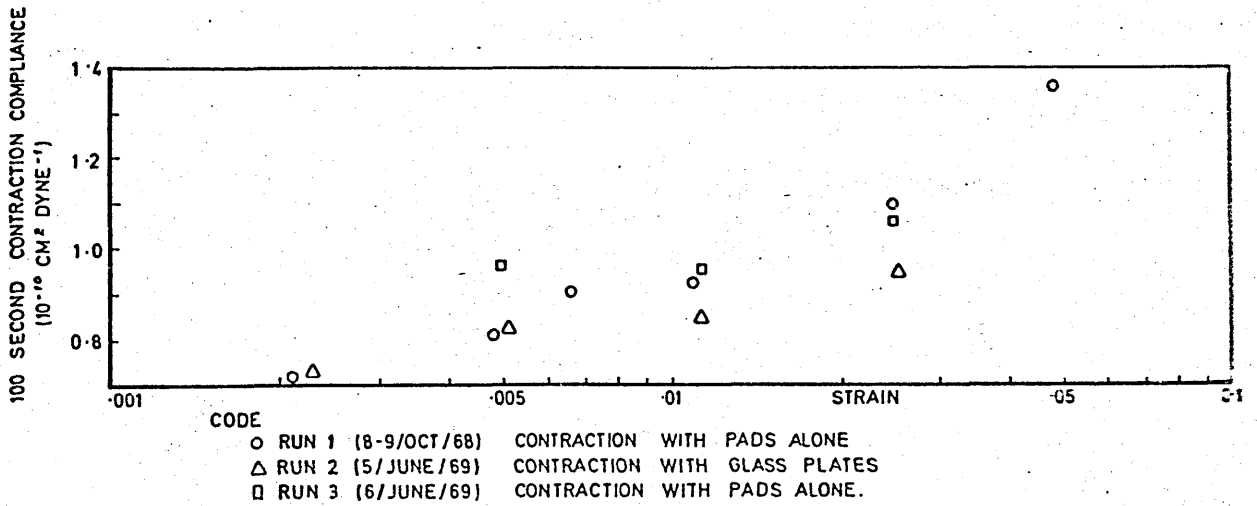
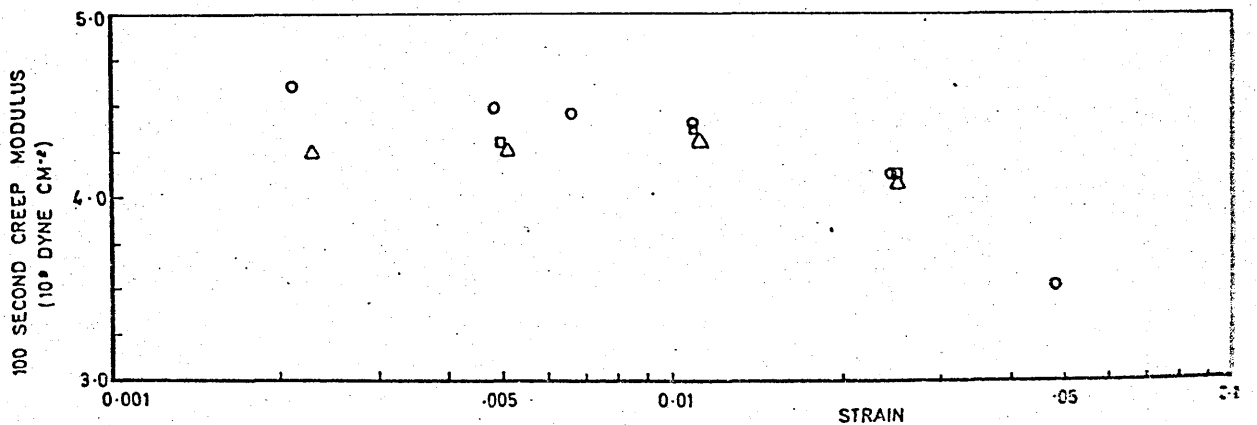


FIG5.15 THE VARIATION OF THE 100 SECOND CREEP MODULUS, E_0 , AND THE CONTRACTION COMPLIANCE, S_{13} , WITH 100 SECOND STRAIN, FOR A D.R. 3-8, 0° SPECIMEN.

6. SAMPLE PREPARATION AND CHARACTERISATION

6.1 Preparation of the Isotropic Sheets

The grade of polymer chosen was I.C.I. 'Alkathene' WJG 11, a low density polyethylene (L.D.P.E.) having a melt flow index of 2.0 and a nominal density of 0.918 gm/c.c. at 23°C. It was obtained in the form of cube granules, and isotropic sheets were prepared by compression moulding the granules between highly polished aluminium plates at 160°C. Thin sheets of polyethylene terephthalate 'Melinex' were used between the polymer and the plates to avoid adhesion problems when removing the pressed polymer sheets. The molten polymer was held in the press at 160°C for 15 minutes before cooling by passing water through the press platens. This heating period was necessary to remove strains caused by the flow pattern of the polymer during pressing. The isotropic sheets have a nominal thickness of 0.166 cms. The mechanical isotropy of the sheets was checked by measuring the variation of the isochronous modulus with strain for samples cut at various angles and positions in several sheets. No systematic variation with angle or position could be detected. (See Section 5). The density of the isotropic sheet was measured from 20 hours to 500 hours after preparation and a steady value was not attained. The variation was small, however, being less than 0.0004 gm/c.c. The mean density was 0.917 gm/c.c. which corresponds to a crystallinity of approximately 47%.

6.2 Preparation and Characterisation of the Drawn Samples

After the isotropic sheets had been in storage for a period of four to five weeks anisotropic sheets were prepared by selecting uniform isotropic sheets of length 15 to 24 cms, and width 6 to 8 cms., and cold drawing in uniaxial tension. The resultant material is transversely isotropic with the plane of isotropy perpendicular to the draw direction. A grid of half centimetre squares marked on each sheet prior to the drawing process was used in the determination of the final draw ratio. The draw ratio is defined as the ratio of the final length of a line in the direction of draw to the initial length, and is a convenient measure of the degree of anisotropy. (Raumann and Saunders, 1961). Raumann and Saunders, 1961, also reported that the moduli of anisotropic samples, prepared in this way, increased slightly during the first three weeks after drawing, but then remained substantially constant. The drawn sheets were therefore stored at room temperature for over two months before measurements of the draw ratios, or any tensile tests, were made.

Specimens for the uniaxial tensile creep studies were prepared from the sheets using a microspecimen tensile cutter (A.S.T.M. designation O.1708 - 59 T) having an overall length of 3.8 cms., a gauge length of 1.96 cms., and a width of 0.478 cms in the test section. The specimens were cut with their long axes at angles of 0°, 45°, and 90° to the draw direction.

Parallel sided specimens, which were cut at 0° to the draw direction, were used for the torsional creep studies. The nominal sample length was approximately 5 cms.

All specimens were stored in a temperature controlled room at $20.0^{\circ}\text{C} \pm 0.5^{\circ}$ until required.

SECTION 7. EXPERIMENTAL RESULTS

The experimental data is presented in two main sections. The first section concerns the variation of the measured compliance parameters with time at two stress levels, and the second, the variation of the measured parameters with strain at constant time. The test procedure is described in Section 5.

The time dependent behaviour under load is presented in the form of Creep Compliance data, and on the removal of applied load as a Recovery Compliance. The recovery compliance is a computed parameter calculated assuming the Boltzmann Superposition Principle, but represents the most convenient form in which to express the recovery data and avoid repetition of results. Details of a representative calculation are shown in Appendix A.3. The experimental results for specimens cut at 0° to the draw direction are shown in Figures 7.1 to 7.8, and both the longitudinal and the contraction creep and recovery compliances, $S_{33}(t)$, and $S_{13}(t)$ respectively, are presented at 0.5% and 1.0% 100 second strain. The longitudinal creep compliance $S_{33}(t)$ - (Fig. 7.1 to Fig. 7.4) - is calculated from the longitudinal creep deflection as follows:-

$$S_{33}(t) = \frac{\epsilon_{33}(t)}{\text{applied stress}} \quad 7.1$$

$$\text{where } \epsilon_{33}(t) = \frac{\text{Longitudinal Creep Deflection}}{\text{Gauge Length}} \quad 7.2$$

and the creep contraction compliance $S_{13}(t)$ is given by

$$S_{13}(t) = \frac{\epsilon_{11}(t)}{\text{applied stress}} \quad 7.3$$

$$\text{where } \epsilon_{11}(t) = \frac{\text{Through Thickness Creep Contraction}}{\text{Original Thickness}} \quad 7.4$$

The main features of Figures 7.1 to 7.4 are the variation of the time dependence of the compliance with draw ratio, and the marked similarity between the magnitude and shape of the 0.5% and 1.0% 100 second strain curves in creep and recovery, and also between the creep and recovery curves. At low draw ratios the creep rate increases with increasing draw ratio up to DR 1.25 and thereafter decreases, and at high draw ratios the compliance is relatively time independent. The trends at low draw ratios are explained in terms of a c-axis shear mechanism, and at high draw ratios by a chain extension mechanism. The variation of the contraction compliance, $S_{13}(t)$, with time and draw ratio, Figure 7.5 - 7.8, shows similar trends as above and may be explained by invoking the

same mechanisms (Section 9.1). The similarity of the creep and recovery compliances at the two strain levels indicate that all mechanisms governing the deformation are reversible. The Figures 7.1 - 7.8 are shown on the following pages and are preceded by the figure captions.

Exactly similar experiments were carried out on specimens cut at 90° and 45° to the draw direction and these results are shown in Figure 7.9 to 7.16 and Figures 7.17 to 7.24 respectively. The longitudinal creep compliance, $S_{22}(t)$, and the creep contraction compliance, $S_{12}(t)$ are calculated using equations 7.5 to 7.7 below:-

$$S_{22}(t) = \frac{\epsilon_{22}(t)}{\text{applied stress}} \quad 7.5$$

$$\text{where } \epsilon_{22}(t) = \frac{\text{longitudinal creep deflection}}{\text{gauge length}} \quad 7.6$$

$$\text{and the compliance } S_{12}(t) = \frac{\epsilon_{11}(t)}{\text{applied stress}} \quad 7.7$$

where $\epsilon_{11}(t)$ is defined in 7.4.

Similar equations are used for the 45° specimens viz.

$$\frac{1}{E_{45}(t)} = \frac{\epsilon_{45^\circ}(t)}{\text{applied stress}} \quad 7.8$$

$$\text{where } \epsilon_{45^\circ}(t) = \frac{\text{Longitudinal creep deflection}}{\text{gauge length}} \quad 7.9$$

$$\text{and the contraction compliance, } \left(\frac{\Delta t}{\sigma} \right)_{45^\circ} = \frac{\text{Through thickness Creep Contraction}}{\text{Original Thickness}} \times \frac{\text{Applied stress}}{\text{Applied stress}} \quad 7.10$$

The variation of the creep rate of the longitudinal compliance, $S_{22}(t)$, with draw ratio, is similar to that for the compliance, $S_{33}(t)$, (Figure 7.9 - 7.12), and is shown to be a manifestation of the c-axis shear mechanism at low draw ratios. However, there is a marked anisotropy of creep rates at the low draw ratio and this is a consequence of the cone distribution of c-axes about the draw direction. (Section 9.1). The

contraction compliance for 90° specimens shows an apparently anomalous behaviour (Fig. 7.13 to 7.16). The instantaneous contraction is followed by a time-dependent thickening. On removal of the applied load, the specimen instantaneously recovers to a thickness which is greater than the original thickness followed by a time-dependent recovery to the original dimensions.

For 45° specimens only selected draw ratios were investigated and the longitudinal compliance data, $\frac{1}{E_{45}(t)}$ is presented in Fig. 7.17 to 7.20, and the contraction $E_{45}(t)$ results, which were taken mainly at the 1% 100 second strain level, are shown in Figure 7.21 - 7.24. The creep rates are similar at all the low draw ratios, unlike the 0° and 90° specimens, whilst at high draw ratios the time dependence is again relatively small but the magnitude of the compliance is increased considerably. Also, at high draw ratios the contraction strains were negligible at DR 3.8 and result in a very low compliance value.

The Figures 7.9 to 7.16 for the 90° specimens, and Figures 7.17 to 7.24 for the 45° specimens are presented on the following pages and are preceded in each case by a list of figure captions.

The shear compliance, $S_{44}(t)$ is derived from torsional creep experiments on rectangular cross-sectioned specimens, cut at 0° to the draw direction, from measurements of the applied torque and the time dependent angular deflection as shown in Section 2. The results of these computations are shown in Figure 7.25 and 7.26. The creep tests were carried out on specimens where the maximum shear strain was approximately 0.2%, and at a temperature in the range $19.3 \pm 0.5^\circ\text{C}$. The results of tests on more than one specimen at the same draw ratio are shown to demonstrate the reproducibility of the tests. The sensitivity and accuracy of the results is fully discussed in Section 5.2. The figures 7.25 and 7.26 and the figure captions are shown on the following pages.

The variation of the isochronous creep modulus and creep contraction compliance with strain for specimens cut at 0° , 90° and 45° to the draw direction are shown in Figures 7.27 to 7.32. For each angular position the isochronous modulus and contraction compliance is presented as a function of the 100 second longitudinal strain, for all the draw ratios investigated, and allows an examination of the non-linearity at each draw ratio. A linear continuum would be represented by a straight line parallel to the strain axis. The variation of the isochronous shear compliance with strain at all draw ratios is shown in Figure 7.33. The isochronous tests in torsional creep

were carried out at $20.5 \pm 0.5^{\circ}\text{C}$. However, the ambient temperatures in the laboratory dropped to $19.3 \pm 0.5^{\circ}\text{C}$ when the long term tests were performed and accounts for the slight differences in values for the shear compliances presented in 7.25 and 7.33. The reproducibility of results and the effect of sample geometry on the end effects were examined by testing many samples at each draw ratio and varying the length to width, (L/W), and the width to thickness, (W/t), ratios. The results of these investigations are shown in Figure 7.34 to 7.36, and it was concluded that no errors were introduced due to the St. Venant's type end effects. (See also Section 5.2). The effect of axial loads on the torsional rigidity was also examined and some results are presented in Figure 7.37 and 7.38.

The isochronous data for all tests - Figures 7.27 to 7.38 - are presented on the following pages and each specimen angle is preceded by a list of figure captions.

Tensile Specimens - 0°

Fig. 7.1 The variation of the longitudinal creep compliance $S_{33}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.2 The variation of the longitudinal recovery compliance $S_{33}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.3 The variation of the longitudinal creep compliance $S_{33}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.4 The variation of the longitudinal recovery compliance $S_{33}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.5 The variation of the creep contraction compliance $S_{13}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.6 The variation of the recovery contraction compliance $S_{13}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.7 The variation of the creep contraction compliance $S_{13}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.8 The variation of the recovery contraction compliance $S_{13}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Tensile Specimens - 90°

Fig. 7.9 The variation of the longitudinal creep compliance $S_{22}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.10 The variation of the longitudinal recovery compliance, $S_{22}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.11 The variation of the longitudinal creep compliance, $S_{22}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.12 The variation of the longitudinal recovery compliance, $S_{22}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.13 The variation of the creep contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.14 The variation of the recovery contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.15 The variation of the creep contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.16 The variation of the recovery contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.

Tensile Specimens - 45°

Fig. 7.17 The variation of the longitudinal creep compliance, $\frac{1}{E_{45}(t)}$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.18 The variation of the longitudinal recovery compliance, $\frac{1}{E_{45}(t)}$, with time, for different draw ratios, at 0.5% 100 second strain.

Fig. 7.19 The variation of the longitudinal creep compliance, $\frac{1}{E_{45}(t)}$, with time, for different draw ratios, at 1.0% 100 second strain.

Fig. 7.20 The variation of the longitudinal recovery compliance, $\frac{1}{E_{45}(t)}$, with time, for different draw ratios, at 1.0% 100 second strain.

$\left(\frac{\Delta \epsilon}{\sigma}\right)_{45^\circ}$ Fig. 7.21 The variation of the creep contraction compliance, with time, for DR. 2.65 at 0.5% 100 second strain.

$\left(\frac{\Delta \epsilon}{\sigma}\right)_{45^\circ}$ Fig. 7.22 The variation of the recovery contraction compliance, with time, for DR. 2.65 at 0.5% 100 second strain.

$\left(\frac{\Delta \epsilon}{\sigma}\right)_{45^\circ}$ Fig. 7.23 The variation of the creep contraction compliance, with time, for different draw ratios, at 1% 100 second strain.

$\left(\frac{\Delta \epsilon}{\sigma}\right)_{45^\circ}$ Fig. 7.24 The variation of the recovery contraction compliance, with time, for different draw ratios, at 1% 100 second strain.

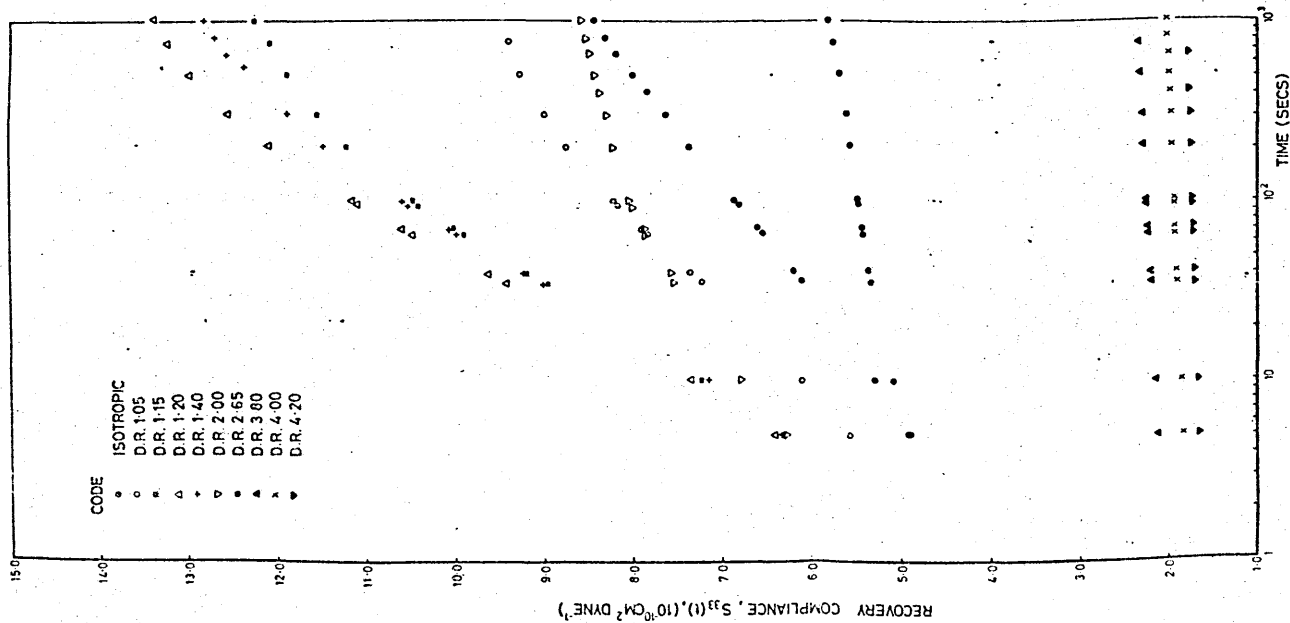


FIG. 72 THE VARIATION OF THE LONGITUDINAL RECOVERY COMPLIANCE, $S_{33}(t)$ WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

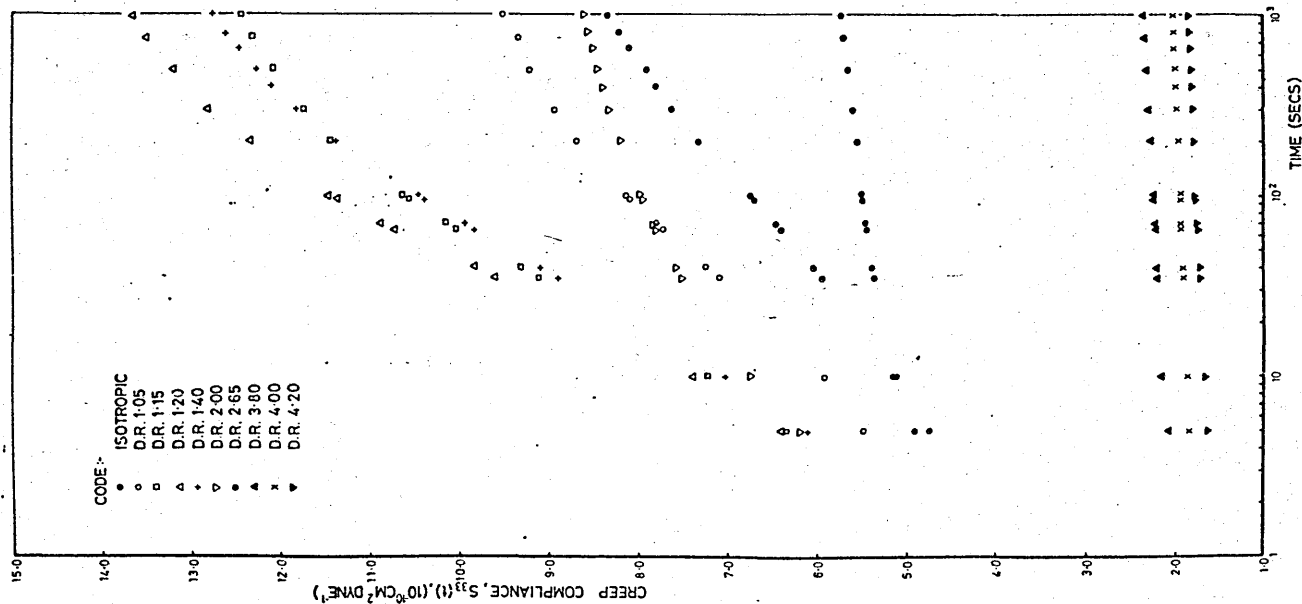


FIG. 73 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE, $S_{33}(t)$ WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

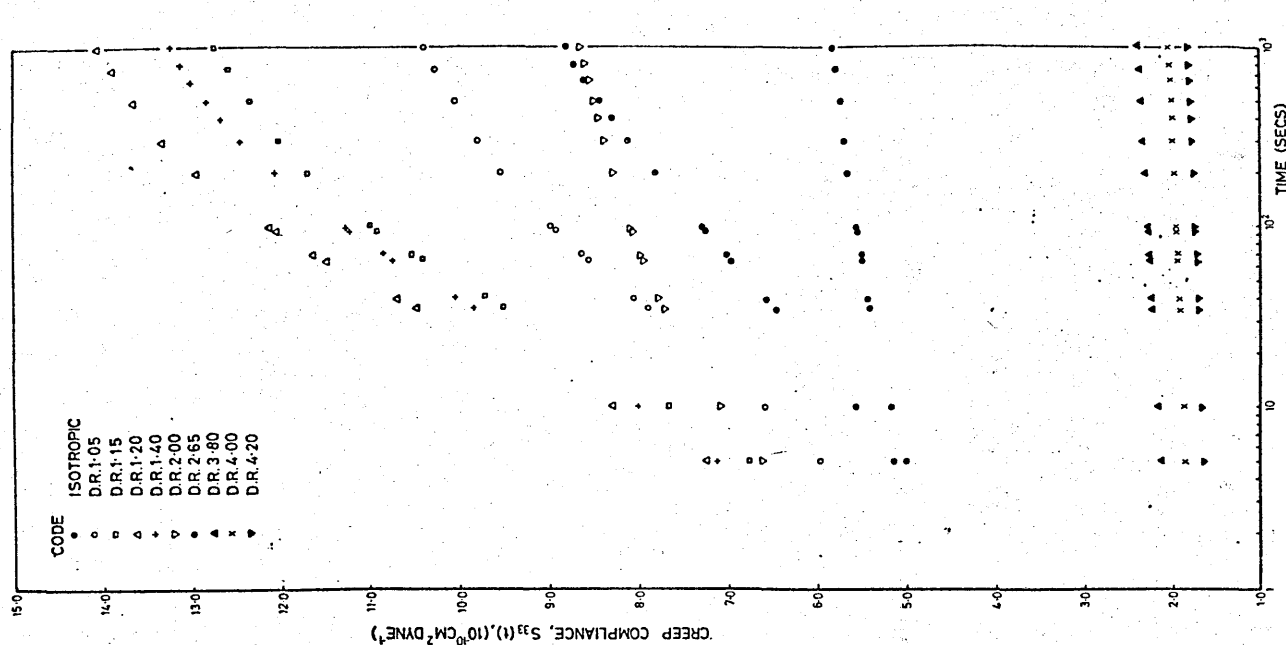


FIG. 74 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE, $S_{33}(t)$ WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

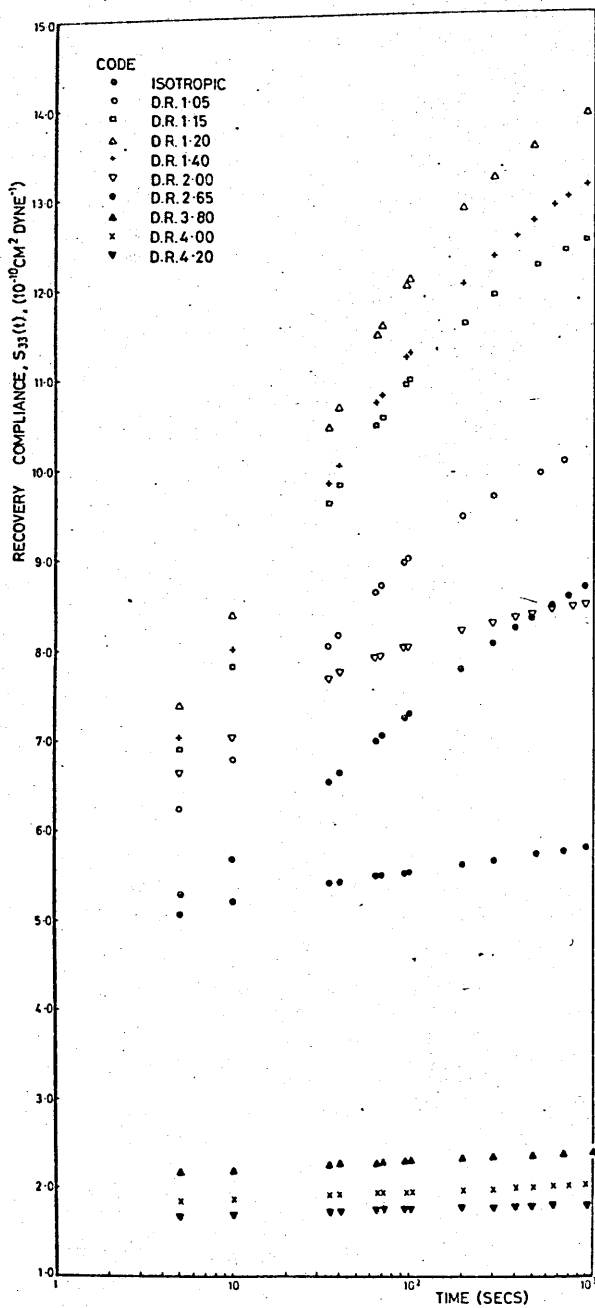


FIG 74 THE VARIATION AT LONGITUDINAL RECOVERY COMPLIANCE, $S_{33}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 10% 100 SECOND STRAIN.

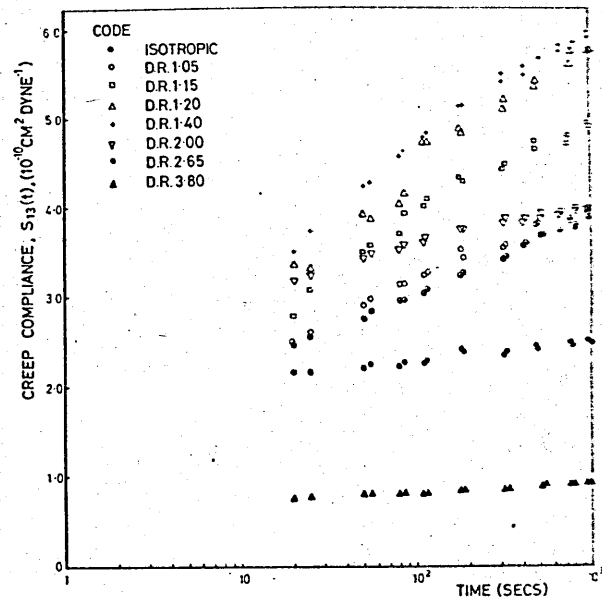


FIG 75 THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE, $S_{33}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

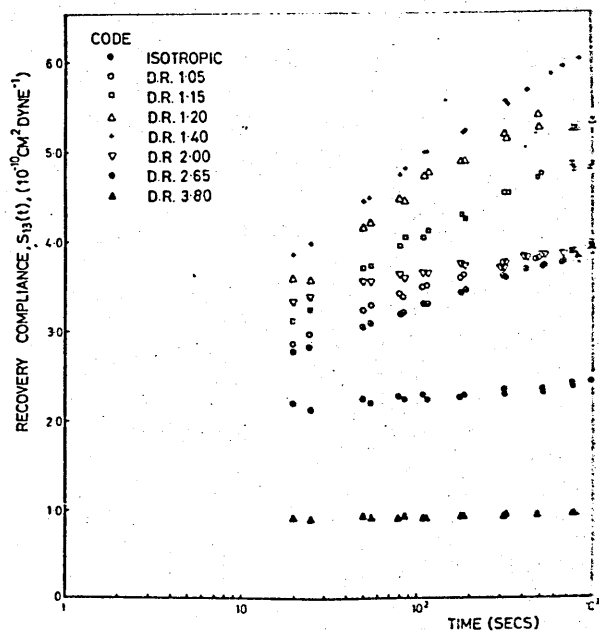


FIG 76 THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE, $S_{33}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

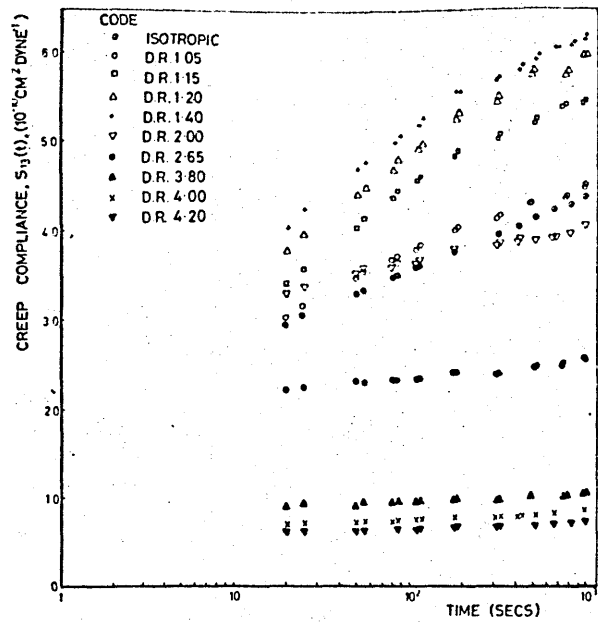


FIG 77 THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE, $S_{13}(t)$, WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

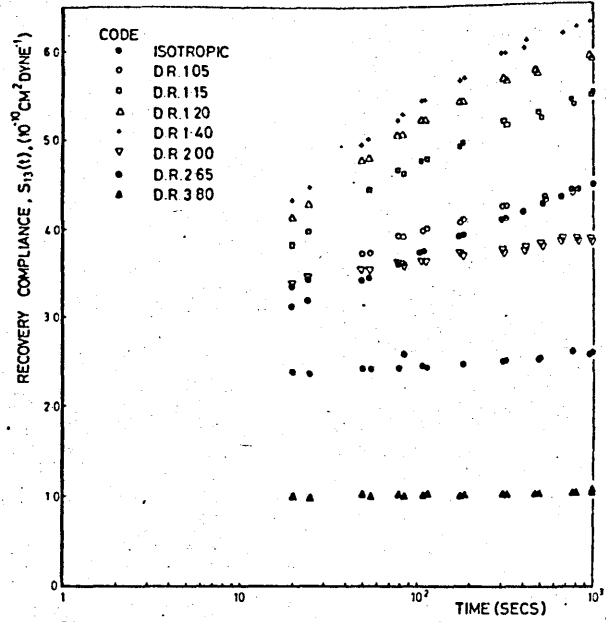


FIG 78 THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE, $S_{13}(t)$, WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN LEVEL.

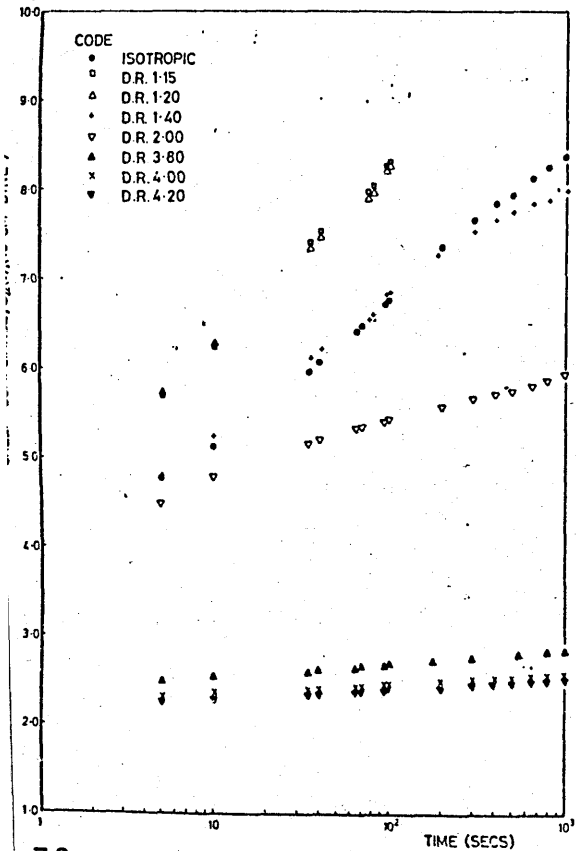


FIG 79 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE, $S_{22}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

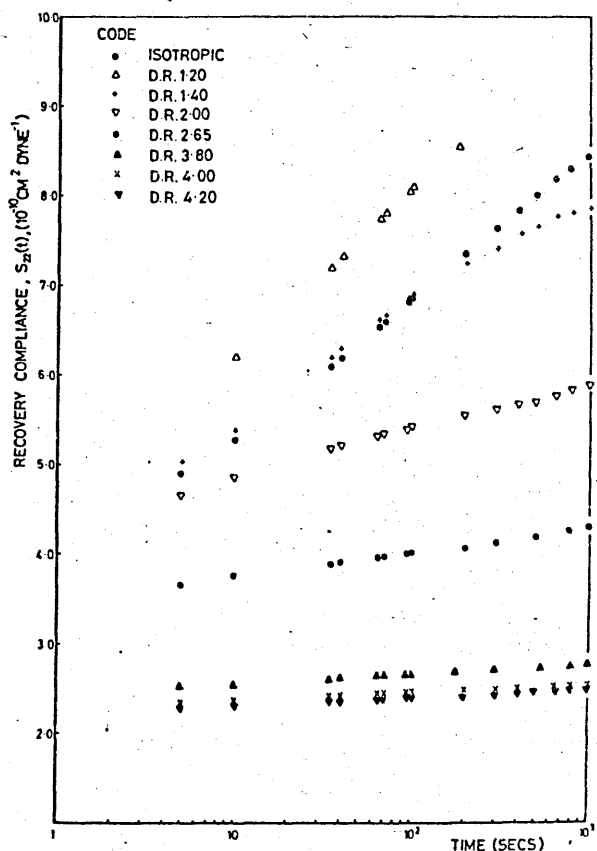


FIG 80 THE VARIATION OF THE LONGITUDINAL RECOVERY COMPLIANCE, $S_{22}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

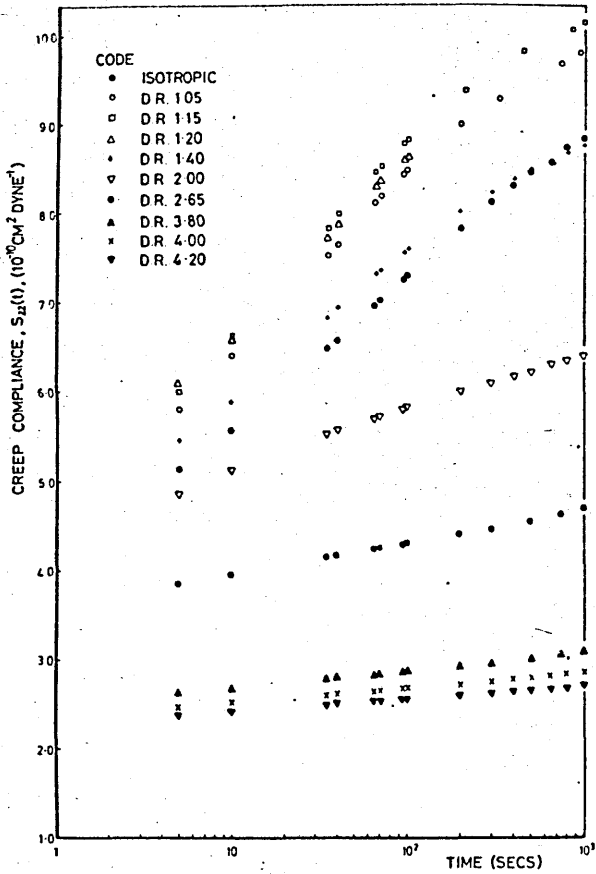


FIG 7 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE, $S_{11}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS AT 1.0% 100 SECOND STRAIN.

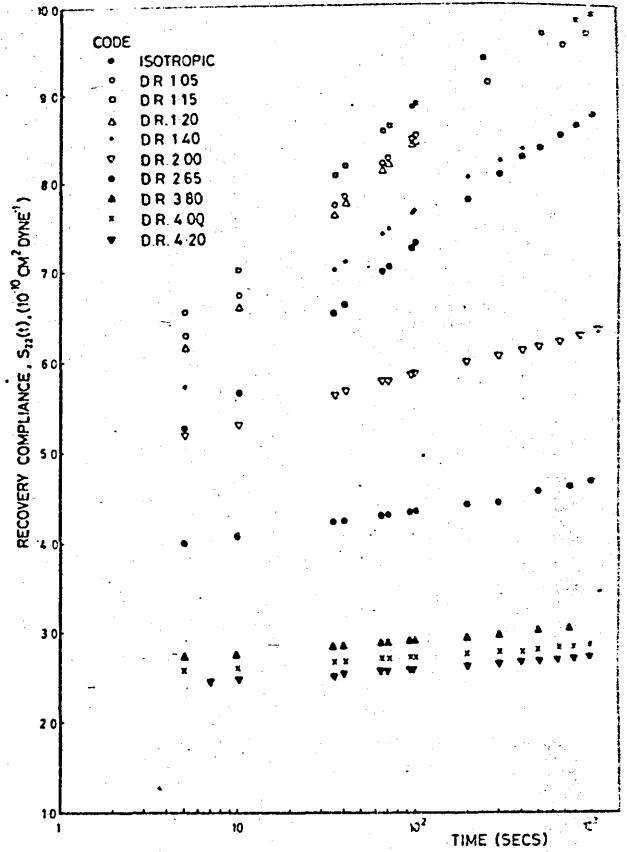


FIG 12 THE VARIATION OF THE LONGITUDINAL RECOVERY COMPLIANCE, $S_{11}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1.0% 100 SECOND STRAIN.

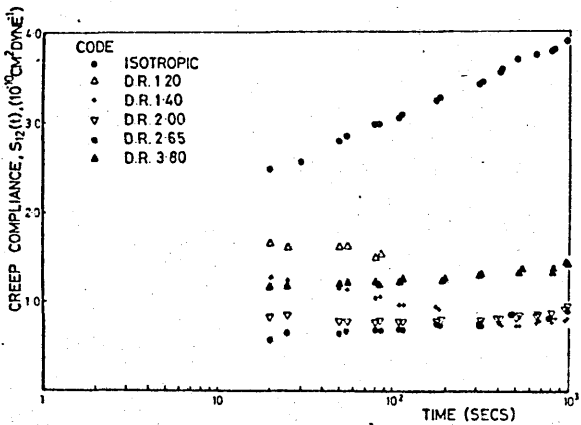


FIG 13 THE VARIATION AT THE CREEP CONTRACTION COMPLIANCE, $S_{12}(t)$, WITH TIME AT DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

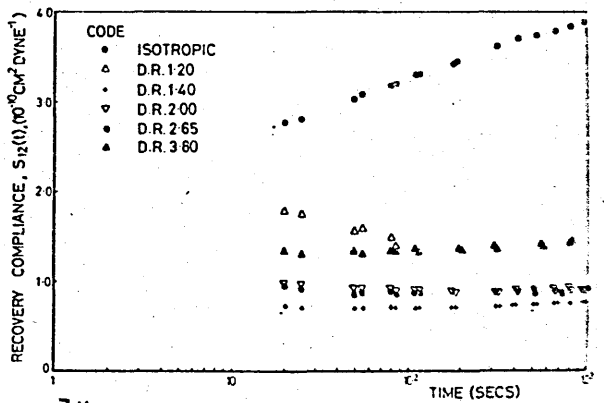


FIG 14 THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE, $S_{12}(t)$, WITH TIME, AT DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

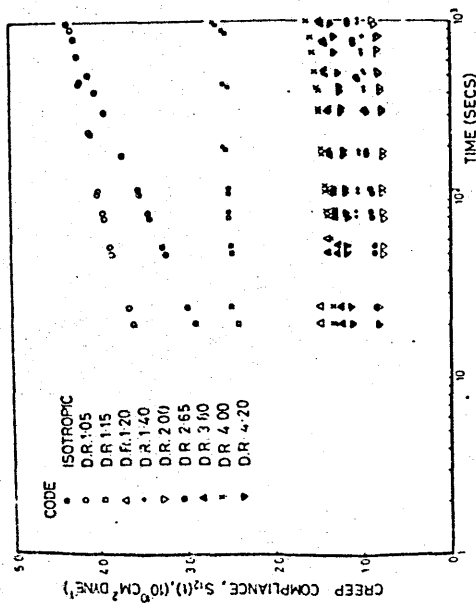


FIG 7-15 THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE, $S_{12}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN

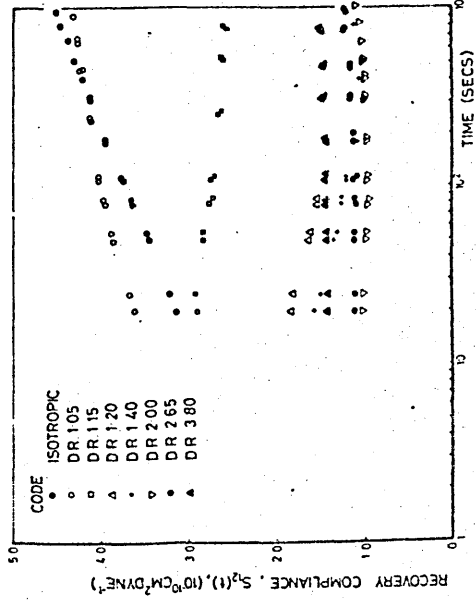


FIG 7-16 THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE, $S_{12}(t)$, WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN LEVEL

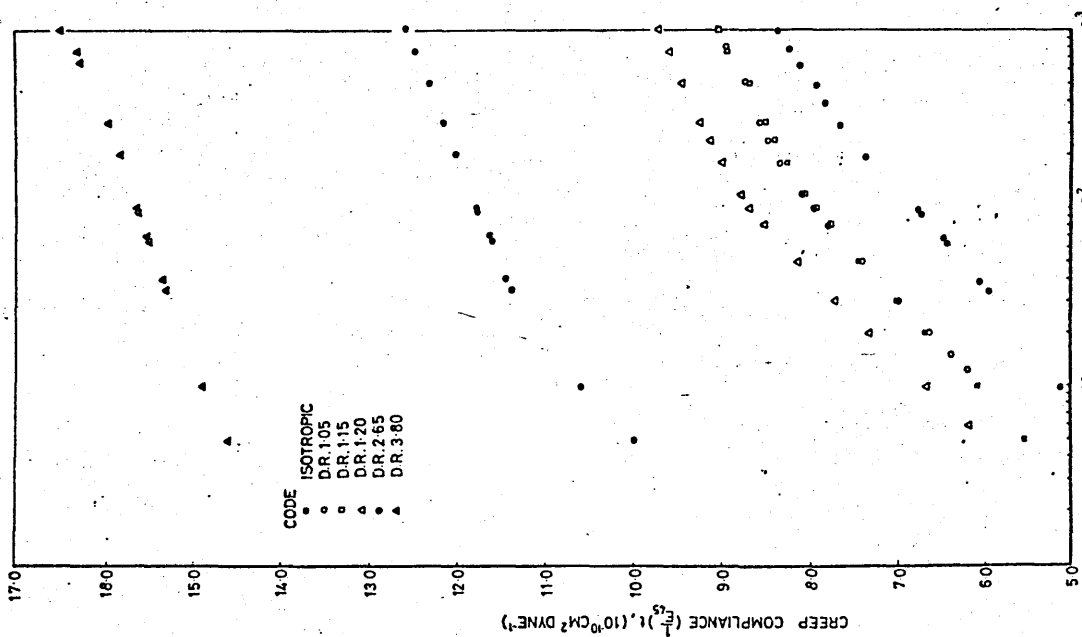


FIG 7-17 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE, $E_{13}^{-1}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN

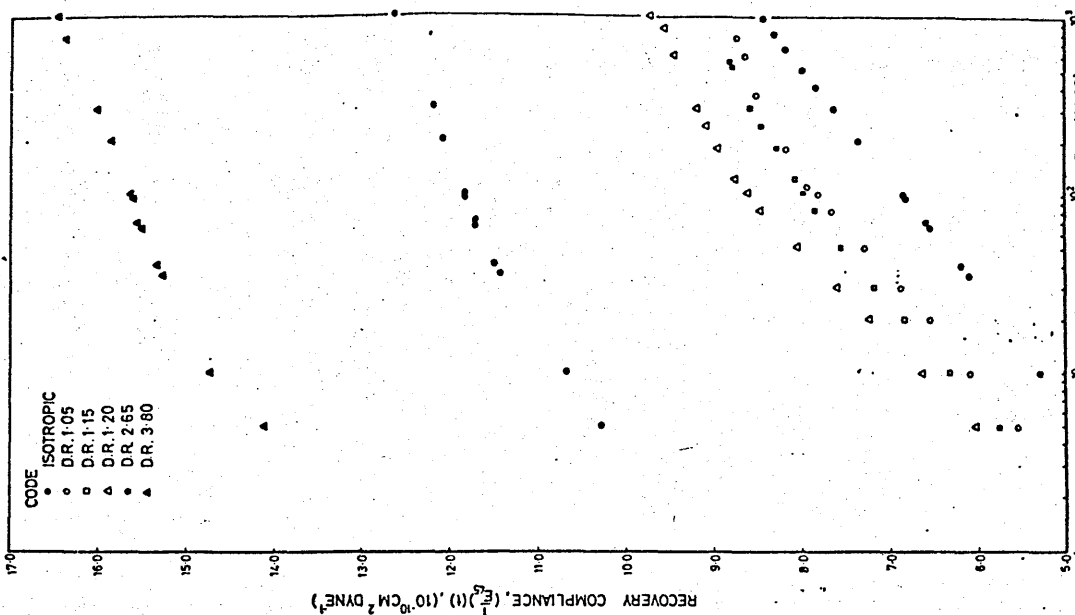


FIG 7-18 THE VARIATION OF LONGITUDINAL RECOVERY COMPLIANCE, $E_{13}^{-1}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN

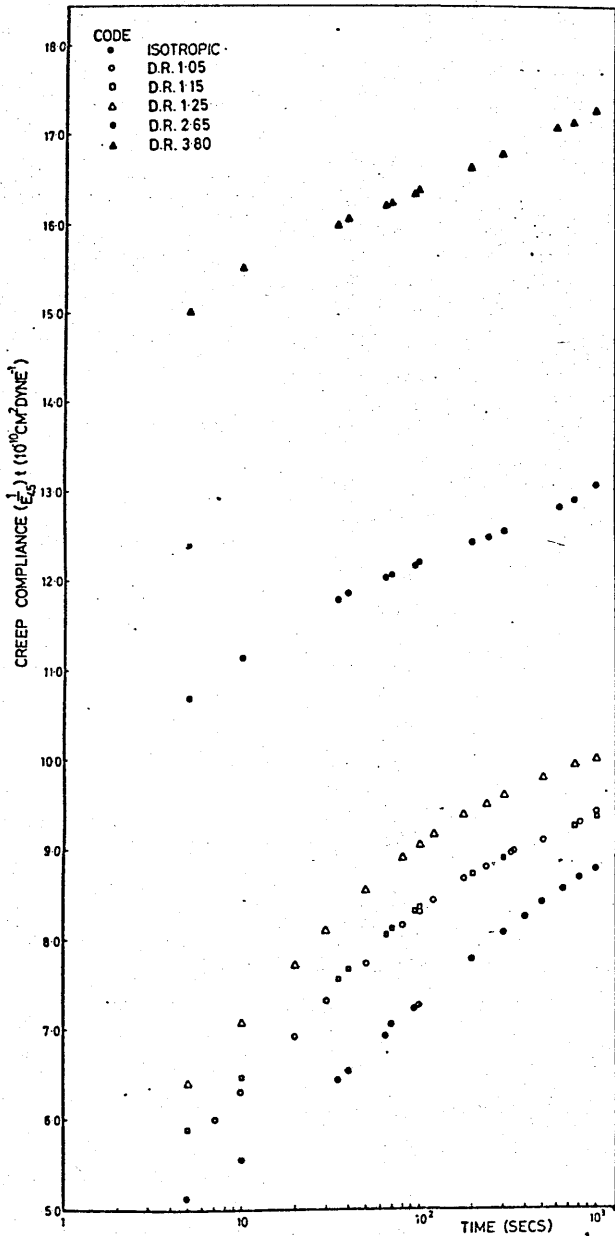


FIG. 19 THE VARIATION OF THE LONGITUDINAL CREEP COMPLIANCE (J_c), WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

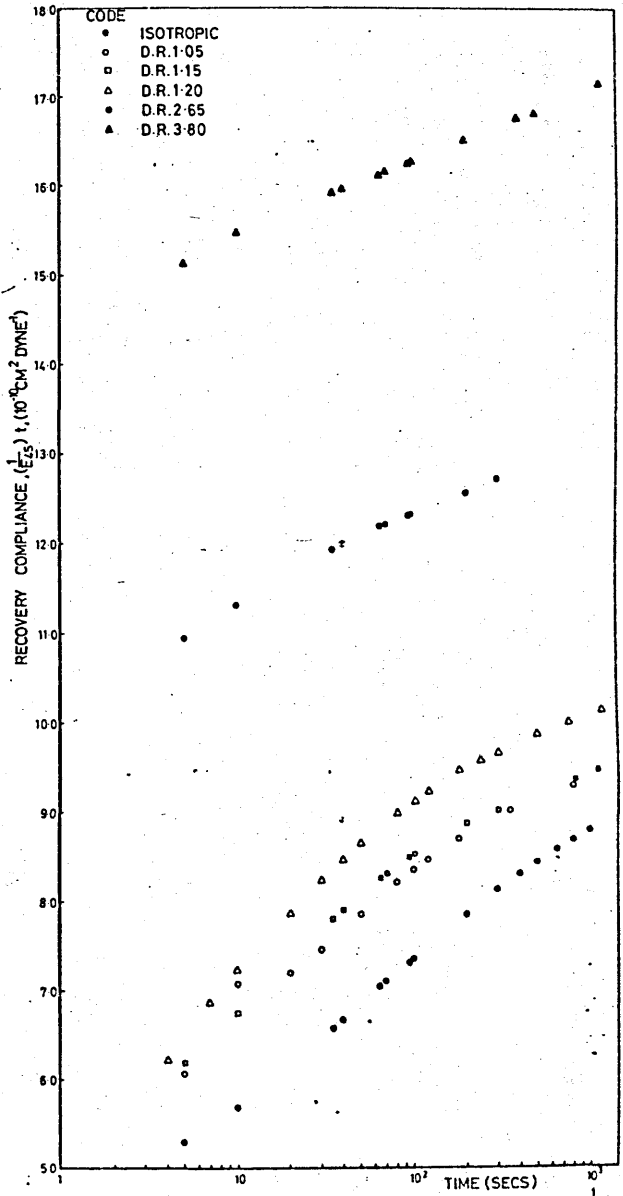


FIG. 20 THE VARIATION OF THE LONGITUDINAL RECOVERY COMPLIANCE (J_r), WITH TIME, FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

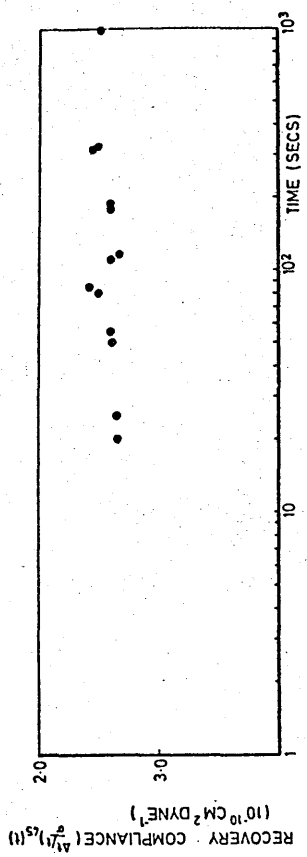


FIG 722 THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE ($\frac{A_{1/2}}{A_0}$) WITH TIME, FOR D.R. 2.65, AT 0.5% 100 SECOND STRAIN.

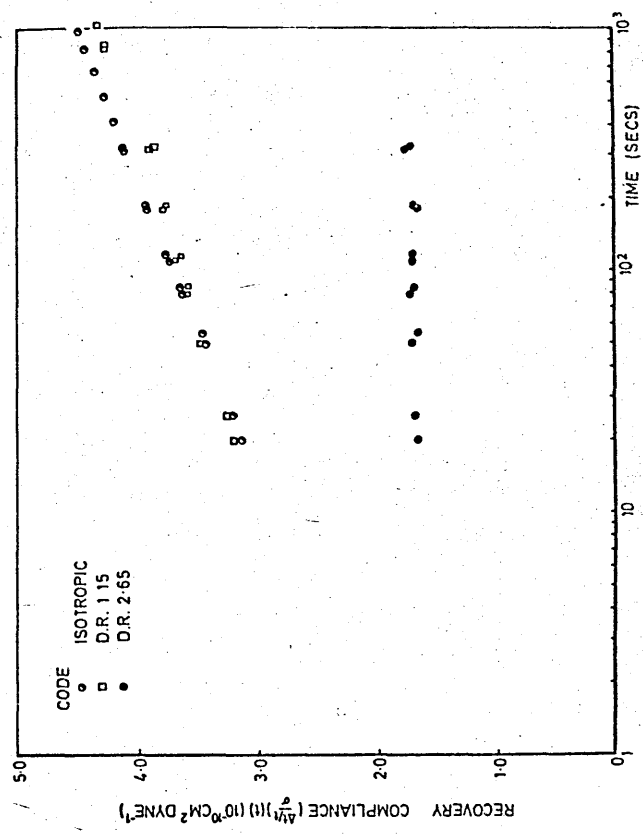


FIG 724 THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE ($\frac{A_{1/2}}{A_0}$) WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 10% 100 SECOND STRAIN.

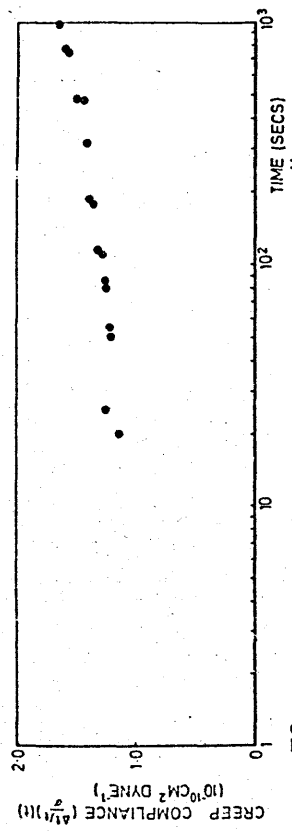


FIG 721 THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE ($\frac{A_{1/2}}{A_0}$) WITH TIME, FOR D.R. 2.65, AT 0.5 % 100 SECOND STRAIN.

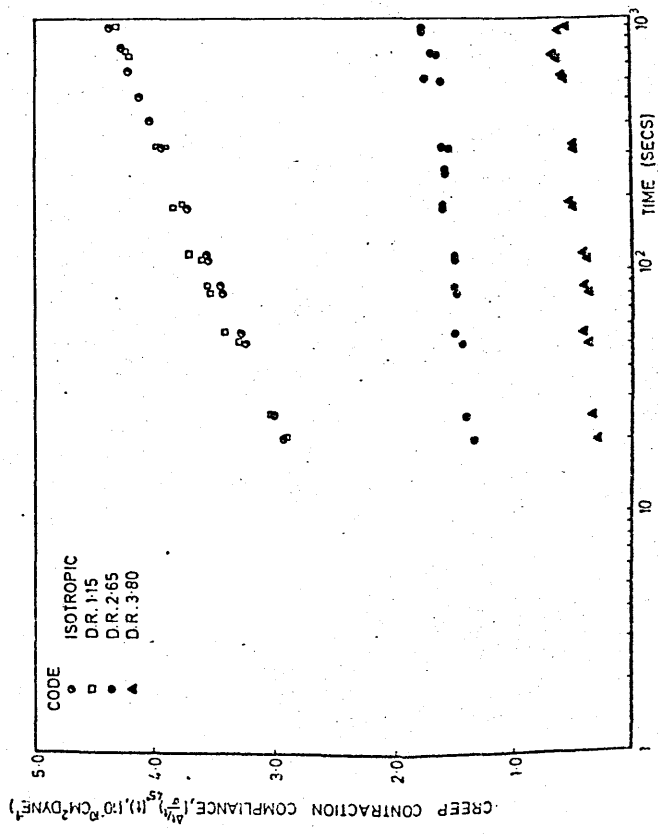


FIG 723 THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE ($\frac{A_{1/2}}{A_0}$) WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

Torsional Creep Specimens

Fig. 7.25 The variation of the shear creep compliance $S_{44}(t)$, with time, for different draw ratios.

Fig. 7.26 The variation of the shear recovery compliance, $S_{44}(t)$, with time, for different draw ratios.

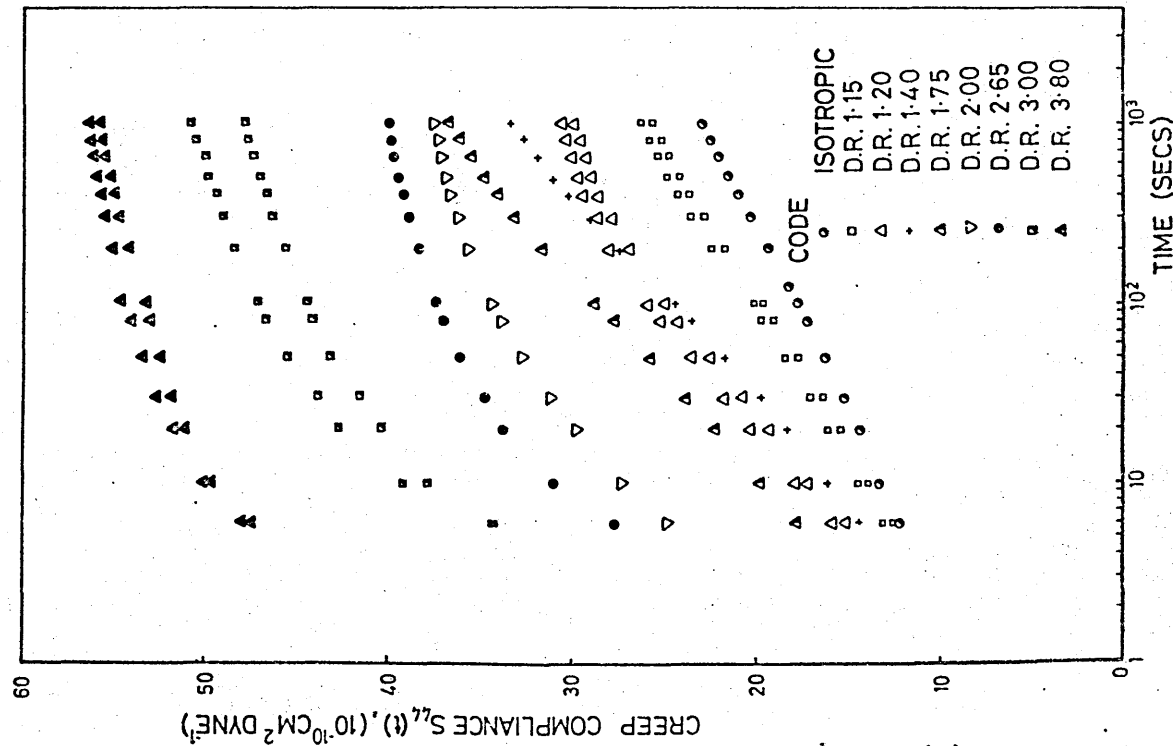


FIG.7-25 THE VARIATION OF THE SHEAR CREEP COMPLIANCE $S_{44}(t)$, WITH TIME FOR DIFFERENT DRAW RATIOS.

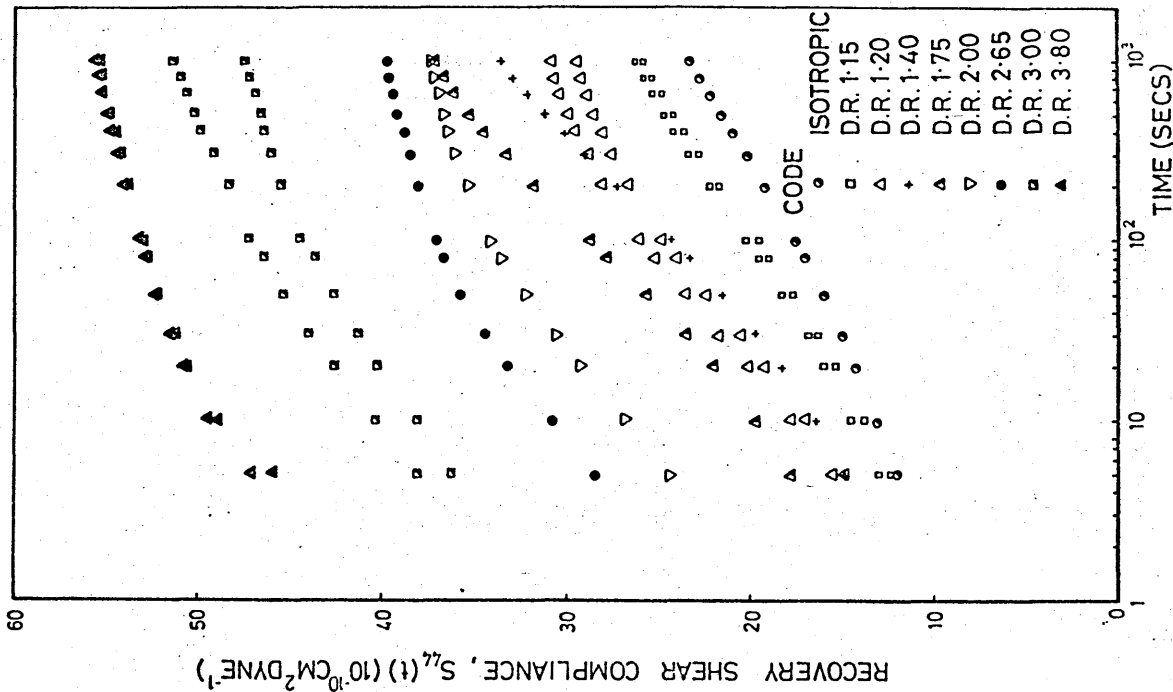


FIG.7-26 THE VARIATION OF THE SHEAR RECOVERY COMPLIANCE, $S_{44}(t)$, WITH TIME FOR DIFFERENT DRAW RATIOS.

Tensile Specimens - 0°

Fig. 7.27 The variation of the 100 second longitudinal modulus, $E_0(t)$, with 100 second strain, $e_0(t)$ for different draw ratios.

Fig. 7.28 The variation of the 100 second contraction compliance, $S_{13}(t)$, with 100 second strain, $e_0(t)$ for different draw ratios.

Tensile Specimens - 90°

Fig. 7.29 The variation of the 100 second longitudinal modulus, $E_{90}(t)$, with 100 second strain, $e_{90}(t)$, for different draw ratios.

Fig. 7.30 The variation of the 100 second contraction compliance, $S_{12}(t)$, with 100 second strain, $e_{90}(t)$, for different draw ratios.

Tensile Specimens - 45°

Fig. 7.31 The variation of the 100 second longitudinal modulus, $E_{45}(t)$, with 100 second strain, $e_{45}(t)$, for different draw ratios.

Fig. 7.32 The variation of the 100 second contraction compliance, $(\Delta t/t)_{45^\circ}$, with 100 second strain, $e_{45}(t)$, for different draw ratios.

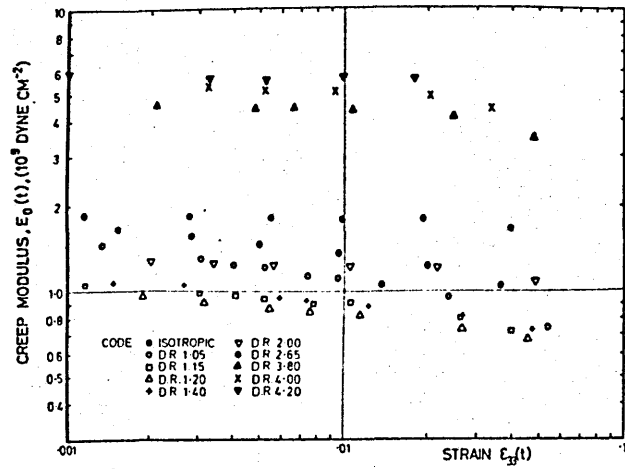


FIG 7-27 THE VARIATION OF THE 100 SECOND CREEP MODULUS, $E_0(t)$, WITH 100 SECOND STRAIN, $\epsilon_{33}(t)$, FOR DIFFERENT DRAW RATIOS.

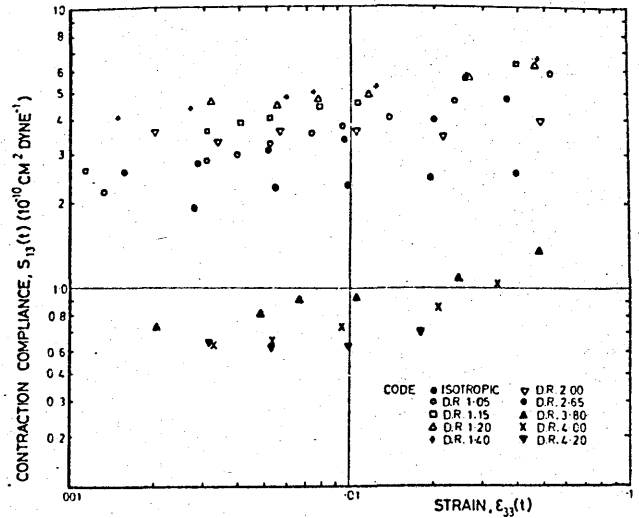


FIG 7-28 THE VARIATION OF THE 100 SECOND CREEP CONTRACTION COMPLIANCE, $S_{13}(t)$, WITH 100 SECOND LONGITUDINAL STRAIN, $\epsilon_{33}(t)$, FOR DIFFERENT DRAW RATIOS.

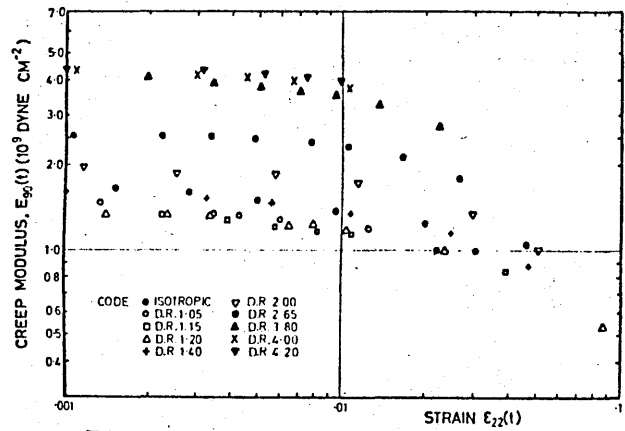


FIG 7-29 THE VARIATION OF THE 100 SECOND CREEP MODULUS, $E_{90}(t)$, WITH 100 SECOND STRAIN, $\epsilon_{22}(t)$, FOR DIFFERENT DRAW RATIOS.

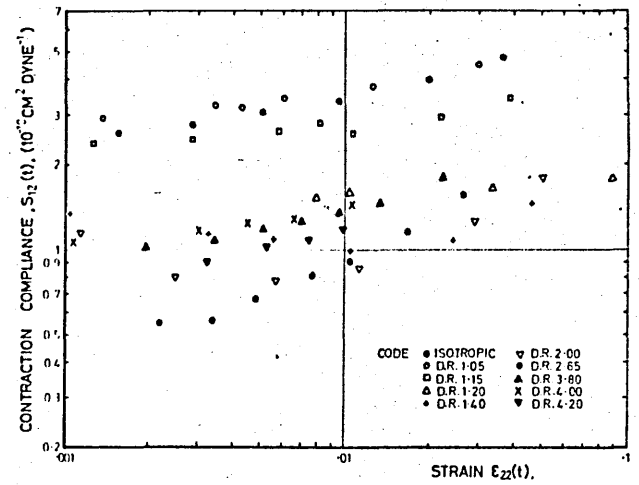


FIG 7-30 THE VARIATION OF THE 100 SECOND CREEP CONTRACTION COMPLIANCE, $S_{12}(t)$, WITH 100 SECOND LONGITUDINAL STRAIN, $\epsilon_{22}(t)$

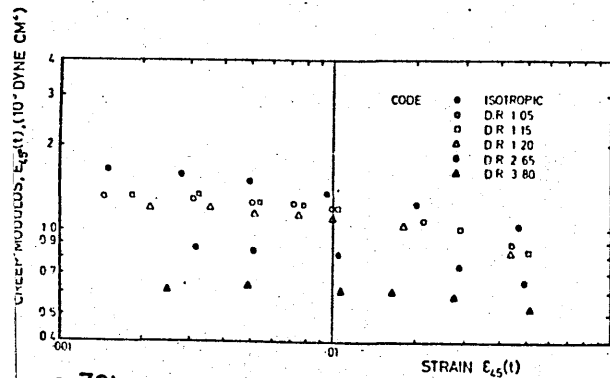


FIG 7-31 THE VARIATION OF THE 100 SECOND CREEP MODULUS, $E_{45}(t)$, WITH 100 SECOND STRAIN, $\epsilon_{45}(t)$, FOR DIFFERENT DRAW RATIOS.

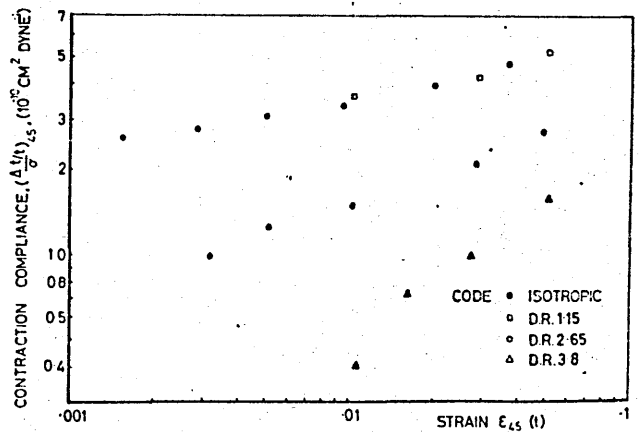


FIG 7-32 THE VARIATION AT THE 100 SECOND CREEP CONTRACTION COMPLIANCE, $(\frac{\Delta u_i}{\sigma})_{45}$, WITH 100 SECOND LONGITUDINAL STRAIN, $\epsilon_{45}(t)$ FOR DIFFERENT DRAW RATIOS.

Torsion Specimens

Fig. 7.33 The variation of the 100 second shear compliance $S_{44}(t)$, with 100 second maximum shear strain, $\gamma(t)_{\max}$, for different draw ratios.

Fig. 7.34 The variation of the 100 second shear compliance $S_{44}(t)$, with 100 second maximum shear strain, $\gamma(t)_{\max}$, at $DR = 1.00$ (Isotropic), for different width to thickness, and length to width ratios.

Fig. 7.35 The variation of the 100 second shear compliance $S_{44}(t)$, with 100 second maximum shear strain, $\gamma(t)_{\max}$, at $DR = 1.05$, for different width to thickness, and length to width ratios.

Fig. 7.36 The variation of the 100 second shear compliance $S_{44}(t)$, with 100 second maximum shear strain, $\gamma(t)_{\max}$, at $DR = 1.15$, for different width to thickness and length to width ratios.

Fig. 7.37 The variation of the 100 second shear compliance $S_{44}(t)$, with 100 second maximum shear strain, $\gamma(t)_{\max}$, at $DR = 2.65$, for different applied loads.

Fig. 7.38 The variation of the 100 second shear compliance $S_{44}(t)$, with 100 second maximum shear strain, $\gamma(t)_{\max}$, at $DR = 3.0$, for different loads.

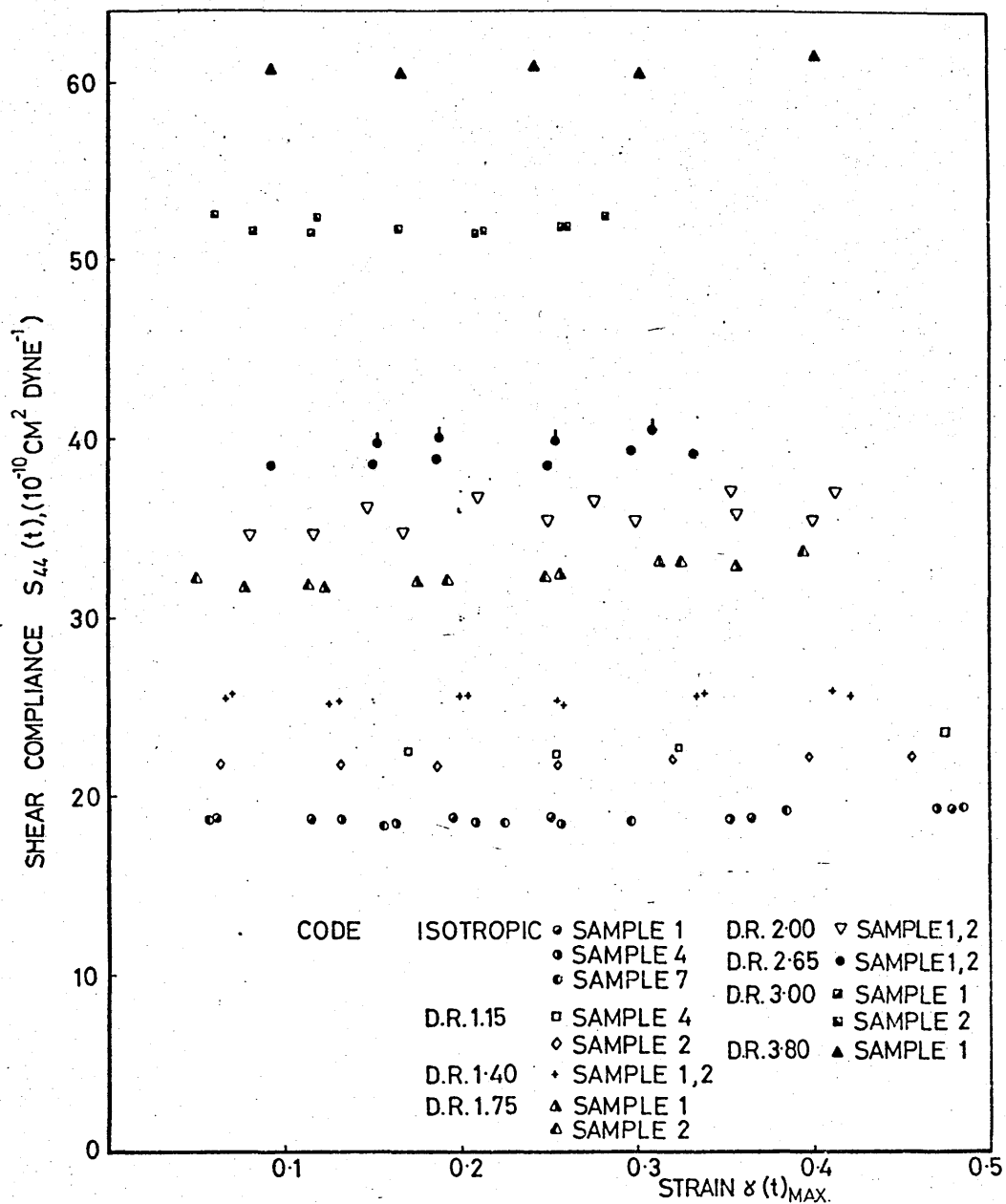


FIG733 THE VARIATION OF THE 100 SECOND SHEAR CREEP COMPLIANCE $S_{44}(t)$, WITH 100 SECOND MAXIMUM SHEAR STRAIN, ϵ_{MAX} , FOR DIFFERENT DRAW RATIOS.

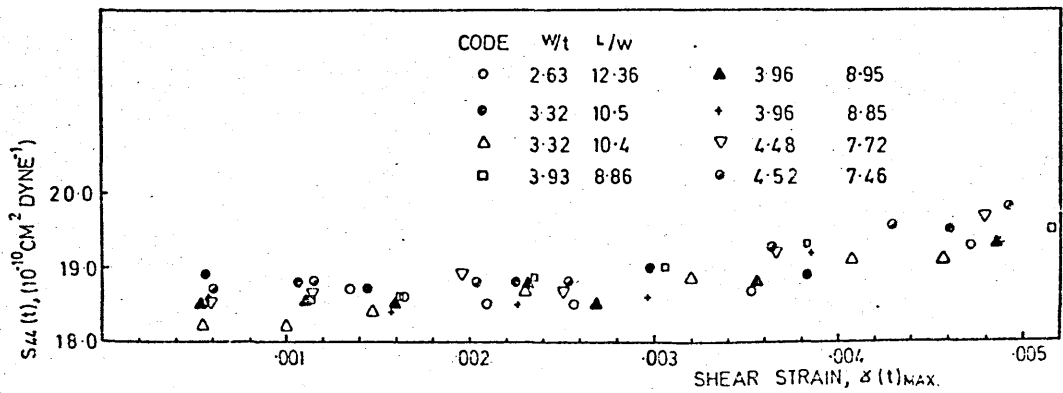


FIG734 THE VARIATION OF THE 100 SECOND SHEAR CREEP COMPLIANCE, $S_{44}(t)$, WITH 100 SECOND MAXIMUM SHEAR STRAIN, $\epsilon_{MAX}(t)$, AT DRAW RATIO 1.00 (ISOTROPIC), FOR DIFFERENT WIDTH TO THICKNESS AND LENGTH TO WIDTH RATIOS.

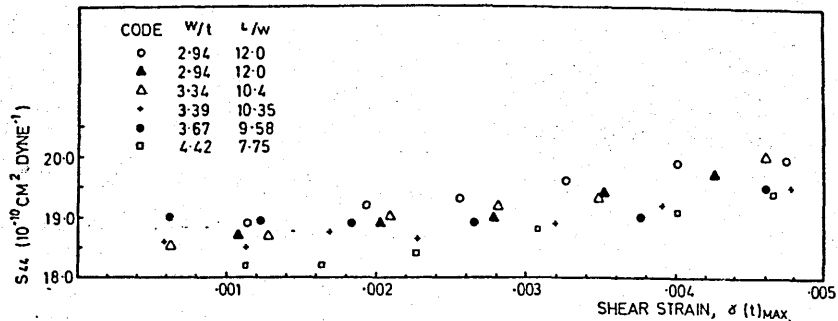


FIG735 THE VARIATION OF THE 100 SECOND SHEAR CREEP COMPLIANCE, $S_{44}(t)$, WITH 100 SECOND MAXIMUM SHEAR STRAIN, $\epsilon_{MAX}(t)$, AT DRAW RATIO 1.05, FOR DIFFERENT WIDTH TO THICKNESS AND LENGTH TO WIDTH RATIOS.

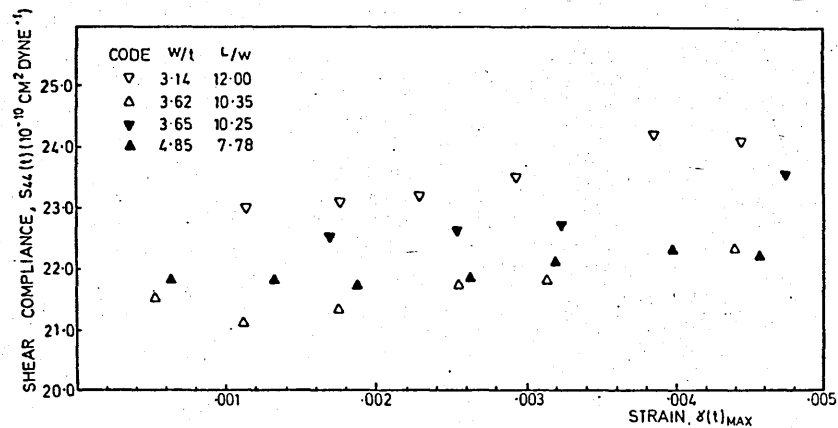


FIG736 THE VARIATION OF THE 100 SECOND CREEP SHEAR COMPLIANCE, $S_{44}(t)$, WITH 100 SEC. MAXIMUM SHEAR STRAIN, $\epsilon_{MAX}(t)$ D.R. 1.15, FOR DIFFERENT WIDTH TO THICKNESS AND LENGTH TO WIDTH RATIOS.

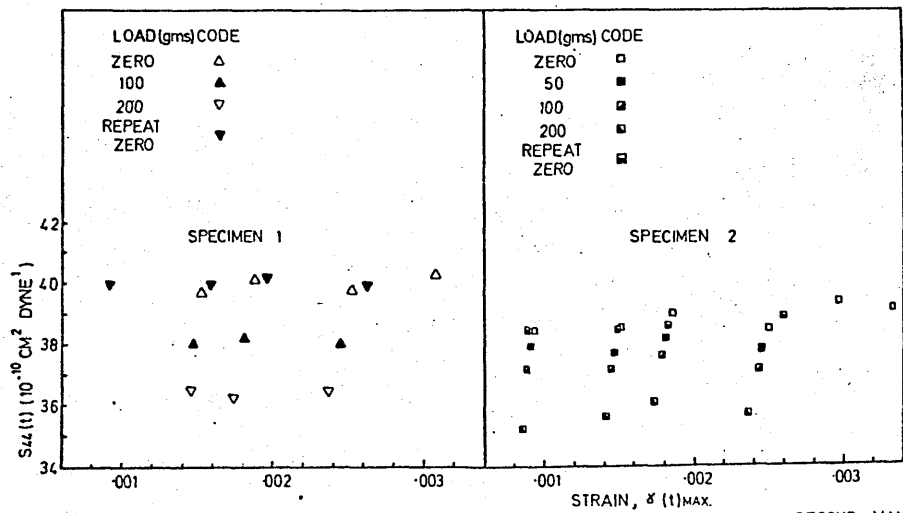


FIG737 THE VARIATION OF 100 SECOND SHEAR CREEP COMPLIANCE, $S_{44}(t)$, WITH 100 SECOND MAXIMUM SHEAR STRAIN, $\epsilon_{MAX}(t)$, AT D.R. 2.65, FOR DIFFERENT APPLIED LOADS.

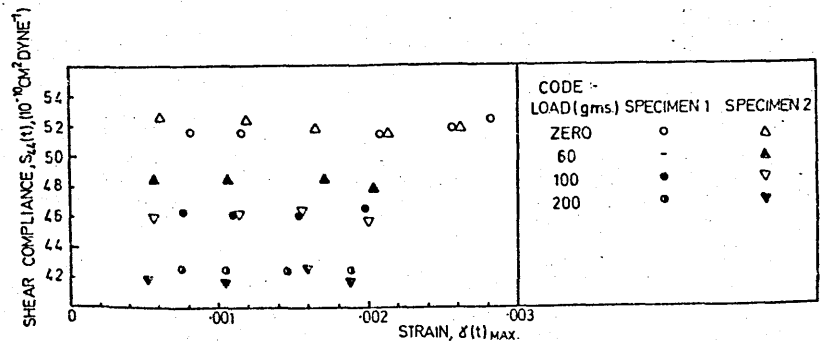


FIG738 THE VARIATION OF THE 100 SECOND SHEAR CREEP COMPLIANCE, $S_{44}(t)$, WITH 100 SECOND MAXIMUM SHEAR STRAIN, $\epsilon_{MAX}(t)$, AT D.R. 3.0, FOR DIFFERENT APPLIED LOADS

SECTION 8. ANALYSIS OF RESULTS

- 8.1 Retardation Spectra and Mechanical Energy Loss Data
- 8.2 Isochronous Data : the Dependence upon Draw Ratio
- 8.3 A Comparison of Creep and Recovery Compliance Parameters
- 8.4 Volume Compliance and Bulk Modulus
- 8.5 Calculations based upon assumptions of Linearity and Constant Volume Deformation.

In this section the experimental data has been analysed into forms which make it possible to identify the mechanisms of deformation, and the associated volume changes dominant in cold drawn L.D.P.E. Detailed interpretation of the data is left until Section 9. The data also allows an analysis based on the assumptions of linearity and constant volume deformation.

The section may be conveniently subdivided, and each subdivision may be used to demonstrate some special feature or derive a specific conclusion. Analysis of the time-dependent data demonstrates a c-axis shear process, and an anomalous relaxation mechanism in low draw ratio specimens, and is collated with the mechanical energy loss data in Section 8.1. An inter-lamellar shear mechanism is identified in Section 8.2 using the isochronous compliance data. The short-term isochronous and the time-dependent behaviour exhibit different degrees of non-linearity, and the creep and recovery data are examined in Section 8.3 and collated with the above deformation mechanisms in Section 9.15. The contraction compliance data reported in Section 7 has enabled the bulk moduli and the volume changes occurring during deformation to be calculated. This analysis is described in Section 8.4, and the structural interpretation is discussed in Section 9.16. Some simple calculations based on the assumptions of linearity and constant volume deformation are reported in Section 8.5. Each subsection is presented below and the significance of the data is discussed.

8.1 Retardation Spectra and the Mechanical energy loss data

The rate of change of compliance with log time, $\frac{dS_{ij}}{d \log t}$, is the first approximation of the retardation spectrum of a linear visco-elastic material and indicates the presence of the major transitions on the time axis at constant temperature. The major transitions are usually associated with the dominant deformation mechanisms which govern deformation behaviour. Due to the difficulties associated with creep measurements, it has been usual in the past to locate the transitions using dynamic test methods and monitor the variation of the mechanical energy loss factor, $\tan \delta$, with temperature at constant frequency. The latter approach has been used by other workers investigating highly drawn L.D.P.E. (See Section 4). In this study both approaches have been used and the results are collated in Figures 8.1 to 8.10. Both techniques have shown that the magnitudes of the transition peaks are anisotropic.

The first approximation to the retardation spectrum of samples cut at 0° , 90° , and 45° degrees to the draw direction, over a range of draw ratios are shown in Figure 8.1 to 8.3. The transition is seen to be anisotropic. The major differences are in 0° and 90°

specimens and this is shown to be due to the cone distribution of c-axes about the draw direction. As the cone develops, and the c-axes become more ordered, the peak height increases in magnitude at low draw ratios, and moves to shorter times at high draw ratios.

A similar treatment of the contraction compliances, S_{13} , S_{12} , and the shear compliances, S_{44} and S_{66} are shown in Figure 8.4 to 8.5 and Figure 8.6 to 8.7, respectively. The spectra are again anisotropic. The 90° specimens at low draw ratios exhibit an anomalous behaviour which is a result of a relaxation mechanism in these specimens. Values of $S_{66}(t)$, and hence $\frac{d S_{66}(t)}{d \log t}$, were obtained from the tensile results using the equation (2.45).

The variation of the mechanical loss factor, $\tan \delta$, with temperature, at different angles and at four draw ratios, is shown in Figure 8.8 to 8.10. The data was obtained using a commercially available Rheovibron apparatus. A sinusoidal tensile stress is applied to a specimen and the out of phase sinusoidal strain response, and the phase angle, δ , are automatically recorded. In the isotropic material two transitions are apparent (Figure 8.8), which at D.R. 1.4 are anisotropic (Figure 8.9) and tend to merge at D.R. 2.00 (Figure 8.10). At high draw ratios, D.R. 4.00, only 1 peak is apparent around 0°C . The isotropic and high draw ratio peaks have been reported previously by other workers (See Section 4); however, the intermediate draw ratio peaks appear for the first time.

Figures 8.1 to 8.10 are now presented preceded by a list of figure captions.

LIST OF FIGURES

- Figure 8.1 The variation of the rate of change of creep compliance, $\frac{d S_{33}(t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.2 The variation of the rate of change of creep compliance, $\frac{d S_{22}(t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.3 The variation of the rate of change of creep compliance, $\frac{d \frac{1}{E_{45}}(t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.4 The variation of the rate of change of creep contraction compliance, $\frac{d (S_{13} t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.5 The variation of the rate of change of the creep contraction compliance, $\frac{d (S_{12} t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.6 The variation of the rate of change of the shear creep compliance, $\frac{d S_{44}(t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.7 The variation of the rate of change of shear creep compliance, $\frac{d S_{66}(t)}{d \log t}$, with time, for different draw ratios.
- Figure 8.8 The variation of the mechanical loss factor, $\tan \delta$, with temperature at constant frequency, (3.5 c/s), for isotropic and draw ratio 4.0
- Figure 8.9 The variation of the mechanical loss factor, $\tan \delta$, with temperature at constant frequency (3.5 c/s)
- Figure 8.10 The variation of the mechanical loss factor, $\tan \delta$, with temperature, at constant frequency (3.5 c/s) for D.R. 2.0.

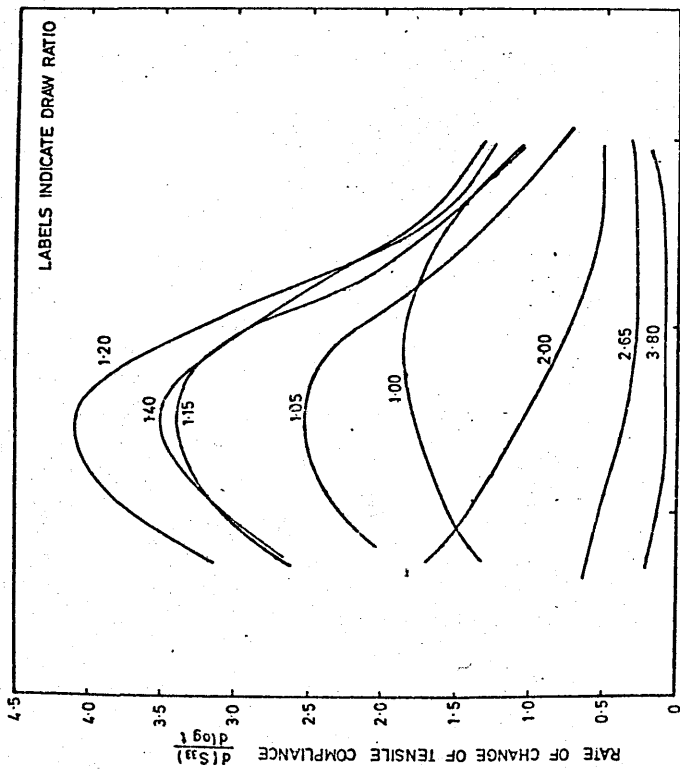


FIG.8.1 THE VARIATION OF THE RATE OF CHANGE OF TENSILE COMPLIANCE $\frac{dS_{33}(t)}{d \log t}$ WITH TIME FOR DIFFERENT DRAW RATIOS.

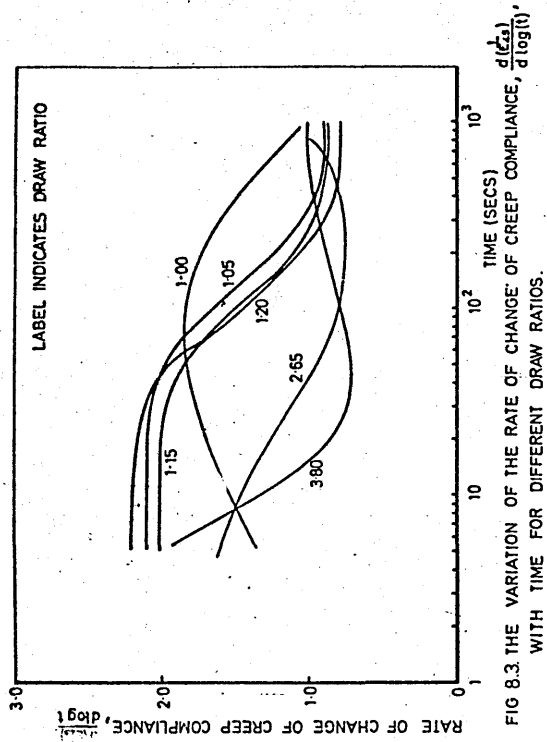


FIG 8.3 THE VARIATION OF THE RATE OF CHANGE OF CREEP COMPLIANCE, $\frac{d(\epsilon_{33})}{d \log t}$, WITH TIME FOR DIFFERENT DRAW RATIOS.

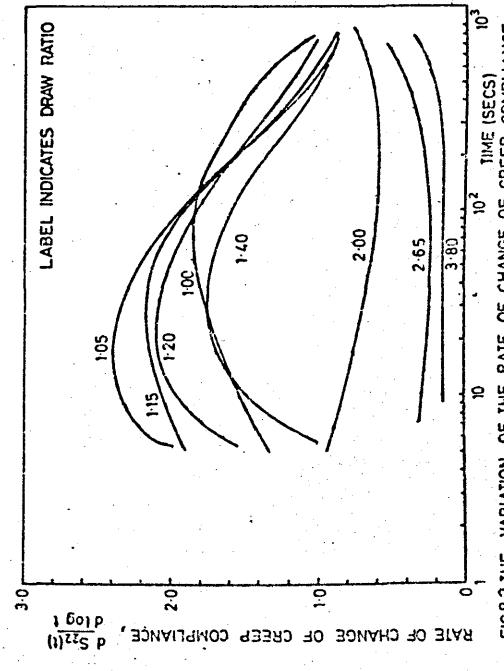


FIG.8.2 THE VARIATION OF THE RATE OF CHANGE OF CREEP COMPLIANCE, $\frac{d(S_{22}(t))}{d \log t}$, WITH TIME, FOR DIFFERENT DRAW RATIOS.

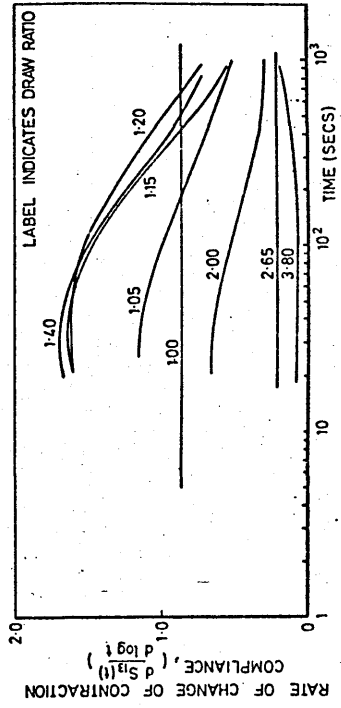


FIG 8.4 THE VARIATION OF THE RATE OF CHANGE OF THE CREEP CONTRACTION COMPLIANCE, $\frac{d(S_{11}(t))}{d \log t}$, WITH TIME, FOR DIFFERENT DRAW RATIOS

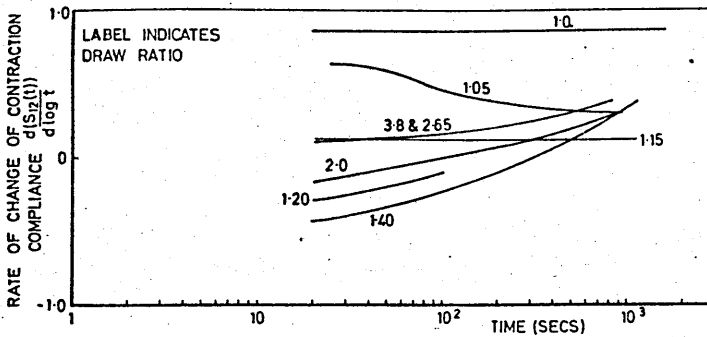


FIG 8.5 THE VARIATION OF THE RATE OF CHANGE OF THE CREEP CONTRACTION COMPLIANCE, $\frac{d[S_{12}(t)]}{d \log t}$, WITH TIME, FOR DIFFERENT DRAW RATIOS.

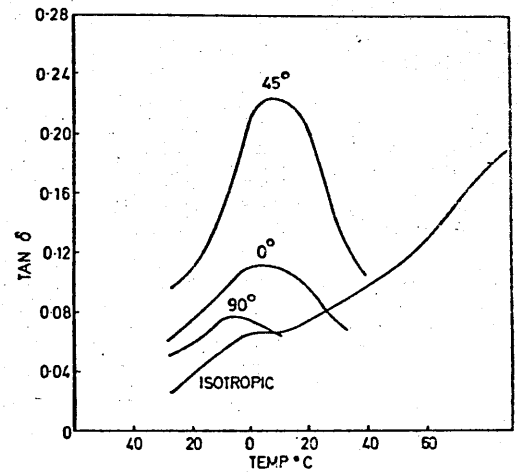


FIG 8.8 THE VARIATION OF MECH LOSS TANGENT, $\tan \delta$, WITH TEMPERATURE AT CONSTANT FREQUENCY (35 c/s) FOR DRAW RATIO 4.0 AND ISOTROPIC $\rho_{12} G_{11}$

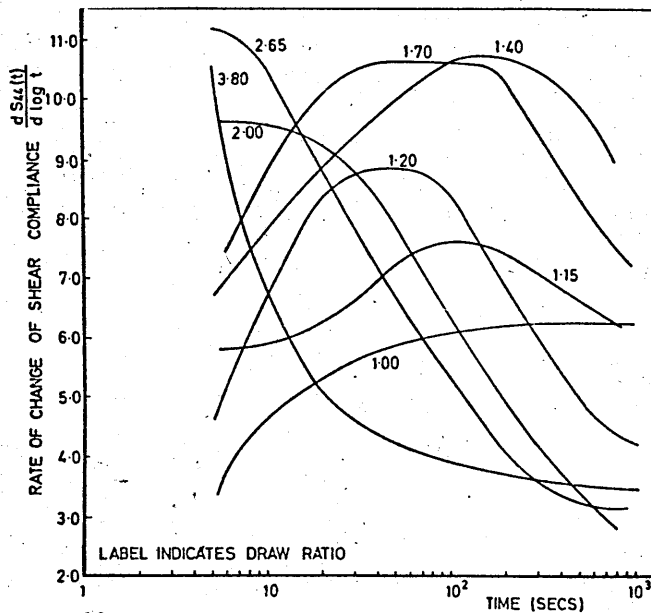


FIG 8.6 THE VARIATION OF THE RATE OF CHANGE OF SHEAR COMPLIANCE $\frac{d[S_{44}(t)]}{d \log t}$, WITH TIME FOR DIFFERENT DRAW RATIOS.

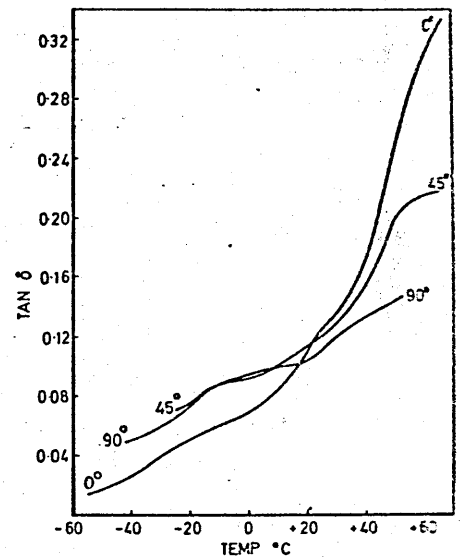


FIG 8.9 THE VARIATION OF MECH. LOSS FACTOR, $\tan \delta$, WITH TEMPERATURE AT CONSTANT FREQUENCY (35 c/s) FOR DRAW RATIO 14

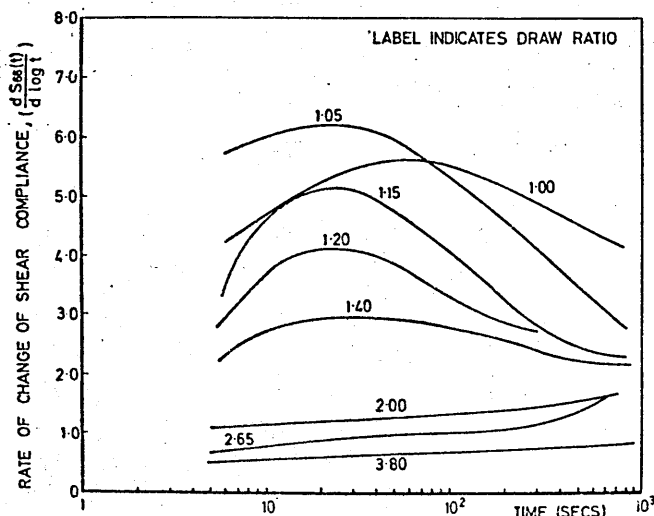


FIG 8.7 THE VARIATION OF THE RATE OF CHANGE OF SHEAR COMPLIANCE, $\left(\frac{d[S_{44}(t)]}{d \log t}\right)$ WITH TIME, FOR DIFFERENT DRAW RATIOS.

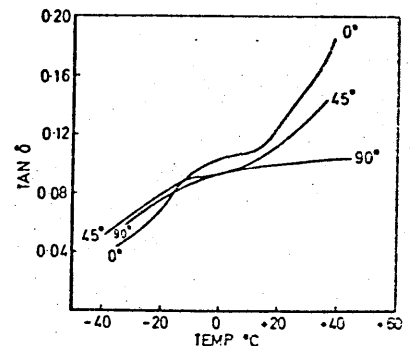


FIG 8.10 THE VARIATION OF MECH. LOSS FACTOR $\tan \delta$, WITH TEMPERATURE AT CONSTANT FREQUENCY (35 c/s) FOR DRAW RATIO 2.0.

8.2 Isochronous Data: The Dependence upon Draw Ratio

The isochronous data presented in Figure 8.11 to 8.16 is a cross-plot of the data in Section 7 which shows clearly the variation with draw ratio of the isochronous moduli and compliance parameters at a constant strain level. The 1% 100 second strain data are presented here. The data is used to identify the inter-lamellar shear mechanism at low draw ratios, and interfibrillar shear and other mechanisms at high draw ratios. A simple analysis also enables a comparison between the calculated and measured values of both the shear compliance, $S_{44}(t)$, and the creep contraction compliance, $v_{45}(t)$. The usefulness of a constant volume deformation assumption is also considered.

At low draw ratios the moduli decrease with increasing draw ratio (Figure 8.11). The behaviour is indicative of an inter-lamellar shear process, and the anisotropy is associated with the cone distribution of lamellae. At intermediate and high draw ratios the original crystalline spherulitic structure is broken down and the resultant crystalline units are aligned in fibrils parallel to the draw direction. The low value of $E_{45}(t)$ at high draw ratios is a result of inter-fibrillar shear. The anisotropy of E_0 , E_{90} , E_{45} is discussed in Section 9.2. The trend in these curves has been reported by other workers, (see for example, Raumann and Saunders, 1961), but is presented here at a well defined strain level. The cone distribution of lamellae and the inter-lamellar shear mechanism is also responsible for the anisotropy of the contraction compliances at low draw ratios (Figure 8.12). The continuous lines represent the values predicted using constant volume assumptions and are derived from equations 8.1 and 8.2 below.

$$(S_{13})_{c.v.} = \left(\frac{-S_{33}}{2} \right) \quad 8.1$$

$$(S_{12})_{c.v.} = \left(S_{11} - \frac{S_{33}}{2} \right) \quad 8.2$$

A comparison of the measured and calculated values demonstrates that the mechanism governing deformation at short times is at no stage approximated by a constant volume process. The usefulness of the constant volume assumption is discussed in Section 9.3.

The variation of the measured S_{44} with draw ratio is shown in Figure 8.13 and may be compared with the values computed from the tensile measurements using equations 8.3 and 8.4 below (Figure 8.14).

$$S_{44} = \frac{4}{E_{45}} - S_{22} - S_{33} - 2 S_{13} \quad 8.3$$

$$(S_{44})_{c.v.} = \frac{4}{E_{45}} - S_{22} \quad 8.4$$

The rapid increase of S_{44} with draw ratio is due to the inter-fibrillar shear mechanism. The variation with draw ratio compares favourably with that obtained by Raumann and Saunders (1961). Due to the difficulties involved in measuring S_{66} directly, the computed values only are shown in Figure 8.15 and are compared with the values calculated using constant volume assumptions.

$$S_{66} = 2 (S_{22} - S_{12}) \quad 8.5$$

$$(S_{66})_{c.v.} = 2 (S_{22} - S_{12} \text{ c.v.}) \quad 8.6$$

The creep contraction ratios v_0, v_{90}, v_{45} , are given by equations 8.7 to 8.9 below.

$$v_0 = S_{13}/S_{33} \quad 8.7$$

$$v_{90} = S_{12}/S_{22} \quad 8.8$$

$$v_{45} = -\frac{1}{2} E_{45} [S_{13} + S_{12}] \quad 8.9$$

The results of these computations at different draw ratios and the corresponding values calculated using constant volume assumptions are shown in Figure 8.16 and Table 8.1. This analysis is discussed in Section 9.3.

The variation of the isochronous data with DR is now presented preceded by a list of figure captions.

- Figure 8.11 The variation of the creep moduli, E_0 , E_{90} , and E_{45} with draw ratio at 1% 100 second strain.
- Figure 8.12 The variation of the 100 second creep contraction compliance, $S_{13}(t)$, and $S_{12}(t)$, with draw ratio, at 1% 100 second strain.
- Figure 8.13 The variation of the 100 second shear creep compliance, S_{44} with draw ratio at 0.3% 100 second shear strain.
- Figure 8.14 The variation of the calculated 100 second shear compliance, S_{44} , with draw ratio, at 1% 100 second strain.
- Figure 8.15 The variation of the calculated 100 second shear compliance, S_{66} , with draw ratio at 1% 100 second strain.
- Figure 8.16 The variation of the 100 second creep contraction ratios $\nu_0(t)$ and $\nu_{90}(t)$, with draw ratio at 1% 100 second strain.
- Table 8.1 A comparison of the measured and calculated creep contraction ratio, $\nu_{45}(t)$ with strain, at different draw ratios.

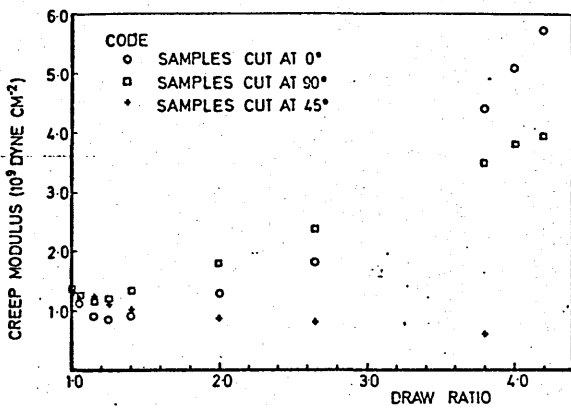


FIG 8.11. THE VARIATION OF THE CREEP MODULI, $E_0(t)$, $E_{90}(t)$, & $E_{45}(t)$, WITH DRAW RATIO, AT 1% 100 SECOND STRAIN.

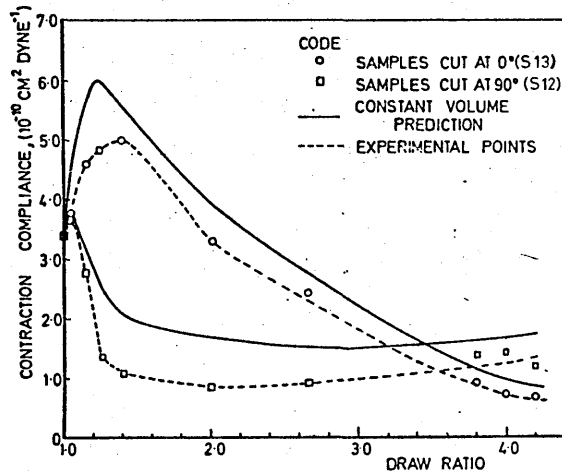


FIG 8.12. THE VARIATION OF THE 100 SECOND CREEP CONTRACTION COMPLIANCE, $S_{13}(t)$, AND $S_{12}(t)$, WITH DRAW RATIO, AT 1% 100 SEC. STRAIN.

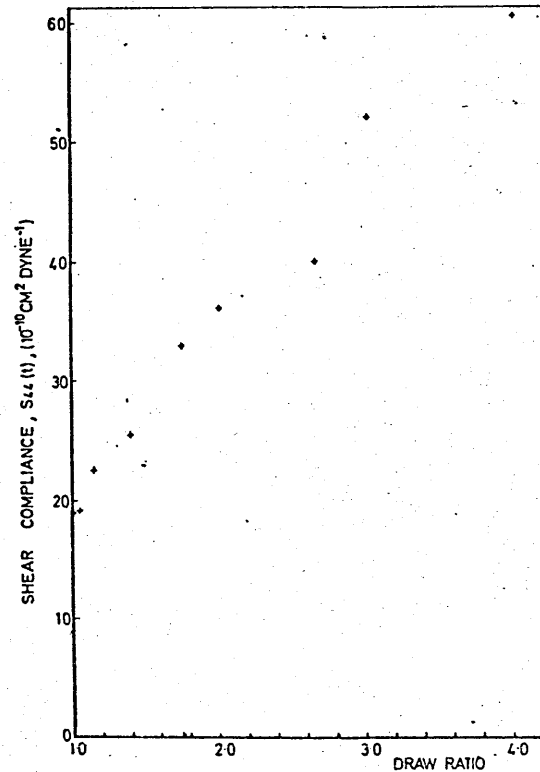


FIG 8.13. THE VARIATION OF THE 100 SECOND SHEAR CREEP COMPLIANCE, $S_{44}(t)$, WITH DRAW RATIO, AT 0.3% MAXIMUM 100 SEC. SHEAR STRAIN.

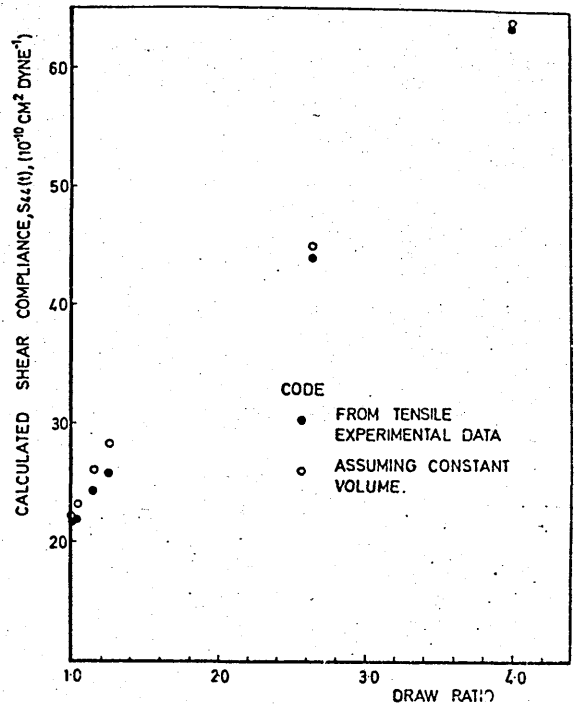


FIG 8.14. THE VARIATION OF THE CALCULATED SHEAR COMPLIANCE, $S_{44}(t)$, WITH DRAW RATIO, AT 1% 100 SECOND STRAIN.

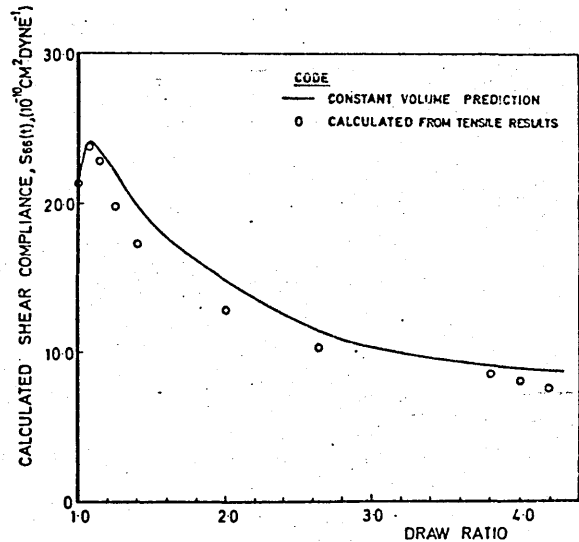


FIG 8.15. THE VARIATION OF THE CALCULATED 100 SECOND SHEAR COMPLIANCE, $S_{66}(t)$, WITH DRAW RATIO AT 1% 100 SECOND STRAIN.

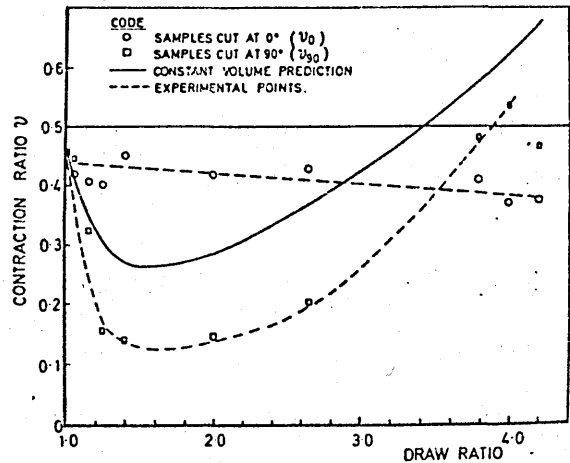


FIG 8.16. THE VARIATION OF THE 100 SECOND CREEP CONTRACTION RATIOS $v_0(t)$ & $v_{90}(t)$, WITH DRAW RATIO, AT 1% 100 SECOND STRAIN.

	ISOTROPIC						D.R. = 1.15						D.R. = 2.65						D.R. = 3.80					
	% STRAIN						% STRAIN						% STRAIN						% STRAIN					
	0.3	0.5	1.0	2.0	5.0	0.3	0.5	1.0	2.0	5.0	0.3	0.5	1.0	2.0	5.0	0.3	0.5	1.0	2.0	5.0	0.3	0.5	1.0	2.0
CALCULATED $v_{45}(t)$	-	-	-	-	-	.376	.388	.420	.428	.432	.122	.124	.133	.137	.165	.058	.062	.070	.080					
CONSTANT VOLUME $v_{45}(t)$	0.5	0.5	0.5	0.5	0.5	.464	.480	.496	.508	.560	.170	.170	.174	.192	.252	.080	.0819	.086	.103					
MEASURED $v_{45}(t)$	.448	.448	.454	.470	.480	-	-	.430	.430	.430	.084	.100	.123	.145	.175	.00	.00	.022	.045					

TABLE 6.1 A COMPARISON OF THE MEASURED & CALCULATED CREEP CONTRACTION RATIO, $v_{45}(t)$, WITH STRAIN, AT DIFFERENT DRAW RATIOS.

8.3 A Comparison of Creep and Recovery Compliance Parameters

The recovery compliance data has been calculated assuming the material deforms in a linear visco-elastic manner, and that the Boltzmann superposition principle may be invoked. This assumes that the strain varies linearly with applied stress and that the time dependence may be described by a function of time alone. Thus for a linear visco-elastic material the time dependence of the compliance at the 0.5% 100 second strain level will be identical to that at the 1% 100 second strain level. Also the creep and recovery compliances will superpose. However, none of the materials tested here were truly linear and several forms and degrees of non-linearity were observed and are discussed in Section 9.1.5. The non-linearity of the isochronous data is presented in Section 7, and in this section the time-dependent data is compared. The linearity or non-linearity of the deformation mechanisms are deduced from these comparisons (Section 9.1.5), and the usefulness of the linearity assumptions for engineering purposes are discussed in Section 9.2.

In the following figures the longitudinal and contraction creep and recovery compliances are compared for specimens cut at 0° , 90° and 45° to the draw direction, at selected draw ratios. A comparison of the creep and recovery compliances and also the creep compliances at two strain levels has been made and is summarized in Table 9.2 and discussed in Section 9.1.5. The following comparisons of the longitudinal creep and recovery compliances have been made:-

1. Isotropic material (Figure 8.17)
2. 0° , 90° and 45° samples at DR=1.15 (Figure 8.18 and 8.19)
3. 0° , 90° and 45° samples at DR = 1.25 (Figure 8.20 to 8.22)
4. 0° and 90° samples at DR = 1.40 (Figure 8.23)
5. 0° and 90° samples at DR = 2.00 (Figure 8.24)
6. 0° , 90° and 45° samples at DR = 2.65 (Figure 8.25)
7. 0° , 90° and 45° samples at DR = 3.80 (Figure 8.26 and 8.27)

Also comparisons of the creep and recovery contraction compliances have been made as follows:-

1. 0° specimens at DR = 1.25 (Figure 8.28)
2. 0° and 90° specimens at DR = 1.40 (Figure 8.29)
3. 0° and 90° specimens at DR = 2.00 (Figure 8.30)
4. 0° , 90° and 45° specimens at DR = 2.65 (Figure 8.31)
5. 0° , 90° and 45° specimens at DR = 3.80 (Figure 8.32)

The detailed comparisons are shown in the subsequent figures preceded by a list of figure captions.

- Figure 8.17 The variation of the creep and recovery compliance, $S_{11}(t)$, with time, at 0.5% and 1.0% 100 second strain for Isotropic (DR = 1.00) material.
- Figure 8.18 The variation of the creep and recovery compliance $S_{33}(t)$ and $S_{22}(t)$, with time, at 0.5% and 1.0% 100 second strain for DR 1.15.
- Figure 8.19 The variation of the creep and recovery compliance $\frac{1}{E_{45}}(t)$, with time, at 0.5% and 1.0% 100 second strain levels, for draw ratio 1.15.
- Figure 8.20 The variation of the creep and recovery compliance, $S_{33}(t)$, with time, at 0.5% and 1.0% 100 second strain, for DR 1.25.
- Figure 8.21 The variation of the creep and recovery compliance $S_{22}(t)$, with time, at 0.5% and 1.0% 100 second strain for draw ratio 1.25.
- Figure 8.22 The variation of the creep and recovery compliance $\frac{1}{E_{45}}(t)$, with time, at 0.5% and 1.0% 100 second strain levels, for DR 1.25.
- Figure 8.23 The variation of the creep and recovery compliance $S_{33}(t)$, and $S_{22}(t)$, with time, at 0.5% and 1.0% 100 second strain for DR 1.4.
- Figure 8.24 The variation of the creep and recovery compliance, $S_{33}(t)$, and $S_{22}(t)$, with time, at 0.5% and 1.0% 100 second strain for DR 2.00.
- Figure 8.25 The variation of the creep and recovery compliance, with time at 0.5% and 1.0% 100 second strain levels, for 0°, 90° and 45° specimens at DR 2.65.
- Figure 8.26 The variation of the creep and recovery compliance, $S_{33}(t)$ and $S_{22}(t)$, with time, at 0.5% and 1.0% 100 second strain, for DR 3.8.
- Figure 8.27 The variation of the creep and recovery compliance $\frac{1}{E_{45}}(t)$, with time, at 0.5% and 1.0% 100 second strain, for draw ratio 3.8.

- Figure 8.23 The variation of the creep and recovery contraction compliance, $S_{13}(t)$, with time, at 0.5% and 1.0% 100 second strain, for D.R. 1.25.
- Figure 8.29 The variation of the creep and recovery contraction compliances, $S_{13}(t)$ and $S_{12}(t)$, with time, at 0.5% and 1.0% 100 second strain, for draw ratio 1.4.
- Figure 8.30 The variation of the creep and recovery contraction compliances, $S_{13}(t)$ and $S_{12}(t)$, with time, at 0.5% and 1.0% 100 second strain, for D.R. 2.00.
- Figure 8.31 The variation of the creep and recovery contraction compliances, with time, at 0.5% and 1.0% 100 second strain, for 0° , 90° and 45° specimens, at D.R. 2.65.
- Figure 8.32 The variation of the creep and recovery contraction compliance, with time, at 0.5% and 1.0% 100 second strain, for 0° , 90° and 45° specimens, at D.R. 3.8.

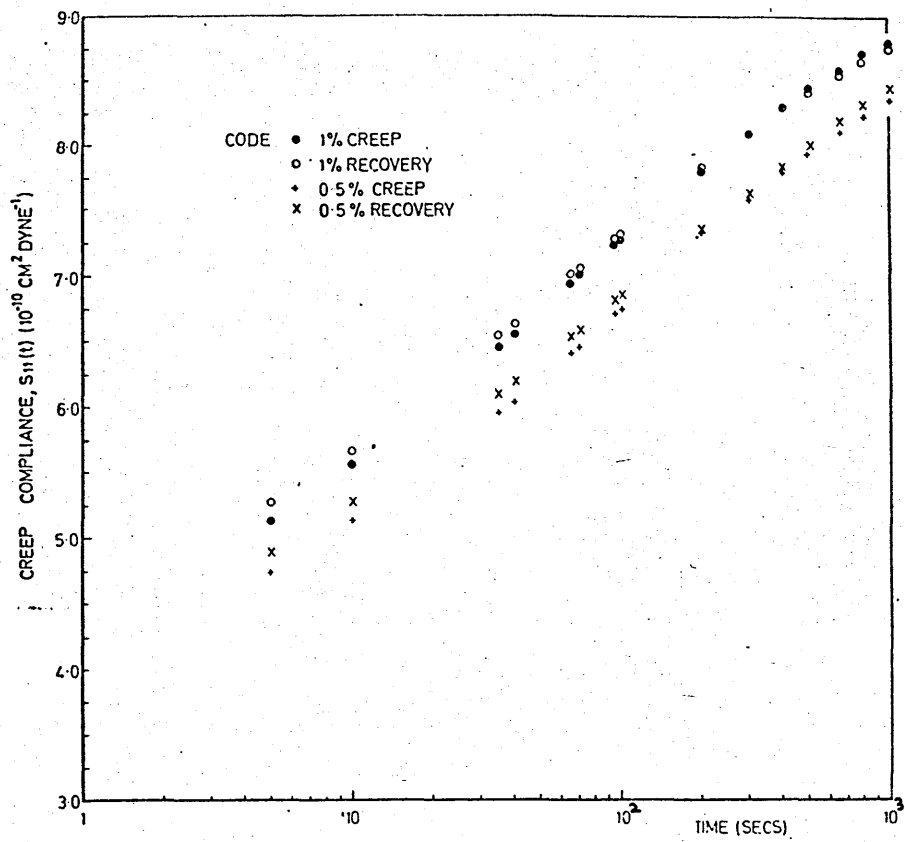


FIG.8.17 THE VARIATION OF THE CREEP & RECOVERY COMPLIANCE, $S_{11}(t)$ WITH TIME AT 0.5% & 1.0% 100 SECOND STRAIN FOR ISOTROPIC D.R. 1.00

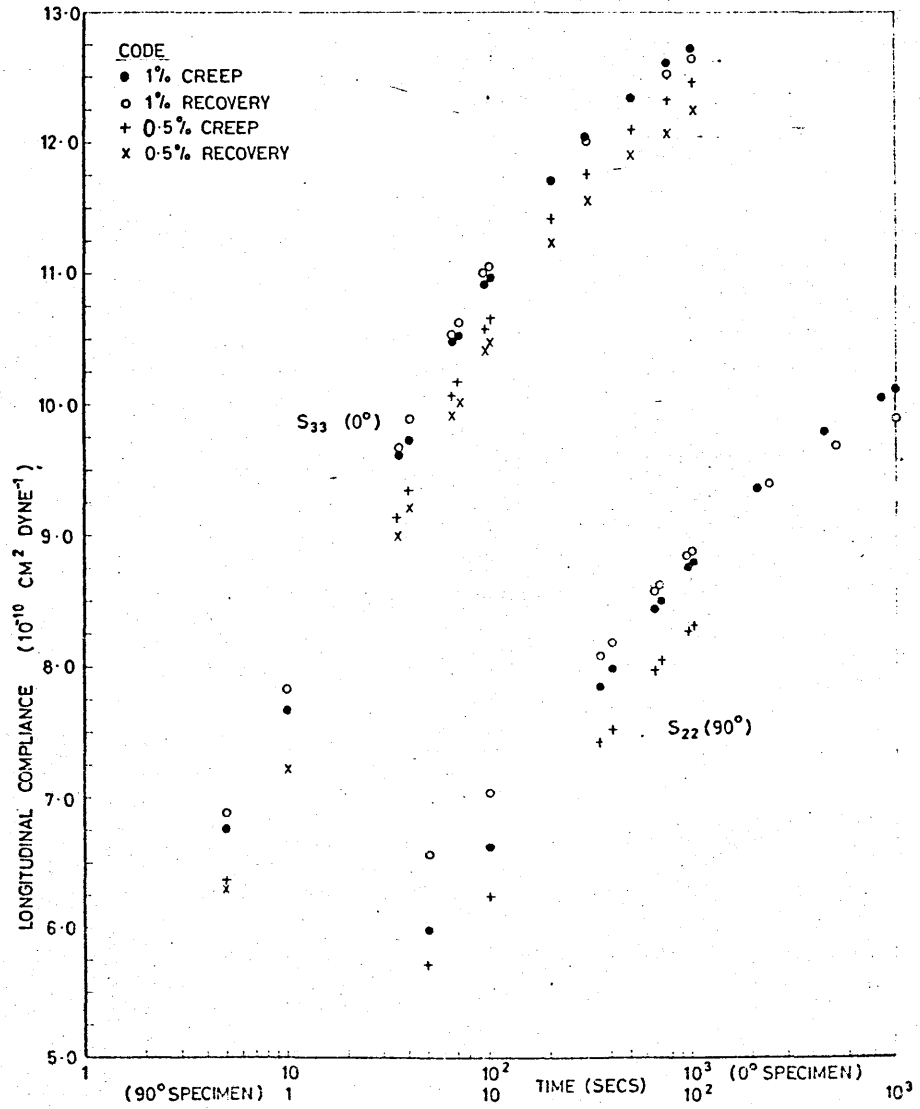


FIG.8.18 THE VARIATION OF THE CREEP AND RECOVERY COMPLIANCE $S_{33}(t)$ AND $S_{22}(t)$ WITH TIME AT 0.5% AND 1% 100 SECOND STRAIN FOR D.R. (1.15)

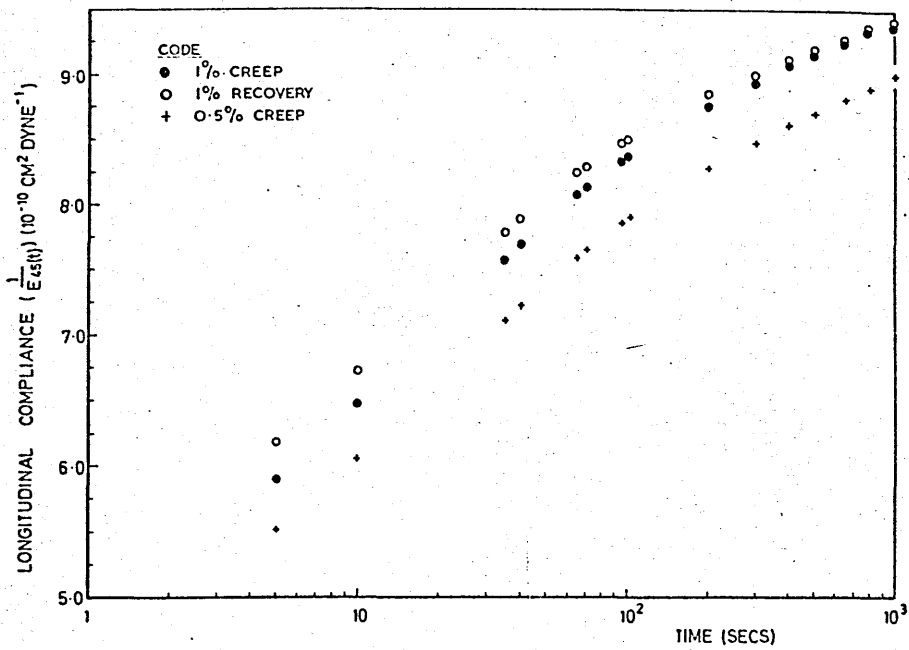


FIG.8.19 THE VARIATION AT THE CREEP AND RECOVERY COMPLIANCE, $(\frac{1}{E_{45}(t)})$, WITH TIME, AT 0.5% AND 1% 100 SECOND STRAIN LEVELS, FOR DRAW RATIO 1.15

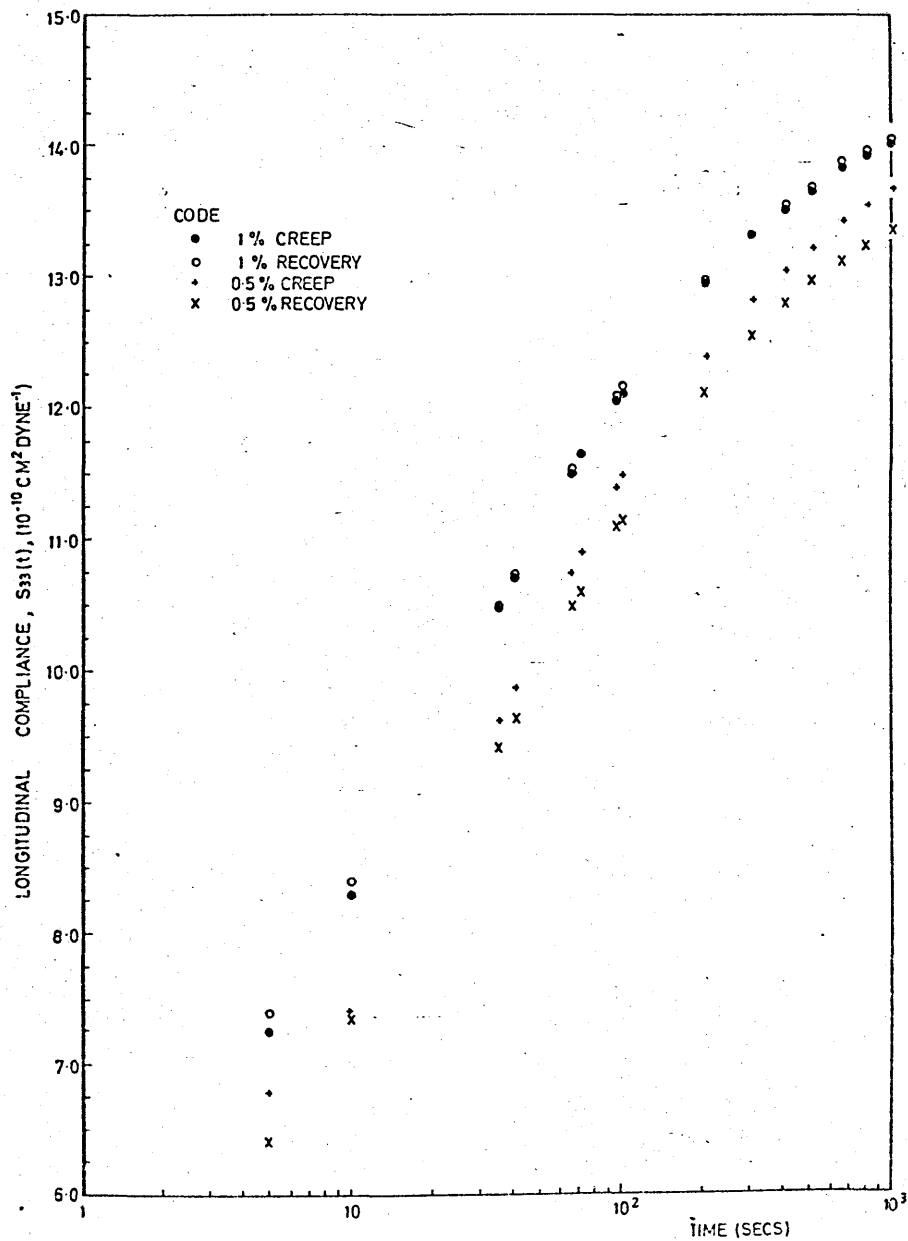


FIG.8.20 THE VARIATION OF THE CREEP & RECOVERY COMPLIANCE, $S_{33}(t)$, WITH TIME AT 0.5% & 1% 100 SECOND STRAINS, FOR D.R. 1.25

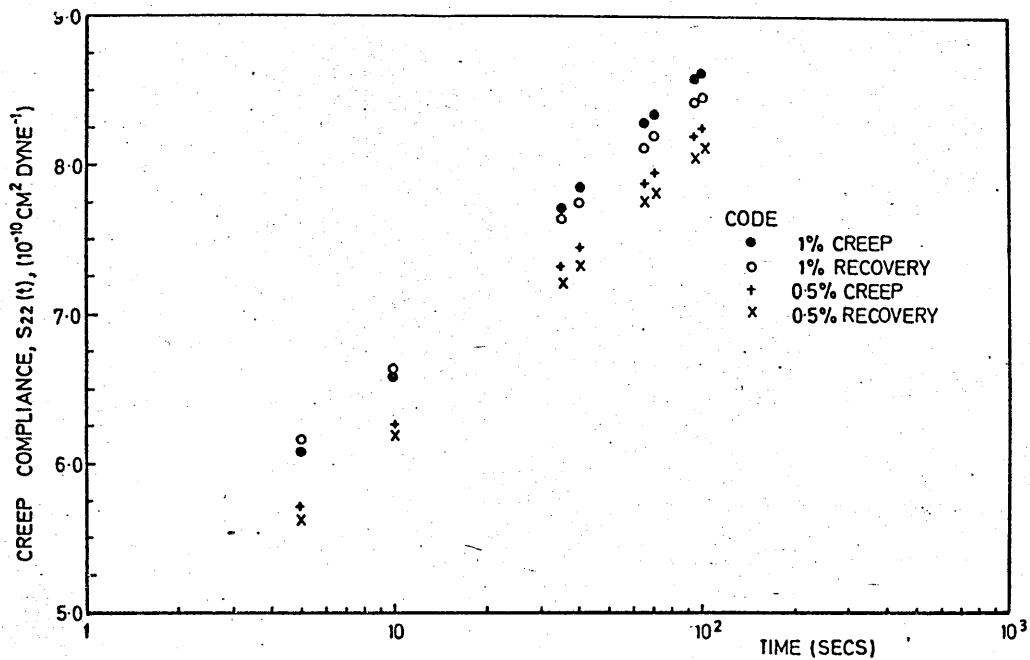


FIG.8.21. THE VARIATION OF THE CREEP AND RECOVERY COMPLIANCE, $S_{22}(t)$, WITH TIME AT 0.5% & 1.0% 100 SECOND STRAIN FOR DRAW RATIO, DR.1.25

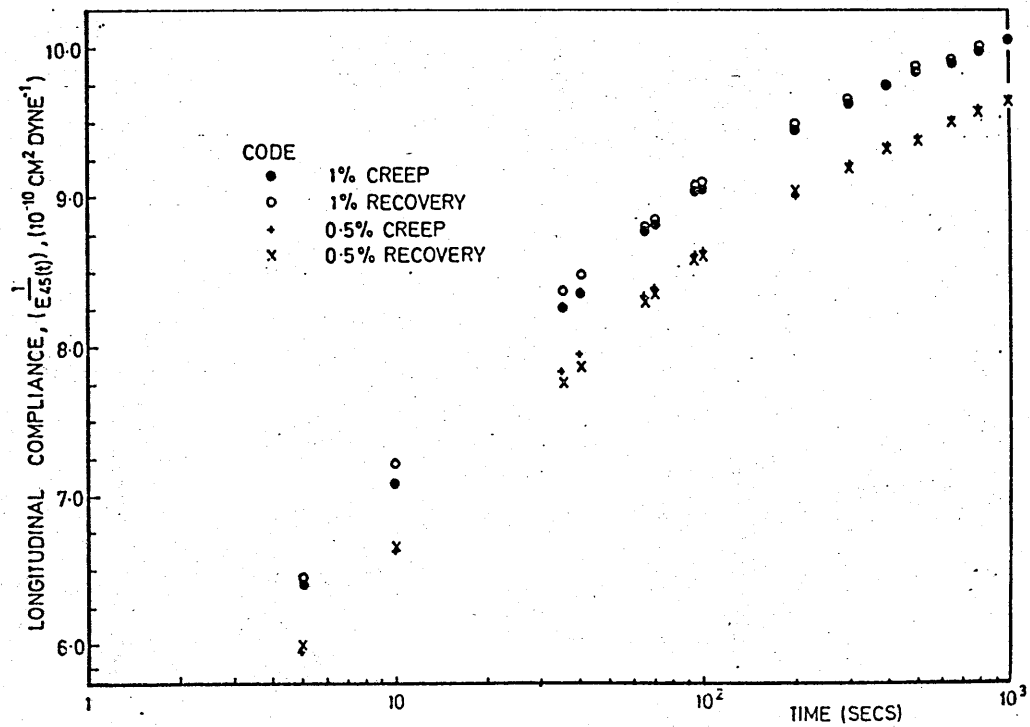


FIG.8.22 THE VARIATION OF THE CREEP AND RECOVERY COMPLIANCE, $(\frac{1}{E_{45}t})$ WITH TIME, AT 0.5% AND 1.0% 100 SECOND STRAIN LEVELS, FOR DRAW RATIO 1.25

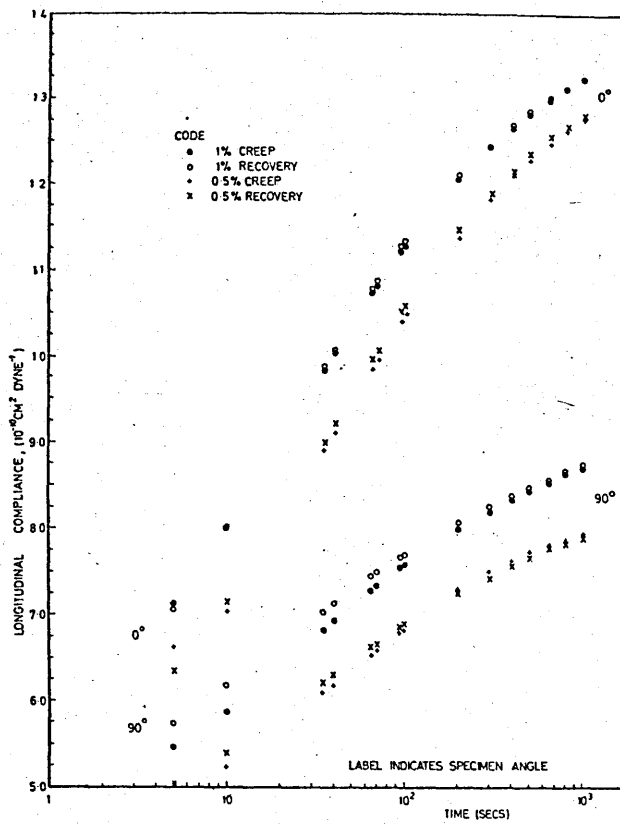


FIG.8.23 THE VARIATION OF THE CREEP & RECOVERY COMPLIANCE, $S_{33}(t)$ & $S_{22}(t)$, WITH TIME, AT 0.5% & 1.0% 100 SECOND STRAIN FOR D.R.1.4

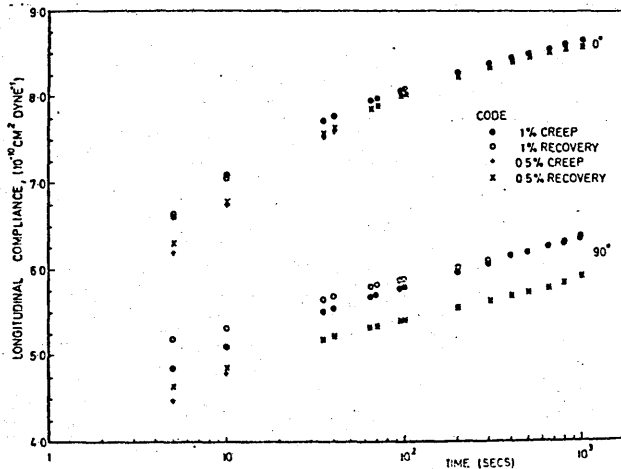


FIG.8.24 THE VARIATION OF THE CREEP & RECOVERY COMPLIANCE $S_{33}(t)$ & $S_{22}(t)$, WITH TIME, AT 0.5% & 1.0% 100 SECOND STRAIN, FOR DRAW RATIO 2.00

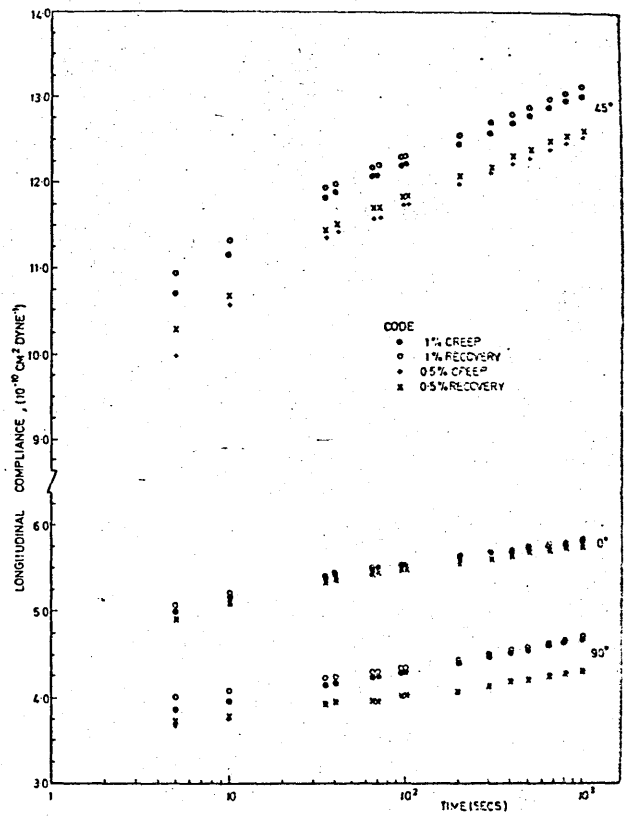


FIG.8.25 THE VARIATION OF THE CREEP AND RECOVERY COMPLIANCE WITH TIME AT 0.5% AND 1% 100 SECOND STRAIN LEVELS, FOR D.R.2-65 0°, 90° AND 45° SPECIMENS.

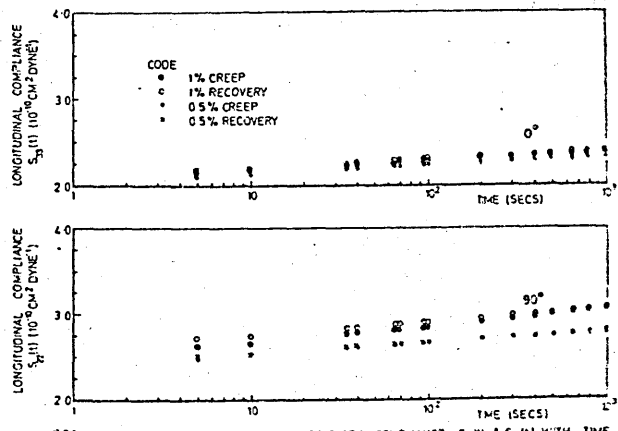


FIG.8.26 THE VARIATION OF THE CREEP AND RECOVERY COMPLIANCE, $S_{33}(t)$ & $S_{22}(t)$ WITH TIME AT 0.5% & 1% 100 SECOND STRAIN, FOR D.R.3.8

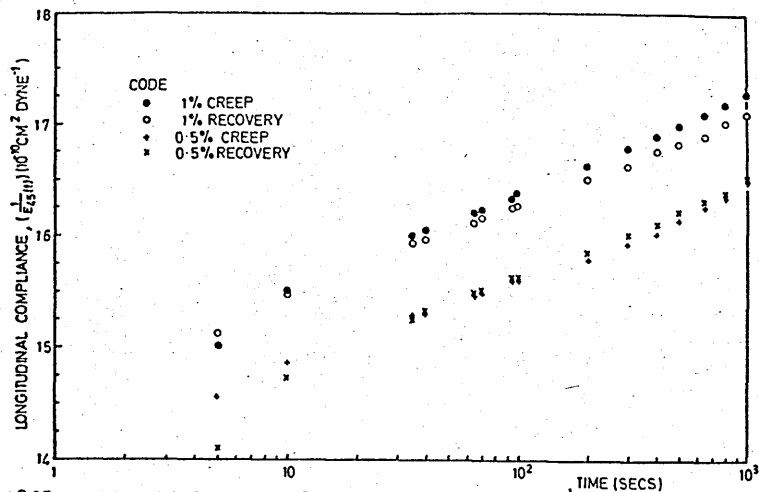


FIG.8.27 THE VARIATION OF THE CREEP & RECOVERY COMPLIANCE, $(\epsilon_{45}^L(t))$, WITH TIME AT 0.5% AND 1% 100 SECOND STRAIN, FOR DRAW RATIO 3.8

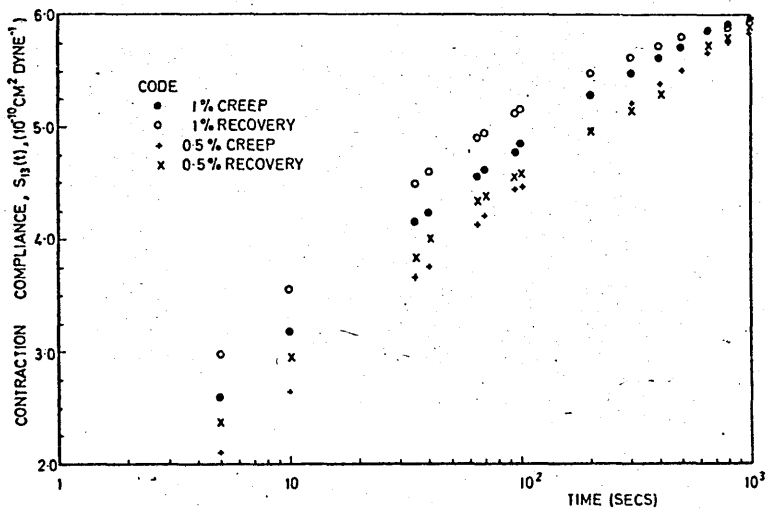


FIG.8.28 THE VARIATION OF THE CREEP & RECOVERY CONTRACTION COMPLIANCE, $S_{13}(t)$, WITH TIME, A 0.5% & 1.0% 100 SECOND STRAIN, FOR DRAW RATIO 1.25.

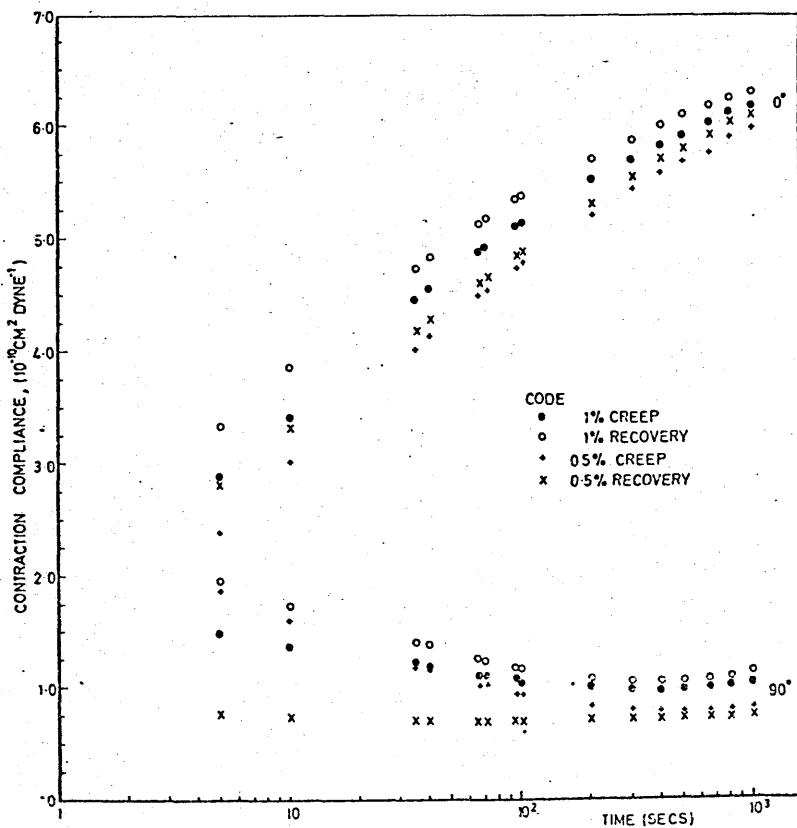


FIG.8.29 THE VARIATION OF THE CREEP AND RECOVERY CONTRACTION COMPLIANCE, $S_{13}(t)$, AND $S_{12}(t)$, WITH TIME, AT 0.5% & 1.0% 100 SECOND STRAIN, FOR DRAW RATIO, D.R. 1.4

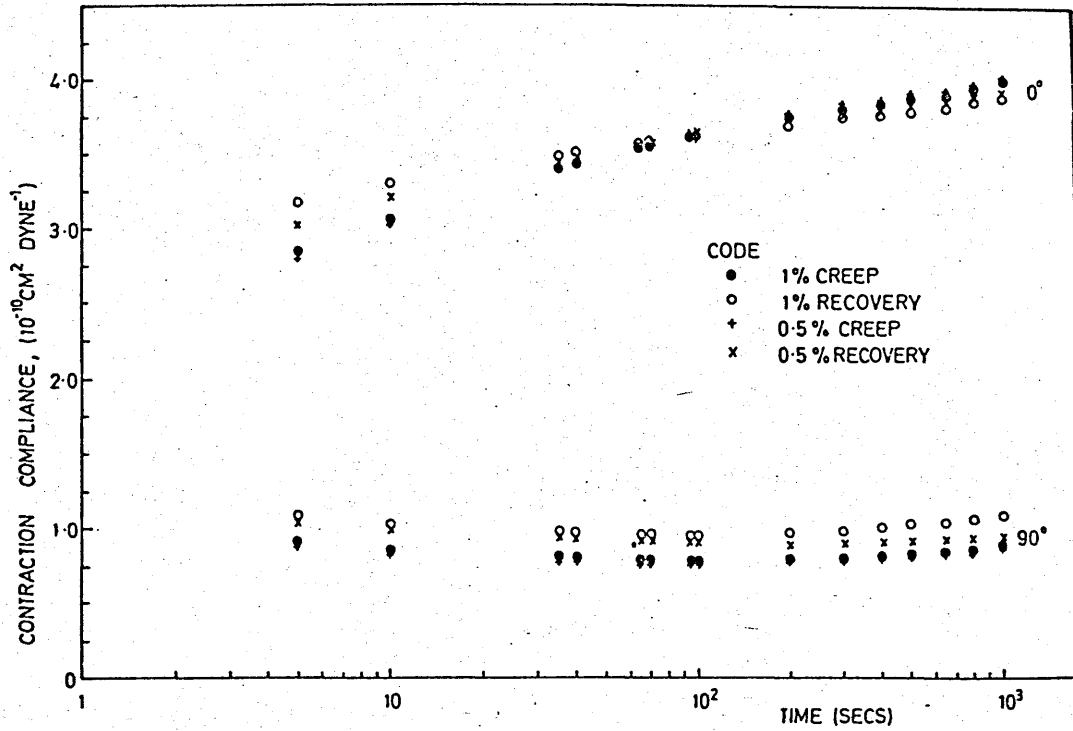


FIG.8.30 THE VARIATION OF THE CREEP AND RECOVERY CONTRACTION COMPLIANCE, $S_{13}(t)$, AND $S_{12}(t)$, WITH TIME, AT 0.5% AND 1.0% 100 SECOND STRAIN, FOR D.R. 2.0

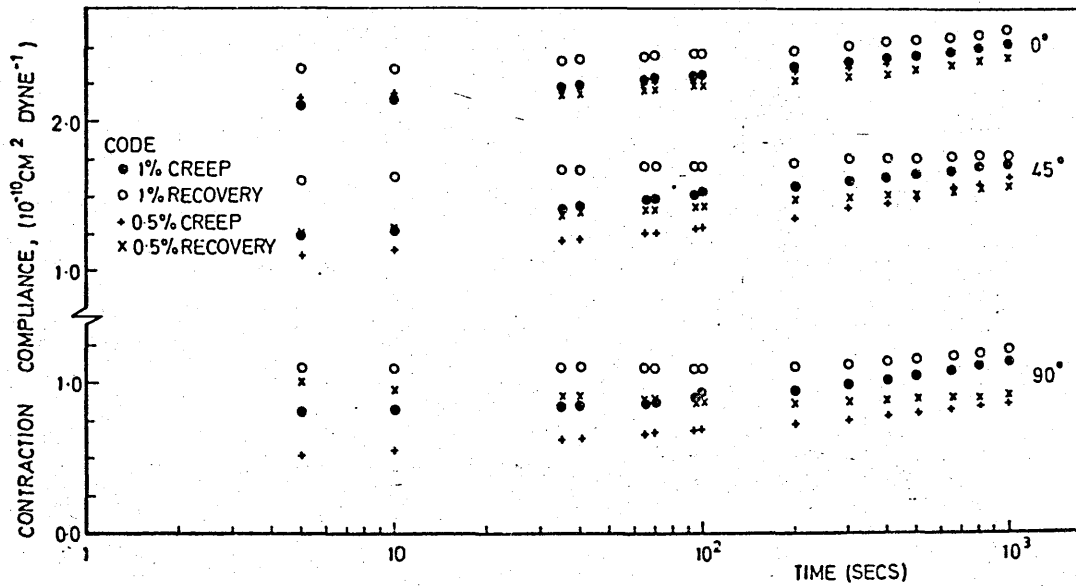


FIG.8.31. THE VARIATION OF THE CREEP & RECOVERY CONTRACTION COMPLIANCE $S_{13}(t)$, $(\frac{\Delta l}{l})_{45^\circ}$, $S_{12}(t)$, WITH TIME, AT 0.5% & 1.0% 100 SECOND STRAIN FOR D.R. 2.65

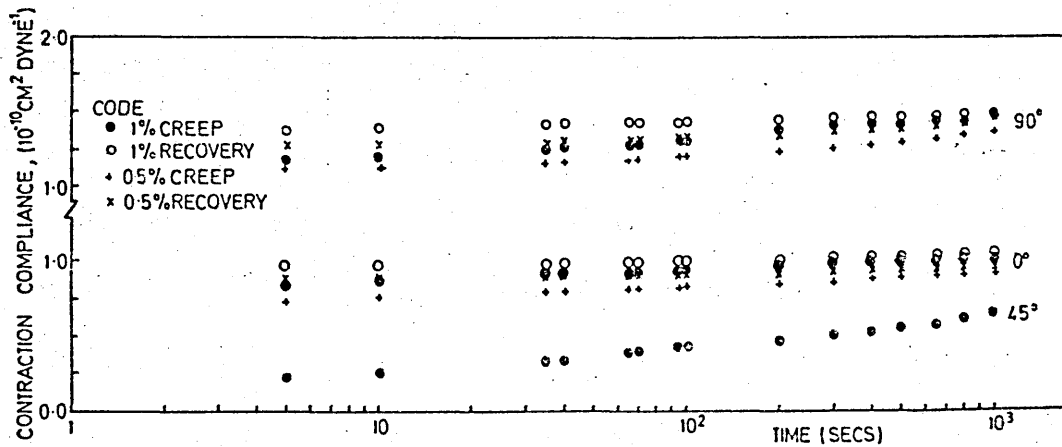


FIG.8.32 THE VARIATION OF THE CREEP AND RECOVERY CONTRACTION COMPLIANCE, WITH TIME, AT 0.5% AND 1.0% 100 SECOND STRAIN, FOR D.R. 3.8, AND SPECIMENS CUT AT 0°, 45°, AND 90° TO THE DRAW DIRECTION

8.4 Volume Compliance and Bulk Modulus

The simultaneous measurement of the longitudinal and contraction strains has enabled the determination of the volume strain changes during uniaxial creep deformation. The data is conveniently presented in terms of the volume compliances $V_0(t)$ and $V_{90}(t)$ for 0° and 90° specimens respectively, and the bulk modulus, $K(t)$. The parameters are computed as follows. (See Section 2):-

$$V_0(t) = S_{33}(t) + 2 S_{13}(t) \quad 8.10$$

$$V_{90}(t) = S_{11}(t) + S_{12}(t) + S_{13}(t) \quad 8.11$$

$$\text{and bulk modulus } K(t) = \left[S_{33}(t) + 2S_{11}(t) + 4 S_{13}(t) + 2 S_{12}(t) \right]^{-1} \quad 8.12$$

$$= \left[V_0(t) + 2V_{90}(t) \right]^{-1} \quad 8.13$$

Consistent with previous analysis both isochronous and time-dependent data are presented.

The isochronous data has been computed using the mean isochronous values of the longitudinal and contraction compliances over a range of 100 second strain levels. The accuracy of the individual compliance parameters varies with draw ratio and strain level, (See Section 5) but, in general, is $\pm 5\%$ for the contraction compliance and $\pm 3\%$ for the longitudinal compliance at 1% 100 second strain. The accuracy decreases at lower strain levels and increases at higher strain levels. Table 8.2 shows the values of the compliance parameters at the 0.5% and 1.0% 100 second strain levels. The computed volume compliances $V_0(t)$ and $V_{90}(t)$ are also shown with their respective error bands. The error limits have been determined using the following simple error analysis:-

$$\frac{d V_0(t)}{V_0(t)} = \frac{d S_{33}(t)}{V_0(t)} + 2 \frac{d S_{13}(t)}{V_0(t)} \quad 8.14$$

$$\frac{d V_{90}(t)}{V_{90}(t)} = \frac{d S_{11}(t)}{V_{90}(t)} + \frac{d S_{12}(t)}{V_{90}(t)} + \frac{d S_{13}(t)}{V_{90}(t)} \quad 8.15$$

It has been assumed that the longitudinal compliances have errors of 4% at 0.5% 100 second strain and 3% at 1% 100 second strain, and that the contraction compliance has an error of 7% at 0.5% 100 second strain and 5% at the 1% 100 second strain level.

The error limits calculated in this way indicate the maximum possible errors that could be obtained from arbitrary tests. However, the compliance values used in computation are average values of the experimental data and should not have large errors and thus the accuracies of the volume compliances are better than those quoted in Table 8.2. The trends with strain and draw ratio shown in the following figures are therefore significant.

The variation of the isochronous volume compliances V_0 , V_{90} with draw ratio, are shown in Figure 8.33. The peak in the volume compliance at D.R. 1.25 is shown to be due to the large volume changes associated with an interlamellar shear process. Up to D.R. 1.25 the volume change in 0° specimens is greater than that for 90° specimens. At draw ratios up to D.R. 2.65 V_{90} is greater than V_0 , and at higher draw ratios the two values are similar. These results are discussed in Section 9.1.6. The corollary to this behaviour is that the isochronous bulk modulus $K(t)$, shows a minimum value around D.R. = 2.00. The variation of $K(t)$, with draw ratio is shown in Figure 8.34.

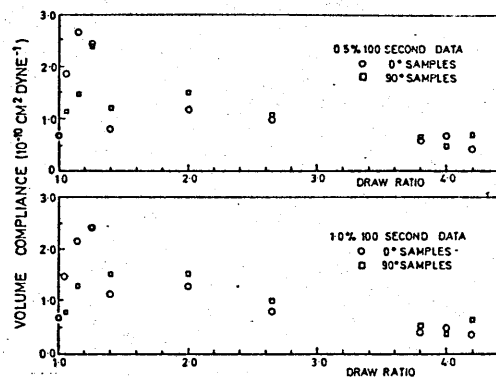
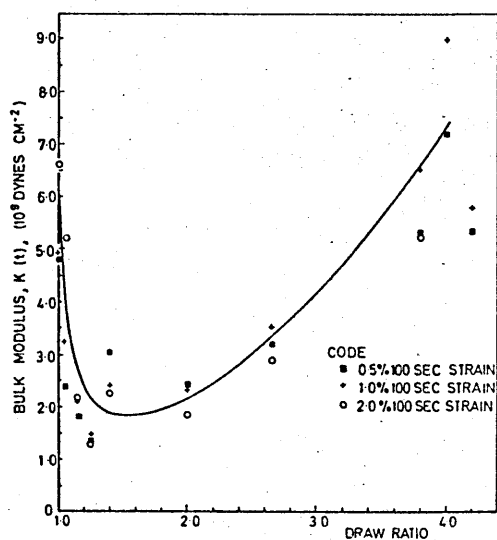
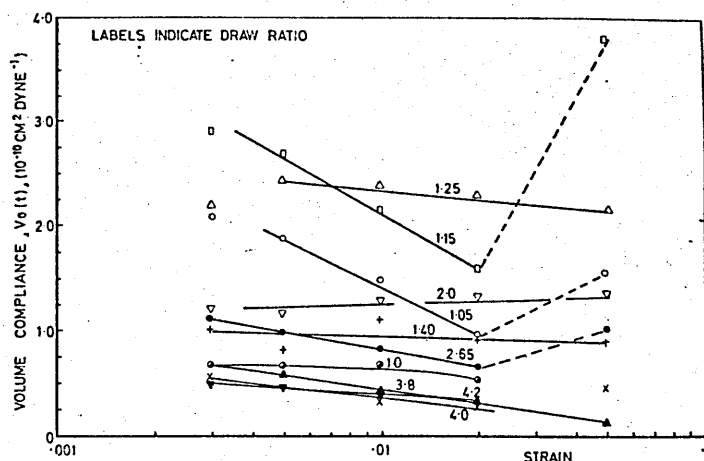
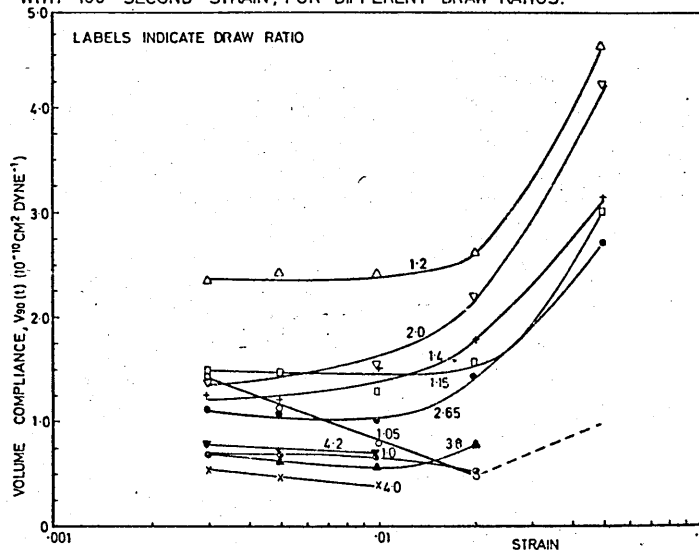
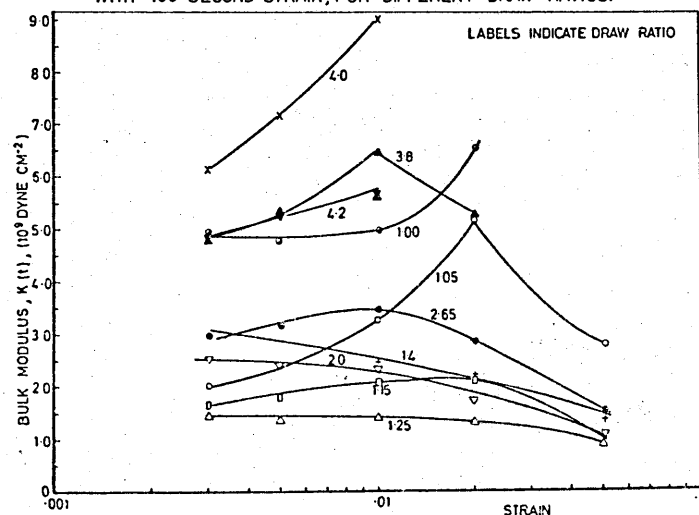
The variation of $V_0(t)$, $V_{90}(t)$ and $K(t)$, with 100 second strain are shown in Figure 8.35 to 8.37. With the exception of D.R. 1.05 and D.R. 1.15, $V_0(t)$ is approximately independent of the strain level. However, $V_{90}(t)$ is independent of strain up to 1% 100 second strain, and increases rapidly thereafter. The full lines in Figures 8.35 - 8.37 have been drawn "by eye" and are included for identification purposes only.

The repeatability and reproducibility of the time dependence in creep and recovery for all compliance parameters has been shown to be excellent (Section 5). The time dependence of $V_0(t)$ and $V_{90}(t)$ are derived from a simple time addition of the compliance parameters and the trends of $V_0(t)$ and $V_{90}(t)$ with time and draw ratio are significant. The creep and recovery behaviour of V_0 , V_{90} and $K(t)$ at different draw ratios is shown in Figures 8.38 to 8.49 at two strain levels. $V_0(t)$ is in general time-independent, however, a 12% increase in volume is apparent at D.R. 1.2 between 10 and 10^2 seconds, but the value at 10 and 10^3 seconds is the same. The increase is not consistent with the general trend in $V_0(t)$ and may be fortuitous. $V_0(t)$ is dominated by the c-axis shear process which is shown to be a constant volume deformation mechanism (Section 9.1.6). In contrast $V_{90}(t)$ increases between 10 and 10^3 seconds by 20% for D.R. 1.05 to 40% at D.R. 1.4 and exhibits a definite trend with draw ratio and is consistent with large time-dependent volume changes associated with a relaxation process discovered in 90° specimens (Section 9.1.3). As the draw ratio increases above DR 1.40 this

relaxation process is diminished and at D.R. 2.00 the volume increase is only 25% and at higher draw ratios V_{90} is independent of time. The large volume increases in 90° specimens give rise to a decreasing $K(t)$ with time. (Figure 8.48).

- Figure 8.33 The variation of the volume compliances $V_0(t)$ and $V_{90}(t)$, with draw ratio, at 0.5% and 1.0% 100 second strain levels.
- Figure 8.34 The variation of the bulk modulus, $K(t)$ with draw ratio, at 0.5%, 1.0% and 2.0% 100 second strain levels.
- Figure 8.35 The variation of the 100 second volume compliance, $V_0(t)$, with 100 second strain, for different draw ratios.
- Figure 8.36 The variation of the 100 second volume compliance, $V_{90}(t)$, with 100 second strain, for different draw ratios.
- Figure 8.37 The variation of the 100 second bulk modulus, $K(t)$, with 100 second strain, for different draw ratios.
- Figure 8.38 The variation of the volume creep compliance, $V_0(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.39 The variation of the volume recovery compliance, $V_0(t)$, with time, for different draw ratios, at 0.5%, 100 second strain.
- Figure 8.40 The variation of the volume creep compliance, $V_0(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.41 The variation of the volume recovery compliance, $V_{90}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.42 The variation of the volume creep compliance, $V_{90}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.43 The variation of the volume recovery compliance, $V_{90}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.44 The variation of the volume creep compliance, $V_{90}(t)$, with time, for different draw ratios, at 1% 100 second strain.
- Figure 8.45 The variation of the volume recovery compliance, $V_{90}(t)$, with time, for different draw ratios, at 1% 100 second strain.

- Figure 8.46 The variation of the creep bulk modulus, $K(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.7 The variation of the recovery bulk modulus, $K(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.48 The variation of the creep bulk modulus, $K(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.49 The variation of the recovery bulk modulus, $K(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Table 8.2 Error analysis on $V_0(t)$, and $V_{90}(t)$ for different draw ratios, at 0.5% and 1.0% 100 second strain levels.



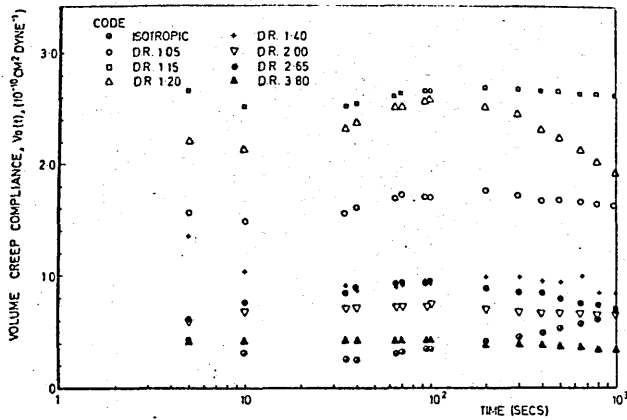


FIG. 8.38. THE VARIATION OF THE VOLUME CREEP COMPLIANCE, $V_0(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

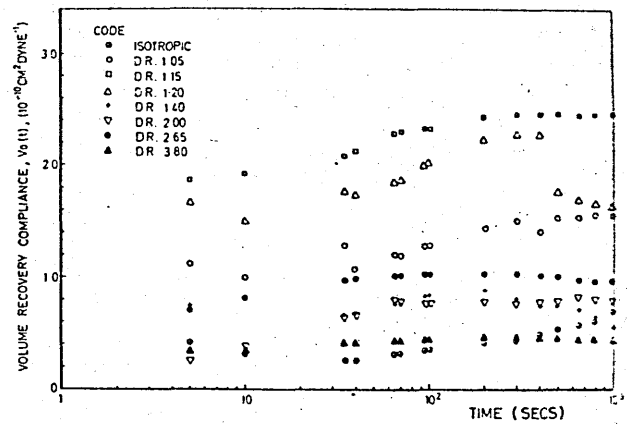


FIG. 8.39. THE VARIATION OF THE VOLUME RECOVERY COMPLIANCE, $V_0(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

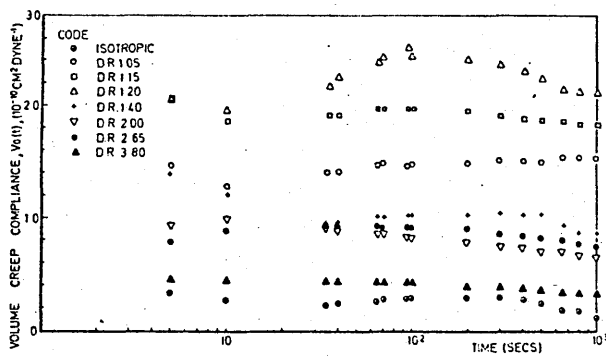


FIG. 8.40. THE VARIATION OF THE VOLUME CREEP COMPLIANCE, $V_0(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

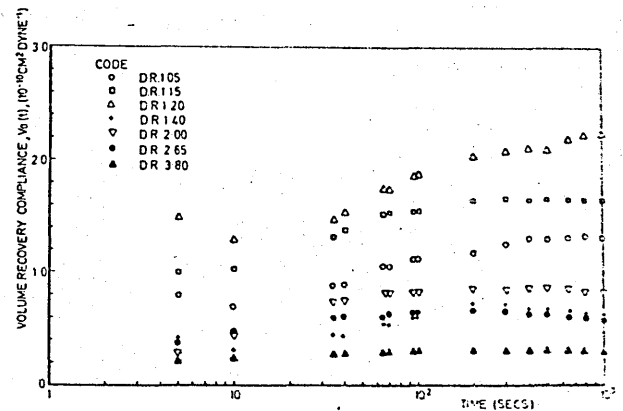


FIG. 8.41. THE VARIATION OF THE VOLUME RECOVERY COMPLIANCE, $V_0(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

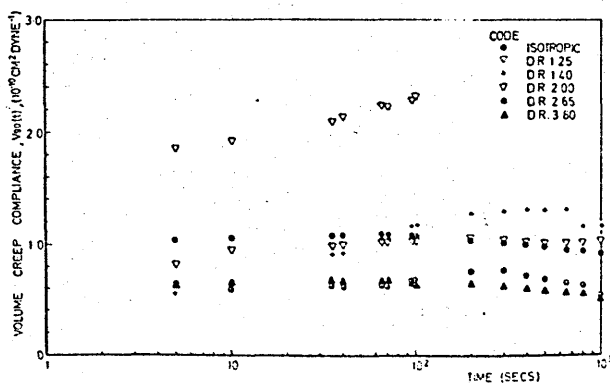


FIG. 8.42. THE VARIATION OF THE VOLUME CREEP COMPLIANCE, $V_0(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

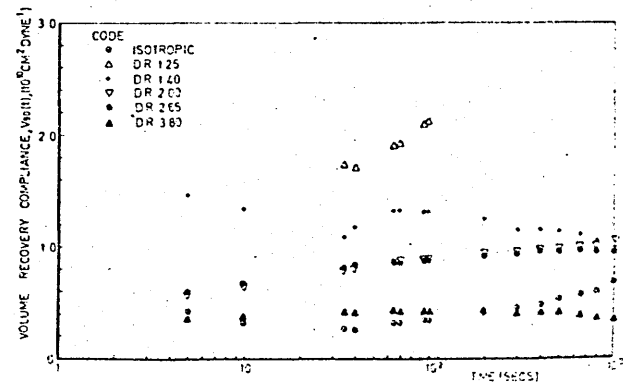


FIG. 8.43. THE VARIATION OF THE VOLUME RECOVERY COMPLIANCE, $V_0(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

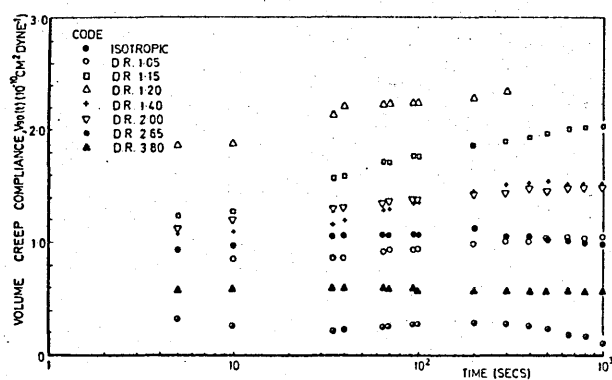


FIG844 THE VARIATION OF THE VOLUME CREEP COMPLIANCE, $V_{90}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIO, AT 1% 100 SECOND STRAIN.

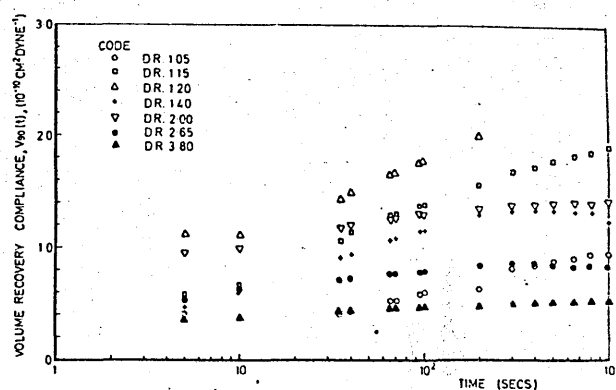


FIG845 THE VARIATION OF THE VOLUME RECOVERY COMPLIANCE, $V_{90}(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

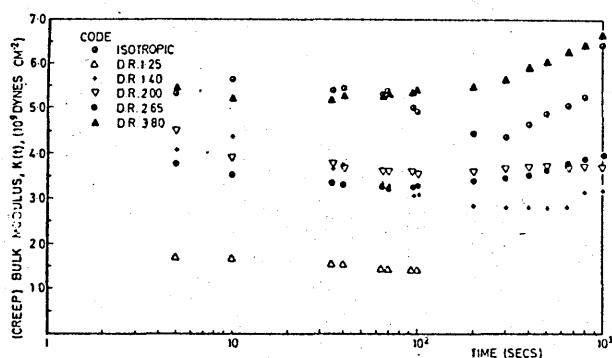


FIG846 THE VARIATION OF THE (CREEP) BULK MODULUS, $K(t)$, WITH TIME FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

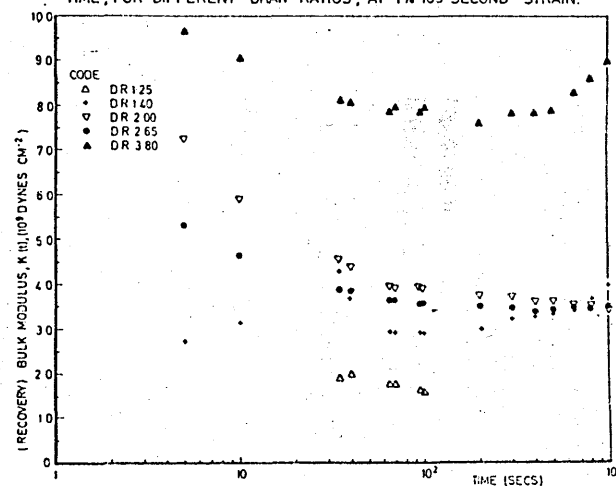


FIG847 THE VARIATION OF THE (RECOVERY) BULK MODULUS, $K(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 0.5% 100 SECOND STRAIN.

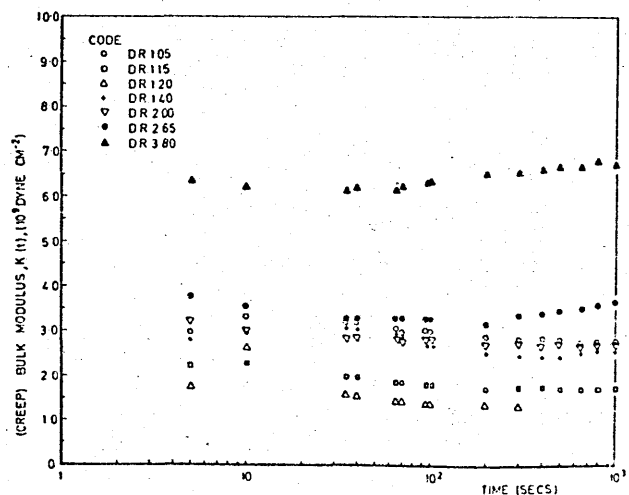


FIG848 THE VARIATION OF THE (CREEP) BULK MODULUS, $K(t)$, WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

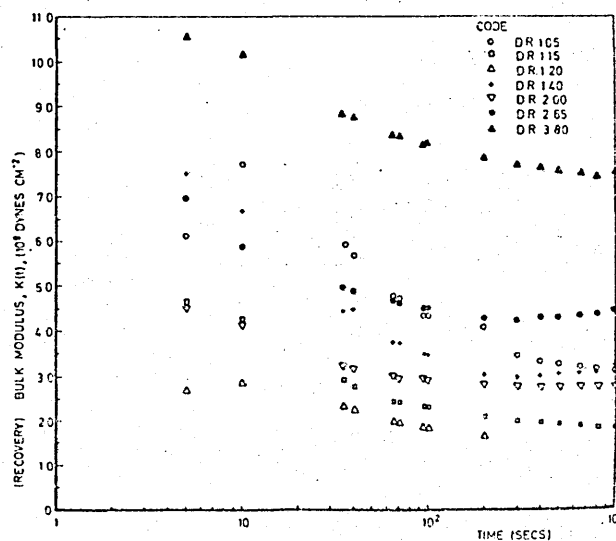


FIG849 THE VARIATION OF THE (RECOVERY) BULK MODULUS, $K(t)$ WITH TIME, FOR DIFFERENT DRAW RATIOS, AT 1% 100 SECOND STRAIN.

ISOTROPIC		D.R. 1.05		D.R. 1.15		D.R. 1.25		D.R. 1.40	
STRAIN %		STRAIN %		STRAIN %		STRAIN %		STRAIN %	
0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
S33	6.78	7.35	9.09	10.75	11.36	11.24	11.98	10.20	11.11
S22			8.30	8.13	8.70	8.00	8.55	6.90	7.58
S13	3.04	3.34	3.81	4.03	4.60	4.40	4.80	4.70	5.00
S12			3.70	2.62	2.80	1.19	1.35	0.98	1.00
V ₀	0.67±23.6%	0.67±14.8%	1.47±7.5%	2.69±4.8%	2.16±5.6%	2.44±7.0%	2.38±5.0%	0.8±31.3%	1.11±1.1%
V ₉₀			0.79±17.7%	1.48±9.1%	1.30±8.5%	2.41±3.0%	2.40±2.1%	1.22±11.5%	1.51±4.4%
D.R. 2.00		D.R. 2.65		D.R. 3.80		D.R. 4.00		D.R. 4.20	
STRAIN %		STRAIN %		STRAIN %		STRAIN %		STRAIN %	
0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
S33	7.58	7.87	5.59	2.25	2.28	1.95	1.97	1.748	1.754
S22	5.46	5.65	4.27	2.68	2.88	2.47	2.63	2.38	2.55
S13	3.20	3.30	2.38	0.84	0.93	0.64	0.73	0.63	0.66
S12	0.77	0.83	0.88	1.20	1.39	1.24	1.41	1.02	1.19
V ₀	1.18±12%	1.27±8.1%	0.83±4%	0.58±5.0%	0.42±5.7%	0.67±1.5%	0.51±1.9%	0.49±4.9%	0.43±2.7%
V ₉₀	1.50±3%	1.52±2.6%	1.01±3.6%	0.65±4.6%	0.56±5.3%	0.47±8.9%	0.40±6.8%	0.70±2.8%	0.66±2.4%

TABLE 8.2 The Variation of the Compliance Parameters with Draw Ratio

8.5 Calculations based upon Assumptions of Linearity and Constant Volume

The formalisms of classical elasticity theory (C.E.T.) have been extended to describe the matrix of the time dependent compliance parameters for a linear visco-elastic transversely isotropic material, and the inter-relations between these material parameters. (See Section 2). The usefulness of C.E.T. has been examined in the linear and non-linear region by comparing measured and calculated compliance parameters. The inter-relations examined are as follows:-

$$S_{44} = \frac{4}{E_{45}} - S_{33} - S_{22} - 2 S_{13} \quad 8.16$$

$$S_{66} = 2 (S_{11} - S_{12}) \quad 8.17$$

$$\nu_{45} = -\frac{1}{2} E_{45} [S_{13} + S_{12}] \quad 8.18$$

Often in polymer engineering practice the assumption of deformation at constant volume (c.v.) is made which reduces the number of independent compliance parameters since:-

$$(S_{13})_{c.v.} = -\frac{1}{2} (S_{33}) \quad 8.19$$

$$\text{and } (S_{12})_{c.v.} = -\left(S_{11} - \frac{S_{33}}{2}\right) \quad 8.20$$

Hence equations 8.16 to 8.18 may be written:-

$$(S_{44})_{c.v.} = \frac{4}{E_{45}} - S_{22} \quad 8.21$$

$$(S_{66})_{c.v.} = 2 (S_{11} - S_{12} \text{ c.v.}) \quad 8.22$$

$$\text{and } (\nu_{45})_{c.v.} = -\frac{1}{2} E_{45} S_{11} \quad 8.23$$

The above time-dependent parameters defined by equation 8-16 - 8.18 and 8.21 to 8.23 have been calculated from tensile creep and recovery data at the 0.5% and 1.0% 100 second strain level and are presented in the following pages.

The values of S_{44} calculated using equation 8.16 from the creep and recovery data at 0.5% and 1.0% strain levels are shown in Figure 8.50 - 8.53, and show a similar variation with time and draw ratio as those reported in Section 7. Also the values of S_{44} predicted using constant volume assumptions and equation 8.21 are similar and are shown in Figure 8.54 - 8.57. A direct comparison of creep and recovery data at selected draw ratios is shown in Figure 8.58 - 8.60 and will be discussed in Section 9.2. A similar series of calculations for S_{66} based on equations 8.17 and 8.22 are shown in Figure 8.61 to 8.68.

The time-dependent values of S_{13} and S_{12} , calculated using equations 8.19 and 8.20, and the creep and recovery data at 0.5% and 1.0% 100 second strain levels, are shown in Figure 8.69 to 8.76. A comparison of selected draw ratios at the 1.0% level is shown in Figure 8.77 for S_{13} and Figure 8.78 for S_{12} . The structural interpretation is discussed in Section 9.1, and the engineering implications in Section 9.2. Similar calculations and comparisons of S_{13} were also made at 100 second strain levels in the region of 2% and 4% and are shown for D.R. 1.05, 1.15, and D.R. 1.25 only in Figure 8.79 to 8.81 respectively. The relevance of these figures is discussed in Section 9.1.6.

The measurement of the contraction compliance and the longitudinal compliance has enabled the calculation of the creep contraction ratios v_o , v_{90} , and v_{45} , which are material parameters more familiar to the engineer, and are calculated as follows:-

$$v_o = S_{13}/S_{33} \quad 8.24$$

$$v_{90} = S_{12}/S_{22} \quad 8.25$$

$$v_{45} = -\frac{1}{2} E_{45} (S_{13} + S_{12}) \quad 8.26$$

The values obtained by assuming constant volume may also be calculated viz:-

$$(v_o)_{c.v.} = 0.5 \quad 8.27$$

$$(v_{90})_{c.v.} = 1 - \frac{S_{33}}{2S_{11}} \quad 8.28$$

$$(v_{45})_{c.v.} = -\frac{1}{2} E_{45} S_{11} \quad 8.29$$

The values of the creep contraction ratio calculated using equation 8.24 to 8.27 are shown in Figure 8.82 to 8.105 and the variation of the isochronous values with strain are shown in Figure 8.106 to 8.108.

The above figures will now be presented, preceded by a list of figure captions.

- Figure 8.50 The variation of the calculated shear creep compliance, $S_{44}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.51 The variation of the calculated shear recovery compliance $S_{44}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.52 The variation of the calculated shear creep compliance, $S_{44}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.53 The variation of the calculated recovery compliance, $S_{44}(t)$, with time, for different draw ratios, at 1% 100 second strain.
- Figure 8.54 The variation of the shear creep compliance, $S_{44}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.55 The variation of the shear recovery compliance, $S_{44}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.56 The variation of the shear creep compliance, $S_{44}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.57 The variation of the shear recovery compliance, $S_{44}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.58 The variation of the measured and calculated shear compliance, S_{44} , with time, for isotropic material.
- Figure 8.59 The variation of the measured and calculated shear compliance, S_{44} , with time for D.R. = 2.65.
- Figure 8.60 The variation of the measured and calculated shear compliance, S_{44} with time, for D.R. = 3.80.
- Figure 8.61 The variation of the calculated shear creep compliance, $S_{66}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.62 The variation of the calculated recovery compliance, $S_{66}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

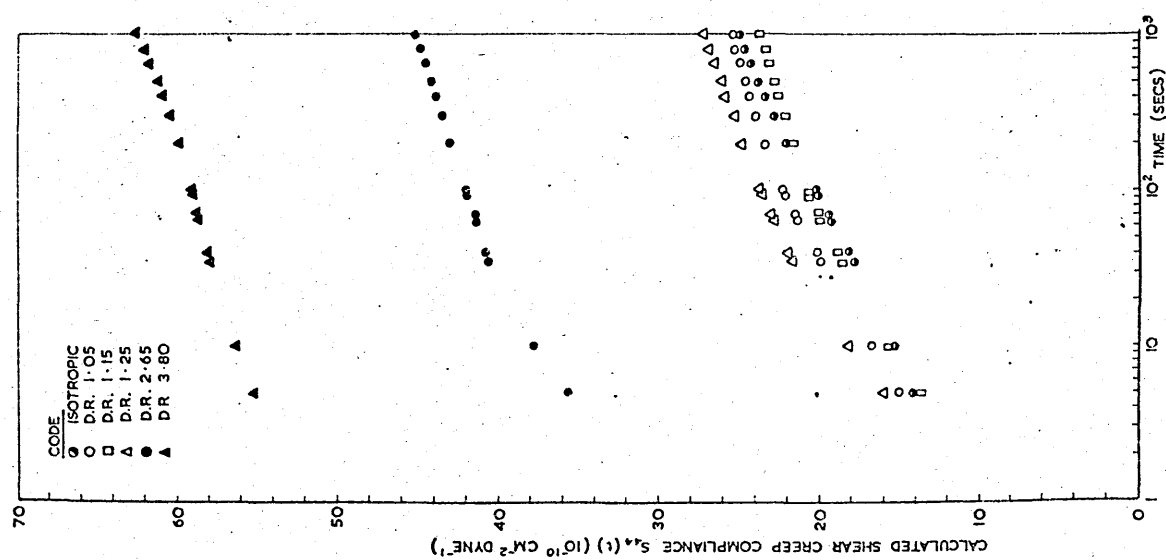


FIG.850. THE VARIATION OF THE CALCULATED SHEAR CREEP COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN.

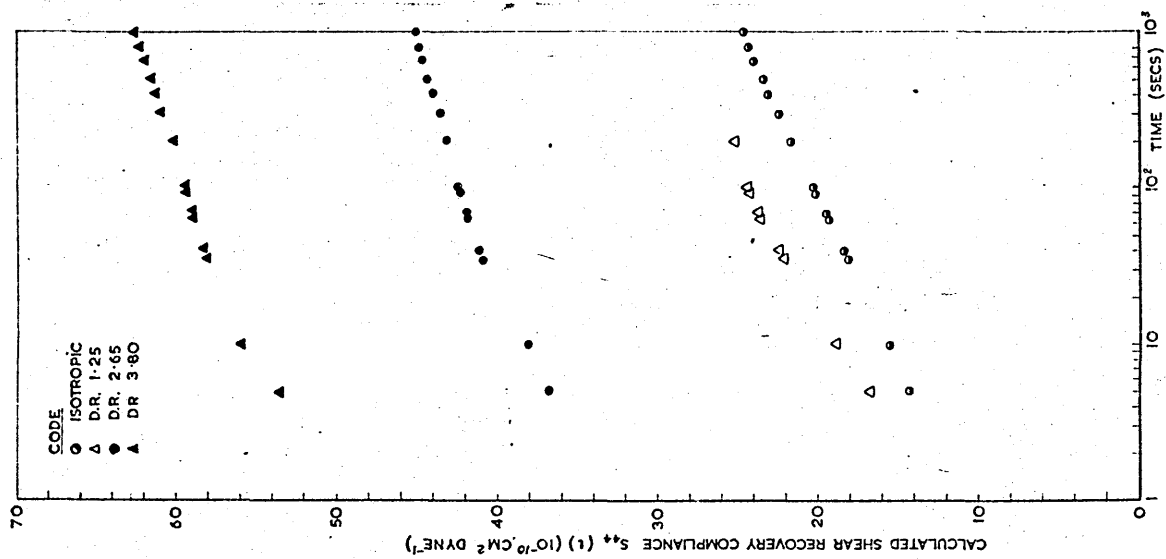


FIG.851. THE VARIATION OF CALCULATED SHEAR RECOVERY COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIO AT 0.5% 100 SECOND STRAIN.

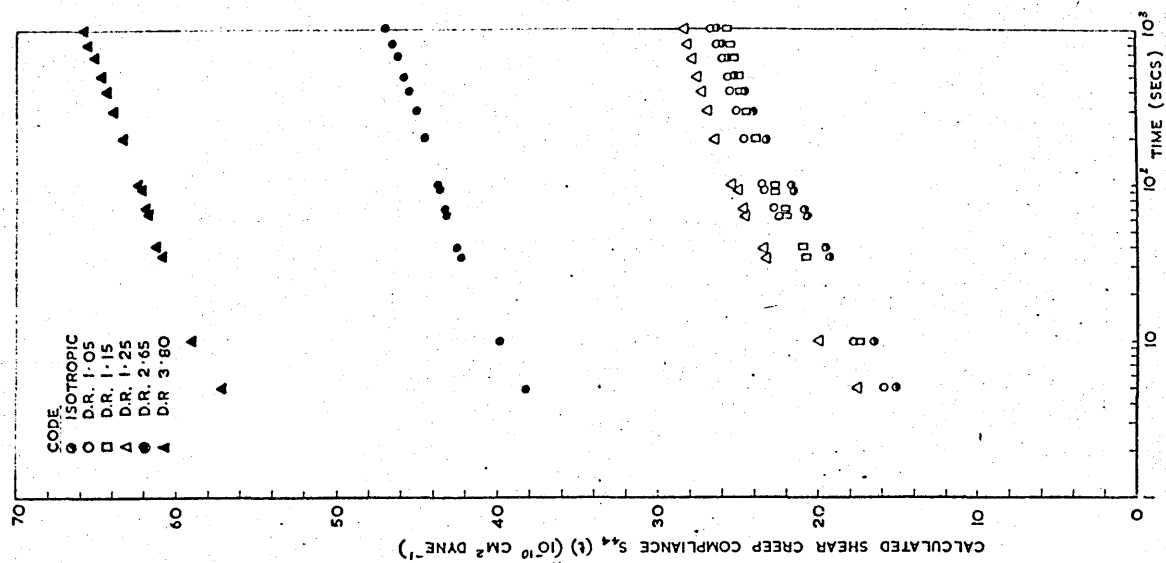


FIG.852. THE VARIATION OF THE CALCULATED SHEAR CREEP COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

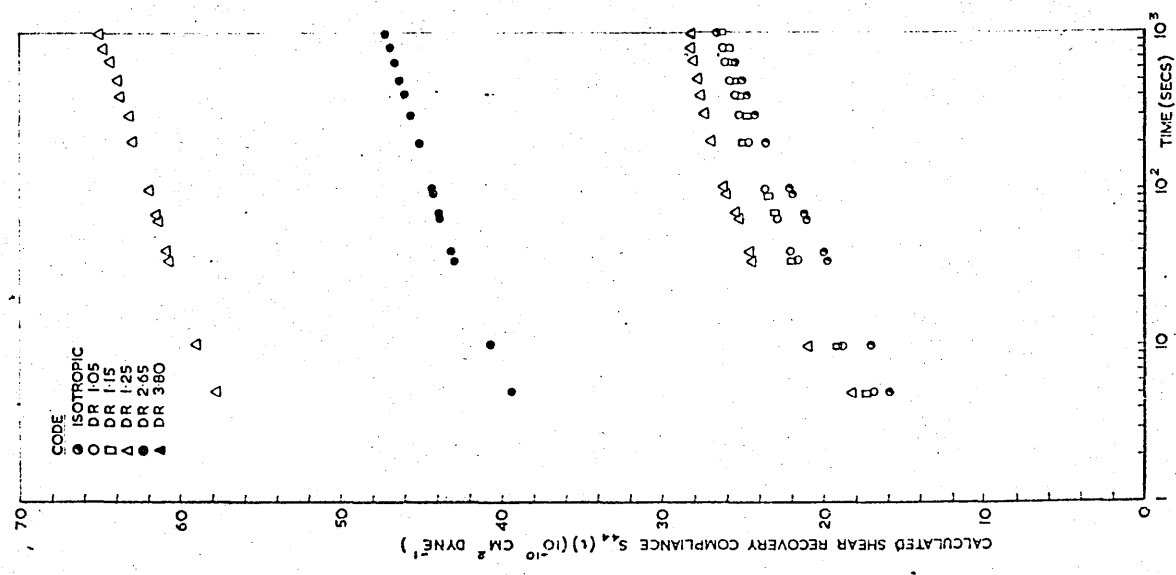


FIG.8.53 THE VARIATION OF THE CALCULATED RECOVERY COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN

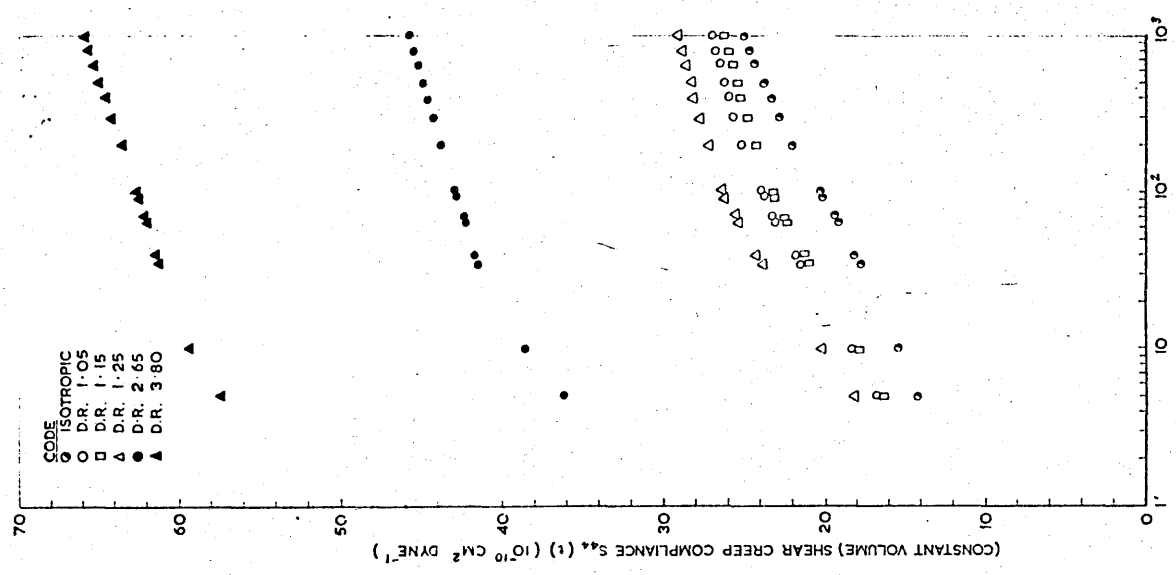


FIG.8.54. THE VARIATION OF THE SHEAR CREEP COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPT.

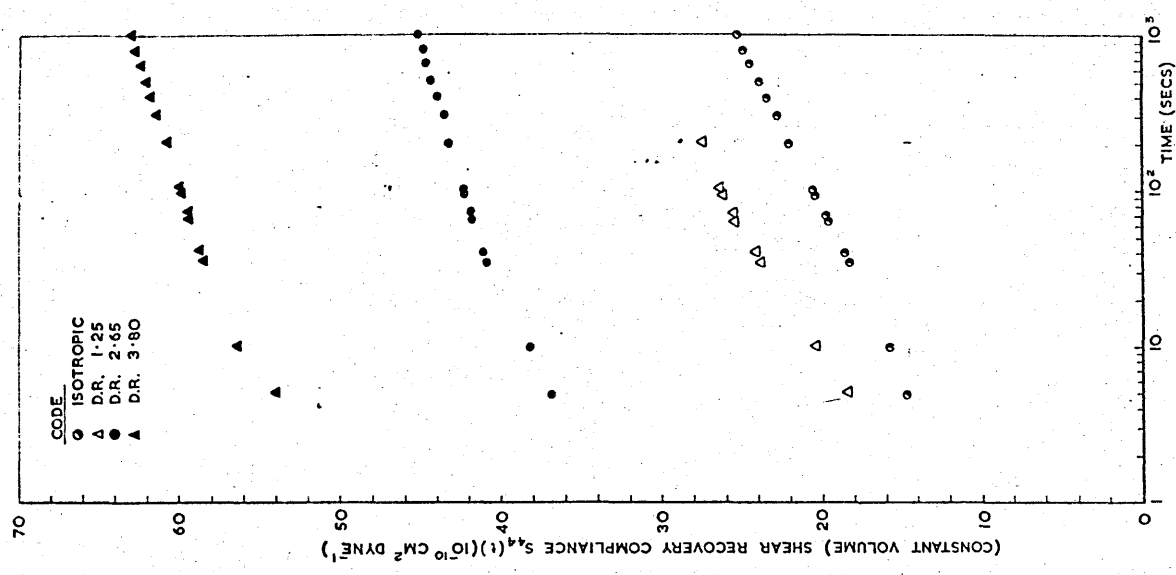


FIG.8.55 THE VARIATION OF THE SHEAR RECOVERY COMPLIANCE $S_{44}(t)$ WITH TIME PREDICTED USING CONSTANT VOLUME ASSUMPTIONS AT 0.5% 100 SECOND STRAIN.

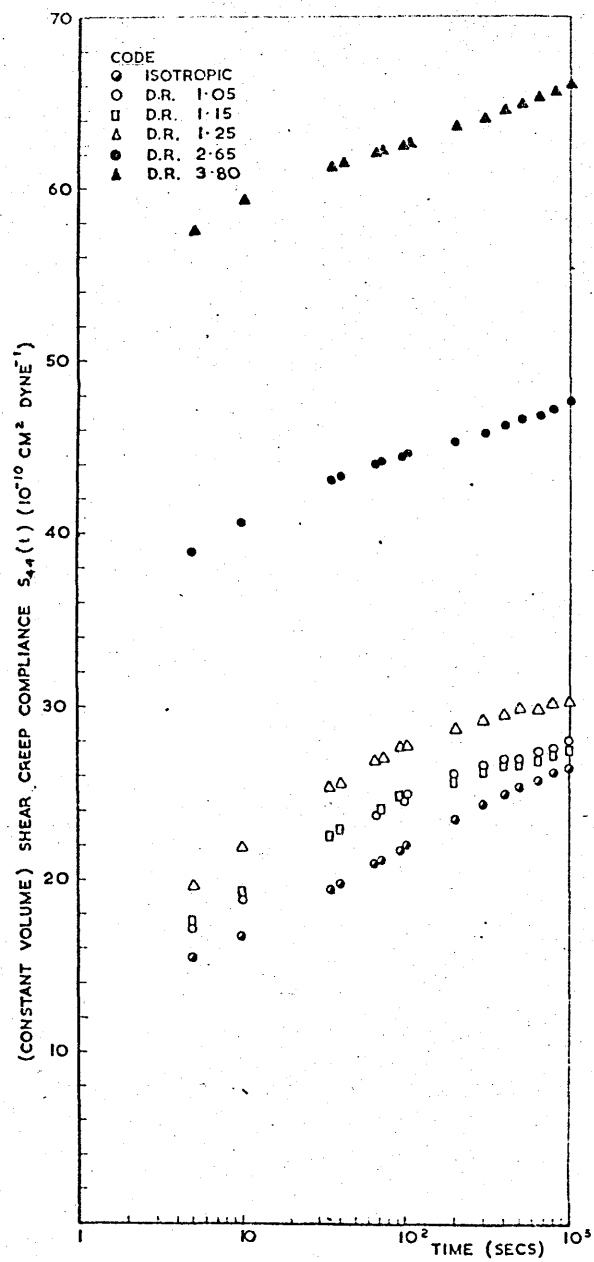


FIG.8.56. THE VARIATION OF THE SHEAR CREEP COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS PREDICTED USING CONSTANT VOLUME ASSUMPTIONS AT 1%, 100 SECOND STRAIN

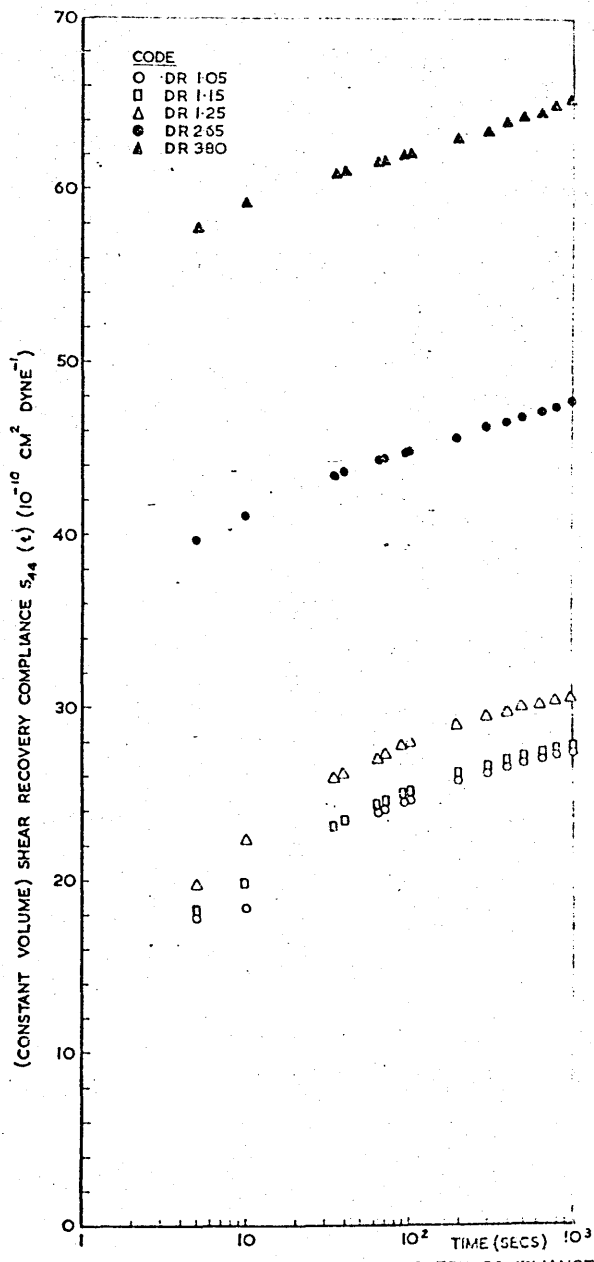


FIG.8.57. THE VARIATION OF THE SHEAR RECOVERY COMPLIANCE $S_{44}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS PREDICTED USING CONSTANT VOLUME ASSUMPTIONS AT 1.0%, 100 SECOND STRAIN

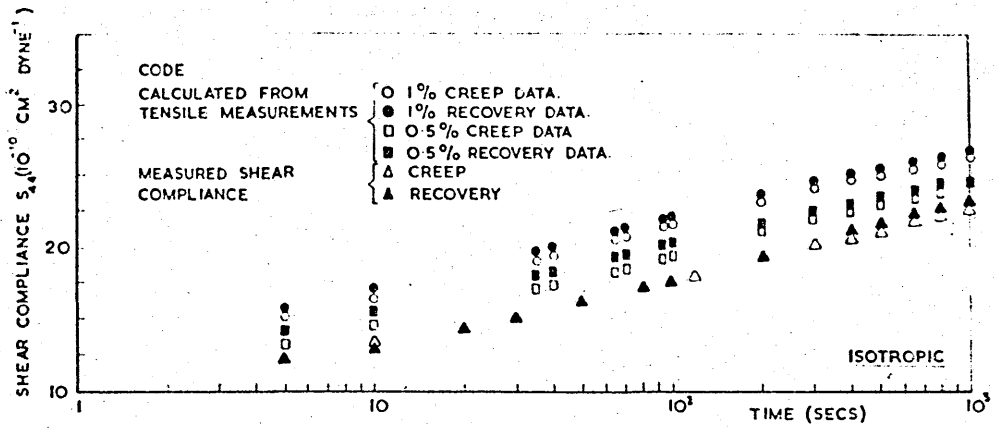


FIG.8.58. THE VARIATION OF THE MEASURED AND CALCULATED SHEAR COMPLIANCE S_{44} WITH TIME FOR ISOTROPIC MATERIAL.

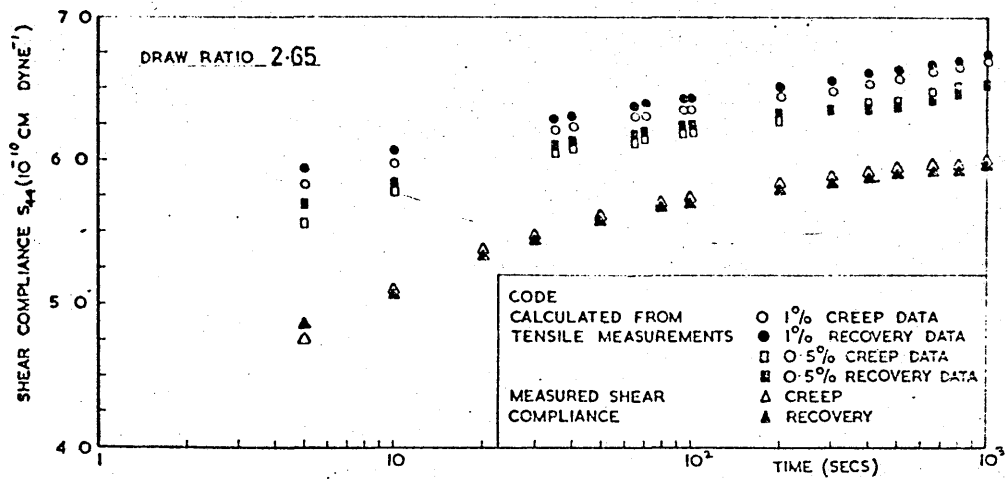


FIG.8.59. THE VARIATION OF THE MEASURED AND CALCULATED SHEAR COMPLIANCE S_{44} WITH TIME FOR D.R. 2.65.

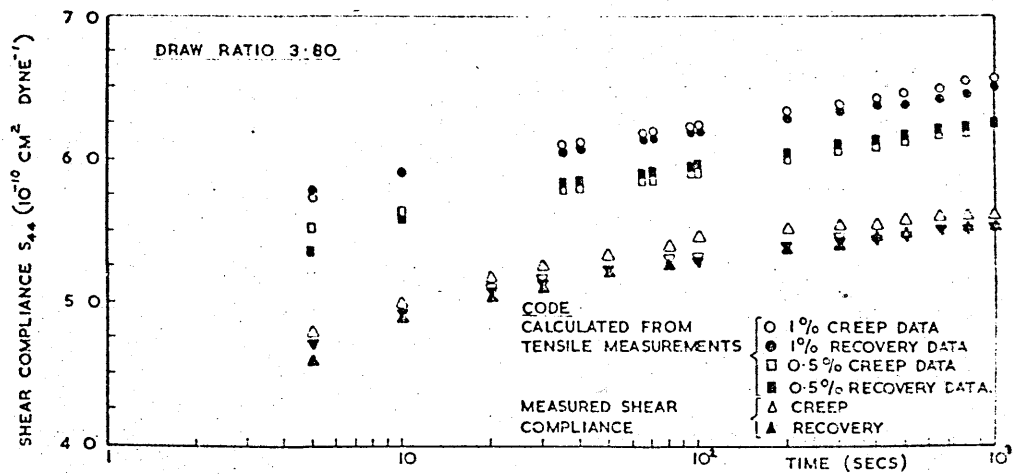


FIG.8.60. THE VARIATION OF THE MEASURED AND CALCULATED SHEAR COMPLIANCE S_{44} WITH TIME FOR D.R. 3.80.

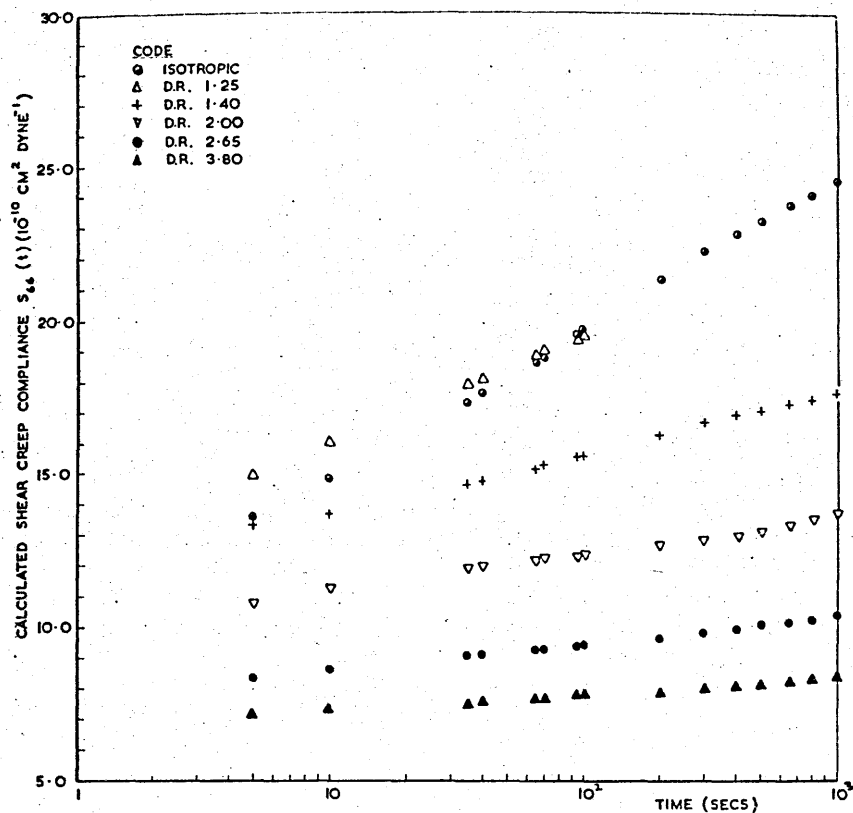


FIG.8.61. THE VARIATION OF THE CALCULATED SHEER CREEP COMPLIANCE $S_{ee}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN.

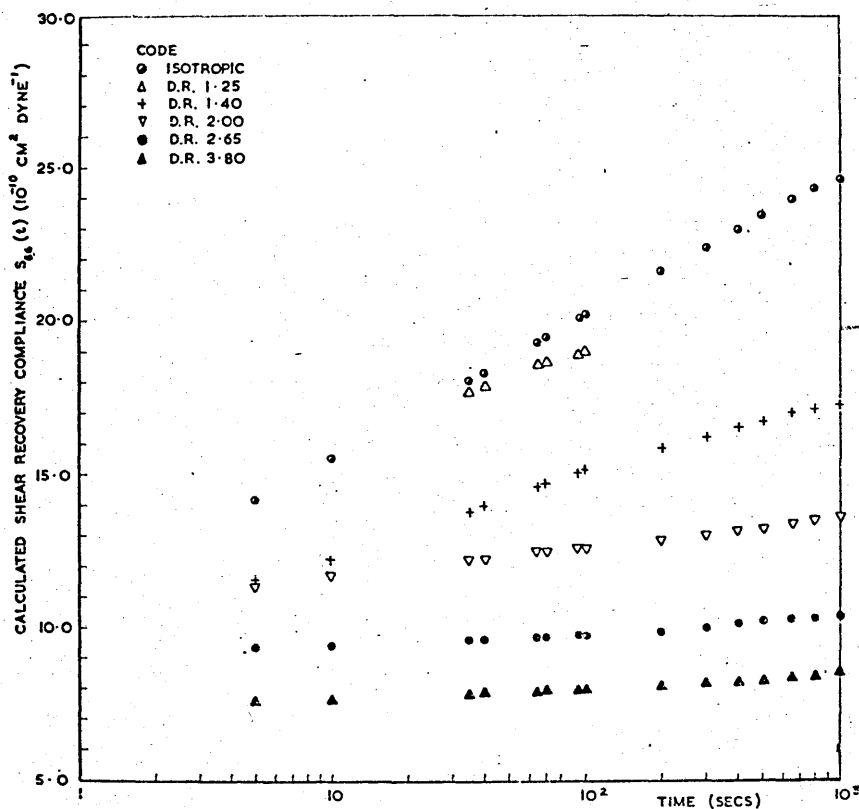


FIG.8.62 THE VARIATION OF THE CALCULATED SHEAR RECOVERY COMPLIANCE $S_{ee}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN.

- Figure 8.63 The variation of the calculated shear creep compliance, $S_{66}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.64 The variation of the calculated shear recovery compliance, $S_{66}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.65 The variation of the shear creep compliance, $S_{66}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.66 The variation of the shear recovery compliance $S_{66}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.67 The variation of the shear creep compliance, $S_{66}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.68 The variation of the shear recovery compliance, $S_{66}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.69 The variation of the creep contraction compliance, $S_{13}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.70 The variation of the recovery contraction compliance, $S_{13}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.71 The variation of the creep contraction compliance, $S_{13}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.72 The variation of the recovery contraction compliance, $S_{13}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.

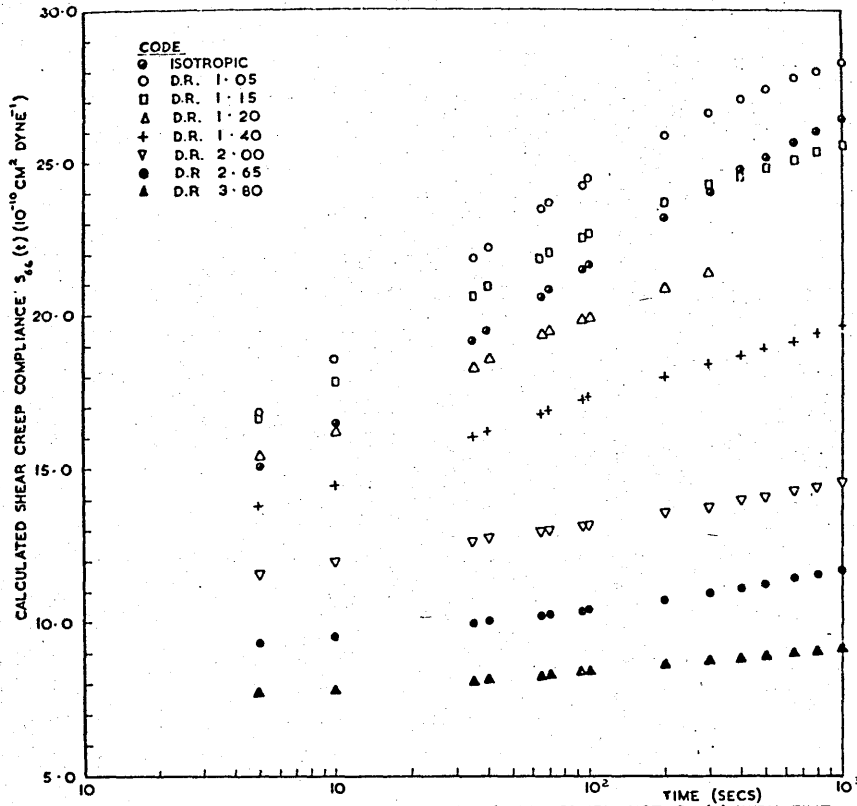


FIG.8.63 THE VARIATION OF THE CALCULATED SHEAR CREEP COMPLIANCE $S_{ee}(t)$ WITH TIME FOR DRAW RATIOS AT 1% 100 SECOND STRAIN.

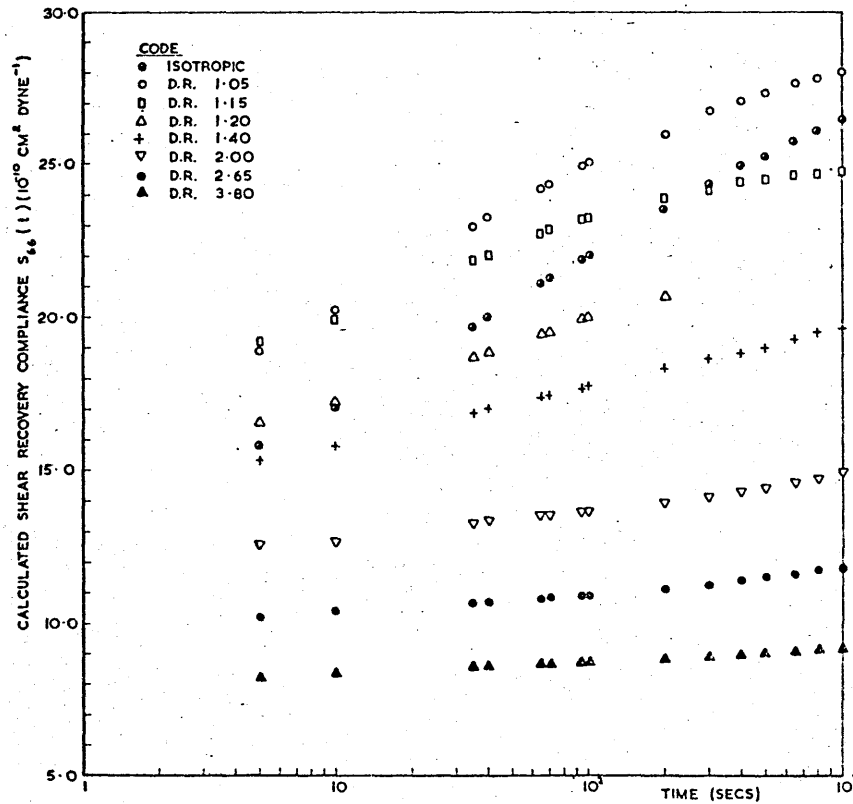


FIG.8.64 THE VARIATION OF THE CALCULATED SHEAR RECOVERY COMPLIANCE $S_{ee}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

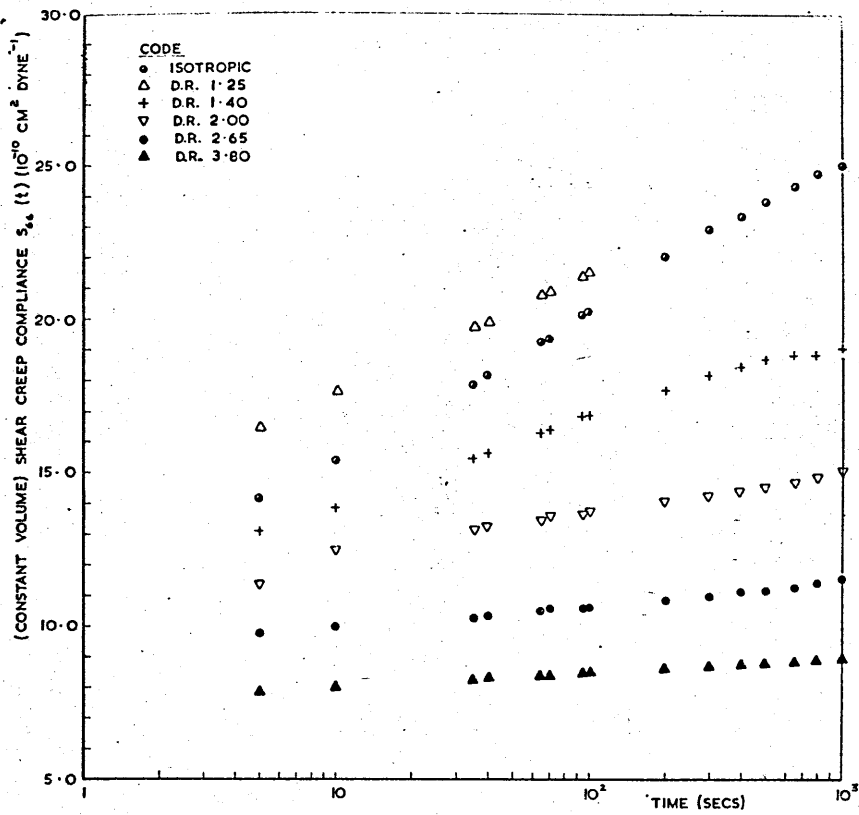


FIG.8.65 THE VARIATION OF THE SHEAR CREEP COMPLIANCE $S_{66}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

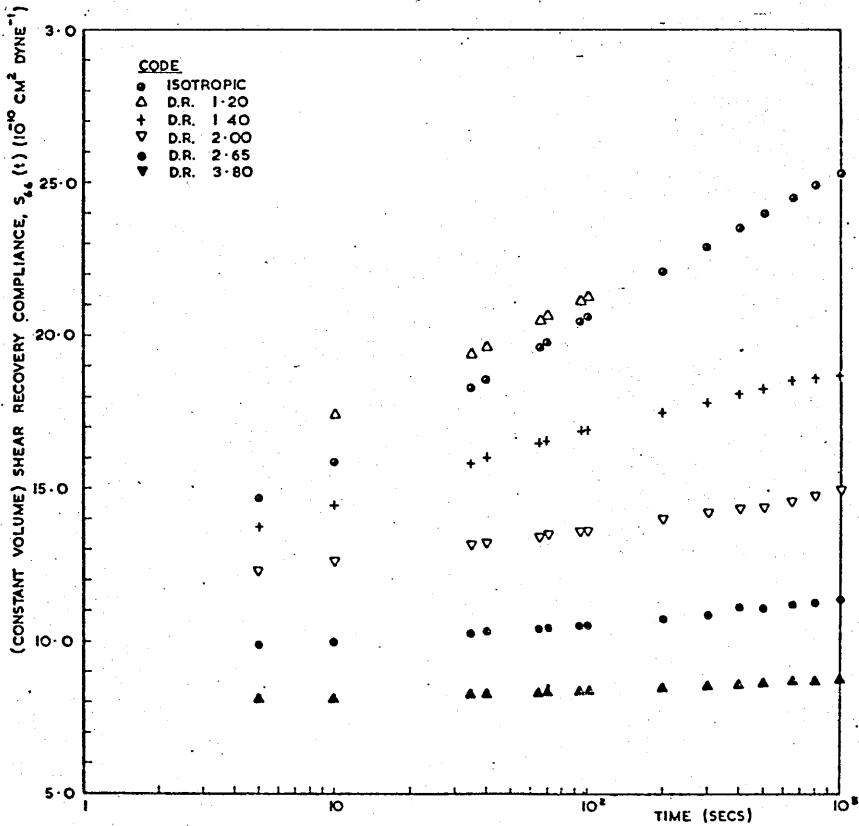


FIG.8.66 THE VARIATION OF THE SHEAR RECOVERY COMPLIANCE $S_{66}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

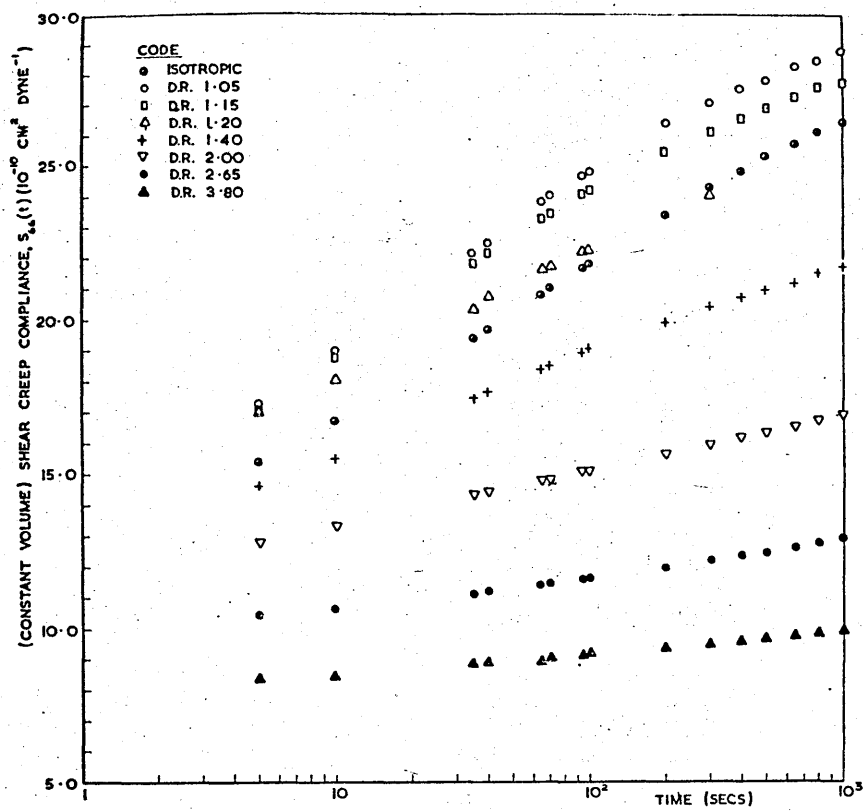


FIG.8.67. THE VARIATION OF THE SHEAR CREEP COMPLIANCE $S_{\epsilon\epsilon}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN, PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

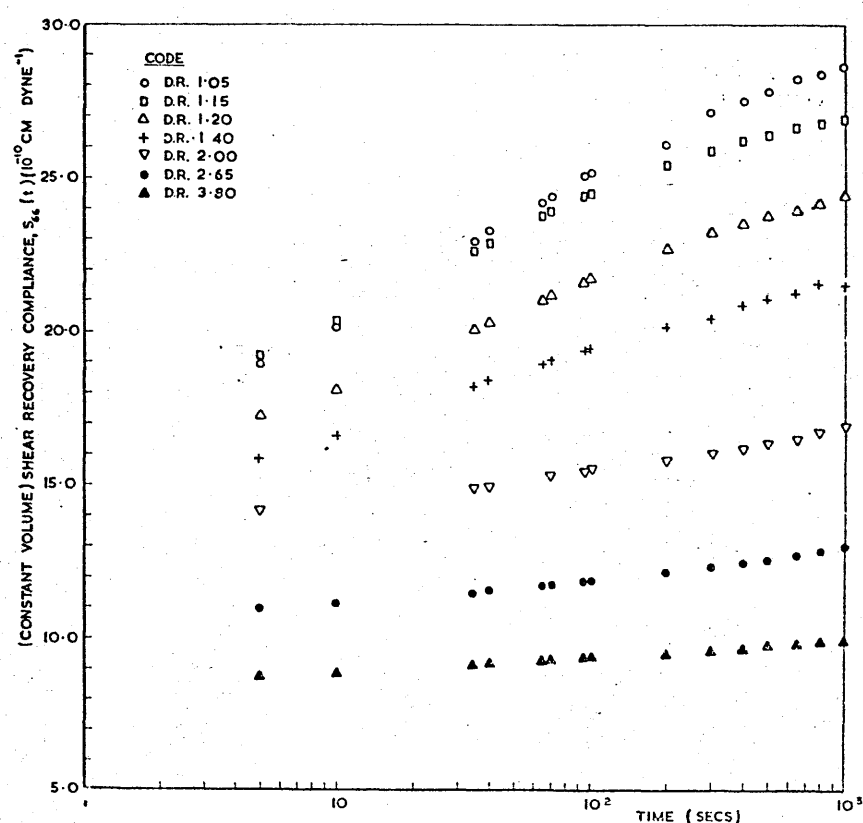


FIG.8.68. THE VARIATION OF THE SHEAR RECOVERY COMPLIANCE $S_{\epsilon\epsilon}(t)$ WITH TIME FOR DIFFERENT DRAW RATIO AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

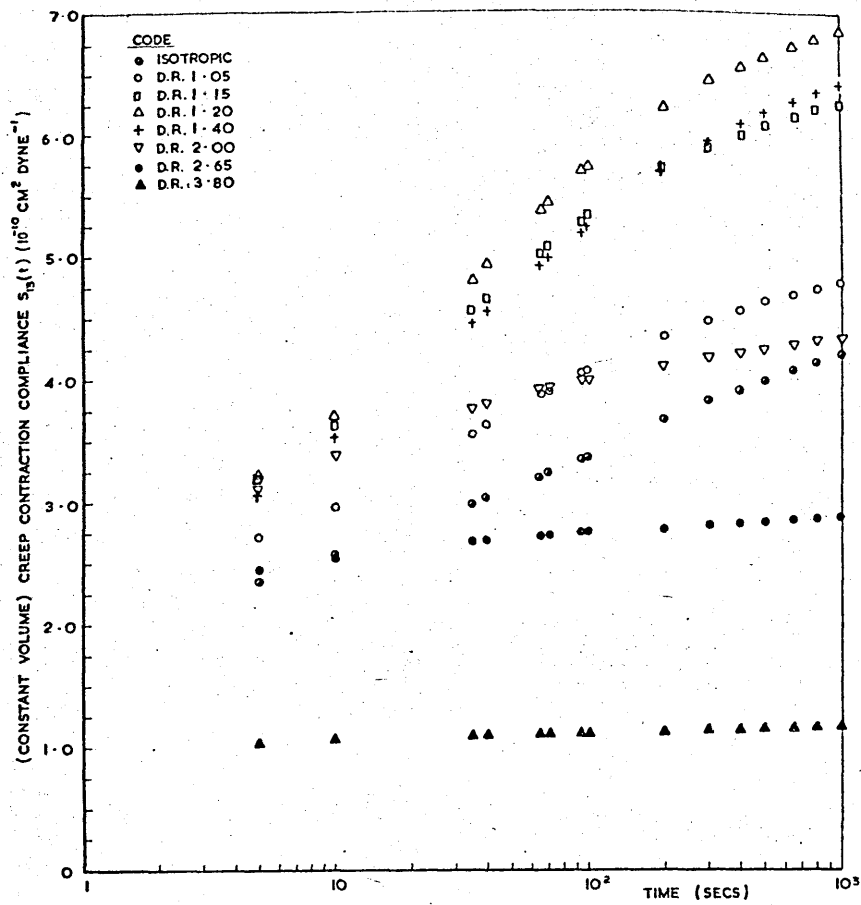


FIG.8.69. THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE $S_3(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

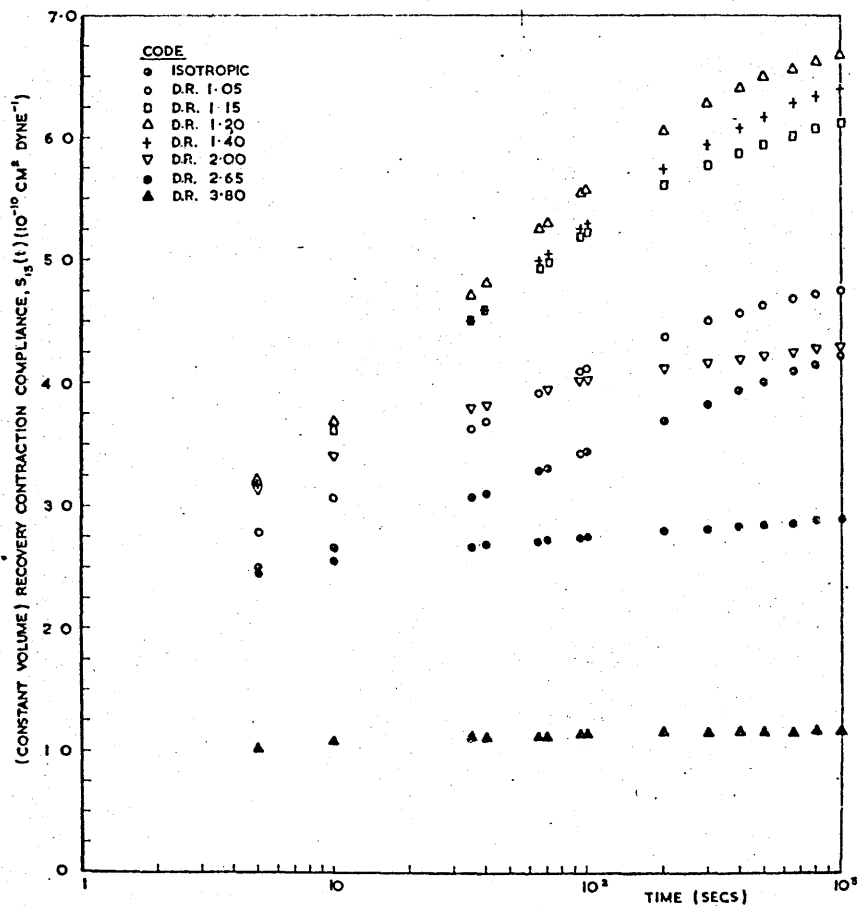


FIG.8.70. THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE, $S_3(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

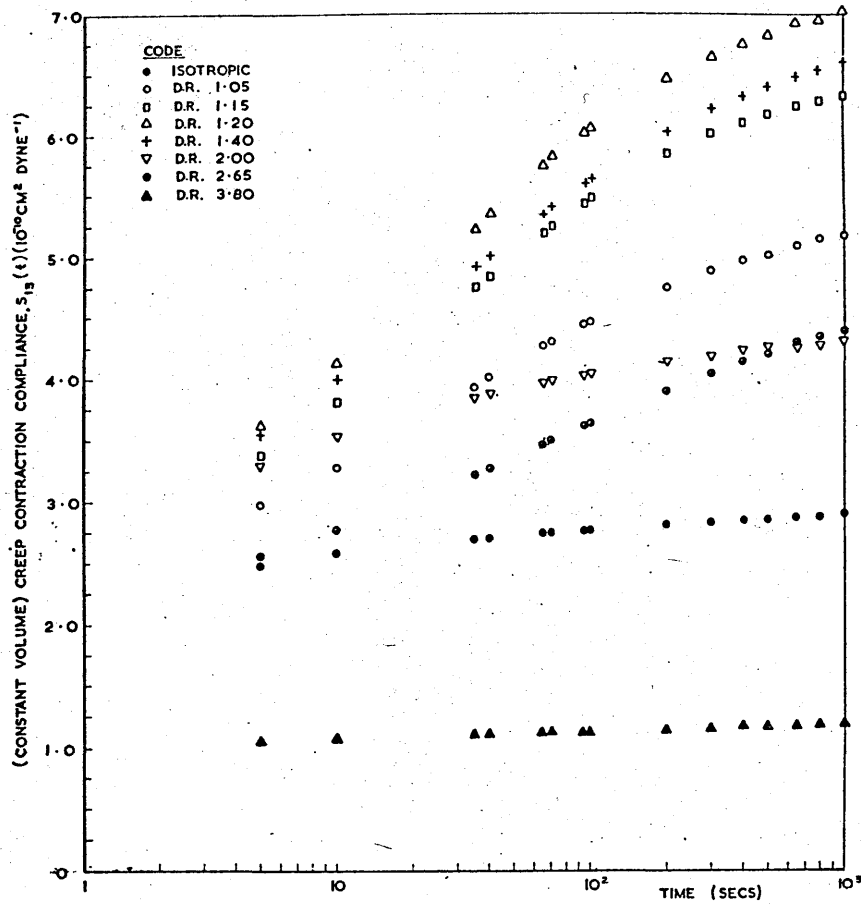


FIG.8.71. THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE $S_{13}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

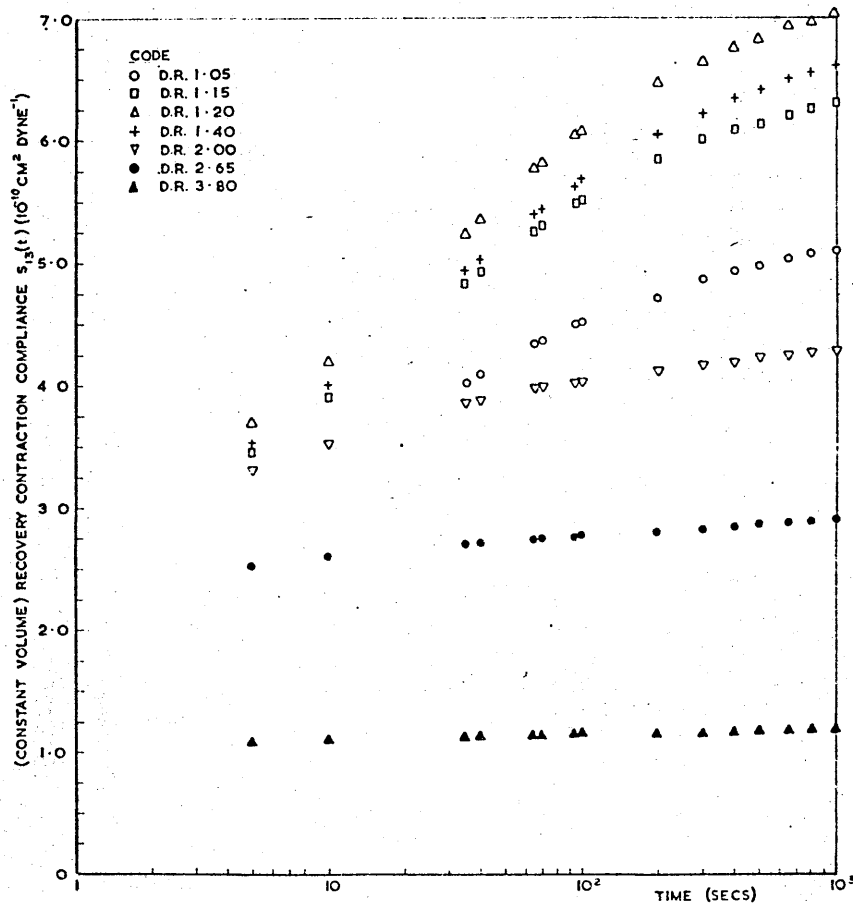


FIG.8.72. THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE $S_{13}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

- Figure 8.73 The variation of the creep contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.74 The variation of the recovery contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumption
- Figure 8.75 The variation of the creep contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.75 The variation of the recovery contraction compliance, $S_{12}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.77 The variation of the measured and constant volume creep contraction compliance, $S_{13}(t)$, with time, at 1.0% 100 second strain, at different draw ratios.
- Figure 8.78 The variation of the measured and constant volume creep contraction compliance, $S_{12}(t)$, with time, at 1.0% 100 second strain, at different draw ratios.
- Figure 8.79 The variation of the measured and constant volume creep contraction compliance, $S_{13}(t)$, with time, at high strains, for D.R. 1.05.
- Figure 8.80 The variation of the measured and constant volume creep contraction compliance, $S_{13}(t)$, with time, at high strains, for D.R. 1.15.
- Figure 8.81 The variation of the measured and constant volume creep contraction compliance, $S_{13}(t)$, with time, at high strains, for D.R. 1.25.
- Figure 8.82 The variation of the creep contraction ratio, $v_o(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.83 The variation of the recovery contraction ratio, $v_o(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.84 The variation of the creep contraction ratio $v_o(t)$, with time, for different draw ratios, at 1% 100 second strain.
- Figure 8.85 The variation of the recovery contraction ratio, $v_o(t)$, with time, for different draw ratios, at 1% 100 second strain.
- Figure 8.86 The variation of the creep contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

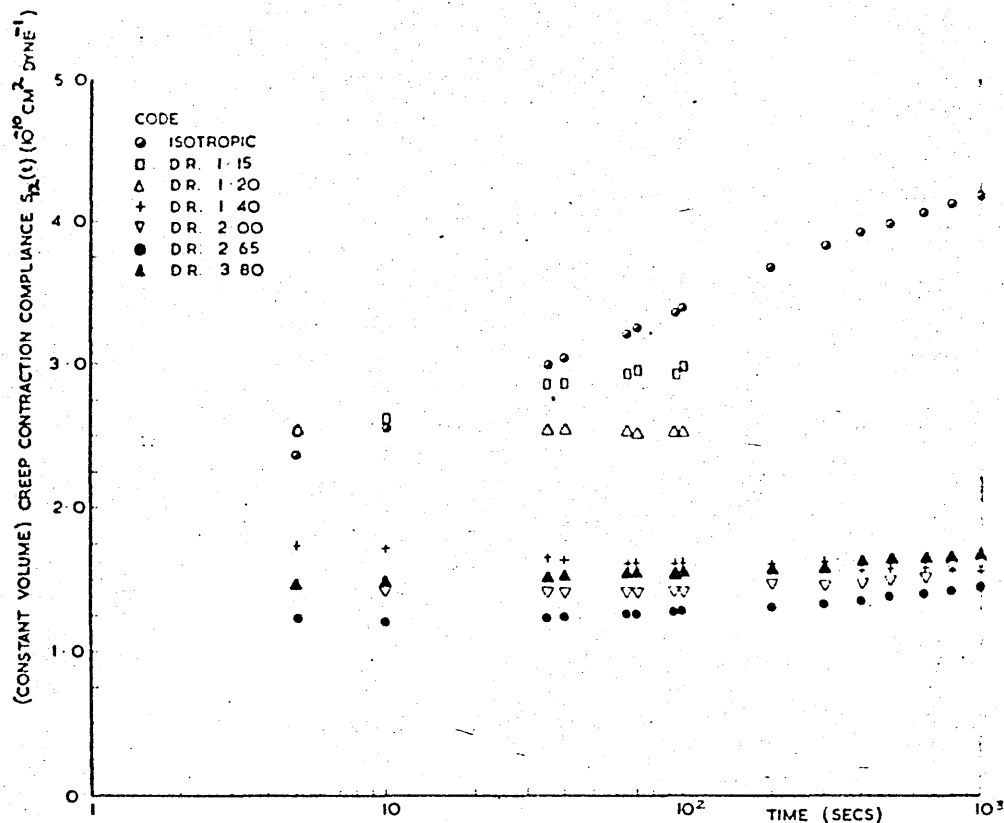


FIG.873. THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE $S_{12}(t)$ WITH TIME FOR DIFFERENT DRAW RATIO AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

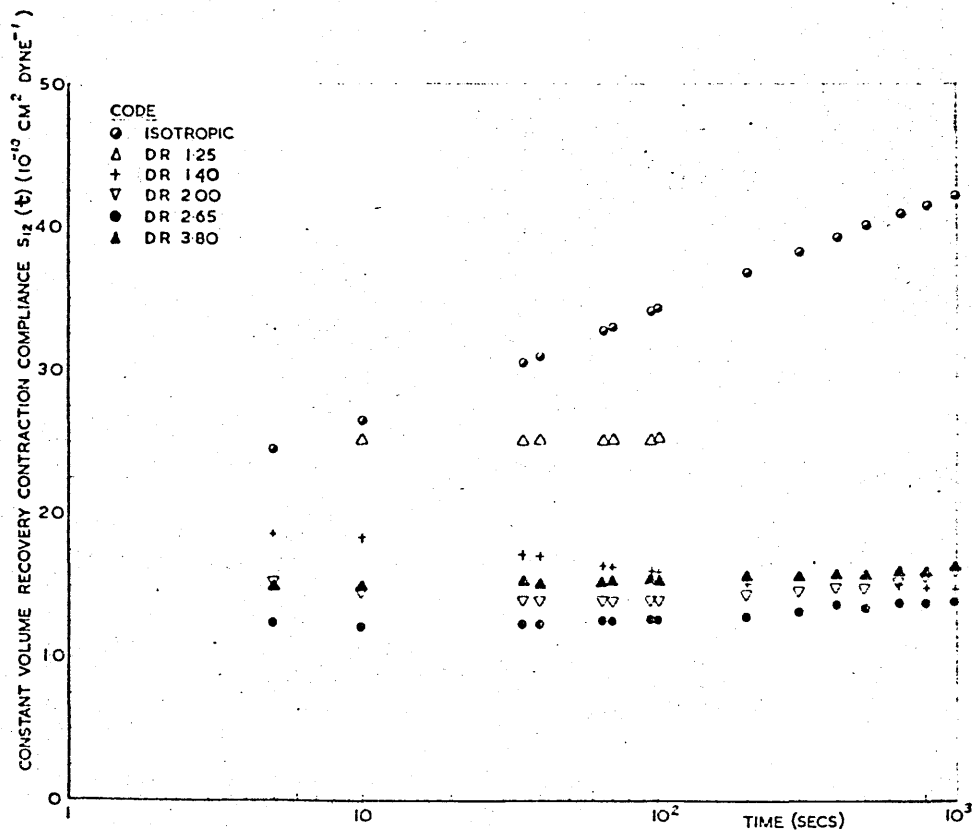


FIG.874. THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE $S_{12}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS

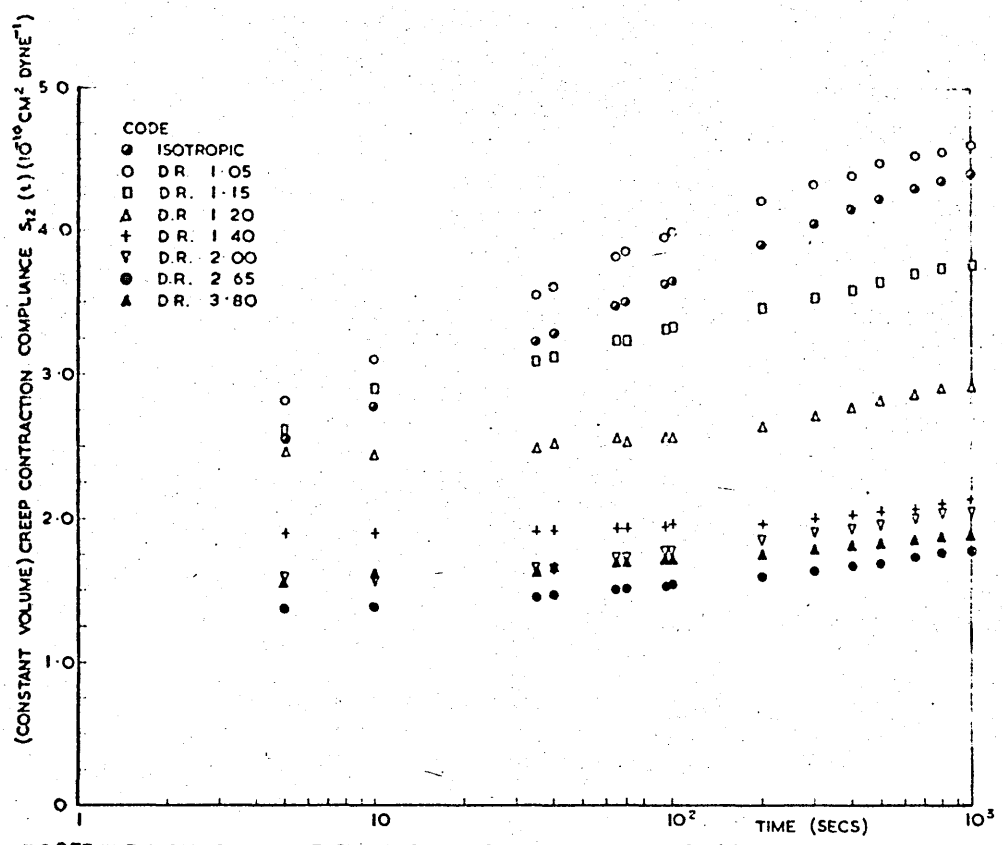


FIG.8.75. THE VARIATION OF THE CREEP CONTRACTION COMPLIANCE $S_{12}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

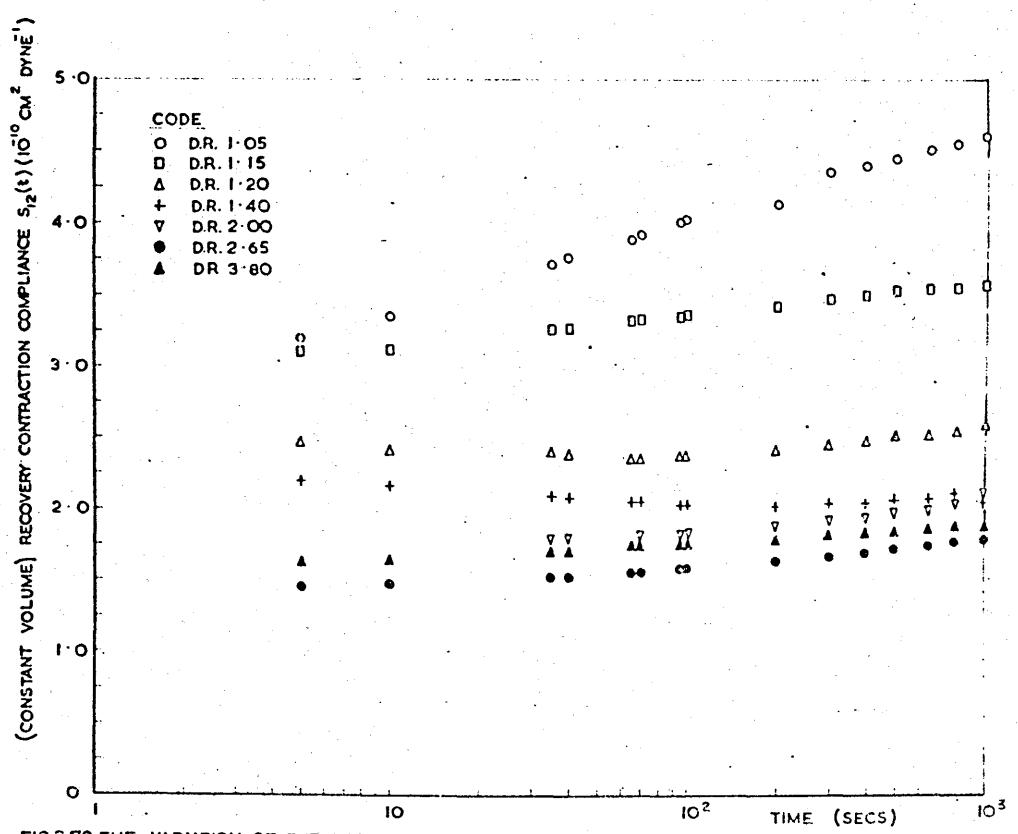


FIG.8.76. THE VARIATION OF THE RECOVERY CONTRACTION COMPLIANCE $S_{12}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

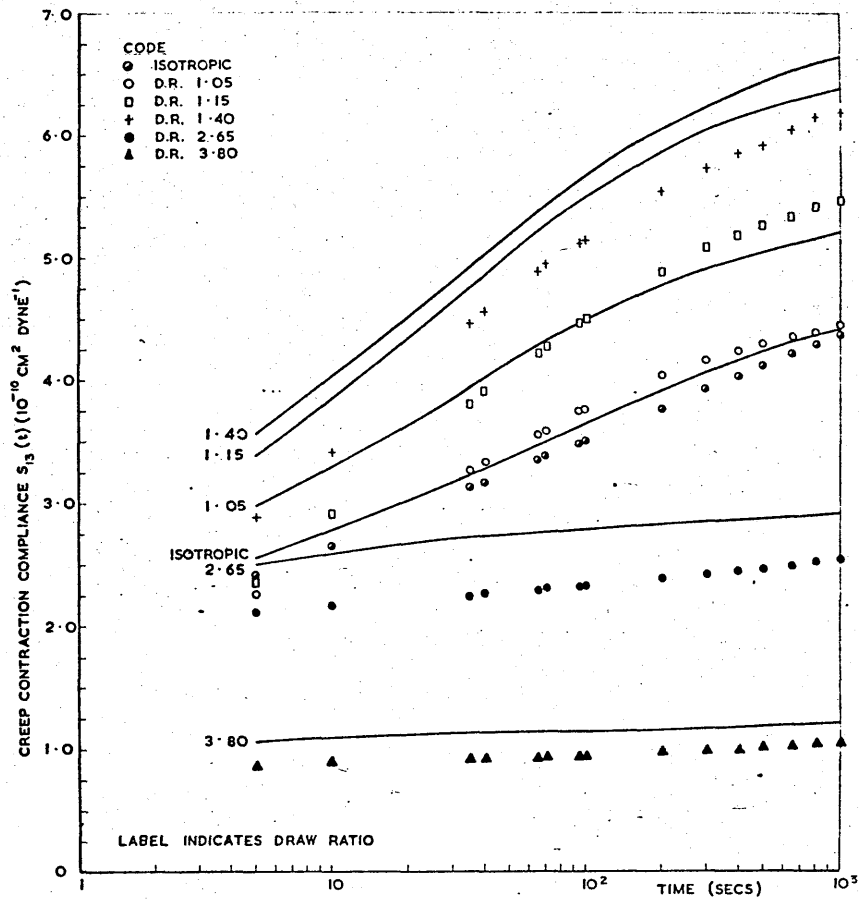


FIG.8.77. THE VARIATION OF THE MEASURED AND CONSTANT VOLUME CREEP CONTRACTION COMPLIANCE $S_{13}(t)$ WITH TIME AT 1% 100 SECOND STRAIN AT DIFFERENT DRAW RATIOS (FULL LINE REPRESENTS CONSTANT VOLUME PREDICTION)

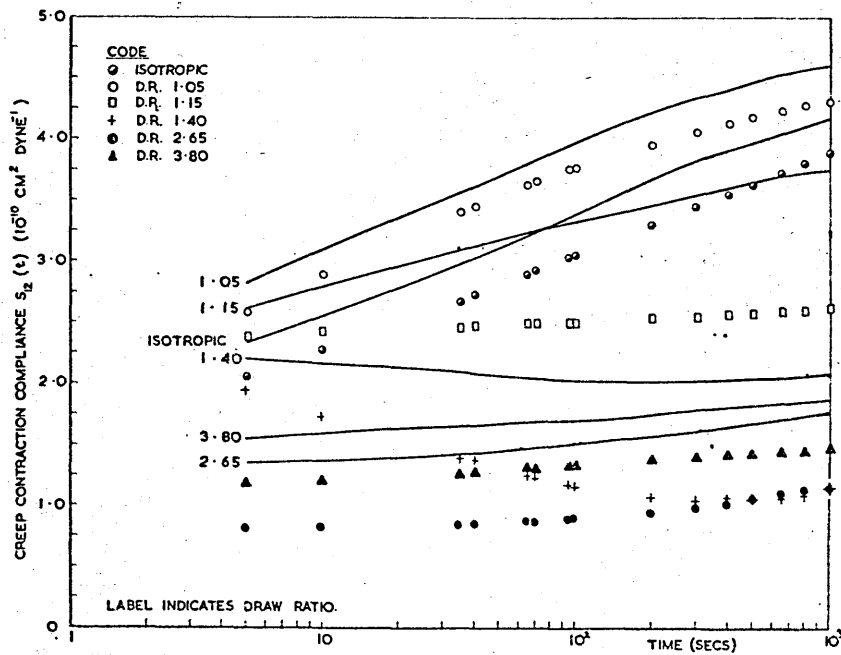


FIG.8.78. THE VARIATION OF THE MEASURED AND CONSTANT VOLUME CREEP CONTRACTION COMPLIANCE $S_{12}(t)$ WITH TIME AT 1% 100 SECOND STRAIN AT DIFFERENT DRAW RATIOS (FULL LINE REPRESENTS CONSTANT VOLUME PREDICTION)

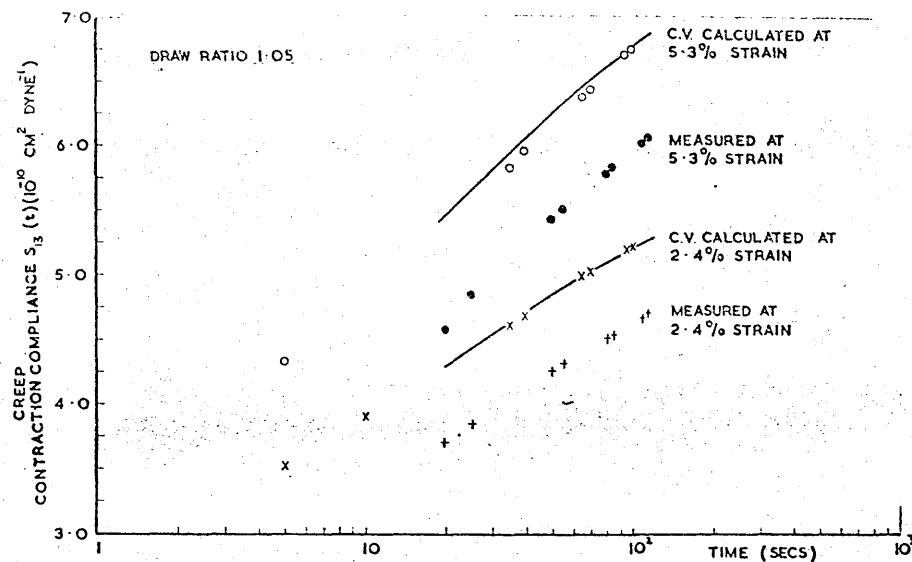


FIG879. THE VARIATION OF THE MEASURED AND CONSTANT VOLUME CREEP CONTRACTION COMPLIANCE $S_{13}(t)$ WITH TIME AT HIGH STRAINS FOR D.R. 1.05 (FULL LINE INDICATES OFF-SET MEASURED CURVES)

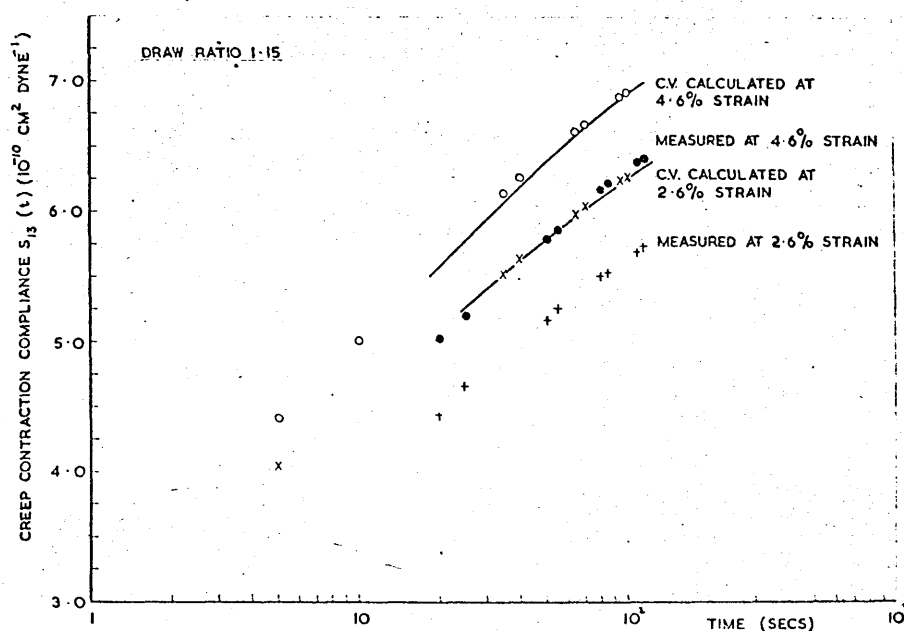


FIG880. THE VARIATION OF THE MEASURED AND (CONSTANT VOLUME) CALCULATED CREEP CONTRACTION COMPLIANCE $S_{13}(t)$ WITH TIME AT HIGH STRAINS FOR D.R. 1.15 (FULL LINE INDICATES OFF-SET MEASURED CURVES)

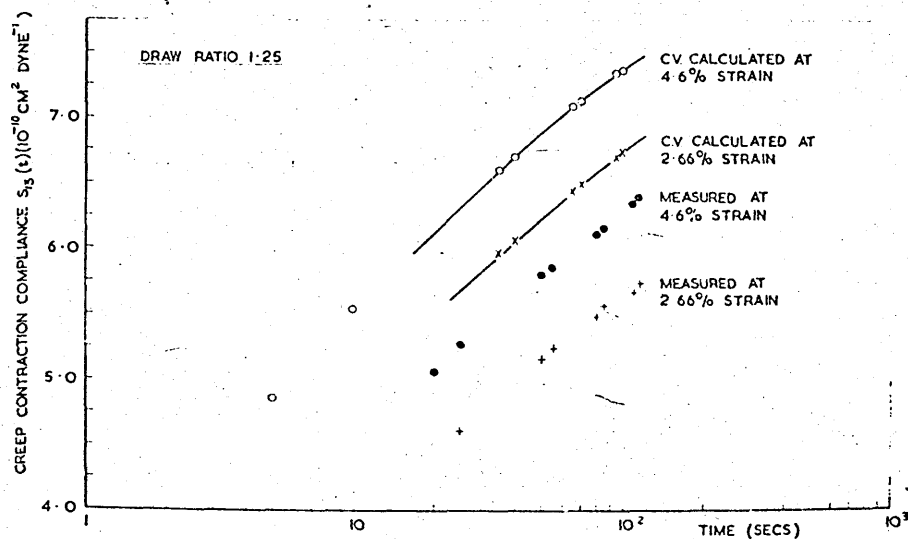


FIG881. THE VARIATION OF THE MEASURED AND CALCULATED (C.V.) CREEP CONTRACTION COMPLIANCE $S_{13}(t)$ WITH TIME AT HIGH STRAINS FOR D.R. 1.25 (FULL LINES INDICATE OFF-SET MEASURED CURVES)

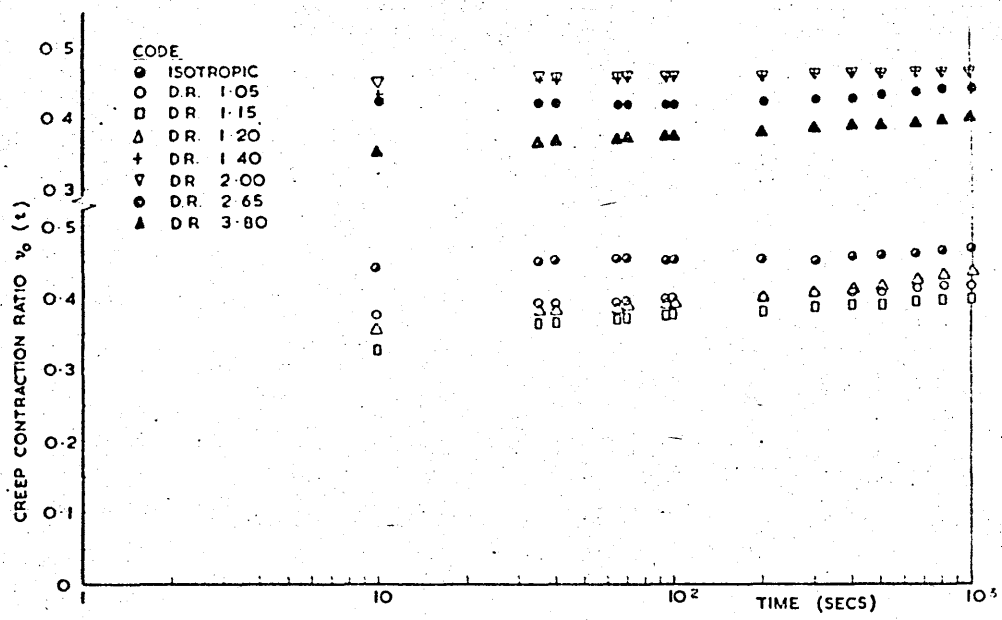


FIG882. THE VARIATION OF THE CREEP CONTRACTION RATIO $v_c(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5%, 100 SECOND STRAIN.

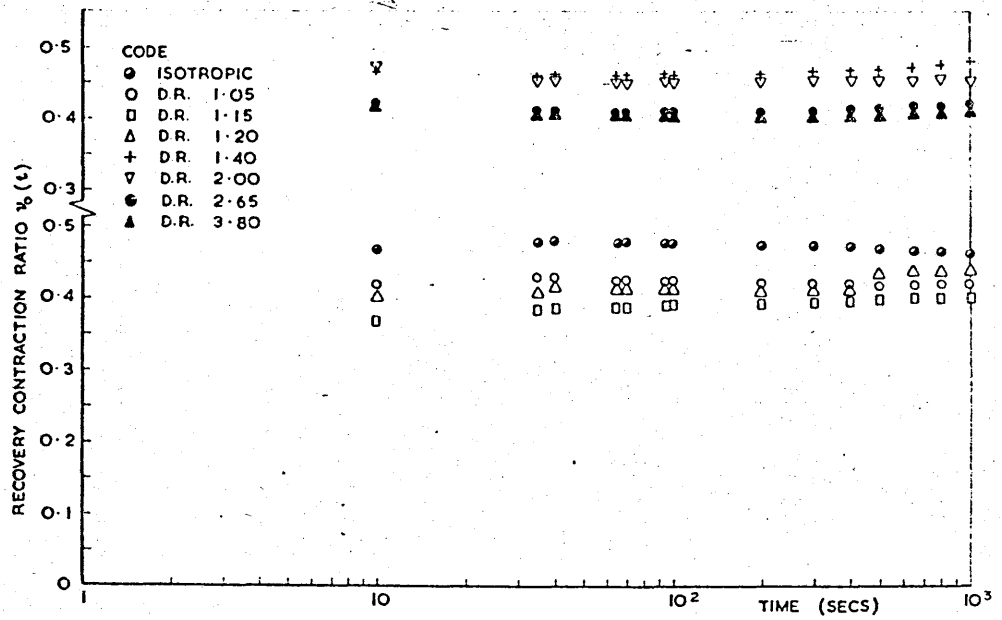


FIG883. THE VARIATION OF THE RECOVERY CONTRACTION RATIO $v_r(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5%, 100 SECOND STRAIN.

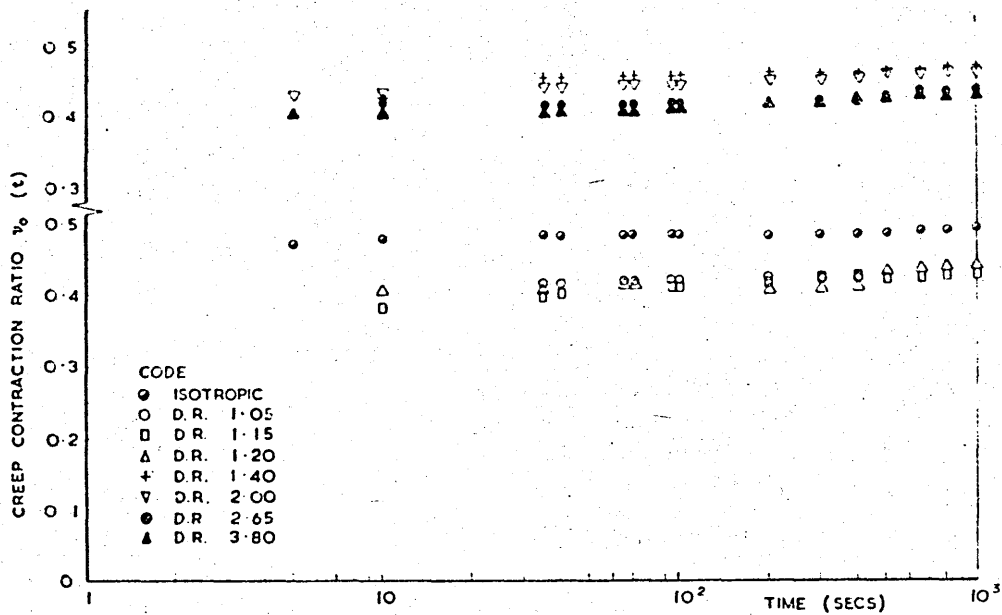


FIG.884 THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_0(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

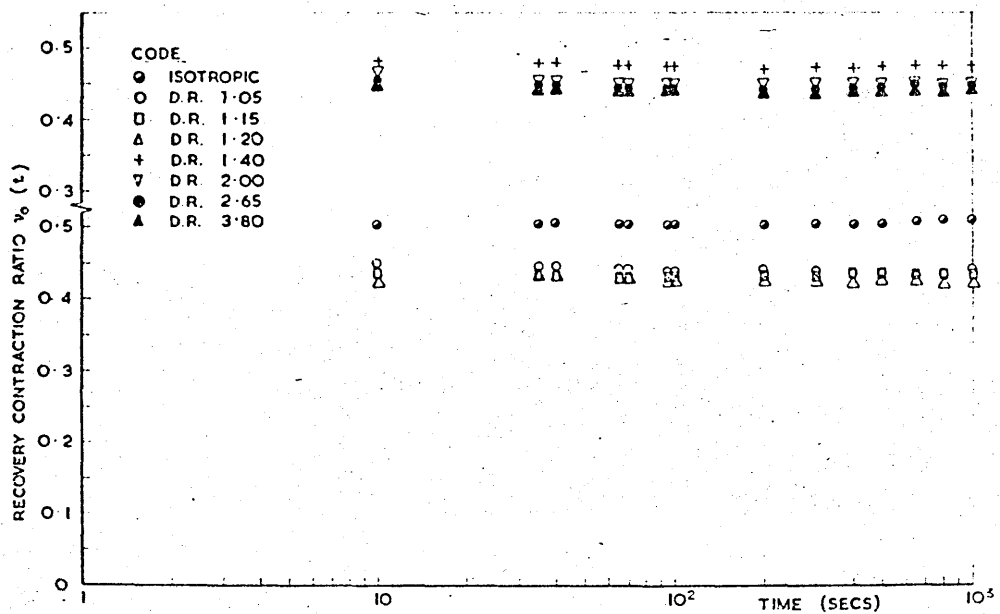


FIG.885 THE VARIATION OF THE RECOVERY CONTRACTION RATIOS $\nu_0(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

- Figure 8.87 The variation of the recovery contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.88 The variation of the creep contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.89 The variation of the recovery contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.90 The variation of the creep contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, calculated using constant volume assumptions.
- Figure 8.91 The variation of the recovery contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, calculated using constant volume assumption.
- Figure 8.92 The variation of the creep contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, calculated using constant volume assumptions.
- Figure 8.93 The variation of the recovery contraction ratio, $v_{90}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, calculated using constant volume assumptions.
- Figure 8.94 The variation of the creep contraction ratio, $v_{45}(t)$, with time, for D.R. = 2.65, at 0.5% 100 second strain.
- Figure 8.95 The variation of the recovery contraction ratio, $v_{45}(t)$ with time, for D.R. = 2.65, at 0.5% 100 second strain.
- Figure 8.96 The variation of the creep contraction ratio, $v_{45}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.97 The variation of the recovery contraction ratio, $v_{45}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.98 The variation of the calculated creep contraction ratio, $v_{45}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.
- Figure 8.99 The variation of the calculated recovery contraction ratio, $v_{45}(t)$, with time, for different draw ratios, at 0.5% 100 second strain.

- Figure 8.100 The variation of the calculated creep contraction ratio, $\nu_{45}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.101 The variation of the calculated recovery contraction ratio, $\nu_{45}(t)$, with time, for different draw ratios, at 1.0% 100 second strain.
- Figure 8.102 The variation of the creep contraction ratio, $\nu_{45}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.103 The variation of the recovery contraction ratio, $\nu_{45}(t)$, with time, for different draw ratios, at 0.5% 100 second strain, predicted using constant volume assumptions.
- Figure 8.104 The variation of the creep contraction ratio, $\nu_{45}(t)$, with time, for different draw ratios, at 1% 100 second strain, predicted using constant volume assumptions.
- Figure 8.105 The variation of the recovery contraction ratio, $\nu_{45}(t)$, with time, for different draw ratios, at 1.0% 100 second strain, predicted using constant volume assumptions.
- Figure 8.106 The variation of the 100 second creep contraction ratio, $\nu_o(t)$, with 100 second strain, at different draw ratios.
- Figure 8.107 The variation of the 100 second creep contraction ratio, $\nu_{90}(t)$, with 100 second strain, at different draw ratios.
- Figure 8.108 The variation of the 100 second creep contraction ratio, $\nu_{45}(t)$, with 100 second strain, at different draw ratios.

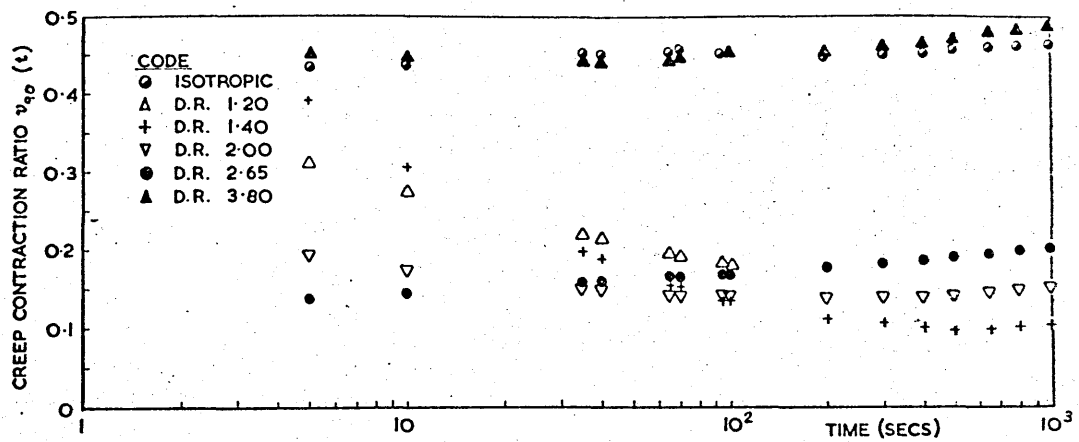


FIG.8.86 THE VARIATION OF THE CREEP CONTRACTION RATIO $v_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN

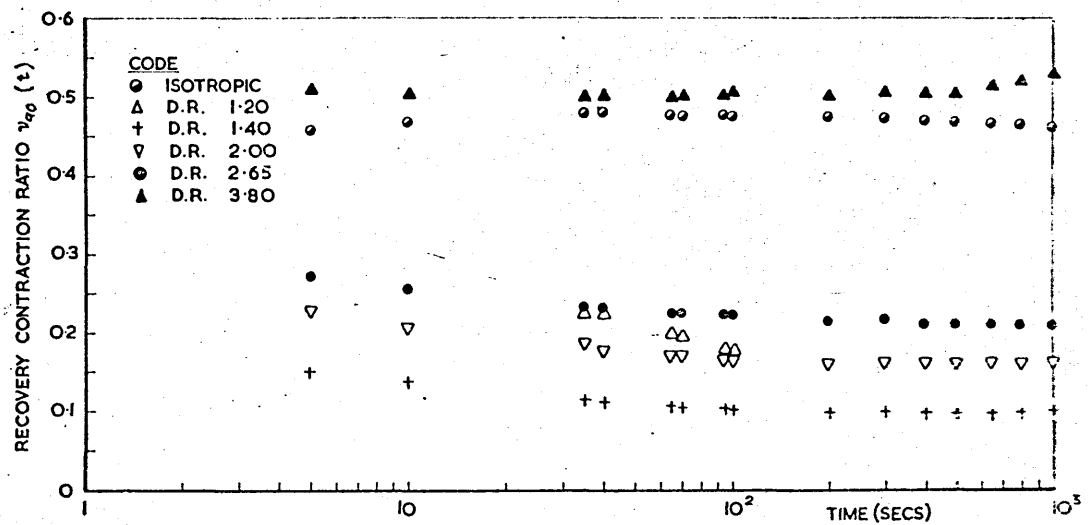


FIG.8.87 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $v_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN.

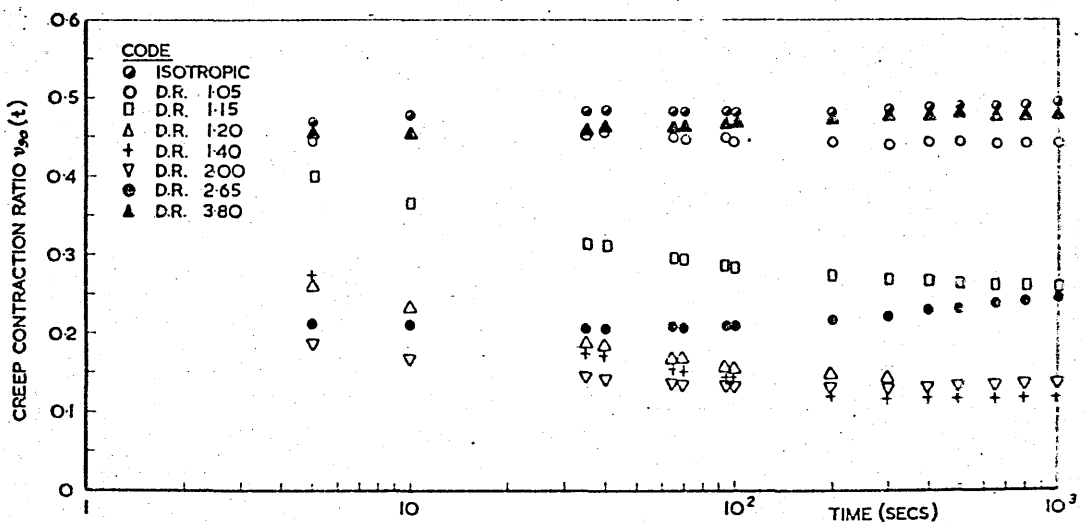


FIG.8.88 THE VARIATION OF THE CREEP CONTRACTION RATIO $v_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1.0% 100 SECOND STRAIN

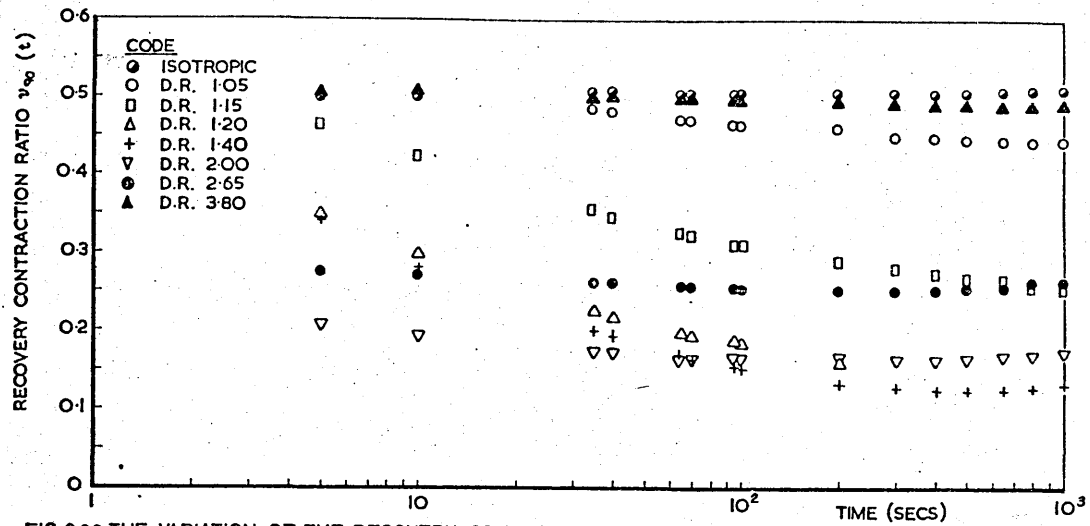


FIG.889 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1.0% 100 SECOND STRAIN

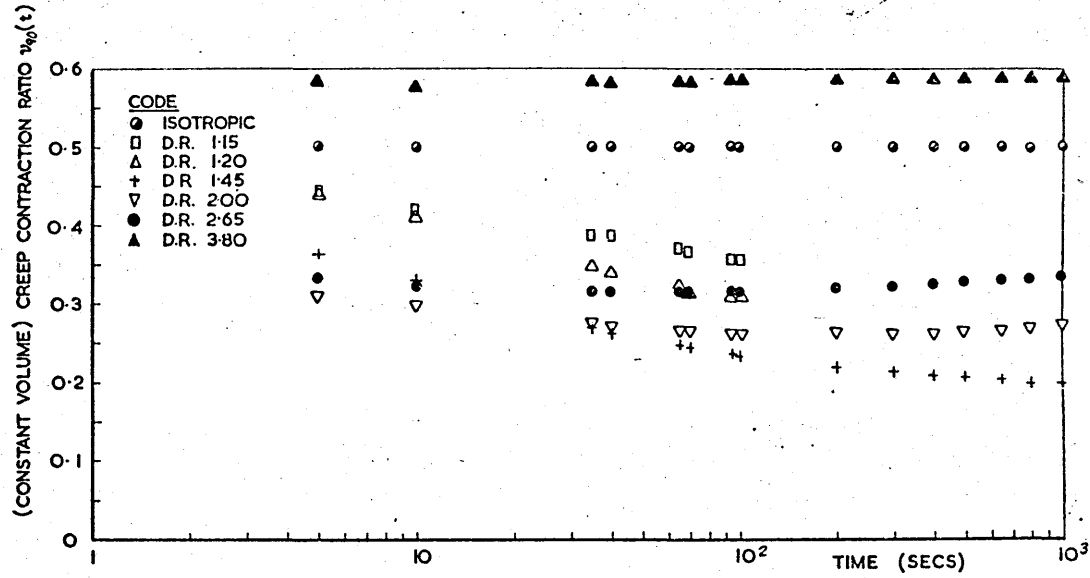


FIG.890 THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN CALCULATED USING CONSTANT VOLUME ASSUMPTIONS

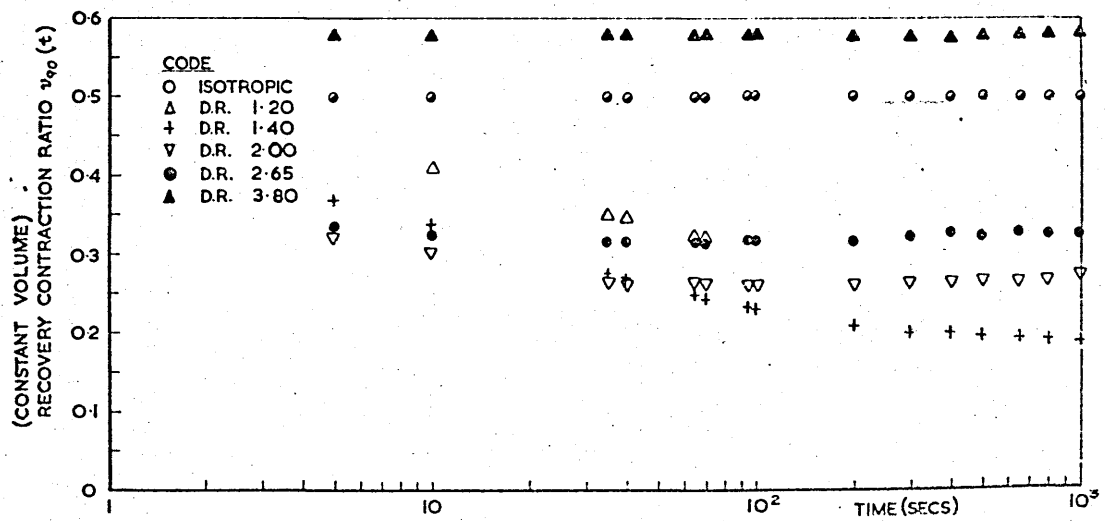


FIG.891 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN CALCULATED USING CONSTANT VOLUME ASSUMPTIONS

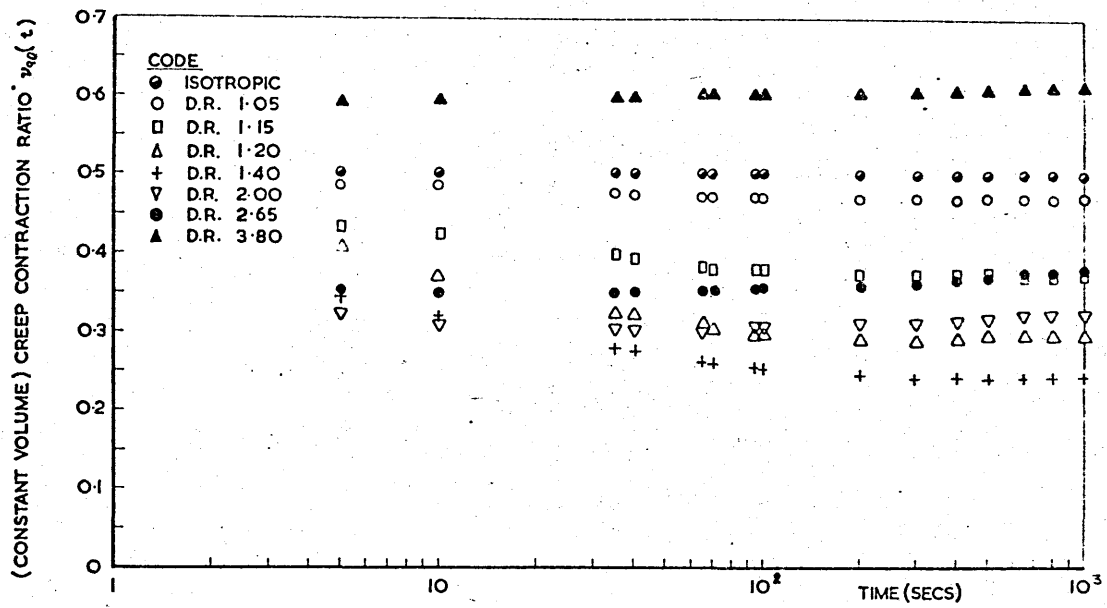


FIG.8.92 THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1.0% 100 SECOND STRAIN CALCULATED USING CONSTANT VOLUME ASSUMPTIONS

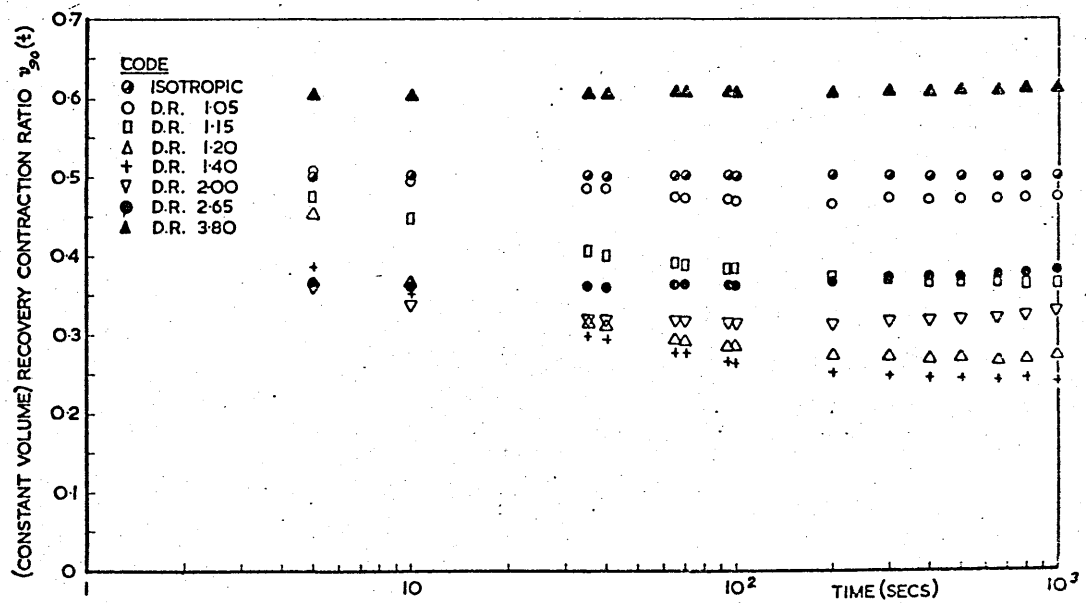


FIG.8.93 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{90}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1.0% 100 SECOND STRAIN CALCULATED USING CONSTANT VOLUME ASSUMPTIONS

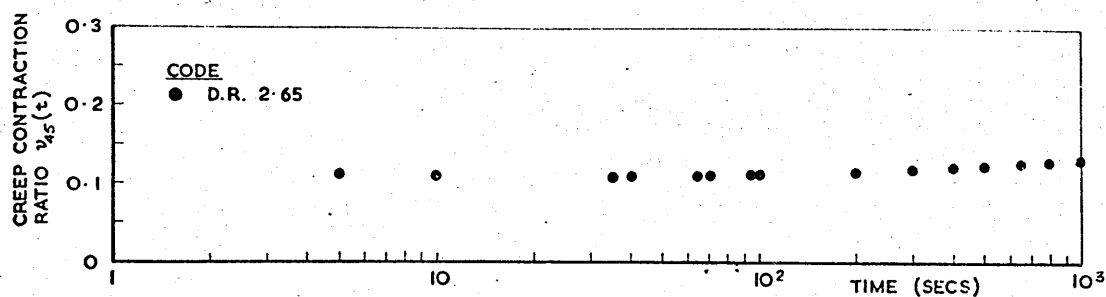


FIG.8.94. THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR D.R. = 2.65 AT 0.5% 100 SECOND STRAIN.

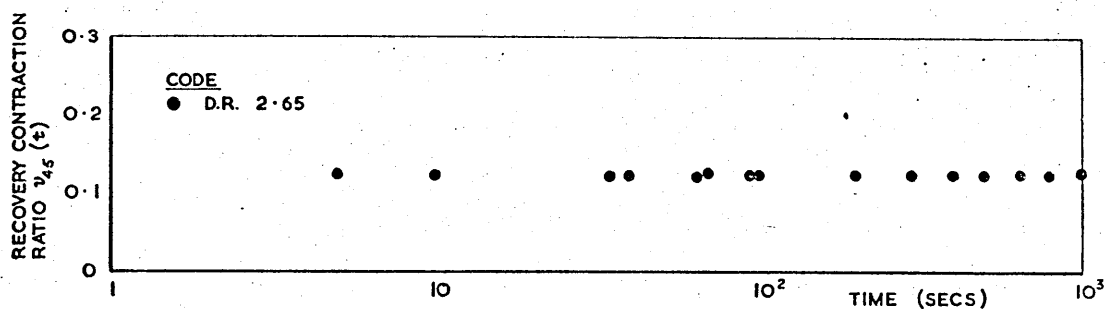


FIG.8.95 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR D.R. 2.65 AT 0.5% 100 SECOND STRAIN.

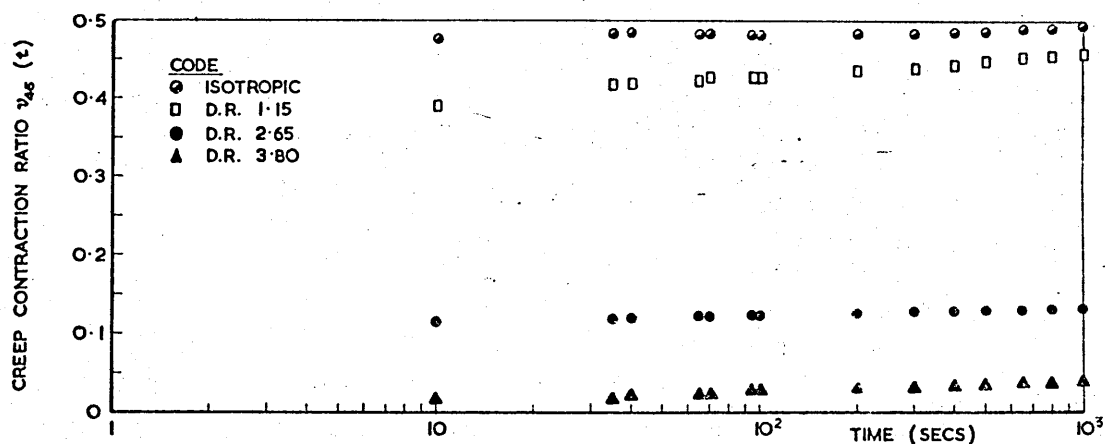


FIG.8.96 THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

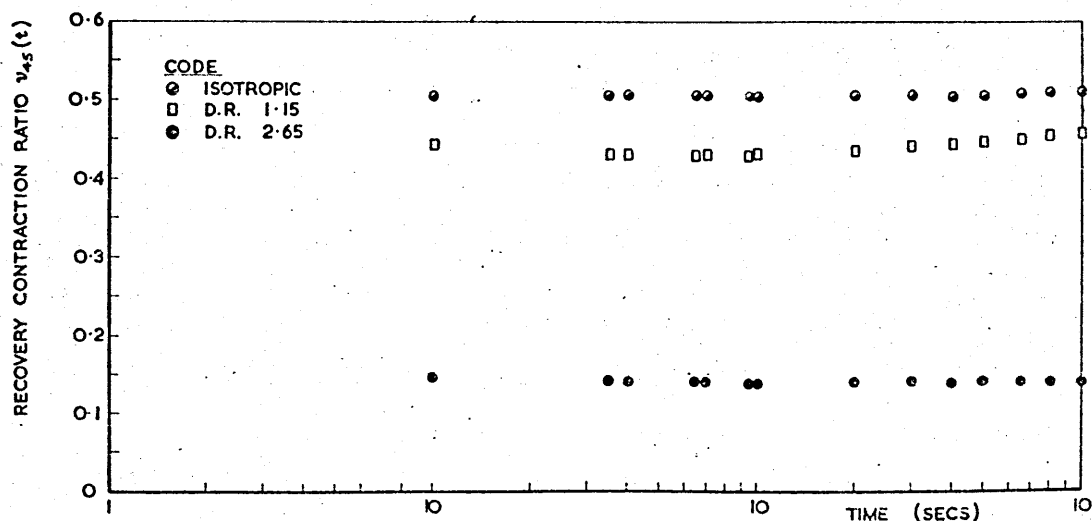


FIG.8.97 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

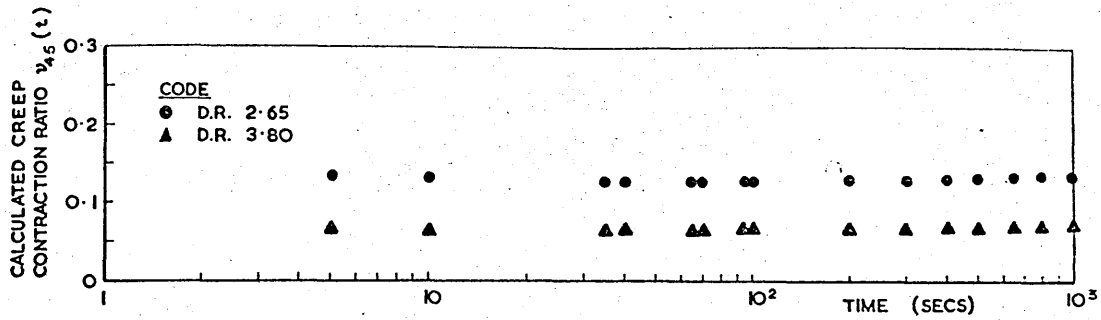


FIG. 8.98 THE VARIATION OF THE CALCULATED CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN.

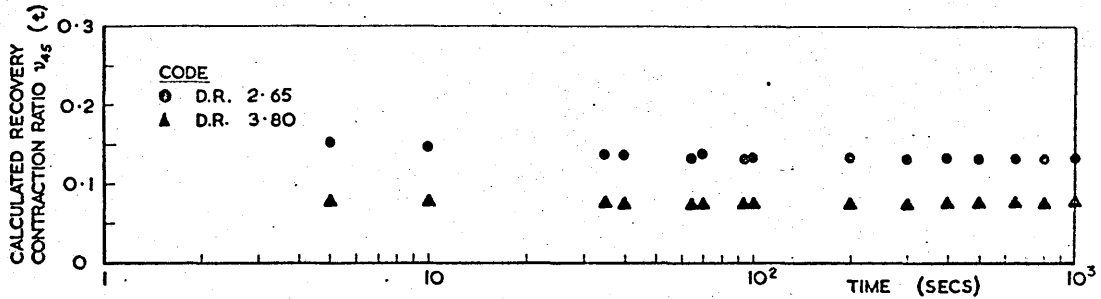


FIG. 8.99 THE VARIATION OF THE CALCULATED RECOVERY CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN

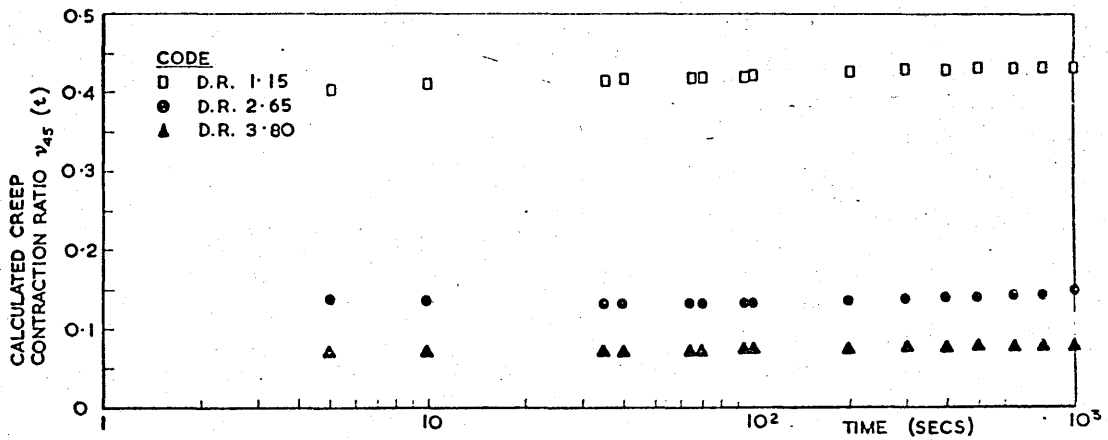


FIG. 8.100 THE VARIATION OF THE CALCULATED CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN

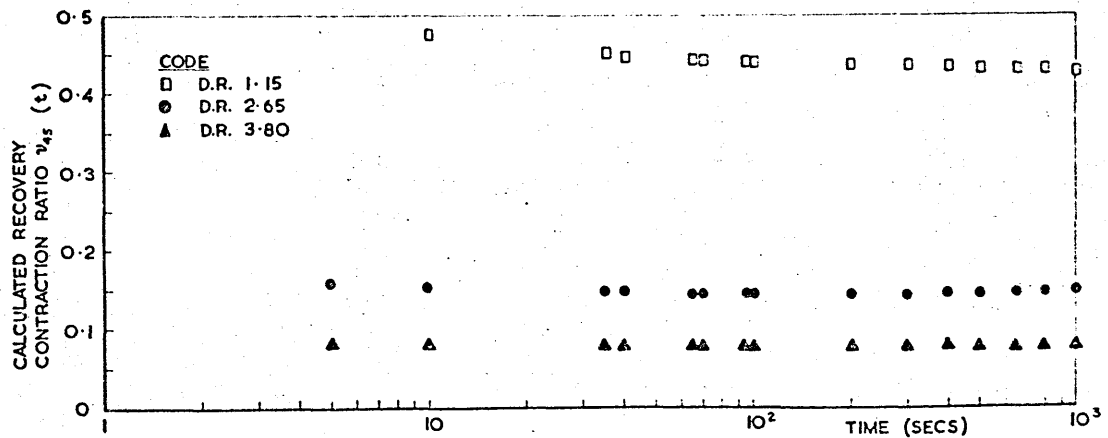


FIG. 8.101 THE VARIATION OF THE CALCULATED RECOVERY CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN.

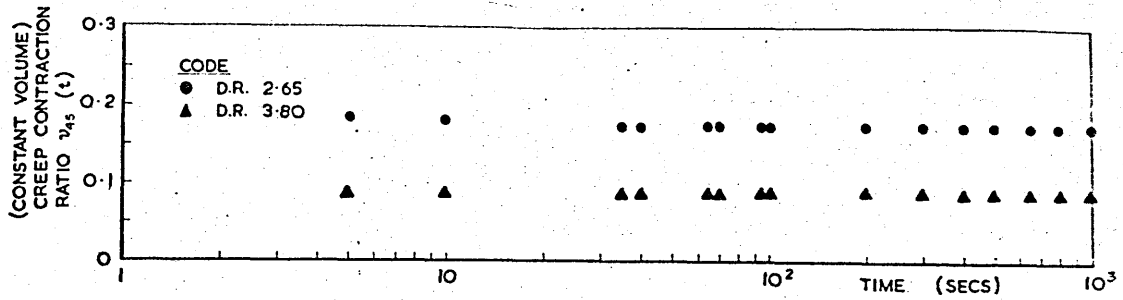


FIG.8102 THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

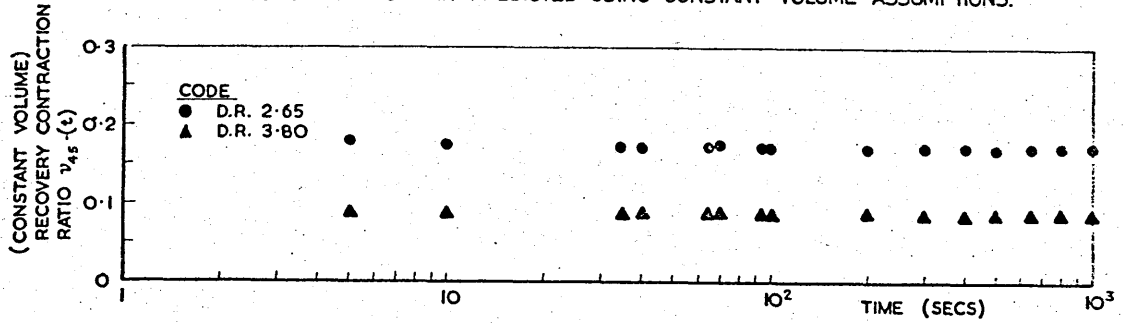


FIG.8103 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 0.5% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

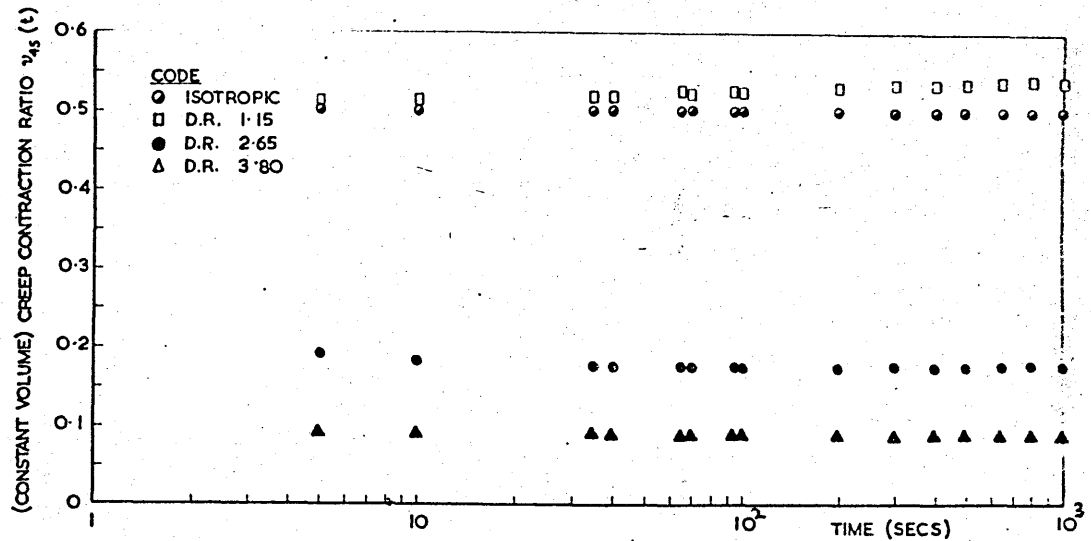


FIG.8104 THE VARIATION OF THE CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

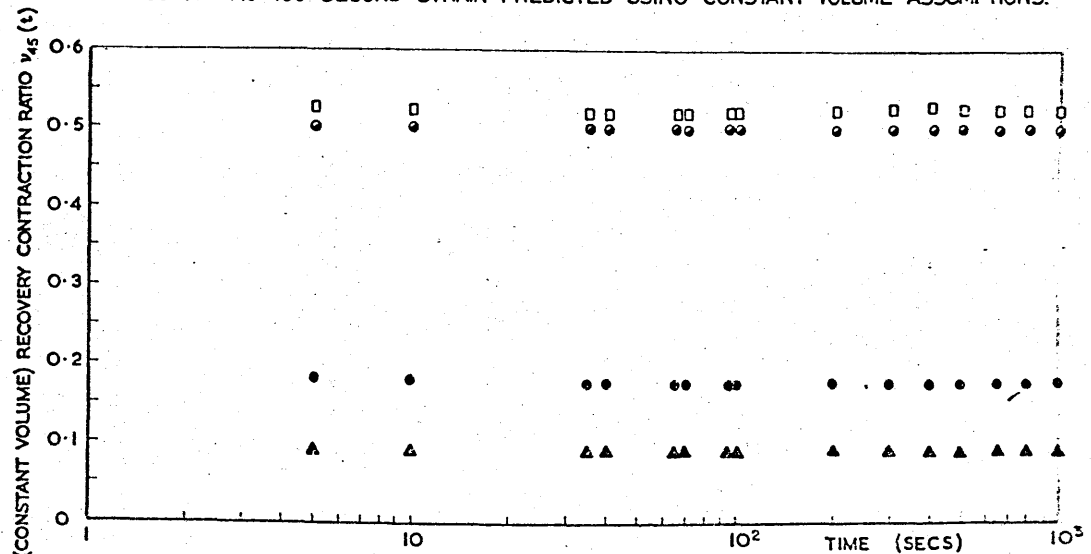


FIG.8105 THE VARIATION OF THE RECOVERY CONTRACTION RATIO $\nu_{45}(t)$ WITH TIME FOR DIFFERENT DRAW RATIOS AT 1% 100 SECOND STRAIN PREDICTED USING CONSTANT VOLUME ASSUMPTIONS.

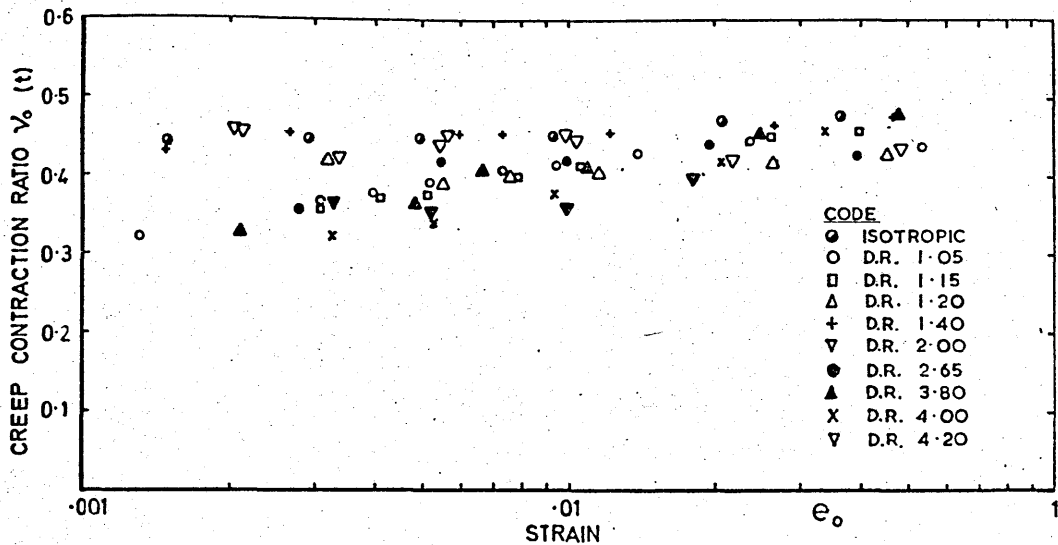


FIG.8.106 THE VARIATION OF THE 100 SECOND CREEP CONTRACTION RATIO, $\nu_0(t)$, WITH 100 SECOND TENSILE STRAIN, $e_0(t)$ FOR DIFFERENT DRAW RATIOS.

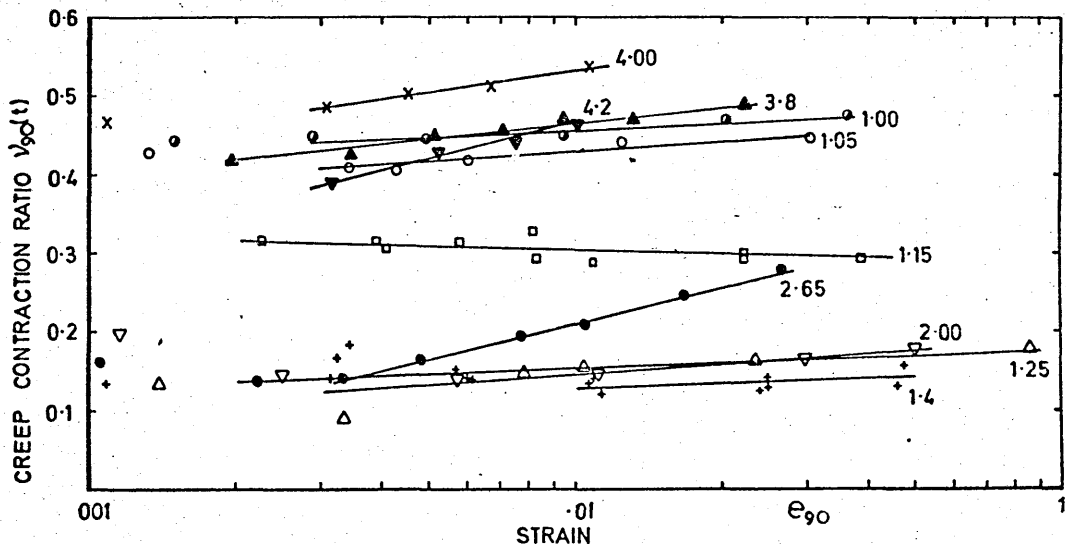


FIG.8.107 THE VARIATION OF THE 100 SECOND CREEP CONTRACTION RATIO, $\nu_{90}(t)$, WITH 100 SECOND TENSILE STRAIN, $e_{90}(t)$ FOR DIFFERENT DRAW RATIOS.

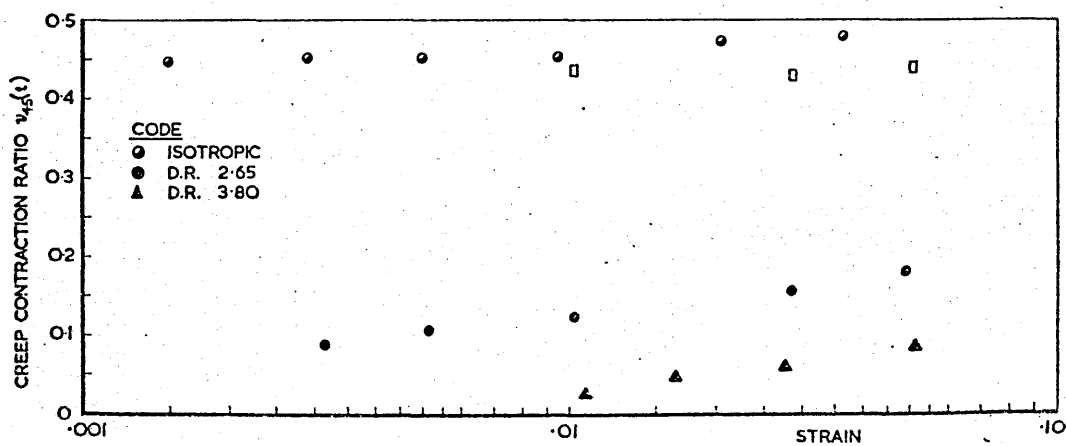


FIG.8.108 THE VARIATION OF THE 100 SECOND CREEP CONTRACTION RATIO $\nu_{45}(t)$ WITH 100 SECOND STRAIN $e_{45}(t)$ FOR DIFFERENT DRAW RATIOS

SECTION 9. DISCUSSION OF RESULTS

9.1 The Mechanisms of Deformation in Oriented Low Density Polyethylen

- 9.1.1 The c-axis shear mechanism
- 9.1.2 The inter-lamellar shear mechanism
- 9.1.3 An anomalous relaxation process in 90° specimens
- 9.1.4 The inter-fibrillar shear mechanisms
- 9.1.5 Interpretation of the non-linearity in terms of structure
- 9.1.6 Interpretation of the volume changes in terms of structure

9.2 Simple Engineering Considerations

- 9.2.1 The applicability of the formalisms of classical elasticity and linear viscoelasticity theory to non-linear anisotropic visco-elastic continua.
- 9.2.2 The constant volume assumption
- 9.2.3 Other considerations with anisotropic materials

The results and calculations which have been presented earlier in Sections 7 and 8 are discussed in the following section in terms of current structural knowledge, (Section 9.1), and the simple engineering implications of the results are presented in Section 9.2.

9.1 THE MECHANISMS OF DEFORMATION IN ORIENTED L.D.P.E.

The results and computed parameters presented in Sections 7 and 8 are interpreted in terms of current structural knowledge and a simple model is presented which serves to interpret the mechanical properties reported in this thesis.

Isotropic L.D.P.E. exhibits two prominent transitions in the mechanical and dielectric loss spectra; a β transition below room temperature, which is attributed to the amorphous content, and an α transition at room temperature attributed to an intra-crystalline mechanism. (Section 4).

At low draw ratios the initial spherulitic structure is oriented and the c-axes have a cone distribution about the draw direction with a cone-half-angle of approximately 40° , and a maximum population density of c-axes about this angle (Stein and Norris, 1956, Keller, 1955, Keller et al, 1968). The α and β loss transitions are still apparent but are now anisotropic. The α peak has an anisotropy $\tan \delta_0 > \tan \delta_{45} > \tan \delta_{90}$ and is consistent with an easy-shear deformation on planes parallel or perpendicular to the c-axes (Section 9.1.1). The anisotropy of the β peak is shown to be attributable to an inter-lamellar shear mechanism (Section 9.1.2). A third mechanism has been discovered in specimens cut at 90° to the draw direction at low draw ratios and is attributed to a relaxation process occurring on planes in the draw direction, but at an angle to the applied stress direction, especially those perpendicular to the applied stress direction (Section 9.1.3). All three mechanisms have been shown to be recoverable.

At intermediate draw ratios the spherulitic superstructure is broken down and the lamellae decrease in size and perfection and the β peak is less prominent and merges with the dominant α peak which moves to shorter times. Both peaks retain the above anisotropy.

In the highly drawn material the c-axes are oriented in the draw direction and current models proposed in the literature

envisage a fibrillar structure with fragments of the initial lamellae oriented about the draw direction. The material exhibits a single prominent transition with anisotropy of mechanical loss factor $\tan \delta_{45} > \tan \delta_0 > \tan \delta_{90}$ and is consistent with an easy-shear mechanism parallel to the c-axes which may be inter-fibrillar shear, (Section 9.1.4.). This mechanism has been shown to be fully recoverable over the range of strains and times investigated.

The above mechanisms have been successfully invoked to explain the variations of non-linearity with draw-ratio and angle, (Section 9.1.5), and the volume changes occurring during deformation (Section 9.1.6).

Individual features of the results will now be discussed and evidence for the above hypotheses will be presented.

9.1.1 The α Peak and the C-Axis Shear Mechanism

Analysis of the time-dependent behaviour of the compliance matrix, $S_{ij}(t)$, for uniaxially cold-drawn L.D.P.E., and studies of the temperature dependence of the mechanical energy losses have identified the α transition as an easy-shear process on planes parallel or perpendicular to the c-axes.

The rate of change of compliance with logarithmic time, $\frac{d S_{ij}(t)}{d \log(t)}$, is the first approximation to the retardation spectra

of a linear visco-elastic material and indicates the presence of the transitions on the time axis at constant temperature. The transitions may also be identified using dynamic test techniques at constant frequency and determining the change of the mechanical loss factor, $\tan \delta$, with temperature. By invoking the equivalence of time and temperature the two sets of data may be compared and are seen to show similarities in trend with draw ratio. The time-dependence of, $\frac{d S_{ij}(t)}{d \log t}$, for all five compliance parameters

is shown in Figures 8.1 to 8.7. The mechanical loss factor, $\tan \delta$, measured on the Rheovibron, using specimens cut at 0° , 90° , and 45° to the draw direction, at selected draw ratios, is shown in Figures 8.8 to 8.10.

The isotropic mechanical loss peak of L.D.P.E. shows the α transition at room temperature and above. At low draw ratios, up to D.R. 2.0, the α peak is still present at room temperature and exhibits an anisotropy $\tan \delta_0 > \tan \delta_{45} > \tan \delta_{90}$.

A corresponding behaviour is observed in the time-dependent behaviour of the compliance parameters at room temperature. The change of creep rate with time for the compliances of specimens cut at 0° and 90° to the draw direction, viz. $\frac{d S_{33}(t)}{d \log t}$, and

$\frac{d S_{22}(t)}{d \log t}$ respectively, over a range of draw ratios are shown in Figure 8.1 and 8.2. The peak height and the anisotropy of the peak heights increases with increasing draw ratio up to D.R. 1.25, and thereafter the peak height decreases in magnitude and shifts to shorter times. At low draw ratios the anisotropy of the peak heights, viz. $0^\circ > 90^\circ \gg 45^\circ$, is similar to the mechanical loss peaks

The anisotropy in creep rates and $\tan \delta$ data for the low draw ratio material, and the position of the peaks on the time and temperature axes, are consistent with an easy-shear deformation on planes parallel or perpendicular to the c-axes, which may be identified with the α transition. At low draw ratios the c-axes are oriented in a cone distribution about the draw direction with a maximum c-axis population density at around 40° . As the draw ratio increases from isotropic to low draw ratios, (approximately D.R. 1.4), the angular spread of the c-axes about 40° is reduced. (Section 3). Thus, for a 0° specimen, the applied uniaxial stress has a large resolved shear stress along the c-axes which facilitates an easy shear process either parallel or perpendicular to the c-axes. The increased draw ratio from D.R. 1.05 to D.R. 1.25 orients more c-axes in a more favourable position for easy shear and consequently increases the creep rate and the ease of deformation. This is consistent with the increase in peak height of the $S_{ij}(t)$ data over this draw ratio range. A further increase in draw ratio to D.R. 2.00 decreases the cone angle and orients the c-axes towards the draw direction; the c-axes are at a less favourable angle for easy shear and the creep rate is decreased and the peak is seen to move to shorter times.

For 90° specimens, the c-axes are less favourably oriented for easy shear due to the cone distribution about the draw direction. Hence the c-axis shear process is less dominant, accounting for the marked anisotropy of creep rate and mechanical loss factor of the 0° and 90° specimens. The 45° specimens are affected in a similar way resulting in an anisotropy of creep rate, $\dot{S}_{33}(t) > \dot{S}_{22}(t) \gg \left(\frac{1}{E_{45}(t)} \right)$, and loss factor $\tan \delta_0 > \tan \delta_{45} > \tan \delta_{90}$. Furthermore, as the cone angle at low draw ratios is nominally constant the creep rates of the 45° specimens are similar. (Figure 8.3).

It is concluded that the α transition at low draw ratios is a manifestation of an easy-shear mechanism parallel or perpendicular to the c-axes, and that as the isotropic α peak is attributed to the crystalline regions it is postulated that the mechanism is an intra-crystalline c-axis shear or slip.

The variation of $\dot{S}_{13}(t)$ with draw ratio and time, Figure 8.4 is a further manifestation of the c-axes shear process. As the cone distribution develops and the c-axes are ordered about the cone-angle the creep rate and peak height increase in a similar fashion to the longitudinal compliances. At intermediate and high draw ratios the peak decreases and moves to shorter times. The variation of $\dot{S}_{12}(t)$, with draw ratio and time is shown in Figure 8.5 and is discussed in Section 9.1.3.

A similar analysis of the shear creep compliances, $S_{44}(t)$, and $S_{66}(t)$, is shown in Figures 8.6 and 8.7. The shear compliances exhibit the highest peak heights, which are again anisotropic. At low draw ratios the deformation mechanisms are not known. The applied shear stresses are not suitably distributed to facilitate the c-axes shear mechanism and other mechanisms must be dominant. From intermediate to high draw ratios the high creep rates in the short time end of the $\dot{S}_{44}$ spectrum are a manifestation of the loss peak associated with the inter-fibrillar shear mechanism in the 1, 3 and 2,3 planes. The compliance, S_{66} , governs laminar shear in the 1,2 plane, the plane of isotropy, and is dominated by other mechanisms. The anisotropy of the creep rates at high draw ratios is a manifestation of the above different mechanisms.

9.1.2 The β Peak and the Inter-Lamellar Shear Mechanism

The instantaneous values of the compliance parameters at room temperature are affected by those transitions with relaxation times less than experimental times. An insight into the short-time behaviour can be gained by studying the transitions occurring below room temperature, the β peaks, and assuming the equivalence of time and temperature. The anisotropy of the β peaks has been examined, together with the instantaneous compliance parameters at room temperature, over a range of draw ratios. It is concluded that the β transition is a manifestation of an inter-lamellar shear mechanism.

The variation of the loss factor with temperature at D.R. 1.4 and D.R. 2.00 is presented in Figures 8.9 and 8.10, and the variation with draw ratio of the instantaneous compliance parameters, in the form of 1% 100 second isochronous values, is shown in Figures 8.11 to 8.15. The anisotropy of the β peak at

D.R. 1.4 is $\tan\delta_{45} \gg \tan\delta_{90} > \tan\delta_0$, and with an increase of the orientation to D.R. 2.0, the anisotropy of the peak is difficult to determine, and at higher draw ratios is no longer apparent, Figure 8.8. With increase in the draw ratio the α peak shifts to lower temperatures and the two peaks merge and result in a single loss peak at high draw ratios. At low draw ratios the compliance parameters increase with increasing draw ratio with the exception of the 90° contraction compliance, $S_{12}(t)$. Further orientation causes a reversal in this trend with the exception of $S_{12}(t)$, and the 45° longitudinal compliance, $\frac{1}{E_{45}}(t)$. The anisotropy of the moduli at low draw ratios is $E_{90} > E_{45} > E_0$, and is similar to the anisotropy of the loss factors.

At low draw ratios these results have been interpreted in terms of an inter-lamellar shear process. Isotropic L.D.P.E. has a spherulitic superstructure composed of crystalline lamellae regions separated by an amorphous inter-phase. The crystallographic c-axes are, in general, perpendicular to the lamellae surfaces, (Section 3). Detailed studies on the mechanical and dielectric loss peaks attribute the β transition to the amorphous regions, (Section 4). On uniaxially drawing to low draw ratios, it may be argued that the spherulitic structure is retained, but the lamellae which dominate the deformation are oriented in a cone distribution about the draw direction, (Section 3.). At low draw ratios the β peak is anisotropic with $\tan\delta_{90} > \tan\delta_{45} > \tan\delta_0$ and is manifest in the anisotropy of the instantaneous values of the moduli at room temperature. Due to the cone distribution of lamellae about the draw direction the 0° specimens have a high resolved shear stress on the lamellae planes and an inter-lamellar shear process is readily activated. However, for 90° and 45° specimens only a section of the cone distribution is favourably oriented for inter-lamellar shear and other mechanisms are activated on planes perpendicular to the applied stress, and the resultant deformation is due to a combination of inter-lamellar shear and other mechanisms. The dominance of the inter-lamellar shear process on all cone sections containing the draw direction in the 0° specimens leads to the anisotropy of moduli $E_{90} > E_{45} > E_0$. On increasing the draw ratio from isotropic to draw ratio 1.4 the cone develops and the lamellae take up a more ordered configuration thus facilitating the shear mechanism; consequently those compliance parameters affected by the process increase with increasing draw ratio at low draw ratios. The intermediate draw ratio material has a complicated structure and is prepared by necking, which destroys the original spherulitic superstructure and large lamellae fibrils and orients the amorphous regions. The resultant structure has not been identified or reported in the literature. The available information identifies a rapid orientation of c-axes towards the draw direction again with a cone distribution with a cone half angle

of around 10° . The decrease prominence of the β peak is due to the orientation and the diminution of the number and size of the remaining lamellae.

The other mechanisms invoked above, for the 90° and 45° specimens, may account for the difference in anisotropy of the compliances - $(S_{33} > \frac{1}{E_{45}} > S_{22})$ - & the loss factor, $\tan \delta_{90} > \tan \delta_{45} > \tan \delta_0$.

These unidentified mechanisms may have loss factors greater than that attributed to the inter-lamellar shear process, and the experimentally measured loss factors $\tan \delta_{90}$ and $\tan \delta_{45}$ are a result of the contributions of both mechanisms. However, $\tan \delta_0$, is due primarily to inter-lamellar shear and is consequently lower valued. Increasing the draw ratio from D.R. 1.4 to D.R. 2.0 decreases the cone angle and the perfection of the lamellae, and orients the lamellae towards the draw direction, consequently the inter-lamellar shear process becomes less dominant at 0° and other mechanisms are activated resulting in an increase in $\tan \delta_0$ to the values measured for $\tan \delta_{45}$ and $\tan \delta_{90}$. The eventual disappearance of the β peak is due to the break-down of the original lamellae structure.

It is concluded that the β transition in L.D.P.E. is due to an inter-lamellar shear process.

The isochronous contraction compliance, $S_{13}(t)$, exhibits a similar behaviour with draw ratio, at low draw ratios, as the longitudinal compliances (Fig. 8.12). The contraction compliance shows a rapid increase with draw ratio as the cone distribution of lamellae develops and the lamellae become more favourably oriented for easy-shear. The variation of $S_{13}(t)$, with draw ratio, at low draw ratios, is consistent with an inter-lamellar shear process.

The contraction behaviour of the 90° specimens at low draw ratios is contrary to the other compliance parameters. At draw ratio, D.R. 1.05, the contraction compliance, $S_{12}(t)$, increases slightly above the isotropic value. However, with increasing draw ratio, as the cone distribution develops, the value falls rapidly with draw ratio, and cannot be reconciled with the inter-lamellar shear process. Another mechanism is proposed in Section 9.1.3.

9.1.3 An Anomalous Relaxation Process in 90° Specimens

Contraction studies on 90° specimens at low draw ratios indicated the anomalous behaviour of $S_{12}(t)$. Analysis of the instantaneous and time-dependent values of $S_{12}(t)$, over a range of draw ratios suggests that the behaviour is controlled by a relaxation process on planes parallel to the draw direction and nominally at 90° to the applied stress direction.

At low draw ratios, the increase with draw ratio of the 100 second compliance parameters, $1/E_0$, $1/E_{90}$, $1/E_{45}$, and S_{13} , has been explained in terms of the inter-lamellar shear process. The c-axis shear process explains the increasing creep rate with draw ratio, up to D.R. 1.25. However, S_{12} , (and S_{66}), decrease with increasing draw ratio and do not exhibit the peak attributed to c-axes shear - except for the apparent peak at D.R. 1.05. At draw ratios greater than D.R. 1.05, the instantaneous contraction is followed by a time-dependent thickening, which increases with increasing draw ratio up to D.R. 1.4. (Figure 7.13 to 7.16). These two factors indicate that the observed behaviour of S_{12} is not attributable to inter-lamellar shear, or c-axes shear, and other processes must be dominant.

A model for the low draw ratio material is shown in Figure 9.1 and is a schematic representation of the cone distribution of c-axes about the draw direction, and the oriented lamellae. It is realized that the proposed model is grossly over-simplified, and that the true aggregation of the structural units in both isotropic and cold drawn L.D.P.E. is extremely complex. (Section 3). In reality a preponderance of c-axes have an angular distribution of around 35° - 40° degrees to the draw direction. Also, there would presumably be a distribution of the angle between the c-axes and the plane of the lamellae, but here it is shown as 90° for clarity. However, as little structural information is available in the literature, and the structure is still ill-defined, it is difficult to propose a more involved model. The simple model will be shown to be adequate to describe the features of the results, but no attempt has been made to reconcile the model with X-ray data, birefringence measurements, and other physical measurements reported in the literature.

For a 90° specimen the observed thickening with time, and the decreasing compliance with draw ratio, at low draw ratios, may be explained using the above model. Consider the application of a uniaxial stress to a 90° specimen. In the plane contained by the draw direction and the applied stress direction there is a large resolved shear stress on lamellar planes, and an instantaneous deformation occurs due to inter-lamellar shear, which is manifest in the instantaneous compliance, $1/E_{90}$. On planes which contain the

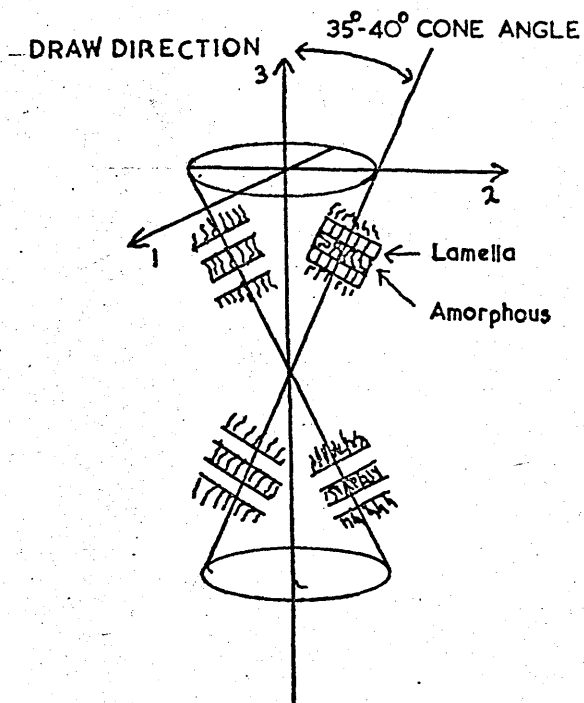


FIGURE 9.1 A Simple Model Showing the Cone Distribution of C-Axes and Lamellae for Low Draw Ratio Cold Drawn L.D.P.E.

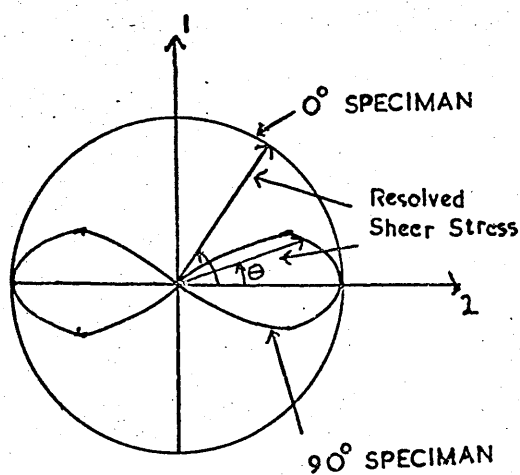


FIGURE 9.2 The Distribution of Resolved Shear Stress on Planes Containing the Lamellae and C-Axes in Low Draw Ratio Cold Drawn L.D.P.E.

draw direction, but are at an angle to the applied stress direction, the resolved shear stress on lamellar planes decreases with increasing angle, and is zero on planes perpendicular to the applied stress. Thus, on planes perpendicular to the applied stress an instantaneous contraction occurs, not due to inter-lamellar shear, but due to another unidentified mechanism - a 90° instantaneous mechanism. On planes at intermediate angles the contraction will be due to a combination of the 90° instantaneous mechanism, and inter-lamellar shear. It has been shown, (Stein and Norris, 1956), that by increasing the draw ratio from D.R. 1.00 to D.R. 2.00 both the crystalline and the amorphous phase become rapidly ordered in a cone distribution about the draw direction. It follows that as the draw ratio increases, and the cone develops and becomes more ordered, that the 90° instantaneous mechanism is impeded as the amorphous regions become more aligned. Consequently, the instantaneous contraction falls rapidly with increasing draw ratio, and is responsible for the sharp fall of the contraction compliance, $S_{12}(t)$, with draw ratio up to draw ratio 1.4.

The time-dependent deformation on a plane defined by the draw direction and the applied stress direction on a 90° specimen is governed by the c-axis shear mechanism, due to the high resolved shear stress in the c-axes direction, and is reflected in an increasing length with time (i.e. an increasing S_{22} with time). At angles away from the applied stress direction, resolved shear stress on planes containing the c-axes decreases, and on planes perpendicular to the applied stress, the resolved shear stress is zero. A relaxation of the instantaneously strained structure occurs and is reflected in the experimentally observed thickening with time.

The contraction studies on 90° specimens have indicated an instantaneous mechanism, and a relaxation mechanism, on planes containing the draw direction and perpendicular to the applied stress direction, but neither mechanism has been identified with a particular structural process. Both mechanisms are recoverable at all draw ratios over the range of experimental times and strains investigated. In the recovery cycle the instantaneous component of the recovery compliance will now make the specimen thickness greater than the original thickness, and the relaxation process is manifest in a time-dependent decrease in thickness to the original thickness.

At strains around 5% 100 second strain, an instantaneous contraction was recorded followed by a time-dependent contraction. However, on removal of the applied stress the instantaneous thickness is greater than the original thickness and relaxes back to the original thickness. It is believed that at high strains the relaxation process is shifted to shorter times and is reflected in the instantaneous deformation, and within experimental time other

mechanisms are activated. This factor would also explain the fact that the creep rate at 0.5% 100 second strain is greater than at 1% 100 second strain. At 1% strain the relaxation process is shifted to shorter times and does not have its full effect within experimental time at this strain level.

9.1.4 The Inter-Fibrillar Shear Mechanism

Deformation studies on highly drawn L.D.P.E. have been reported previously by Darlington and Saunders, (1970), and the anisotropy of the mechanical loss peaks has been characterised in this thesis and by Ward and co-workers, (Stachurski and Ward, 1968, a). Darlington and Saunders have shown that an easy shear mechanism parallel to the c-axes was the dominant deformation mechanism at angles away from the 0° and 90° directions. The work reported here substantiates these findings, and it is postulated that the easy-shear mechanism is an inter-fibrillar shear process.

The highly drawn material exhibits a single transition below room temperature with an anisotropy of mechanical loss factor $\tan \delta_{45} > \tan \delta_0 > \tan \delta_{90}$. (Figure 8.8). Assuming the equivalence of time and temperature this transition will be manifest in the anisotropy of the instantaneous moduli at room temperature. (Figure 8.11). The longitudinal compliance parameters have creep rates which are essentially independent of time, (Section 7), and the contraction compliances are very small with almost zero creep rate. For 45° specimens, the contraction compliance is nearly zero at 1.0% 100 second strain; at 0.5% 100 second strain there was no measurable contraction. (Figure 7.23 to 7.24).

The highly drawn material has the c-axes oriented in the draw direction with fragmentary lamellae blocks ordered about the draw direction, and the angle between the lamellae planes and the c-axes is nominally 50° (McConkey, 1970). The lamellae blocks are ordered in fibrils in the draw direction and the inter-fibrillar material is the highly oriented amorphous phase. (Section 3). The anisotropy of the mechanical loss peaks and the moduli are consistent with an easy shear mechanism parallel to the c-axes. For the 45° specimens there is a high resolved shear stress along the draw direction which facilitates the easy shear mechanism, resulting in a low modulus and an almost zero contraction compliance. The easy shear mechanism may be interpreted either as intra-crystalline c-axes shear, or an inter-fibrillar shear. However, in the highly drawn state the crystalline units are small and do not have a high degree of perfection (Section 3), and consequently an inter-fibrillar shear process is favoured, the relative fibrillar movement occurring via the oriented inter-fibrillar amorphous regions.

For 0° specimens, the molecular chains are aligned along the direction of the applied stress and the high modulus may be associated with a chain extension mechanism.

Deformation studies on 90° specimens of highly drawn material have shown that the specimen necks at 5% strain, and the chains are re-aligned in the direction of applied stress and the lamellae blocks are re-oriented about the new draw direction. Also, it has been observed during the course of this current work that the highly drawn 90° specimens have failed at instantaneous strains of approximately 1% strain. Clearly, the deformation mechanisms at 90° are complicated and may be associated with chain and lamellae re-orientation or other mechanisms associated with yield behaviour. It is not clear without further studies, which, if any, of these mechanisms is operative. However, the mechanisms are fully recoverable within the sensitivity of the apparatus.

9.1.5 Interpretation of the Non-Linearity in Terms of Structure

The deviation from linear deformation behaviour of a continuum may be determined by an examination of the isochronous modulus-strain plot. In this form a linear continuum would be represented by a straight line parallel to the strain axis and, in general, a non-linear material will exhibit a decreasing modulus with increasing strain and the extent of non-linearity is determined by the deviation from a straight line. The variation of the longitudinal moduli, $E_0(t)$, $E_{90}(t)$ and $E_{45}(t)$, with strain are shown in Figure 7.27, 7.29 and 7.31. The following measures of non-linearity have been tabulated. Firstly, the slopes of the lines between the 0.1% and 1.0%, and the 1.0% and 3.0% 100 second strain moduli, have been measured, and secondly, the percentage change between the 1.0% and 0.1% and 3.0% and 1.0% moduli has been calculated. The results of these calculations are shown in Table 9.1. (The contraction compliances have not been treated in this manner, as the low strain values may be subject to errors which would mask the relative values of non-linearity). The isochronous moduli are representative of the instantaneous moduli are governed by the mechanisms occurring at temperatures below room temperature. In the case of the highly drawn material, the structure is highly ordered and the dominant mechanism is inter-fibrillar shear. This mechanism occurs at sub-ambient temperatures, and is manifest in the isochronous longitudinal modulus of the 45° specimens, and imparts linear deformation behaviour up to strains of 3.0%. However, for 0° and 90° specimens other mechanisms are operative and the non-linearity is increased, especially above the 1% strain level. Notably, the 90° specimens show a pronounced non-linearity, since strains at 1% are near the yield strain for the material and many mechanisms are activated which are associated with the re-orientation of the chains and lamellae, and yielding. In the region of strains between 1.0% and 1.5% 100 second strains, 90° specimens of D.R. 4.00 and D.R. 4.20, have been observed to fail in a brittle manner at the high initial rates of loading used in a creep test. However, for an almost similar rate of loading for a 1.0% 100 second strain test, the specimens do not fail, and creep for times greater than 10^5 seconds. At slow rates of loading, using, for example a constant rate of elongation test, a highly drawn 90° specimen will yield in a ductile manner and draw up to 700% elongation. It is

DRAW RATIO	1.0% — 1.0% 0°		1.0% — 3.0% 0°		0.1% — 1.0% 90°		1.0% — 3.0% 90°		0.1% — 1.0% 45°		1.0% — 3.0% 45°	
	A1	B1	A2	B2	A3	B3	A4	B4	A5	B5	A6	B6
ISOTROPIC												
1.05	•37	23.7%	1.85	30.8%	•37	23.7%	1.85	30.8%	•37	23.7%	1.85	30.8%
	•39	29.8%	1.0	20.0%	•30	22.1%	1.1	20.0%	•17	13.2%	1.35	23.8%
1.15	•18	18.2%	•625	15.0%	•30	23%	1.25	24.4%	•2	15.4%	1.0	18.2%
1.25	•15	16.2%	•35	8.6%	•26	20%	1.25	24.0%	•13	11.1%	•8	15.5%
1.40	•18	17.9%	•6	14.0%	•23	15.5%	1.5	24.4%				
2.0	•10	7.8%	•25	4.2%	•20	10.7%	2.2	28.8%				
2.65	•10	5.4%	•5	5.7%	•23	9.5%	3.1	30.5%	•1	11.5%	•45	11.6%
3.8	•20	4.4%	2.0	9.5%	•95	24.8%	5.0	34.5%	•02	3.1%	•2	6.8%
4.0	•25	4.75	2.75	11.5%	•62	15.2%	4.4*	26.2%				
4.2	•25	4.3%	1.5	5.45%	•45	10.1%	3.5*	19.5%				

TABLE 9.1 The Non-Linearity of the Isochronous Moduli

(* Extrapolated Values)

clear that highly drawn 90° specimens are near failure at the 1% strain level, and it is believed that this factor accounts for the observed marked non-linearity.

It is postulated that when the simple inter-fibrillar shear mechanism is operative the material behaves linearly, but when the relatively complicated mechanisms in the 0° and 90° specimens are operative the material behaves non-linearly.

At low draw ratios the structure is rapidly oriented and ordered into a cone distribution about the draw direction and the dominant mechanism below room temperature is then inter-lamellar shear. Consequently, there is a marked decrease in non-linearity from the isotropic case to the low draw ratio 0° specimens. Deformation of the former is influenced by a wide spectrum of possible retardation processes due to the random orientation of the structural units; for the latter a single inter-lamellar shear mechanism is dominant. The 90° specimens exhibit a similar degree of non-linearity to the isotropic case as both the inter-lamellar shear process and a further mechanism on planes perpendicular to the applied stress direction are dominant. With increasing draw ratio from 1.15 to 2.0 it has been shown that this second contributory mechanism is less dominant and consequently the behaviour becomes more linear. The linearity of the 45° specimens is similar to those at 0° in the strain range up to 1%. However, thereafter the 45° specimens are much more linear.

At intermediate draw ratios all the moduli are relatively linear up to 1%, but little is known about the structure in this region.

At strains greater than 1% it is shown for the low drawn materials that the c-axis shear mechanism is shifted to shorter times (Section 9.1.6), and it may be that the 100 second modulus at high strains is a manifestation of the inter-lamellar shear process and a contribution from the c-axis shear process, and would thus account for the high non-linearity at strains greater than 1%. At these high strains other mechanisms may also be operative.

The non-linearity of the deformation mechanisms occurring within experimental time have been examined by comparing the shapes of the compliance - time curves at 0.5% and 1.0% 100 second strain levels. The compliance-time curves for a linear

deformation mechanism would be similar in shape, and non-linearity is manifest in diverging or converging time-dependent compliances. In all cases both creep and recovery compliances have been examined at the two strain levels which enables the following comparisons. Firstly, a comparison between the 0.5% and 1.0% creep compliance curves, and the 0.5% and 1.0% recovery compliance curves, to estimate the extent of the linearity of the time dependent deformation mechanisms. Secondly, a comparison between creep and recovery compliances at the 0.5% strain level, and again at the 1.0% strain level to confirm, or otherwise, the effect of the instantaneous deformation mechanisms. The details of the comparisons are presented in Figure 8.17 to 8.32 and are summarized in Table 9.2. The columns labelled 'A' indicate which strain level has the greater creep rate, if any, and column B indicates whether the recovery compliance is greater than or equal to the creep compliance at short times. (At times approaching 10^3 seconds the recovery compliance was found to equal the creep compliance within experimental error). The figures in brackets indicate the percentage divergence in the shape of the compliance-time curves.

For low draw ratio 0° specimens it may be seen that the c-axis shear mechanism is non-linear. The compliance-time curves at the 0.5% and 1.0% strain levels converge; the 0.5% compliance creeps faster than that at the 1.0% level for both the longitudinal compliance, $S_{33}(t)$, - column A₁ - and the contraction compliance, $S_{13}(t)$, - column A₄. However, both 90° and 45° specimens show similarity of time-dependence of the longitudinal compliances even though this involves deformation perpendicular to the cone axis where more than one process is operative. The time dependent non-linearity of the 0° specimens is attributed to a shift in the c-axes peak to shorter times at the higher stress levels. (Section 9.1.6). The creep rate at 0.5% 100 second strain was greater than that at the 1.0%, 2.0% or 4.5% strain level. It is possible that the c-axis shear is still dominant, but at high stress levels the peak may shift to shorter times, and the retardation times associated with the short time end of the c-axis retardation spectrum no longer contributes to the time dependent behaviour in our experimental time and temperature region. Consequently, the creep rate would decrease. The 90° and 45° specimens should exhibit a similar non-linear effect. However, it is believed that the two time-dependent processes operative in these specimens, have contrary effects and combine to realize a linear time-dependent behaviour.

At high draw ratios the 0° and 45° specimens show a similarity of time-dependent behaviour at the two strain levels, but the 90° specimens show a divergence of the compliance curves. The former specimens have relatively simple linear deformation mechanisms. However, the 90° specimens are near yield point and many mechanisms may be operative.

DRAW RATIO	S33 (0°)		S22 (90°)		1/E45 (45°)		S13 (0°)		S22 (90°)		$\left(\frac{\Delta\epsilon/\epsilon}{\sigma}\right)_{45^\circ}$	
	A1	B1	A2	B2	A3	B3	A4	B4	A5	B5	A6	B6
ISO	0.5 > 1.0 (2.0%)	Rec > Creep (2.5%)										
1.05												
1.15	0.5 > 1.0 (6.5%)	Rec > Creep (3.5%)	0.5 = 1.0	Rec > Creep (10%)	0.5 = 1.0	Rec > Creep (6%)		Rec > Creep	-	Rec > Creep		
1.25	0.5 > 1.0 (7%)	Rec > Creep (1.5%)	0.5 = 1.0	Rec > Creep (1% → 2%)	0.5 = 1.0	Rec > Creep (2%)	0.5 > 1.0 (16%)	Rec > Creep (15%)				
1.40	0.5 > 1.0 (8%)	Rec = Creep	0.5 = 1.0	Rec > Creep (7%)			0.5 > 1.0 (15%)	Rec > Creep (12%)	0.5 > 1.0	Rec > Creep		
2.00	0.5 > 1.0 (15%)	Rec = Creep	1.0 > 0.5 (10%)	Rec > Creep (13%)			0.5 = 1.0	Rec > Creep (15%)	0.5 = 1.0	Rec > Creep		
2.65	0.5 = 1.0	Rec = Creep	1.0 > 0.5 (33%)	Rec > Creep (14%)	0.5 = 1.0	Rec > Creep (10%)	0.5 = 1.0	Rec > Creep (20%)	0.5 = 1.0	Rec > Creep (60%)	0.5 = 1.0	Rec Creep (30)
3.8	0.5 = 1.0	Rec = Creep	1.0 > 0.5 (32%)	Rec > Creep (25%)	0.5 = 1.0	Rec = Creep	0.5 = 1.0	Rec Creep	1.0 > 0.5	Rec > Creep	-	-

TABLE 9.2 The Non-Linearity of the Time Dependent Compliances

A comparison of the short-time isochronous moduli and the time-dependent creep and recovery behaviour, over a range of draw ratios, shows that several forms of non-linearity are encountered.

1. Linear behaviour

The 0° and 45° specimens at D.R. 2.65 and D.R. 3.8 have a linear isochronous behaviour and a linear time-dependent behaviour, and consequently, since the deformation is at all times recoverable, the creep and recovery compliance curves superpose. The creep rates encountered at D.R. 2.65 are greater than those at D.R. 3.8.

2. Pseudo-Linear isochronous and non-linear time-dependent behaviour

The low draw ratio 0° specimens exhibit almost linear short-time isochronous behaviour, but a non-linearity of time-dependence. The creep and recovery curves do not superpose at short times. However, as the time-dependent mechanism is the same at both 0.5% and 1.0% strain levels, and the non-linearity arises only from a shift of the peak to shorter times, the discrepancy between the creep and recovery compliance is only small. The time dependence of the compliance parameters in this case is quite marked.

3. Non-linear isochronous and linear time dependent behaviour

The low draw ratio 90° specimens show a marked non-linearity of the 100 second isochronous moduli due to the two mechanisms manifest in the instantaneous deformation, but a fortuitous linear time dependent behaviour due to the contrary effects of the time-dependent mechanisms. In this case the creep and recovery compliances do not superpose and the discrepancy is much greater than in the case of the 0° specimens, and may be due to the relatively large number of dominant mechanisms involved.

4. Non-linearity of instantaneous and time-dependent behaviour

The isotropic and the 90° specimens at D.R. 3.8 exhibit overall non-linearity. The isotropic has marked time dependence and the highly drawn material shows only a slight variation of compliance with time. In both cases, both the instantaneous moduli, and the time-dependence show non-linear effects. Consequently, the creep and recovery compliances do not superpose at short times. However, the deformation is fully recoverable at longer times.

9.1.6 Structural Interpretation of the Volume Changes

The instantaneous deformation at low draw ratios is attributed to an inter-lamellar shear process and it is shown that the mechanism is associated with large volume changes. In 90° specimens a further mechanism is apparent whose effect on the volume change is small, and it is found that $V_0(t)$ is greater than $V_{90}(t)$, where $V_0(t)$ and $V_{90}(t)$, are the volume compliances for 0° and 90° specimens respectively. (Section 2). At intermediate draw ratios the inter-lamellar shear process is less dominant and the volume compliances decrease, but now $V_{90}(t)$ is greater than $V_0(t)$. At high draw ratios the instantaneous volume changes are small for the mechanisms operative in the 0° , 90° , and 45° specimens. The time dependent deformation mechanisms at low draw ratios are dominated by a c-axis shear process and a relaxation process on planes perpendicular to the applied stress direction in 90° specimens. The c-axis shear is shown to be a constant volume deformation, but in 90° specimens the mechanism is associated with a large time-dependent volume change. At high draw ratios there is little variation of volume with time.

To understand the nature of the volume changes occurring on deformation at low draw ratios it is necessary to consider the distribution of the resolved shear stress components on planes containing the lamellae and the c-axes. (Figure 9.2). For 0° specimens there is a high resolved shear stress on all lamellae and c-axis planes about the cone distribution and thus, the instantaneous and time-dependent volume changes are primarily due to the inter-lamellar shear process, and the c-axis shear mechanism respectively. The mechanisms are activated by the resolved shear stress component of the applied stress. However, for 90° specimens the distribution of the resolved shear stress on the lamellae and c-axes, on planes parallel to the draw direction but at an angle θ to the applied shear direction is shown schematically in Figure 9.2. When $\theta = 0^\circ$ there is a maximum resolved shear stress which falls gradually as θ approaches 90° . Consequently, the instantaneous and time-dependent volume changes are attributed to the inter-lamellar and c-axis shear mechanisms respectively, and also, mechanisms on planes at an angle to the applied stress direction.

Instantaneous Volume Changes

The variation with draw ratio of the instantaneous values of the volume compliance, $V_0(t)$, $V_{90}(t)$, and the bulk modulus, $K(t)$, in the form of 0.5% and 1.0% 100 second strain values are shown in Figures 8.33 and 8.34, and the variation with draw ratio of the measured and calculated - using constant volume assumptions - values of the contraction compliances $S_{13}(t)$, and $S_{12}(t)$, are shown in Figure 8.12. The volume compliances $V_0(t)$, and $V_{90}(t)$, increase

with increasing draw ratio, at low draw ratios, but become more divergent, up to D.R. 1.15, with $V_0(t)$, greater than $V_{90}(t)$. Over the same range of draw ratios - up to D.R. 1.15 - there is a larger discrepancy between the measured and constant volume values of the contraction compliance of 0° specimens, $S_{13}(t)$, than those at 90° , $S_{12}(t)$. Above D.R. 1.25, $V_{90}(t)$, becomes greater than $V_0(t)$, but at high draw ratios the values are inseparable. Also, the measured values of $S_{13}(t)$, are a closer approximation to the constant volume predictions than $S_{12}(t)$. The corollary to the above behaviour is that the bulk modulus falls rapidly with increasing draw ratio, at low draw ratios, and increases with further increase in draw ratio. (Figure 8.34).

The 100 second volume changes are associated with the inter-lamellar shear process, and as the cone distribution of lamellae develops with increasing draw ratio, the volume compliances increase as a result of the more perfect distribution of lamellae about the cone angle. The divergence of the values of $V_0(t)$, and $V_{90}(t)$, arises since at 0° the volume change is due primarily to inter-lamellar shear, but at 90° , $V_{90}(t)$, is associated partially with the inter-lamellar shear, and partially with other mechanisms on planes nominally at 90° to the applied stress direction. It is postulated that at draw ratios up to D.R. 1.15, the contribution to the volume change of these other mechanisms is small. The increasing discrepancy between the measured and constant volume values of the contraction compliance of 0° specimens, $S_{13}(t)$, up to D.R. 1.15, is due to the increasing importance of the inter-lamellar shear process. The relatively small discrepancy in the measured and constant volume values of the contraction compliance at 90° , up to D.R. 1.15, is due to the small contribution to the volume change of the second mechanism. However, at D.R. 1.25, the amorphous and crystalline regions become more oriented and the cone distribution becomes less diffuse, and so the contribution to the volume change of the second mechanism in 90° specimens becomes more dominant and $V_{90}(t) = V_0(t)$. Also, at D.R. 1.25, there is a large discrepancy in the measured and constant volume values of the contraction compliances due to the inter-lamellar shear in 0° specimens, and the combined contribution of the inter-lamellar shear and the second mechanism in 90° specimens. At intermediate draw ratios, D.R. 1.4, D.R. 2.00, and D.R. 2.65, the volume compliances decrease as the inter-lamellar shear process becomes less dominant, but $V_{90}(t)$ is greater than $V_0(t)$, as the second mechanism contributing to the volume change in 90° specimens becomes more dominant. The overall volume change is a maximum around D.R. 1.25 to D.R. 1.4 and is shown as a minimum in bulk modulus $K(t)$. (Figure 8.34).

At high draw ratios the volume change is relatively small, and the volume compliances are similar valued, but the measured contraction compliances still deviate from the constant volume values. At 45° the deformation is dominated by the inter-fibrillar shear process and there is no volume change associated with this mechanism.

The variation of the isochronous volume compliances with strain are more difficult to reconcile, but two types of variation with strain are apparent for the 0° specimens, corresponding to the range of draw ratios above, namely isotropic to D.R. 1.15, and D.R. 1.25 and above. For the range of draw ratios isotropic to D.R. 1.15, $V_0(t)$ decreases with increasing strain up to 2% 100 second strain, and thereafter the volume compliance increases markedly with increasing strain. At higher draw ratios (D.R. 1.25 and above) the volume compliance, $V_0(t)$, is virtually constant with strain. (Figure 8.35). The following tentative explanation is suggested. At low draw ratios, up to 1.15, the cone distribution of lamellae is developing, and there is a wide distribution of lamellae about the cone angle, and the effect of the mechanisms contributing to the volume change is decreased with increasing strain, since the time constant of the instantaneous strain rate is less than the retardation time of the mechanisms. At strains greater than 2% other mechanisms are operative which lead to an increased volume change with strain. At D.R. 1.25 the cone distribution has developed and the structure is more ordered, thus the volume change mechanism is dominated by the inter-lamellar shear process through the whole range of strains, and leads to the virtually linear variation of $V_0(t)$, with strain.

In common with previous analyses of the 90° specimens, (Section 9.1.2 and 9.1.3), the D.R. 1.05 specimens are contrary to the trend of $V_{90}(t)$, with strain, and resembles the 0° specimens. (Figure 8.36). Over the remaining range of D.R.'s up to D.R. 3.8, the volume compliance, $V_{90}(t)$, is approximately independent of strain up to 1% 100 second strain, and thereafter increases rapidly with increasing strain. It is suggested that up to D.R. 1.15 the inter-lamellar shear is dominant, and at higher draw ratios the dominant volume change contribution derives from mechanisms on planes perpendicular to the applied stress direction, and that both mechanisms show linearity of volume compliance with strain up to 1% 100 second strain. The non-linearity arises as other mechanisms are activated at higher strain levels.

The variation of the bulk modulus with strain is a corollary of the behaviour of $V_0(t)$, and $V_{90}(t)$, and exhibits a low value remaining approximately independent of strain (except D.R. 1.05), at low draw ratios, and increases in magnitude and strain dependence with increasing draw ratios. (Figure 8.37).

It is concluded from the above results that in 0° specimens at low draw ratios, the inter-lamellar shear process is the dominant mechanism contributing to the volume changes. For 90° specimens, up to D.R. 1.15, the inter-lamellar shear is the dominant mechanism contributing to the volume change, and the mechanism on planes at 90° to the applied stress direction makes only a small volume contribution. At D.R. 1.25 this second mechanism makes an increasingly dominant contribution to the volume change. At higher draw ratios the influence of the inter-lamellar shear process is diminished and there is a corresponding decrease in the volume compliance. At all draw ratios the deformation is never consistent with a constant volume process, especially at low draw ratios.

Time-Dependent Volume Changes

At low draw ratios the variation of the volume compliance of 0° specimens, $V_0(t)$, with time is a manifestation of the c-axis shear process. However, for 90° specimens the volume changes with time, $V_{90}(t)$, are due to c-axis shear and a relaxation process on planes perpendicular to the applied stress direction. $V_0(t)$, is approximately independent of time, (Figure 8.33 to 8.41), and it is suggested that the c-axis shear process is a constant volume process. Further evidence for this hypothesis is derived from a comparison of the measured contraction compliance, $S_{13}(t)$, and the contraction compliance calculated using constant volume assumptions, $S_{13}(t)_{c.v.}$. It may be seen from Figure 8.77 to 8.81 that at low draw ratios that the time dependence of $S_{13}(t)$, and $S_{13}(t)_{c.v.}$ are similar at 0.5% and 1.0% 100 second strain, and since $S_{13}(t)$, is a manifestation of the c-axis shear mechanism it is concluded that this process is a constant volume deformation. At high strains, 2.6% and 4.6% 100 second strain, at D.R. 1.25 and D.R. 1.4, the measured and calculated contraction compliance, $S_{13}(t)$, are still identical and thus the c-axis shear is still dominant at high strains. However, at draw ratio D.R. 1.05, and D.R. 1.15 there are deviations from the constant volume predictions at high strains and other mechanisms are activated. The variation of the volume compliance, $V_{90}(t)$, with time, is shown in Figures 8.43 to 8.45, and exhibits a marked increase, with time, for the low draw ratio material; again D.R. 1.05 is contrary to the behaviour of the 90° specimens. The increase in volume with time is more apparent as the draw ratio increases from D.R. 1.05 to D.R. 1.4 where the relaxation process is more dominant, (Section 9.1.3, and Figures 8.42 and 8.44). It is concluded that the relaxation process associated with the 90° specimens is not a constant volume process but leads to large volume changes with time. A comparison of the measured contraction compliance, $S_{12}(t)$, and that calculated using constant volume assumptions, $S_{12}(t)_{c.v.}$ support this hypothesis. The time-dependent variation of the two parameters is shown in Figure 8.78, and the corresponding parameters at a given

draw ratio are seen to diverge rapidly, the greatest divergence being at D.R. 1.4.

The variation of the bulk modulus with time is a corollary of the above behaviour, and shows a decrease with time at low draw ratios due to the increase in volume occurring during experimental time. (Figures 8.46 to 8.49).

At high draw ratios the dominant transitions are below room temperature and the volume changes with time are very small or zero.

9.2 SIMPLE ENGINEERING CONSIDERATIONS

In general the conventional thermoplastics manufacturing techniques induce anisotropy of mechanical properties in the moulded article. However, to date, there has been no attempt to fully characterise the mechanical properties of an anisotropic thermoplastic or determine how these properties vary over a range of strains and times with different degrees of anisotropy. In the current study a form of anisotropy has been adopted which is relatively simple to describe and easy to produce over a range of degrees of anisotropy. The different degrees of anisotropy are induced by uniaxially drawing an isotropic blank at room temperature which produces a transversely isotropic symmetry, and the draw ratio is a measure of the anisotropy. Classical elasticity theory - C.E.T. - has been invoked to describe the form of the isochronous compliance matrix relating strain and stress, and the compliance parameters have been measured over a range of strains and times at different draw ratios. The emphasis throughout the experimental measurements on accuracy and reproducibility has achieved a high degree of internal consistency which allows the following analyses.

1. To assess the applicability of the formalisms of classical elasticity and linear visco-elasticity theory to an anisotropic continuum over a range of strains from the pseudo-linear to the non-linear region.
2. To assess the usefulness of the assumption of constant volume deformation in defining and simplifying the matrix of compliances.
3. The contraction data is the most comprehensive obtained over a range of continua and has been used to compute the more familiar creep contraction ratios and has enabled, for the first time, the determination of the bulk modulus of the materials. The effect of orientation on the anisotropy of the material parameters which are more familiar to the engineer are discussed.

It is concluded that over the range of strains and times investigated that the several anisotropic non-linear visco-elastic continua encountered may be described by C.E.T., and may be assumed to be linearly time-dependent with sufficient accuracy for polymer engineering design purposes, and a simple time-addition of compliance parameters suffices to manipulate the inter-relations between the time-dependent material parameters. The constant volume assumption is of limited use to predict the magnitude or time-dependence of the contraction parameters.

The individual points will now be presented and discussed.

9.2.1 The applicability of the Formalisms of Classical Elasticity and Linear Visco Elasticity Theory to Non-Linear Anisotropic Visco-Elastic Continua

For a transversely isotropic continuum C.E.T. shows the following relationships between the measured compliance parameters (see Chapter 2).

$$S_{44} = \frac{4}{E_{45}} - S_{22} - S_{33} - 2 S_{13} \quad 9.1$$

$$\nu_{45} = -\frac{1}{2} (S_{12} + S_{13}) E_{45} \quad 9.2$$

$$\text{and } S_{66} = 2 (S_{11} - S_{12}) \quad 9.3$$

The time-dependent equivalents of the parameters in equations 9.1 to 9.3 have been measured over a range of strains and times, with the exception of S_{44} and S_{66} . The shear compliance, S_{44} , has been measured over a limited range of 100 second isochronous strains up to 0.5% maximum surface shear strain, and the time dependence has been determined only at around 0.15% 100 second strain. Due to experimental difficulties the compliance S_{66} has not been determined directly at all. (See Chapter 2).

The isochronous values of S_{44} at 0.3% 100 second strain have been compared with those calculated from the tensile results at 1.0% 100 second strain using equation 9.1 and the variation of the measured and calculated compliance, $S_{44}(t)$, with draw ratio is shown in Figures 8.13 and 8.14. The agreement between the two sets of data is considered good, since the variations in temperature between experiments, from 20.0°C to 21.5°C, could cause a spread in the compliance values of up to 6% and no correction for temperature variations has been applied. Also, at low draw ratios the principal compliance parameters, S_{22} , S_{33} , and S_{13} , contribute around 25% of the calculated magnitude and thus the value is sensitive to errors contributed from all four compliance parameters. At high draw ratios the contribution from S_{22} , S_{33} , and S_{13} is around 5%. The discrepancy between the values is around 8% at low draw ratios and 2% at high draw ratios.

The variation of the measured and calculated values of the shear compliance, $S_{44}(t)$, with time, at several draw ratios is shown in Figure 7.37 and 7.38 and Figures 8.50 to 8.53 respectively.

The directly measured values were obtained at maximum surface shear strains around 0.15%. The calculated values were obtained from tensile creep curves by substitution of isochronous data into equation 9.1 for each selected creep time, and at each draw ratio the creep data were taken from tests where the 100 second strains were in the region 0.5% and 1.0%. For the low draw ratio material the creep rates of all compliance parameters are relatively high and show a marked anisotropy, but at high draw ratios the creep rates are much lower. However, at all draw ratios the shape of the measured and calculated curves are very similar, and a direct comparison of the time-dependent data, at selected draw ratios, is given in Figures 8.58 to 8.60.

A similar analysis to the one above was adopted for the isochronous and time dependent variations of the creep contraction ratio of a 45° specimen, $\nu_{45}(t)$, with draw ratio. The measurement of lateral contraction involves very small changes in dimensions, typically between 12×10^{-6} and 150×10^{-6} inches at 1% 100 second tensile strain, and it is therefore particularly difficult to check the accuracy of the contraction measurements. However, the internal consistency may be examined using equation 9.2. The isochronous values of the measured and predicted contraction ratio, $\nu_{45}(t)$, are shown in Table 8.1, over a range of strains and draw ratios. The agreement between the directly measured and predicted values is extremely good, as an error in 2×10^{-5} inches would produce a variation in the measured $\nu_{45}(t)$, of 3% at low draw ratios, and 80% at draw ratio D.R. = 3.8, at 1% 100 second strain. The results of the computations of the time dependent variations of the calculated and measured contraction ratio, Figure 8.94 to 8.101, show a remarkable similarity of shape; the main discrepancy is in the magnitude of the sets of data. The fit at low draw ratios is particularly satisfying as the contraction compliances $S_{13}(t)$ and $S_{12}(t)$, have relatively high creep rates and exhibit a marked anisotropy of non-linear behaviour. In contrast, at high draw ratios the creep rates and the magnitude of the contraction compliances is very low and for D.R. 3.8 there was no measureable contraction at 0.5% 100 second strain.

The shear compliance, $S_{66}(t)$, was not measured directly, but the results of the computations to predict the isochronous variation with draw ratio, and the variation with time at different draw ratios are shown in Figure 8.15 and Figures 8.61 to 8.64 respectively.

In a study of highly oriented L.D.P.E. Darlington and Saunders, (1970), predicted the variation of the 1% 100 second isochronous modulus and contraction compliance for specimens cut at different angles to the draw direction using C.E.T., and showed that there was a reasonable agreement between measured and calculated values. However, no time-dependent predictions were reported.

It is concluded from the above sets of data that the formalisms of C.E.T. may be invoked to describe the inter-relationships of the material parameters of a transversely isotropic visco-elastic continuum, and used to predict the creep behaviour in torsion from the creep in uniaxial tension, over a range of strains in both the pseudo-linear and non-linear strain regions

A preliminary attempt has been made to combine the theories of classical elasticity and linear visco-elasticity in an analysis of the recovery compliance data. The Boltzmann superposition principle has been invoked to calculate all the recovery compliances; the recovery shear compliance, $S_{44}(t)$, and the recovery contraction ratio, $\nu_{45}(t)$, obtained directly from the corresponding creep data by the application of the Boltzmann superposition principle, have been compared with those calculated from the recovery compliances $S_{22}(t)$, $S_{33}(t)$, $S_{13}(t)$ and $S_{12}(t)$, using equations 9.1 and 9.2. A good agreement was observed.

The constitutive equation relating strain and stress for a linear visco-elastic material may be written in the form of the Boltzmann superposition principle as follows:-

$$e_i(t) = \int_{\tau = -\infty}^{\tau = +t} S_{ij}(t - \tau) \frac{d\sigma_j}{d\tau} d\tau \quad (i, j = 1 \text{ to } 6) \quad 9.4$$

which reduces to the following for the case of uniaxial and torsional creep and recovery. (See Chapter 2).

$$e_i(t) = S_{ij}(t) \sigma_j^0 \quad 0 < t < t_1 \quad 9.5$$

$$e_i(t) = S_{ij}(t) \sigma_j^0 - S_{ij}(t - t_1) \sigma_j^0 \quad 0 < t_1 < t < \infty \quad 9.6$$

The recovery compliance parameters, $S_{22}(t)$, $S_{33}(t)$, $S_{13}(t)$ and $S_{12}(t)$, have been calculated, using equations 9.5 and 9.6, at the 0.5% and 1.0% 100 second strain levels to examine the usefulness of these equations when combined with C.E.T. in the form of equations 9.1 to 9.3, for the different anisotropy of non-linearities which have been found in the continua studied here. The time dependent data for all the recovery compliance parameters is shown in Section 7. The recovery compliances determined using equation 9.6 have been combined to calculate the recovery shear compliance, $S_{44}(t)$, the recovery contraction compliance, $\nu_{45}(t)$, and the recovery shear compliance, $S_{66}(t)$. The comparison between the recovery

compliances obtained directly from the application of the Boltzmann superposition principle and those computed using Boltzmann and C.E.T. is similar to the comparison made of the corresponding creep data discussed in the first part of this sub-section, and is shown at selected draw ratios in Figure 8.58 to 8.60. Similar comparisons for ν_{45} may be deduced from Figures 8.94 to 8.101. The prediction of the time-dependence of the recovery behaviour is excellent in both cases; the differences in magnitude arise for the same reasons as those observed with the creep data. The recovery shear compliance, $S_{66}(t)$, has been computed for completion and is used to show the similarities between calculated creep and recovery data, and the general applicability of the combination of the Boltzmann superposition principle and C.E.T. over the range of times and strains studied here.

The sets of data in recovery are thus consistent with the conclusions derived from the creep studies, and also demonstrate that C.E.T. may be combined with linear visco-elasticity theory, in the form of the Boltzmann superposition principle, to predict the recovery behaviour of the material parameters of certain linear and non-linear anisotropic visco-elastic continua over the range of strains and times studied here.

9.2.2 The Constant Volume Assumption

A rigorous description of the behaviour of a transversely isotropic continuum requires the knowledge of five independent compliance parameters and previous workers have, in the past, been unable to measure the two contraction compliances. Usually, arbitrary assumptions have been made which allow a first approximation to the contraction compliances without knowing the magnitude of the errors involved. The most common assumption is that the material deforms at constant volume.

When designing with isotropic thermoplastics it is customary to assume either, that the Poisson's ratio, ν , is a time independent constant, or, that the bulk modulus, K , is time independent. A priori, there is no justification to adopt either assumption, however, values of ν or K are required for further calculations and, as satisfactory data is not available to date, this has necessitated an arbitrary assignment of single point values. (The magnitude, strain dependence, and time dependence of the contraction compliances of many isotropic and anisotropic materials have been accumulated in this laboratory by the author and M.W. Darlington, but are unpublished at present). The constant volume assumption, although arbitrary, does specify a value for the Poisson's ratio, which is $\nu = \frac{1}{2}$ for the isotropic case, and which is calculated from the following expressions for the transversely isotropic case:-

$$S_{33} + 2 \cdot S_{13} = 0 \quad 9.7$$

$$\text{and } S_{11} + S_{13} + S_{12} = 0 \quad 9.8$$

which gives the following Poisson's ratios

$$(\nu_o)_{c.v.} = \frac{1}{2} \quad 9.9$$

$$(\nu_{90})_{c.v.} = \left(1 - \frac{S_{33}}{2S_{11}}\right) \quad 9.10$$

where the symbols have the usual meaning discussed in Chapter 2.

Due to the accuracy of the contraction data reported in this study it has been possible to examine the usefulness of the constant volume assumption in determining the magnitude and time dependence of the contraction compliance and the creep contraction ratio - the time dependent analogy of the elastic Poisson's Ratio - at different strain levels for all draw ratios. The constant volume assumption has also been used to calculate the magnitude and time-dependence of $\nu_{45}(t)$, the creep contraction ratio of a 45° specimen, and the shear moduli, $S_{44}(t)$ and $S_{66}(t)$. Using the constant volume assumption the inter-relations between the parameters reduces the equations 9.1 to 9.3 to the following:-

$$(S_{44})_{c.v.} = \frac{4}{E_{45}} - S_{11} \quad 9.11$$

$$(\nu_{45})_{c.v.} = -\frac{1}{2} \left(S_{12 \text{ c.v.}} + S_{13 \text{ c.v.}} \right) E_{45} \quad 9.12$$

$$\text{and } (S_{66})_{c.v.} = 2 (S_{11} - S_{12 \text{ c.v.}}) \quad 9.13$$

The values computed using constant volume assumptions have been compared to the directly measured parameters and those calculated using equations 9.1 to 9.3.

The variation of the isochronous creep contraction compliances, $S_{12}(t)$ and $S_{13}(t)$, and the creep contraction ratios, $\nu_{00}(t)$ and $\nu_{90}(t)$, with draw ratio is shown in Figures 8.12 and 8.16 respectively. The experimentally determined values are shown and the full line represents the values predicted using constant volume assumptions and it is clear that large discrepancies arise between the two values especially at low draw ratios near D.R. 1.25, where differences of around 20% and 100% are observed for the 0° and 90° values respectively. At high draw ratios the differences are approximately 25% in both cases.

The time dependence of the contraction parameters, $S_{12}(t)$, $S_{13}(t)$, $\nu_{00}(t)$, and $\nu_{90}(t)$, determined directly from experimental measurements and calculated from constant volume assumptions are shown in Figures 8.69 to 8.76 and Figures 8.82 to 8.93 at 0.5% and 1.0% 100 second strain levels. For 0° specimens the measured and 'constant volume' time dependences are similar and the differences are within experimental error at all draw ratios. However, the corresponding curves for the low draw ratio 90° specimens show a marked divergence. Direct comparisons of the contraction compliances S_{13} and S_{12} at selected draw ratios for the 0° and 90° specimens are shown in Figure 8.77 to Figure 8.81. The divergence for the 90° specimen at D.R. 1.15 is around 20%, but at D.R. 1.4 the curves diverge by some 100% over the experimental time scale. At high draw ratios the curves are seen to be similar in shape.

It is concluded that, in general, the constant volume assumption, cannot satisfactorily predict the instantaneous nor the time-dependent deformation behaviour of the contraction parameters necessary to describe the transversely isotropic continua used in this study. Only the 0° specimens showed a similarity of time-dependence. The errors involved not only varied with draw ratio and time, but also with the specimen angle, and clearly although the assumption may be satisfactory for one parameter it does not necessarily follow for another.

However, the constant volume assumption should not be discarded altogether, since in most engineering formulae the effect of large errors in the contraction ratio are often minimal in the resultant calculation, and constant volume assumption could be a useful first approximation in these cases. In the event of ν being a dominant factor, of course, the assumption may be unsatisfactory. These points are exemplified by the inter-relations between the material compliance parameters given in equations 9.1 to 9.3 and equations 9.11 to 9.13. In each of these relationships the contraction compliance makes a different contribution to the computed compliance and the effect of substituting the measured value or the constant volume value may be assessed. The computed shear compliance is dominated in equations 9.1 and 9.11 by the compliance, $4/E_{45}$, and the remaining contribution is around 25% at low draw ratios and only 5% at high draw ratios. Thus large errors in the contraction compliance $S_{13}(t)$, have little overall effect, and a comparison of the shear compliance calculated using the experimentally determined contraction compliance, $(S_{44})_{calc.}$, and the shear compliance calculated using constant volume predictions, $(S_{44})_{c.v.}$, does not reflect the large errors inherent in assuming the constant volume compliance, $(S_{13})_{c.v.}$, (See Figures 8.50 to 8.57). The time dependence of $(S_{44})_{calc}$ and $(S_{44})_{c.v.}$ are identical, within experimental error, at all draw ratios since the time dependence of S_{13} and $(S_{13})_{c.v.}$ is similar, and also only makes a small contribution to the total magnitude. Similar conclusions may be derived from the recovery shear compliances $(S_{44})_{calc}$ and $(S_{44})_{c.v.}$, Figures 8.50 to 8.57. The isochronous variation of the two shear compliances, $(S_{44})_{calc}$ and $(S_{44})_{c.v.}$, with draw ratio are shown in Figure 8.14 and at low draw ratios a difference of 3% exists, and at high draw ratios there is only a 1% difference. In the case of the shear compliance, $(S_{66})_{calc}$, calculated using the directly measured contraction compliance, $S_{12}(t)$, and the constant volume predicted value, $(S_{66})_{c.v.}$, the contraction compliance contributes around 10% of the computed value at low draw ratios and around 30% at high draw ratios. At low draw ratios the differences of 100% in the measured and constant volume contraction compliances S_{12} and $(S_{12})_{c.v.}$ are reflected as a difference of 25% between the isochronous values of $(S_{66})_{calc}$ and $(S_{66})_{c.v.}$. However, at high draw ratios the difference in (S_{12}) and $(S_{12})_{c.v.}$ is around 25% which gives rise to 10% differences on $(S_{66})_{calc}$ and $(S_{66})_{c.v.}$ (Figure 8.15). The time dependence of the 'calculated' and the 'constant volume' shear compliance diverge considerably, the amount of divergence depending on the contribution of the contraction compliance to the magnitude, and the divergence between the measured and constant volume contraction values. At low draw ratios the divergence between $(S_{66})_{c.v.}$ and $(S_{66})_{calc}$ is around 30% over the experimental time scale, falling to a few percent at high draw ratios. In both cases

the constant volume compliance has the highest creep rate, (Figure 8.61 to 8.68). Similar conclusions may be derived by examination of the recovery compliances, (S_{12}) and $(S_{12})_{c.v.}$, and $(S_{66})_{calc}$ and $(S_{66})_{c.v.}$, in Figures 8.73 to 8.76 and 8.61 to 8.68 respectively.

The calculated and constant volume creep contraction ratio, $v_{45}(t)$, are dominated by the two contraction compliances S_{12} and S_{13} (Equations 9.3 and 9.13). It has been shown earlier that there is good agreement between the measured v_{45} and the value calculated using experimentally determined contraction compliances. However, there is a large discrepancy between the calculated and constant volume predicted, $v_{45}(t)$ (Table 8.1). At low draw ratios differences of 25% and 5% were noted between the measured and constant volume values of the compliance $S_{13}(t)$, and $S_{12}(t)$ respectively at D.R. 1.15, and these errors are reflected in a difference of 18% in the calculated and constant volume creep contraction ratio, $v_{45}(t)$. At high draw ratios similar analysis shows a difference of 25% in the calculated and constant volume, $v_{45}(t)$, arising from a 25% discrepancy in the measured and constant volume contraction compliances $S_{13}(t)$ and $S_{12}(t)$. The divergence in the time dependent curves of $v_{45}(t)$, in creep and recovery are difficult to assess and no sensible conclusions may be drawn. (Figure 8.94 to 8.105).

It is concluded that the constant volume values of the contraction compliances and creep contraction ratios differ greatly from the measured values, but may be used as a satisfactory first approximation in engineering design formulae where the contribution of the contraction ratio is not dominant. The use of the constant volume parameters does, however, introduce a safety factor into design calculations as the magnitude and the creep rates of the 'constant volume' compliances are greater than those observed experimentally. These observations apply to both the creep and recovery data over the range of strains and times studied here.

9.2.3 Other Considerations with Anisotropic Materials

In a recent paper Bonin et al, (1969), have attempted to determine the Poisson's ratio of an anisotropic injection moulded rectangular specimen. The specimens were cut from an end-gated A.S.T.M. tensile bar where the direction of flow, and hence the orientation direction, is along the direction of the length of the specimen. Thus the specimens are, to a first approximation, transversely isotropic with the plane of isotropy perpendicular to the direction of the length, with the symmetry direction along the length of the specimen. This symmetry is thus analogous to the cold drawn transversely isotropic materials used in this study. Bonin et al have measured the modulus along the length of the prism and determined the shear modulus from torsion about the axis of the prism, and combined these parameters using isotropic theory to

calculate the 'Poisson's ratio, viz:-

$$\nu = 1 - \frac{E}{2G} \quad 9.14$$

Clearly, this analysis is not correct, and the values of ν that these authors have obtained on injection moulded samples are in doubt as large errors may be introduced. Assuming transverse isotropy the relationship involving the measured parameters is given by equation 9.1, viz:-

$$S_{44} = \frac{4}{E_{45}} - S_{22} - S_{33} - 2 S_{13} \quad 9.15$$

where S_{44} and S_{33} , are the reciprocals of the measured moduli. For the transversely isotropic materials used in this study all the parameters in equation 9.1 have been determined and Table 9.3 shows the difference between the contraction ratio calculated using 9.15, ν_{calc} , and those incorrectly calculated using only the moduli, $(1/S_{44})$ and $(1/S_{33})$, and equation 9.14, ν_{ISO} . The bulk moduli calculated using isotropic theory K_{ISO} , and the correct form of anisotropic theory K_{calc} , are also tabulated.

Clearly, the errors involved using isotropic theory for anisotropic L.D.P.E. are large, and the bulk moduli calculated using isotropic theory are valueless. Some oriented polymers at room temperature do not show a marked anisotropy of the compliance parameters, e.g. Polymethyl methacrylate, P.M.M.A., and polyvinyl chloride, P.V.C., (Darlington, 1969), and the above analysis can give what are apparently sensible Poisson's ratio values. However, the values are not a true measure of the ratio and any similarity between the calculated value and the true value is fortuitous.

The variation of the measured creep and recovery contraction ratios with draw ratio, time, and strain are shown in Figure 8.16, Figures 8.82 to 8.97 and Figures 8.106 to 8.107 respectively.

	D R A W R A T I O		
	1.4	2.0	3.8
$E = \frac{1}{S_{33}}$	0.9	1.27	4.38
$G = \frac{1}{S_{44}}$	0.39	0.278	0.165
ν_{ISO}	.15	1.28	12.3
ν_{CALC}	.45	.42	.41
K_{ISO}	.427	- .27	- .0625
K_{CALC}	2.43	2.32	6.47

TABLE 9.3 Calculation of Creep Contraction Ratios and Bulk Moduli.

SECTION 10. CONCLUSIONS

1. Experimental techniques have been developed for use with a tensile and torsional creep apparatus which have enabled the accurate and reproducible measurement of the time-dependent contraction compliances and contraction ratios of anisotropic polymers, over a wide range of strains, for the first time. The internal consistency of the results has been found to be excellent.

2. The compliance matrix necessary to describe a non-linear transversely-isotropic visco-elastic continuum has been characterised at ten different degrees of anisotropy over a range of strains and times for the first time. Different forms of non-linearity have been identified.

3. Three dominant deformation mechanisms have been discovered at low draw ratios.

a) The instantaneous deformation is dominated by an inter-lamellar shear mechanism which is identified with the β transition in L.D.P.E., and gives rise to large instantaneous volume changes.

b) The time-dependent axial deformation behaviour is dominated by an intra-crystalline c-axis shear mechanism which occurs at constant volume, and is identified with the α transition in L.D.P.E.

c) The time-dependent contraction behaviour of specimens cut at 0° to the draw direction is dominated by the c-axis shear mechanism. However, in specimens cut at 90° to the draw direction a further mechanism has been identified which gives rise to a time-dependent thickening under load and large time-dependent volume increases.

All three mechanisms in low draw ratio materials are reversible over the range of strains and times studied in this thesis.

4. At high draw ratios an inter-fibrillar shear mechanism is dominant in specimens cut at angles away from the 0° and 90° directions. For 0° specimens the chains are aligned along the direction of the applied stress and the deformation mechanism may be associated with a chain extension mechanism. The mechanisms of deformation in 90° specimens are complicated and at high strains may be associated with chain and lamellae re-orientation, and other mechanisms associated with yield behaviour. All the mechanisms

in highly drawn materials are reversible over the range of strains and times studied in this thesis.

5. For uniaxial and torsional creep it was found that the formalisms of classical elasticity theory may be invoked to describe the inter-relationships between the material parameters of a transversely isotropic continuum for strain levels in both the pseudo-linear and non-linear strain regions. Also, classical elasticity theory may be combined with linear visco-elasticity theory, in the form of the Boltzmann superposition principle, to predict the recovery behaviour of the material parameters over the same range of strains.

6. The assumption of constant volume deformation has been used to predict the time dependent behaviour of the contraction compliances and the contraction ratios at all draw ratios. It is concluded that the constant volume assumption cannot satisfactorily predict these parameters, and that the errors vary with draw ratio, time, and specimen angle.

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APPENDIX A.I.

CONVERGENCE OF THE SERIES IN THE EXPRESSION
FOR TORSIONAL RIGIDITY

Consider the series in Equation 2.66 viz:

$$\sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh \left(\frac{2n+1}{2} \right) \frac{a}{b} \quad a > b$$

$$= \tanh \frac{a}{2b} + \sum_{n=1}^{\infty} \frac{1}{(2n+1)^5} \tanh \left(\frac{2n+1}{2} \right) \frac{a}{b}$$

Now
$$\sum_{n=1}^{\infty} \frac{1}{(2n+1)^5} \tanh \left(\frac{2n+1}{2} \right) \frac{a}{b} < \sum_{n=1}^{\infty} \frac{1}{(2n+1)^5} = 0.0046$$

and
$$\tanh \frac{a}{2b} \geq 0.917 \quad \text{since } a > b$$

Thus the first term, $n = 0$, gives the sum to within $\frac{1}{2}$ percent, and for practical purposes, equation 2.66, may be approximated to:-

$$D = G a b^3 \left[\frac{16}{3} - \frac{b}{a} \left(\frac{4}{\pi} \right)^5 \tanh \frac{a}{2b} \right] \quad a > b$$

Similarly the series in equation 2.80 and 2.81 may be approximated as

$$D = \frac{ac^3}{S_{66}} \left[\frac{16}{3} - \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \tanh \frac{a}{2} \frac{c}{a} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \right] \frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \geq 1$$

or
$$D = \frac{ca^3}{S_{44}} \left[\frac{16}{3} - \frac{a}{c} \left(\frac{S_{66}}{S_{44}} \right)^{\frac{1}{2}} \left(\frac{4}{\pi} \right)^5 \tanh \frac{a}{2} \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \right] \frac{c}{a} \left(\frac{S_{44}}{S_{66}} \right)^{\frac{1}{2}} \geq 1$$

The exact values of the series were evaluated by St. Venant and have been reproduced by Hearmon, 1961, and Lekhnitski, 1963.

APPENDIX. A2 CALIBRATION OF THE TORSION PENDULUM AND TORSIONAL
CREEP APPARATUS

A.2.1. Simple Theoretical Considerations

The double inverted torsion pendulum used in the calibration comprises an inertial mass attached to two linear visco-elastic samples, namely, the metal shim and the metal suspension element. If the mass-sample system is deformed at zero time and then released it will return to its equilibrium position by means of free-damped vibrations, which are governed by the equation:-

$$I \frac{d^2 \theta}{dt^2} + \left(\frac{K G_2}{w} + \frac{k g_2}{w} \right) \frac{d \theta}{dt} + (K G_1 + k g_1) \theta = 0 \quad \text{A2.1}$$

where I is the moment of inertia of the system,

G_2 and G_1 are the loss and real modulus of the specimen,

g_2 and g_1 are the loss and real modulus of the suspension element,

K and k are geometric factors,

θ is the angular rotation,

and w is the angular frequency of the oscillations.

A solution of A2.1 which describes free vibrations is of the form:-

$$\theta = \theta_0 \exp. \left(-\frac{\Omega w}{2\bar{\Pi}} \right) t. \cos wt \quad \text{A2.2}$$

Substitution of A2.2 into A 2.1 yields

$$K G_2 + k g_2 = I w^2 \left(\frac{\Omega}{\bar{\Pi}} \right) \quad \text{A2.3}$$

$$\text{and } K G_1 + k g_1 = I w^2 \left[1 + \frac{\Omega}{4 \bar{\Pi}^2} \right] \quad \text{A2.4}$$

$$\text{and the system damping, } \tan \delta_s = \frac{\Omega / \bar{\Pi}}{(1 + \Omega^2 / 4 \bar{\Pi}^2)} \quad \text{A2.5}$$

The application of 2.3 to 2.5 enable the calibration of the suspension element of the torsion pendulum and the torsional rigidity of the metal shim. For the suspension and added inertia alone equation A2.4 reduces to:-

$$k g_1 = I \omega^2 \quad \text{A2.6}$$

and measurements of I and ω^2 yield the torsional rigidity of the suspension. For the case of the metal shim A2.4 reads

$$K G_1 + k g_1 = I \omega^2 \quad \text{A2.7}$$

and enables the calculation of the torsional rigidity of the shim. The torsional creep rig may now be used with the calibrated shims to obtain a voltage-deflection characteristic. The applied torque is related to the torsional rigidity and the angular deflection by the equation:-

$$M = k_v V = K G_1 \frac{\theta}{l} \quad \text{A2.8}$$

where M is the applied torque, or twisting moment

k_v is the voltage/torque constant

V is the applied voltage

$K G_1$ is the torsional rigidity of the shim

and $\frac{\theta}{l}$ is the angular deflection per unit length

of the shim sample

$$\text{or, re-arranging } k_v = \frac{K G_1}{l} \left(\frac{\theta}{V} \right) \quad \text{A2.9}$$

where $\frac{\theta}{V}$ is the voltage-deflection characteristic.

Thus, knowing the torsional rigidity and the voltage-deflection constant, the torque-voltage constant, k_v , may be calculated.

A.2.2. Calibration of the Torsion Pendulum Apparatus, and the Torsional Rigidity of the Shims

The results on the free vibration tests on the suspension alone, the shim 1, and shim 2, for different inertia systems are given in Table A.1. Each test was repeated three times and the spread in the frequency of oscillation was always less than 1%. The moment of inertia of the arms and bobs were calculated from a knowledge of the individual weights and measurements of the mass dimensions. The errors involved in the calculations were negligible.

The torsional rigidity of the shims are determined from Table A2.1 and using equation A2.4. (The damping in the metal shims is very small and thus the damping term is ignored). The value of the torsional rigidity for the respective shims is:-

$$\text{SHIM 1} = 4259.9 \text{ grmf cm}^2$$

$$\text{SHIM 2} = 5002.9 \text{ grmf cm}^2$$

Table A 2.1 The Results of Free Vibration on the Pendulum Suspension and Metal Shims

Inertia I	SUSPENSION ALONE		SHIM 1		SHIM 2	
	Frequency ω	$I\omega^2$	Frequency ω	$I\omega^2$	Frequency ω	$I\omega^2$
1,800	11.73	247,662	23.83	1,026,380	-	-
25,850	2.984	246,361				
171,170	1.197	247,693	2.49	1,071,000	2.65	1,210,000
184,600	1.153	247,736	2.394	1,063,000	2.536	1,199,000
423,236	0.766	249,392	1.571	1,049,000	1.663	1,132,000
244,192	1.005	248,451	-	-	-	-
436,674	0.753	248,176	1.549	1,052,000	1.648	1,191,000
257,630	0.981	249,831	2.011	1,049,000	-	-

Average $I\omega^2$ for Suspension alone = $248,163 \pm 0.8\%$

for Suspension and Shim 1 = $1,057,300 \pm 1.0\%$

for Suspension and Shim 2 = $1,195,500 \pm 0.8\%$

A 2.3 The Voltage-Deflection Calibration of the Torsional Creep Apparatus

The voltage-deflection calibration for the creep apparatus was carried out using the two calibrated metal shims. The effect on the calibration on the optical bench arrangements, misalignment of the specimen, and the magnetic field with relation to the coil has been determined.

The results of the voltage-deflection calibration runs on Shims 1 and 2 are shown in Figure A2.1 and A2.2 respectively. The samples were removed and replaced in the apparatus and the results of two runs were found to superpose. The voltage-deflection characteristics for the two shims were found to be:-

Shim 1 4.87 cm/volt $\pm$ 1%

Shim 2 4.10 cm/volt $\pm$ 1%

The following observations were also made during the calibration runs.

1. Gross misalignments of the specimen in planes perpendicular to the cross-section, but containing the plane of the specimen made only a 2.5% spread in the calibration curve at the maximum deflections recorded, with even less scatter at lower deflections. Specimens are aligned perpendicularly by eye with the aid of a set-square and using this method negligible errors are introduced through specimen misalignment.
2. The relative positions of the coil and the magnets does not affect the calibration, for a given separation of the magnetic poles.
3. The errors introduced by reading the tangential movement of the reflected light beam instead of the swept arc are negligible with the optical bench arrangement used here.
4. A procedure was developed for ensuring good alignment of the specimen axis and the torsion axis, which gave repeatable and reproducible results.

A 2.4 Calculation of the Torque Voltage Constant

From the torsion pendulum and the torsional creep calibration runs the following characteristics were derived.

The torsional rigidity, $K G_1$, of the SHIM 1 = 4259.9 grmf. cm²

and for SHIM 2 = 5002.9 grmf. cm²

and the deflection-voltage characteristic, θ/V , for SHIM 1 = 4.87 cm/volt

and for SHIM 2 = 4.10 cm/volt

Now using equation A 2.8

$$T = k_v V = K G_1 \frac{\theta}{l}$$

$$\text{where } \theta \text{ the angle of twist} = \frac{\text{graphspot deflection}}{2 \times \text{optical lever}} = \frac{\theta}{2(O.L.)}$$

the torque-voltage constant k_v , may be calculated as follows:

$$k_v = (K G) \times \frac{\theta}{V} \times \frac{1}{2(O.L.) \times l} \quad \text{gmf.cm. volt}^{-1}$$

Hence, substituting yields for SHIM 1, $k_v = 13.733$ gmf.cm/volt

and for SHIM 2, $k_v = 13.577$ gmf.cm/volt

Thus, the average torque-voltage constant, k_v , is 13,390 dyne cm volt⁻¹

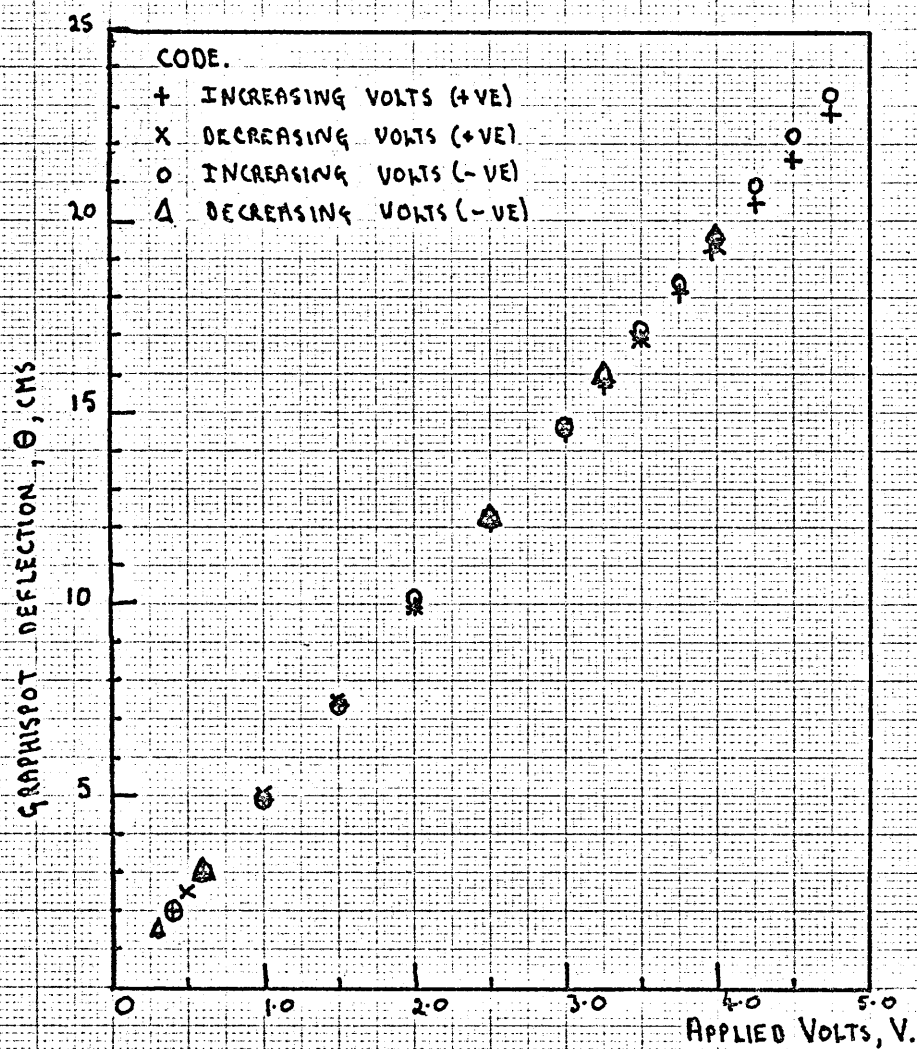


FIGURE A2-1. THE VOLTAGE-DEFLECTION CALIBRATION FOR SHIM 1.

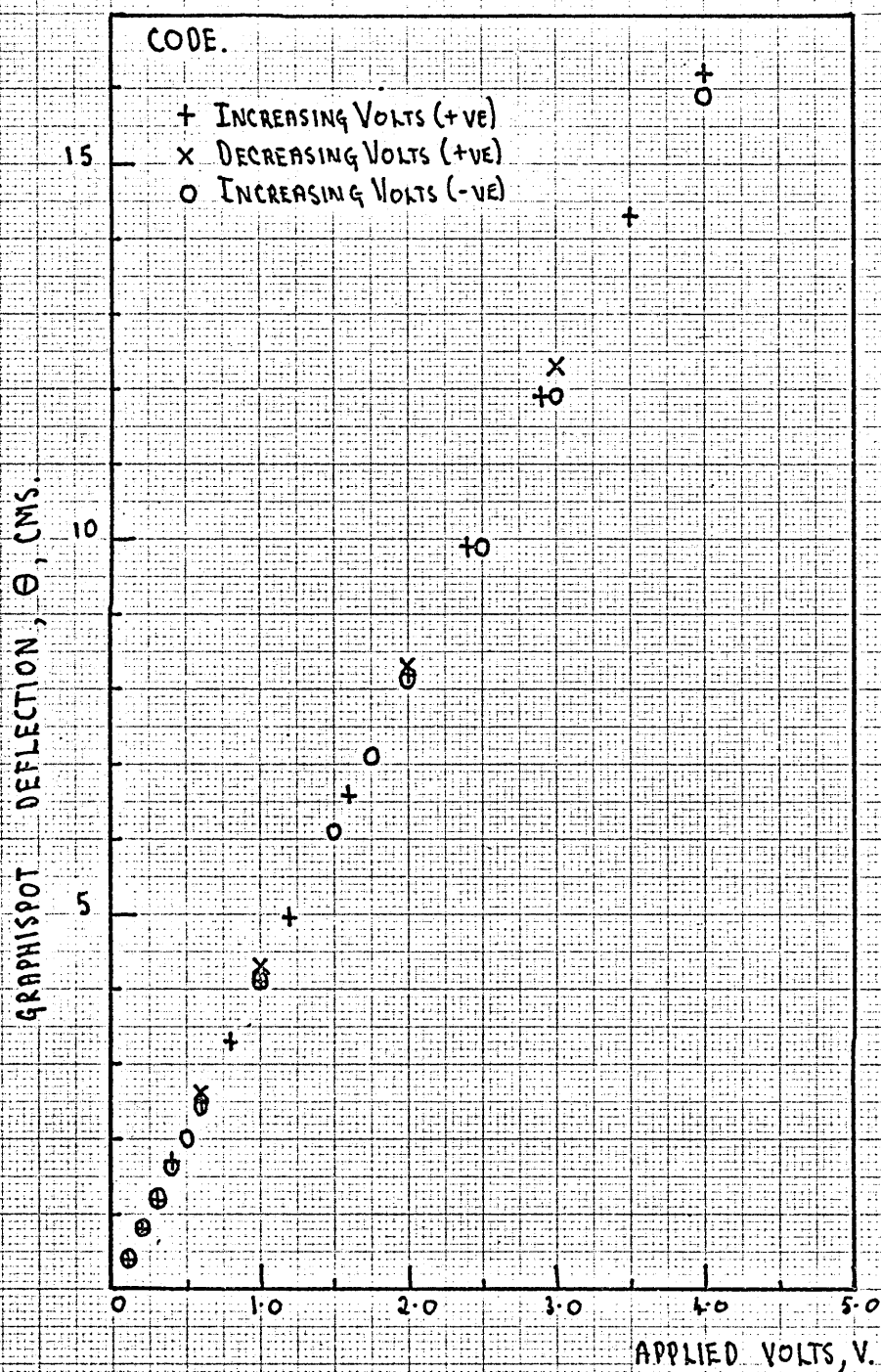


FIGURE A2.2 THE VOLTAGE - DEFLECTION CALIBRATION FOR SHIM2.

APPENDIX A.3 An Example of the Application of the Boltzmann Superposition Principle

For the case of a unit-step input of stress applied to a specimen in its rest state at zero time, $t = 0$, and removed at time $t = t_1$, the Boltzmann superposition integral has been shown to reduce to the following form. (Section 2).

$$\epsilon_i = S_{ij}(t) \sigma_j^0 \quad 0 < t < t_1 \quad A.3.1$$

$$\epsilon_i = S_{ij}(t) \sigma_j^0 - S_{ij}(t - t_1) \sigma_j^0 \quad 0 < t_1 < t < \infty \quad A.3.2$$

where $S_{ij}(t)$ is the creep compliance

and $S_{ij}(t - t_1)$ is the recovery compliance

The recovery compliance is calculated from equation A.3.3 viz

$$S_{ij}(t - t_1) = \frac{(\epsilon_{\text{recovery}})}{\sigma_j^0} \quad A.3.3$$

The recovery strain, $\epsilon_{\text{rec.}}$, is a computed parameter derived from the extrapolated creep/strain time curve and the residual strain/time curve. A typical set of data used in the computation is shown in Figure A.3.1. The data is for the longitudinal strain, ϵ_{33} , for a 0° specimen, D.R. = 2.00, at the 1.0%, 100 second strain level.

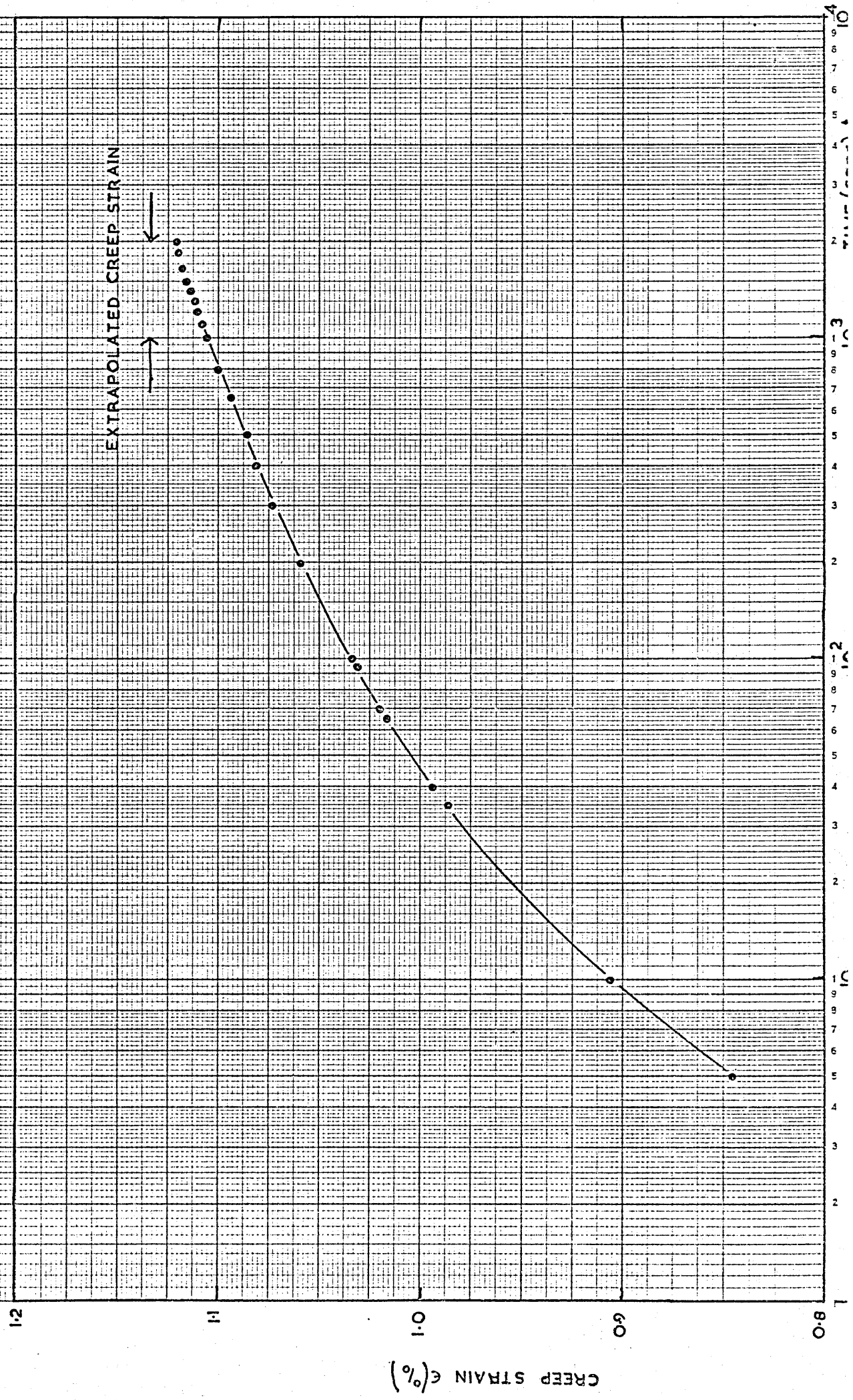
In equation A.3.2 $S_{ij}(t) \sigma_j^0$ is the extrapolated creep strain taken from curve a, ϵ_c , and ϵ_i , is the residual strain taken from curve b. Thus,

$$\epsilon_{\text{rec}} = (\epsilon_c - \epsilon_i) = S_{ij}(t - t_1) \sigma_j^p \quad A.3.4$$

and hence the recovery compliance may be computed.

All the recovery compliance data presented in Section 7 has been calculated in this way. The errors in extrapolating are believed to be negligible.

FIG. A3. THE VARIATION OF THE MEASURED AND EXTRAPOLATED CREEP STRAIN WITH TIME



FIGA 31: THE VARIATION OF THE MEASURED RESIDUAL STRAIN WITH RECOVERY TIME, (t-t₀)

