THE RHEOLOGY OF UNFILLED AND CARBON BLACK LOADED ELASTOMERS

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FOR MY FAMILY

Me gonted ezh eur goñchenn veo
Kredit anezi, re wir eo
Ha n'ez eus enni netra gaou
'Med martenezh eur gër pe zaou

Per-Jakez Hellas
(Merh al Lorh)
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Abstract

This thesis is concerned with the use of rheological equations of state to describe the behaviour of vulcanised elastomers and, in particular, vulcanised elastomers loaded with carbon black. The properties of these materials, are dependent upon the specific combination of elastomer and carbon black, and the effect of carbon black loading is studied by means of experiments on a butadiene-acrylonitrile base polymer KRYNAC 806, unfilled and loaded with 50phr SRF N774 carbon black.

The first part of this work concerns small amplitude oscillatory shear experiments carried out on a Weissenberg rheogoniometer over a range of amplitudes, frequencies, and temperatures. Both materials are found to remain within the linear viscoelastic region for temperatures greater than about -10°C, to obey the time-temperature superposition principle, and to have identical shift factors. Dynamic moduli over a reduced frequency range of about ten decades of log frequency are characterised by the Huet model.

The second part concerns finite deformation experiments consisting of prestraining samples in simple tension and applying small axial oscillations when stress relaxation is almost complete. Dependencies of the incremental dynamic moduli measured in this way are investigated with regard to frequency and extension ratio. Moduli measurements indicate that the time dependence of the materials is unaffected by deformation, although relaxation spectrum functions for the filled sample are strain dependent. A criterion is established for testing whether results can be modelled by a certain class of non-linear viscoelastic constitutive equations. A constitutive equation is proposed which represents the strain dependence of moduli for both the filled and unfilled materials. Other published data are shown not to conform to the above criterion. It is also shown that despite this fact, in some cases at least, the proposed constitutive equation provides a better representation of published data than other constitutive equations which have hitherto been applied.
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CHAPTER 1

INTRODUCTION

The present chapter outlines the plan of this thesis, the aim of which is to develop rheological equations of state to describe the behaviour of vulcanised elastomers, and in particular the behaviour of vulcanised elastomers containing carbon black filler. Vulcanised carbon black filled elastomers have many common applications including tyre treads, power transmission belts, couplings, vibration isolation mountings, absorbers, and dampers. These materials are thus of great industrial importance. They exhibit complex dependencies on temperature, deformation history, frequency, and amplitude of deformation, but in many ways our understanding of their behaviour is incomplete. This has lead Rigbi (1980) to state that 'The mechanism by which carbon black reinforces elastomers is one of the most interesting problems of modern technology and still a subject of much speculation'. The formulation of a rheological equation of state to model the behaviour of carbon black filled elastomers would benefit the prediction of component performance, the production of improved compounds, and the understanding of the microstructure of these materials.

Chapter 2 lays the foundation for this thesis by discussing what is meant by rheology and by the term vulcanised elastomer. This chapter is accordingly divided into two overall sections. The first of these sections aims to facilitate an understanding of rheology. In this section the various quantities which influence the flow and deformation of a material are defined and formulated into the system of equations which specifies a rheological problem. A distinction is made between those equations which express universal physical laws, and those which express particular material properties - the equations of state. Rheological problems are considered within the wider framework of continuum mechanics and it is shown that certain concepts from the fields of thermodynamics and elasticity theory can make an important contribution to the development of a rheological equation of state. The last part of this section discusses the difference between solids and liquids.
The second section of Chapter 2 provides a general description of elastomers - and in particular elastomers containing carbon black - in terms of their chemistry, manufacturing processes, physical properties and applications. Consideration is given to the various behaviours exhibited by different types of carbon black filled elastomers - which shows the need to restrict ourselves to specific compounds, or groups of compounds - and also to the extent to which the observed behaviour is likely to be amenable to description by means of a rheological equation of state. The final part of this section gives details of specific compounds - one filled and one unfilled - which were chosen for the experimental investigations described in Chapter 4 and Chapter 7. These experiments are divided into those carried out at infinitesimal and at finite deformation.

Chapter 3 presents the theory which is applicable to analysis of the infinitesimal deformation experiments described in Chapter 4. Both the frequency and temperature dependencies of the experimental materials are examined, and thus Chapter 3 is divided into two overall sections. The first of these sections reviews how stresses and strains are related in infinitesimal deformation at constant temperature by means of linear viscoelastic theory. The linear viscoelastic moduli and compliances which characterise material behaviour are introduced and defined. Interrelationships between these quantities are presented, and the relaxation spectrum introduced.

The second section of Chapter 3 reviews how isothermal results at different temperatures can be related by means of the time-temperature superposition principle. Published experimental evidence concerning the application of the time-temperature superposition principle to carbon black filled elastomers is presented, and shown to provide a basis for the classification of these materials.

Chapter 4 presents details of the infinitesimal deformation experiments conducted in order to determine the linear properties of the materials chosen for investigation. The significance of such a linear characterisation, and the conditions which must be satisfied in order to achieve this are discussed, together with the relative advantages and disadvantages of experiments in particular modes of deformation. Reasons for choosing an oscillatory (or dynamic) mode of testing are discussed, and techniques and apparatus for dynamic
testing are surveyed. The apparatus used for testing—a Weissenberg rheogoniometer—is described in detail, together with the temperature control and data logging systems. The experimental procedure is described and the theory required for analysis of results is presented. By comparing numerical and approximate analytic solutions it is shown that despite the large samples used in these experiments, large errors are not induced in the analytic solution by neglecting the term associated with the sample density. Other sources of experimental error are also considered. Errors associated with resonance are discussed, and it is demonstrated that the magnitude of this effect varies both with temperature and frequency. Errors due to viscous heating are also discussed.

Chapter 5 presents results of the experiments described in Chapter 4 and models these in terms of the theory reviewed in Chapter 3. The linearity of the results is examined and the effect of errors in the measurement of phase angle discussed. Moduli values from experiments conducted at fixed frequency and at fixed input amplitude are shown to agree well and demonstrate good experimental reproducibility. The time-temperature superposition principle is shown to be applicable to results for both the filled and unfilled materials, and to yield the same shift factors, which are described in the WLF equation. The modified Sprigg's model proposed by Jones and Davies (1982) is shown to represent data only over restricted ranges of temperature and frequency. Relaxation spectra for the filled and unfilled samples are calculated. These spectra constitute a basis for the selection of suitable linear viscoelastic models to represent data over the full ranges of frequency and temperature examined. The relaxation spectrum predictions of a number of reported linear viscoelastic models are considered, and shown not to represent the experimental data. The model due to Huet [Salvia and Duperray (1983)] is shown to represent the dynamic moduli for both the filled and unfilled materials. Exploiting an approximate algebraic relationship between the complex modulus and relaxation modulus, and assuming that temperature dependent behaviour can be expressed by means of a reduced time, enables a temperature-dependent linear viscoelastic equation to be proposed to model the behaviour of the experimental materials in infinitesimal deformation.
Chapter 6 presents non-linear viscoelastic theory relevant to the analysis of the finite deformation experiments of Chapter 7 and reviews published evidence concerning the applicability of this theory to the deformation of carbon black filled elastomers. This chapter is divided into three overall sections. In the first section a number of single integral rheological equations of state (or constitutive equations) are introduced which are explicit in stress. These comprise constitutive equations for multiaxial deformation which feature the 'n' strain measure of Chang, Bloch and Tschoegl (1977a) and the uniaxial constitutive equation of Schapery (1969). It is shown that the constitutive equations featuring the 'n' strain measure can be related to strain energy density functions, and thus satisfy the 2nd law of thermodynamics for purely elastic deformation. The work of Talybly (1978) on temperature dependent non-linear deformation is reviewed. A number of theoretical concepts are defined and considered in terms of the constitutive equations presented. These comprise the modified Boltzmann superposition principle, separability, incremental dynamic moduli, and relaxation spectrum functions.

The second section of Chapter 6 examines published evidence regarding features of the non-linear deformation of carbon black filled elastomers which aid in the development of constitutive equations to model these materials. Evidence regarding the sufficiency of a single integral constitutive equation is gained from consideration of cyclic deformation. The criterion of separability, which has been used to examine the validity of the modified Boltzmann superposition principle is discussed. Results on the static pre-strain dependencies of incremental dynamic moduli are also discussed, and the application of the time-temperature superposition principle to the non-infinitesimal deformation of carbon black filled elastomers is reviewed. The third section of Chapter 6 summarises the main conclusions drawn from this chapter.

In Chapter 7 experiments carried out in simple tension to determine the non-linear properties of the materials chosen for investigation are described, and results for these materials presented and modelled in terms of the non-linear theory presented in Chapter 6. Chapter 7 is divided into four overall sections. In the first section details of the experimental apparatus and procedure are presented and the analysis of the experimental data is
considered. This analysis includes discussion of the effect of the mass of the sample and of the methods used to determine values for incremental dynamic moduli and relaxation spectrum functions.

The second and third sections of Chapter 7 present results obtained for the unfilled and filled materials respectively. These results are for quasi-equilibrium stress, phase angle, incremental dynamic moduli, and relaxation spectrum functions. It is shown that results for the unfilled material can be modelled both by the constitutive equation of Sullivan (1987) and by another constitutive equation proposed in Chapter 6, which also models results for the filled material. The filled material cannot however be modelled by the Sullivan equation. Conclusions pertaining to results on the filled and unfilled materials are presented at the end of the respective sections.

The fourth section of Chapter 7 highlights some of the differences in the observed behaviour of the filled and unfilled materials, and shows that a single constitutive equation could in principle be used to model the behaviour of vulcanised elastomers containing variable amounts of carbon black filler.

Chapter 8 considers the applicability of the theory used to model the results of Chapter 7 to other published data on carbon black filled elastomers. It is shown that generally there is lack of agreement between these data and the incremental dynamic moduli predictions of the Schapery model. Despite this lack of agreement it is attempted to model data both in terms of the Sullivan constitutive equation and the constitutive equation proposed in this thesis. It is shown that these equations afford a representation of the data only over a restricted range of extension ratio, if at all, and that a reasonable fit to simple tension data does not ensure an adequate representation of data in pure shear. Conclusions are presented and further work is discussed.
CHAPTER 2

RHEOLOGY AND ELASTOMERS

INTRODUCTION

This chapter aims to facilitate an understanding of what is meant by rheology and by the term vulcanised elastomer. The chapter is thus divided into two overall sections. The first of these sections is concerned with the subject of rheology, while the second section provides a general description of elastomers, and in particular, elastomers containing carbon black filler.

The first section considers the quantities which influence the deformation and flow of a material, and formulates these into the system of equations which specifies a rheological problem. The position of rheological problems within the wider framework of continuum mechanics is also considered, and it is shown that certain concepts from fields including thermodynamics and elasticity theory can make an important contribution to the development of a rheological equation of state. The final part of this section discusses the difference between solids and liquids.

In the second section elastomers - and in particular elastomers containing carbon black - are described in terms of their chemistry, manufacturing processes, physical properties and applications. Consideration is given to the various behaviours exhibited by carbon black filled elastomers, and to the extent to which such behaviour is likely to be amenable to description by means of a rheological equation of state. The final part of this section gives details of specific compounds chosen for experimental investigation.

2.1 RHEOLOGY

The Supplement to the Oxford English Dictionary defines rheology as 'the study of the deformation and flow of matter, esp. the non-Newtonian flow of liquids and the plastic flow of solids'. The study of the deformational and flow properties of industrial
materials became of increasing technological significance during the early years of this century, with the introduction of new and more sophisticated materials. The importance of this growing science was given concrete expression in 1929 with the foundation in America of the Society of Rheology.

Today deformation and material flow are approached both on the microscopic and macroscopic levels. The microscopic approach is sometimes known as microrheology, and represents an attempt to describe material behaviour in terms of interactions between the structural components of the material at molecular level. It is generally recognised [Buckley (1986)] that this approach may contribute significantly to the understanding of deformatinal and flow processes, but is not yet sufficiently developed to provide practical solutions.

The macroscopic approach consists of treating the material as a continuum. The deformation and flow of such a continuum thus constitutes the branch of continuum mechanics which is known as rheology. It is with such a continuum mechanistic approach that we shall be concerned.

2.1.1 Characterisation: The Fundamental Dynamic and Kinematic Variables

The first step in the rheological characterisation of a material is the identification of the dynamic and kinematic variables which influence flow and deformation.

In order to consider the kinematics of a body it is necessary to introduce a frame of reference. Within this frame of reference we introduce a fixed coordinate system which associates ordered triplets \( x^1, x^2, x^3 \) with points in space. The triplet \( x^1, x^2, x^3 \) may be represented by the vector \( \mathbf{x} \). At a given time \( t_0 \), each position \( \mathbf{x} \) is occupied by a material point, or particle of the body. Thus \( \mathbf{x} = \mathbf{x}(t_0) \) identifies that particle which occupies the position \( \mathbf{x} \) at a given reference time \( t_0 \). The set of points \( \{\mathbf{x}\} \) is known as a reference configuration. At some subsequent time \( \tau \) the position of the particle can be expressed as \( \mathbf{x}(\tau) \), which is the instantaneous position of the particle with respect to the fixed coordinate system.

It is sometimes convenient to write tensor quantities
(including vectors such as \( \mathbf{x} \)) in component notation. The components of tensor quantities may be covariant, contravariant, or mixed. These representations depend formally upon a vector basis, which is generally chosen in association with a particular choice of coordinate system. If the chosen vector basis corresponds to the natural basis, \( \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 \), where

\[
\mathbf{e}_i = \frac{\partial \mathbf{x}}{\partial x^i}, \quad i = 1, 2, 3. \tag{2.01}
\]

then the components of a given vector will be contravariant with respect to this base. However, if the vector basis is chosen as the dual of the natural basis \( \mathbf{e}^1, \mathbf{e}^2, \mathbf{e}^3 \), where

\[
\mathbf{e}^i \cdot \mathbf{e}_j = \delta_{ij}, \quad \text{and} \quad \delta_{ij} \text{ is the Kronecker delta} \tag{2.02}
\]

then the components of a given vector will be covariant. This implies a certain arbitrariness in the representation of tensor components. For this reason a non-component tensor notation might be considered more general, and hence to be preferred. For certain purposes however, component notation does possess advantages, and hence both forms of notation will be exploited.

In the case of a Cartesian coordinate system, covariant and contravariant components coincide, and hence all indices may be written as subscripts. For the purposes of this thesis general curvilinear coordinate systems are not required, and where component notation is used Cartesian coordinates will be adopted and all subsequent indices written as subscripts.

A stress tensor \( \sigma \) describes the force \( d\mathbf{f} \) which acts in a prescribed sense over a surface element \( d\mathbf{s} \) with arbitrary orientation within the body. This is expressed in the relation

\[
d\mathbf{f} = \sigma \cdot d\mathbf{s}. \tag{2.03}
\]

When the stress is calculated with respect to current surface area it is known as the true stress or Cauchy stress. If the stress is calculated with respect to the corresponding element of surface in the reference configuration, then it is generally known as the
nominal stress, or engineering stress. The total stress can be uniquely decomposed into a component corresponding to an isotropic (mechanical) pressure \( p \) and a deviatoric component \( g' \).

\[
\sigma_{ij} = \sigma_{ij}^\prime - p \delta_{ij}
\]

where \( \sigma_{ij}^\prime = 0 \)

[2.04]

Let \( \mathbf{X} \) represent the position of a particle in the reference configuration, and \( \mathbf{x} \) represent the position of this particle at some subsequent time \( \tau \). Then \( \mathbf{x} \) can be written as a function \( \xi \), depending upon \( \mathbf{X} \) - the point occupied in the reference configuration - and the instantaneous time \( \tau \).

\[
\mathbf{x} = \xi(\mathbf{X}, \tau)
\]

[2.05]

The displacement of a particle between the instantaneous time \( \tau \) and the reference time \( t_0 \) is thus given by the displacement vector \( \mathbf{y} \), where

\[
\mathbf{y} = \mathbf{x} - \mathbf{X}
\]

[2.06]

The components of the velocity vector for the particle \( V_i \) are defined by

\[
V_i = \frac{\partial u_i}{\partial t} \bigg|_{\mathbf{X} \text{ = const}}
\]

[2.07]

Equation [2.07] defines the velocity \( \mathbf{v} \) of a material element. The velocity field \( \mathbf{v}(\mathbf{X}, t) \) is defined such that

\[
\mathbf{v}(\mathbf{X}, t) = \mathbf{v}(\xi(\mathbf{X}, t), t) = \mathbf{v}(\mathbf{X}, t)
\]

[2.08]

Formally we may write

\[
\xi(\mathbf{X}, t) = \xi(\mathbf{X}, t) = \mathbf{X}
\]

\[\dagger\] The summation convention applies to repeated suffices.
\[
\begin{align*}
\frac{\partial u_i}{\partial t} \bigg|_{\mathbf{x}} &= \text{const} - \frac{\partial u_i(x,t)}{\partial t} + \frac{\partial u_i(x,t)}{\partial x_j} \frac{\partial x_j}{\partial t} (x,t) \\
\frac{\partial u_i}{\partial t} \bigg|_{\mathbf{x}} &= \text{const} + v_j \frac{\partial u_i}{\partial x_j} \\
\frac{\partial u_i}{\partial t} \bigg|_{\mathbf{x}} &= \text{const} + v_j \frac{\partial u_i}{\partial x_j} - \frac{D u_i}{Dt} . \quad [2.09]
\end{align*}
\]

The operator \( D/Dt \) is known as the substantial or material derivative, and is defined in Cartesian coordinates by

\[
\frac{D}{Dt} = \frac{\partial}{\partial t} + v_j \frac{\partial}{\partial x_j} . \quad [2.10]
\]

Rates of change of other quantities associated with a material particle can be expressed by means of the material derivative. In particular, for the acceleration of a material particle we can write

\[
\frac{\partial v_i}{\partial t} \bigg|_{\mathbf{x}} = \text{const} - \frac{D v_i}{Dt} (x,t) 
\]

and similarly for the rate of change of density of a material particle

\[
\frac{\partial \rho}{\partial t} \bigg|_{\mathbf{x}} = \text{const} - \frac{D \rho}{Dt} \rho(x,t) .
\]

The components of the rate of strain tensor \( \mathbf{d} \) are defined in Cartesian coordinates by

\[
d_{ij} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) .
\]

More generally we may write

\[
\mathbf{d} = \frac{1}{2}(\mathbf{\nabla} + \mathbf{\nabla}^T) , \quad [2.11]
\]

where \( \mathbf{\nabla} \) is the gradient with respect to the coordinate \( \mathbf{x} \).
Considering a particle which is at \( \mathbf{x} \) in the reference configuration, and a neighbouring particle whose position in the reference configuration is given by \( \mathbf{x} + d\mathbf{x} \), the deformation gradient tensor \( \mathbf{F} \) is then defined by

\[
\mathbf{F}(\mathbf{x} + d\mathbf{x}, \tau) = \mathbf{F}(\mathbf{x}, \tau) + \mathbf{F}(\tau).d\mathbf{x} + \ldots \quad [2.12]
\]

If the separation of the two particles at the current time \( \tau \) is given by \( d\mathbf{x} \), then we have the approximate relation,

\[
d\mathbf{x}(\tau) = \mathbf{F}(\tau).d\mathbf{x}(t_0) . \quad [2.13]
\]

The right Cauchy-Green deformation tensor \( \mathbf{C} \) is then defined by

\[
\mathbf{C} = \mathbf{F}^T.\mathbf{F} . \quad [2.14]
\]

A strain measure \( \mathbf{E} \), which is sometimes known as the Lagrangian strain tensor, can now be defined by

\[
\mathbf{E} = \frac{1}{2}(\mathbf{C} - \mathbf{I}) , \quad [2.15]
\]

where \( \mathbf{I} \) is the 2nd order unit tensor.

In the case of infinitesimal deformation [2.14] can be replaced by the approximate relation

\[
\mathbf{C} = \mathbf{F} + \mathbf{F}^T . \quad [2.16]
\]


\[
\mathbf{E} = \frac{1}{2}(\mathbf{F} + \mathbf{F}^T) - \mathbf{I}
\]

and from [2.13] it follows that

\[
\mathbf{E} = \frac{1}{2} \left[ \frac{\partial u_j}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right]
\]

The infinitesimal strain tensor \( \mathbf{\varepsilon} \) is thus defined by
and is a non-frame indifferent tensor.

For the case of the infinitesimal deformation of an isotropic elastic solid, Hooke's law may be formulated as

\[ \sigma_{ij} = 2G\varepsilon_{ij} \]  \hspace{1cm} [2.18]

where \( G \) is the shear modulus.

In infinitesimal deformation, Newton's law for viscous fluids may be represented as

\[ \sigma_{ij} = 2\eta \frac{\partial \varepsilon_{ij}}{\partial t} \]  \hspace{1cm} [2.19]

where \( \eta \) is the viscosity.

Having defined some of the variables which characterise deformation and flow in a continuum, we now turn to the formulation of the system of equations which describes these processes.

2.1.2 Formulation: Universal Physical Laws Applicable to the Mechanics of Continua

There are four physical conservation laws which are applicable to the mechanics of continua. These laws are expressible as balance equations representing the conservation of mass, momentum, moment of momentum, and energy. We shall deal with each of these in turn.

The mass balance equation may be expressed as

\[ \frac{Dp}{Dt} = -\rho \nabla \cdot \mathbf{v} \]  \hspace{1cm} [2.20]

where \( \nabla \cdot \mathbf{v} \) is the divergence calculated with respect to the coordinate \( \mathbf{x} \). This equation is known as the equation of continuity.

The momentum balance equation may be written as

\[ \rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \nabla \cdot \mathbf{g}' + \rho \mathbf{g} \]  \hspace{1cm} [2.21]
where \( g \) is the body force.

This is known as the equation of motion, or dynamical equation. The principle of conservation of momentum only applies within an inertial frame, and thus [2.21] assumes that the reference frame is indeed inertial.

In the absence of body couples and couple stresses (which is known as the non-polar case) the principle of conservation of moment of momentum yields

\[
\sigma_{ij} = \sigma_{ji} \quad [2.22]
\]

In the non-polar case, the energy balance equation may be written as

\[
\rho \frac{D}{Dt} [U + \dot{\gamma} \cdot \dot{\gamma}] = -\nabla \cdot q - \nabla \cdot (p \dot{\gamma}) + \nabla \cdot (g' \cdot \dot{\gamma}) + p \dot{\gamma} \cdot g + Q \quad [2.23]
\]

where \( U \) is the internal energy per unit mass, \( q \) is the heat flux, and \( Q \) is the energy influx per unit volume due to radiation.

The energy balance equation is a statement of the 1st law of thermodynamics. The equations [1.20]-[1.23], which represent the physical conservation laws applicable to a continuum, can also be supplemented by an inequality which represents the 2nd law of thermodynamics:

\[
\dot{S} > \frac{-\nabla \cdot q + Q}{T} \quad [2.24]
\]

where \( \dot{S} \) is the rate of change of entropy and \( T \) is the absolute temperature.

The unknowns appearing in the above formulation of the physical laws applicable to continua are \( \rho, \dot{\gamma}, g, U, q, \) and \( S \). It is assumed that \( g \) and \( Q \) may be assigned arbitrarily. Additional equations are thus required in order to obtain a solution. These additional equations are specific to a particular material or class of materials, and are known generally as equations of state.
2.1.3  **Formulation: Equations of State**

(i)  **The Rheological Equation of State**

The rheological equation of state, or constitutive equation, determines the stress $\sigma$ in terms of the state of deformation and possibly other quantities which may include the history of the deformation and the temperature. The formulations of Hooke's law [2.18] and Newton's law [2.19] are thus examples of simple types of constitutive equations.

Truesdell and Noll (1965) have distinguished three classes of constitutive equation:- differential, integral, and rate equations.

**CONSTITUTIVE EQUATIONS**

- **Differential constitutive equations**
  - express the stress as a function involving the differential kinematics at the instant of observation
  
- **Integral constitutive equations**
  - express the stress in terms of one or more integrals involving the history of kinematics

- **Rate equations**
  - involving at least one time derivative of the stress tensor

The usual rheological approach to problems in continuum mechanics consists of the solution of the rheological equation of state together with the equation of continuity [2.20] and the equation of motion [2.21]. 'Isothermal' experiments can be designed for which the equation of continuity is satisfied, and in which the inertial and gravitational forces in the equation of motion are negligible. Under these conditions, the stresses and strains calculated from observable quantities are related solely by the rheological equation of state.

An important restriction placed upon constitutive equations is that they are required to satisfy the principle of material objectivity, or frame indifference, and should preserve their form under a change of reference frame. Another requirement which may be imposed upon the form of the constitutive relation is that it should not violate the 2nd law of thermodynamics.
The energy balance equation [2.23] may be manipulated to contain the terms \( p(\nabla \cdot \mathbf{v}) \) and \( g' : \nabla \cdot \mathbf{v} \), which represent rates of conversion of energy into internal energy. Under certain conditions, these terms may cause appreciable temperature change in the material. 'Isothermal' conditions thus correspond to the assumption that any temperature change due to the above quantities is negligible.

In general the entropy \( S \) is related to the internal energy \( U \). Thus the rate of change of the entropy \( S \) which appears in the 2nd law of thermodynamics [2.24] is dependent upon the rate of change of internal energy, which is in turn linked to the rheological equation of state via the terms \( p(\nabla \cdot \mathbf{v}) \) and \( g' : \nabla \cdot \mathbf{v} \). Some rheological equations of state which have been proposed thus contravene the 2nd law of thermodynamics [Larson and Monroe (1984)]. This can be avoided by relating the constitutive equation to the equation of state for entropy (see later).

Other material-specific equations, which may be referred to as equations of state, are those which determine the thermodynamic pressure \( P \), the heat flux \( g \), the internal energy \( U \), and the entropy \( S \).

(i) The Thermodynamic Equation of State

The total stress \( g \) can be decomposed into a deviatoric stress \( g' \) and isotropic mechanical pressure \( p \) (see [2.04]). An equation for \( g \) is thus equivalent to a pair of equations which determine \( g' \) and \( p \). The thermodynamic pressure \( P \) however differs in general from the mechanical pressure \( p \). The thermodynamic equation of state determines \( P \) in terms of two other parameters (known as state variables), which may be chosen as the absolute temperature \( T \), and specific volume, or density \( \rho \). For the case of incompressible materials the thermodynamic pressure is undefined, and the mechanical pressure \( p \) is defined only to within an arbitrary constant which is assigned by the boundary conditions.

(iii) The Equation of State for the Heat Flux

The equation of heat transfer relates the heat flux \( g \) to the temperature distribution.
(iv) *The Equation of State for the Internal Energy*

The 'energetic' equation assigns the value of the internal energy $U$. The energetic equation may be written in terms of temperature, density, and the state of deformation. In this case, the four physical balance equations [2.20]-[2.23] and the equations of state for stress $\sigma$, thermodynamic pressure $P$, heat flux $q$, and internal energy $U$ can in principle be solved together. Solution of this system does not guarantee non-violation of the 2nd law of thermodynamics [2.24]. Addition of the 2nd law to this system further requires an equation of state for the entropy $S$, or equivalently an equation of state for the Helmholtz free energy $A$, which is defined by

$$A = U - TS \quad [2.25]$$

Such an equation of state may be called an entropic equation of state.

(v) *Thermodynamic Restrictions on Equations of State*

It has been shown [Astarita and Marrucci (1974)] that for constant density simple fluids with fading memory, the state equations for total stress $\sigma$, thermodynamic pressure $P$, and internal energy $U$ can all be derived from the entropic equation of state.

For incompressible materials the rate of change of entropy $\dot{S}$ may be related to a 'rate of energy dissipation' $\dot{D}$. The rate of energy dissipation may be further decomposed into a mechanical dissipation rate $\dot{D}_M$ and a thermal dissipation rate $\dot{D}_T$. Application of the 2nd law of thermodynamics then leads to the result

$$\dot{D}_M + \dot{D}_T > 0 \quad [2.26]$$

It can be shown that for constant density simple fluids with fading memory $\dot{D}_M > 0$. Since $\dot{D}_M$ may be calculated from the entropic equation of state, the condition $\dot{D}_M > 0$ may thus be regarded as placing a restriction upon the form of the entropic equation. Also, from [2.26]
D_T > -D_M \quad [2.27]

D_T may be calculated from the equation of state for the heat flux, and thus by [2.27] the form of the heat transfer equation is also restricted by the 2nd law of thermodynamics.

The rate of accumulation of elastic energy is defined by

\[ \dot{\varepsilon} = \frac{1}{\rho} \mathbf{a} : \mathbf{d} - D_M \quad [2.28] \]

where \( 1/\rho \mathbf{a} : \mathbf{d} \) is known as the stress power. In the case where \( D_M \) is negligible - such as a sudden deformation, when viscous dissipation tends to zero - the rate of working of the stress is thus proportional to the rate of accumulation of elastic energy. The theory of elasticity makes use of a strain energy function \( W(\varepsilon) \) which represents the elastic energy stored per unit volume as a result of the work done by the stress during deformation. It can be shown \([\text{Larson (1983)}]\) that for simple fluids, compliance with the 2nd law of thermodynamics requires that stresses and strains should be related via a strain energy function.

In the above discussion particular reference has been made to the theory of simple fluids with fading memory. We shall see from §2.2.1, however, that vulcanised elastomers cannot be regarded as fluids. Nevertheless, it is to be expected that similar arguments could be constructed with regard to solid materials, since in the case of a sudden elastic deformation, for example, we would expect to observe no difference in the behaviour of a viscoelastic solid or a viscoelastic liquid. The final part of this section accordingly discusses the distinction between solids and liquids.

2.1.4 The Distinction between Solids and Liquids

The foregoing formulation of continuum mechanics applies equally to all continua, and does not differentiate between those materials which are classed as solids and those which are classed as liquids. It is clear that any distinction between solids and liquids should be reflected in the state equations which embody specific properties of particular classes of materials.
Comparing the infinitesimal deformation formulations of Hooke's law [2.18] and Newton's law [2.19] respectively, it is clear that in the former case a small constantly applied stress produces a strain which is finite (in the sense of being bounded), while in the latter case a similar stress produces a finite strain rate. In itself this does not constrain the resultant strain to be finite. This observation indicates the basis for an experimental criterion for the classification of materials as solids or liquids.

Alternatively, a solid may be defined as possessing a unique reference configuration at a state of zero stress, while a liquid possesses no such unique reference configuration. This constitutes an important distinction in the formulation of constitutive equations.

Another viewpoint is to compare the timescale of a physical deformation with the intrinsic timescale which may be regarded as characteristic of the material. Thus Astarita (1975) remarks '... water, by having an extremely short natural time, from a pragmatical viewpoint, only undergoes very slow processes and can therefore always be regarded as a Newtonian fluid. By analogy, a material such as steel may be considered as having such a large natural time as to undergo in practice only very fast processes, and as such may be always regarded as an elastic solid ...'.

2.2 ELASTOMERS

2.2.1 Elastomers and Carbon Black Fillers

The Supplement to the Oxford English Dictionary defines elastomer as a term coined in 1939 for 'any of various synthetic rubbers or plastic substances resembling rubber'. Hence it is a compound word applied to polymers which exhibit elastic behaviour. The elastic behaviour of such polymers (which may be taken to include natural rubbers) has its origin in the physical constrictions (often referred to by such names as 'entanglements', 'loops', and 'hooks') which arise amongst the molecules of the material. It may thus be appreciated that such elastic behaviour is associated with long chain molecules.

Such long chain molecules can be precipitated by the reaction
of a single monomeric component (resulting in a homo-polymer) or a
number of such components (resulting in a co-polymer). The extent to
which these reactions produce polymer chains of uniform length is
reflected by the molecular mass distribution (M.M.D.) or molecular
weight distribution. The polymers which result from these processes
are of high molecular weight and are sometimes known as high
polymers.

Polymeric systems comprising such molecules have become the
subject of theories describing the behaviour of polymer melts and
concentrated solutions of high polymers. These systems exhibit both
viscous and elastic behaviour, and are hence classed as viscoelastic
liquids. Such molecular entanglements as exist may occur only on a
temporary basis, but it is convenient to conceptualise this system in
terms of 'phantom chains' linked at temporary network points [Wagner
(1979)].

Since elastomers possess both viscous and elastic properties,
it is often desirable that the network associated with the polymer
chains should possess more permanent network points than those
identified with entanglements. To this end chemical bonds, known as
cross-links, may be formed between elastomer molecules. The process
of vulcanisation, or curing, produces cross-linking via an
intermediary such as sulphur. The molecules of vulcanised elastomers
are thus constricted by permanent bonds (eg. sulphur-bonds) as a
result of which these materials exhibit the unique stress-free
configuration which is characteristic of a solid. These materials
may thus be classified as viscoelastic solids, and characterised by a
network of polymer chains possessing permanent network points.

A variety of solid fillers have been compounded with both
vulcanised and unvulcanised elastomers to produce materials which
possess particular properties. These materials are known as filled
elastomers. Carbon black is one such particulate filler, and has
been used in rubber compounds since the early years of this century
to enhance abrasion resistance. It has been observed that many other
material properties are influenced by the inclusion of carbon black.
These include increased damping and an effect upon the temperature
behaviour of the material.

The precise nature of the interaction between carbon black and
the matrix of the polymer chain network is still obscure, and many
investigations have been undertaken to discover the effects which are
Involved [Medalia (1978)]. This situation is further compounded by the fact that many different types of carbon black are in commercial use. With regard to the change in material properties produced by the inclusion of carbon black, Ferry and Fitzgerald (1982) note that this '... depends markedly on the type of rubber for a given carbon black, and on the type of black for a given rubber ...', and further that '... it seems impossible to generalise concerning the temperature and frequency dependencies of dynamic properties of carbon-loaded rubbers'. It is thus necessary to consider the precise structure of carbon black fillers in greater detail, since experimental results must ultimately be interpreted in the light of inferences which may be made about such structures.

The basic unit which is dispersed within the elastomer matrix is known as an aggregate. Aggregates may associate into agglomerates and form networks. Each aggregate is in turn composed of a number of roughly spherical particles and is capable of breaking down to form smaller aggregates. The size of the particles determines the 'grade' of the black eg. coarse, fine, etc, and the number of such particles which comprise the aggregate, together with the voids between them, constitutes the 'structure', or bulkiness of the aggregate. Elastomer molecules are bound to the surface of aggregates by both physical absorption (penetration of the voids within the aggregate by the elastomer molecule) and by chemisorption (formation of a chemical bond between the elastomer molecule and the carbon black). Thus the chemical nature of the carbon black surface is also significant, and is measured by the 'surface activity'. Since individual carbon blacks may differ in many respects, including surface area, grade, structure, and surface activity, it is necessary to assign to each a specific designation such as N770 or SRF [Medalia (1978)].

Before vulcanisation, the various constituents of the elastomer, including curing agents (sulphur, peroxide), filler, and possibly plasticisers and stabilisers, must be mixed by means of a milling process. This process, together with the formation and vulcanisation of the sample, is generally known as processing. The dispersion of the filler in the polymer matrix which is achieved by a

† The designations used in this thesis are quoted from the source materials used, and no attempt has been made to standardise them.
certain degree of milling has an important effect upon the properties of the resulting material [Lee (1985)]. Ferry and Fitzgerald (1982) further observe that 'the black alters the effects of milling'. Chang, Wijayarathna and Salovey (1984) note 'the possible effects of the carbon black on the vulcanisation reaction, leading to characteristic changes in the number and distribution of cross-links in the network'. This phenomenon is due to the physical influence of the carbon black upon the mixing process, and also its chemical influence, depending upon the activity of the black [Medalla (1978)]. Thus Ferry and Fitzgerald conclude that 'it is difficult to make an absolute comparison of a loaded vulcanisate with a corresponding gum vulcanisate'.

2.2.2 Physical Properties of Polymeric Materials and of Carbon Black Filled Elastomers

It is important to note that the physical properties of most elastomers depend strongly upon (i) temperature, (ii) the history of the flow or deformation, (iii) the timescale of the experiment or process under consideration. Let us first consider each of these in turn, and then consider the effects of carbon black loading.

(i) Temperature Dependence

Ward (1979) comments that '... the temperature dependence of polymer properties is of paramount importance because plastics and rubbers show very large changes in properties with changing temperature'. The temperature dependence for a typical polymer - as indicated by the measurement of some appropriate modulus, see Chapter 2 - is shown in Figure 2.1.

Certain ranges of temperature are associated with particular physical states of the material, and are named accordingly (see Figure 2.1). The glass transition region includes the glass transition temperature $T_g$, which is related to the thermal expansion behaviour of the material. $T_g$ corresponds to a discontinuity in the expansion coefficient $\alpha$, measured against temperature. Its exact value depends on the time elapsed between changing the temperature and measuring the value of $\alpha$.
and also upon the rate of cooling. Practically however, values of $T_g$ lie within a narrow band of temperature, and 'are significant within a degree or two' [Ferry (1970)].

The significance of $\alpha$ is outlined by Ferry (1970): 'In polymers, there may be more than one discontinuity in $\alpha$. The highest is usually associated with the loss of the molecular mobility which permits configurational rearrangements of the chain backbones, and it profoundly alters the viscoelastic behaviour; this is "the" glass transition'.

(ii) Dependence upon history of the deformation

Buckley (1986) observes that '... the evolving, non-equilibrium, nature of most polymer structures plays a critical role in determining their properties. A finite stress, applied to such a structure, contributes to its thermo-mechanical history, and hence influences the course of its evolution, in addition to causing a strain directly'.

This observation makes it natural to seek an expression for material behaviour in terms of a rheological equation of state of integral type. It is a constitutive equation of this type which most directly expresses the deformation history dependence of the material.

(iii) Dependence upon timescale of deformation

It has been noted previously (see §2.1.4) that the distinction between solid and liquid-like behaviour may be regarded in terms of the relationship between the intrinsic timescale of the material and the timescale of the imposed deformation. Astarita (1975) describes polymeric materials as having 'natural times in the usual range of experimental timescales'. Thus the observed behaviour will depend strongly upon the timescale of the experiment. Ferry (1970) remarks that 'When the shear creep compliance or the shear relaxation modulus [for definitions see §§3.1.1, 3.1.2] for a particular polymer is plotted against time, or any one of the dynamic functions is plotted against frequency, the most striking feature is the enormous range of magnitudes which the ordinate can assume, changing over several powers of ten'.

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(iv) Properties associated with carbon black loading

Rigbi (1980) comments that 'It may be stated with little likelihood of contradiction, that no other product exists which contributes as much strength and abrasion resistance to non-crystallising rubbers, while maintaining to a large extent their desirable elastic properties, as does carbon black'. Further effects include increased relaxation and creep rates, increased compression or tensile set, and increased hysteresis.

Medalla (1978) lists the principal qualitative effects of carbon black on the dynamic properties of rubber (see §3.1.1) as '(a) an increase in G' (over the gum value); (b) an increase in tanδ; (c) dependence of G' on amplitude (not found with gum).'

Thus carbon black loading modifies the properties of the unfilled material, and also leads to an observed oscillatory amplitude dependence.

2.2.3 Applications of Carbon Black Filled Elastomers

Applications of carbon black filled elastomers which exploit the abrasion resistant properties of these materials include tyre treads, power transmission belts, and couplings. In these applications, other effects of carbon black loading, including increased relaxation and creep rates, increased compression or tensile set, and increased hysteresis (or equivalently increased tanδ), represent undesirable effects. This is particularly true of the latter effect, which represents an increase in the energy dissipation properties of the material, and is associated with viscous heating.

Conversely, the increased energy dissipation properties of these materials are exploited in such applications as vibration isolation mountings, absorbers, and dampers.

Since carbon black filled elastomers are an industrially important class of materials which exhibit complex dependencies upon temperature, deformation history, frequency, and amplitude of deformation, much interest has been generated in the mechanism by which the carbon black filler interacts with the elastomer. Carbon black loading effects will thus be considered in greater detail in

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the following section.

### 2.2.4 Carbon Black Loading Effects

Following Chang, Wijayarathna and Salovey (1984), it is instructive to consider the effect of carbon black loading with respect to a number of regions of deformation, which have been designated by Chang et al as (i) the infinitesimal deformation region, (ii) the finite deformation region, and (iii) the failure region.

#### (1) Infinitesimal Deformation Region

Chang, Wijayarathna and Salovey have demonstrated that the ratio of filled to unfilled modulus for nitrile rubber containing MT or HAF carbon black is independent of sulphur content, provided that equal amounts are contained in both the carbon black loaded and unfilled samples. This suggests that these blacks do not significantly affect the vulcanisation process (see §2.2.1) and that it is possible to adequately describe material behaviour in terms of carbon black loading irrespective of cure and make direct comparison between filled and unfilled samples. Medalla (1978) comments that 'there is good evidence that cross-linking is not materially affected by furnace blacks in conventional sulphur vulcanisation'. The results of Cotten and Boonstra (1965) however, on stress relaxation in butadiene rubber containing 50phr\(^\dagger\) ISAF black, indicate that here the effect of carbon black loading does depend upon the amount of curative (Di-cupR). Medalla reports that this has also been found to be the case in natural rubber loaded with N220 black.

Chang et al found that the Frankel Acivos equation could be used to represent the effect of various volume fractions $\varphi$ of filler

\[^{\dagger}\text{phr - parts per hundred (by weight).}\]
\[ E_0^r = \frac{\text{tensile modulus of filled material}}{\text{tensile modulus of unfilled material}} = \frac{9}{8} \cdot \frac{(\varphi/\varphi_m)^{\frac{3}{5}}}{1-(\varphi/\varphi_m)^{\frac{3}{5}}} \]  

where

\[ \varphi = \frac{\text{volume of filler}}{\text{volume of filled elastomer}} \]

and \( \varphi_m \) is the volume fraction of maximum loading. (\( \varphi_m \) is taken to be 0.65 - the packing density for a random packing of equal spheres).

The Frankel Acrivos equation is derived from lubrication theory, and was found to represent the tensile modulus behaviour of the material for \( \varphi > 0.2 \). Since \( \varphi = 0.1945 \) corresponds to a loading of 50phr it can be seen that the above equation is valid for extremely high filler concentrations only.

An alternative approach, valid for smaller filler loadings (which can be as high as 50phr, depending upon the precise filler-elastomer combination) is given by the various forms of the Guth-Gold equation

\[ E_0^r = 1 + 2.5\varphi + 1.41\varphi^2 \]  

This equation is derived from a consideration of the effect of a distribution of solid spherical particles (which is often termed the hydrodynamic, or strain amplification effect) and their 'next neighbour' interactions [Melnecke and Maksin (1980)] upon the elastic modulus. Values of \( E_0^r \) predicted by the Guth-Gold equation are typically of the order of 2 (being significantly smaller than those predicted by the Frankel Acrivos equation, which essentially relates to the formation of a carbon black network, which can give rise to \( E_0^r \) values of the order of 10 or more). Various modifications have been suggested which involve the replacement of the volume fraction \( \varphi \) by some quantity which better represents the microscopic environment of the material, but since the Guth-Gold equation is based upon dynamic considerations, it cannot predict the much larger increase in modulus which is sometimes associated with the formation of an independent carbon black network [Ferry and Fitzgerald (1982)].

Since the Guth-Gold equation in some cases predicts the value
of the filled tensile modulus from that of the unfilled, especially for smaller loadings, or in the absence of any significant carbon black network structure, it is of interest to enquire to what extent it may be applied in the case of other viscoelastic moduli.

Meincke and Maksin (1980) have investigated the incremental dynamic modulus (see §6.1.5) behaviour of styrene-butadiene copolymers at various loadings of HAF black in small amplitude oscillation about some imposed static strain. They assume that the Guth-Gold equation should account for the relation between the stresses measured in the filled and corresponding unfilled samples, and conclude that the associated ratio of filled to unfilled modulus values depends upon the imposed static strain. The procedure assumes that the loss modulus is negligibly small in comparison to the storage modulus, and that the latter in consequence is approximately equal to the value of the complex modulus. The ratio of energy dissipation per cycle for the filled and unfilled systems is however obtained, and is considered to depend upon the square of the 'amplification factor' which predicts the corresponding ratio for the storage moduli. Since the loss modulus is directly proportional to the energy dissipation [Ward (1979)], this effectively means that different amplification factors are applied to different moduli. It is interesting to note however that the energy dissipation may be related to the square of the dynamic strain amplitude, and thus we conjecture that the strain amplification concept, upon which the Guth-Gold equation is based, may be more fruitfully applied directly to a modification of the strain measure, rather than to modification of the viscoelastic moduli.

Since both components of the complex modulus have been shown by Meincke and Maksin to depend in different ways upon the predicted amplification factor of the Guth-Gold equation, this factor itself being strain-dependent, they conclude that '\(E', E''\) and \(\tan \delta\) are not primary viscoelastic parameters for statically deformed materials' and state further that '\(\tan \delta\) cannot be used, therefore, to describe the influence of strain induced orientation on the energy dissipating process in strained elastomers'. These observations relate essentially to the fact that the Guth-Gold equation is not able to account for strain effects outside the region of infinitesimal deformation.
Chang, Wijayarathna and Salovey (1984) represent the strain amplification concept in the general form

\[ \frac{\varepsilon_{\text{mic}}}{\varepsilon_{\text{mac}}} = f(\varphi), \quad [2.31] \]

where \( \varepsilon_{\text{mic}} \) and \( \varepsilon_{\text{mac}} \) are components of the microscopic and macroscopic strains respectively. They further propose that a component \( \sigma_n \) of the macroscopic nominal stress tensor can be expressed as a function of the corresponding microscopic strain component \( \varepsilon_{\text{mic}} \) such that

\[ \sigma_n = g(\varepsilon_{\text{mic}}). \quad [2.32] \]

Relations [2.31] and [2.32] lead to the conclusion that log-log plots of nominal stress against strain for specific filler loadings should all be superposable by horizontal shifts. For the nitrile rubber filled with MT carbon black studied by Chang et al this was found to hold within certain ranges of deformation, which depended upon the level of loading. (For \( \varphi = 0.2 \) this range corresponds to extension ratios \( \lambda \) such that \( \lambda < 2.1 \). They suggested that the limiting values of these ranges correspond to those values of strain at which the carbon black network is no longer capable of undergoing affine deformation. (This is also proposed as the limiting mechanism on the applicability of the separable time-filler loading-strain expression for stress which was proposed by Smith (1963) to describe his constant strain rate experiments.)

Since the function \( g(\varepsilon_{\text{mic}}) \) is not required to be linear, it is in principle possible to overcome the difficulty of accounting for the strain-dependent strain amplification effect which was investigated by Meinecke and Maksin (1980), subject to the limitations which are apparently imposed by affine deformation of the carbon black network.

(iii) Failure Region

Beyond the limit of affine deformation of the carbon black network, Chang, Wijayarathna and Salovey (1984) claim that the
behaviour of highly filled elastomers ($\phi > 0.25$) depends largely upon microcavitation, which leads to the phenomenon known as stress-softening. Chang et al state that microcavitation under negative hydrostatic pressure depends upon the size of the initial voids, Young's modulus, the tearing energy, the thermodynamic surface energy, and the extensibility of the matrix. They also propose that microcavitation is responsible for their observation that 'the stress-strain curve of highly filled elastomers shows a distinct yield point'. Wool (1978) has developed a theory of material damage for viscoelastic polymers in terms of 'reversible cracks', and Ruberstein and Fitzgerald (1979) have shown that such cracks may be applied to a 3-dimensional treatment of debonding between filler and matrix. Such an approach is thus qualitatively similar to considerations of microcavitation.

Since voids due to cavitation or 3-dimensional cracks are capable of undergoing a healing process which restores the structure of the material, it is not clear to what extent they may be incorporated into a conventional viscoelastic treatment. Wool recognises this fact and states that 'these effects need to be distinguished from similar phenomena in linear viscoelastic materials obtained by varying the deformation history'. Wool claims that surface energy conversion may play an important rôle and can lead to phenomena such as a slower rate of strain recovery following creep for increasingly higher temperatures. Such an effect is not predicted by viscoelastic theory, but neither from the results of Djiauw and Gent (1974) does it appear to have been observed for their filled elastomers. These results are however presented in the form of master curves, and no appropriate isothermal data are presented. It is also possible to consider agglomerate breakdown - reformation as a significant effect [Fitzgerald (1982)].

It has been suggested [Medalia (1978) p.463] that the decrease in storage modulus which is observed upon increasing the strain amplitude during an oscillatory experiment results from the rupture of successive bonds, which reach their limiting extension and subsequently fail. It is further suggested [ibid.] that this response may be associated with a log normal distribution of bond energies. Since damage theories are likely to require some statistical treatment for the rupture occurring in the elastomer matrix, we may speculate whether the above effect could also be
accounted for in terms of such a theory.

Many authors have referred to the phenomenon of stress softening, often without specific reference to the basis upon which it is observed. Rigbi (1980) comments that 'as traditionally studied, stress softening is observed as a shift in the stress-strain curve', but adds that 'Dannenberg and Brennan and Peremsky chose to look upon energy in the first stress cycle as the independent variable for the comparison of stress softening between samples of different rubbers and with varying loading'. This indicates that a comparison between the relative changes in energy dissipation during successive cycles of deformation should be taken as a criterion for stress softening, and explains the statement of Chang et al (1984) that 'energy dissipation in a filled system is often called stress softening'.

It has been proposed that reduction in the storage modulus due to structural damage and the energy dissipation properties of the matrix are related [Medalia (1978)]. This assumption implies that the greater the amount of input energy which is converted into heat, the less is directed to the physical disruption of the elastomer structure.

Consideration has been given to the effects which are likely to occur within filled elastomers in the range of large deformation. A significant degree of cavitation is likely to have a strong influence upon the thermal behaviour of the material, and is also likely to invalidate some basic constitutive assumptions such as incompressibility. Thus although some degree of cavitation might be accommodated within a viscoelastic description of material behaviour, with further damage to the elastomer matrix, a point will be reached at which such a description is invalidated.

In conclusion we state that the Guth-Gold equation [2.30] can be useful in representing material behaviour within the region of small deformation, provided that there is no significant contribution from an independent carbon black network. Although such a contribution exists for many combinations of elastomer matrix and carbon black filler (and is also manifest in the thermal behaviour of the material - see §3.2.2), experimental investigation such as that of Meinecke and Maksin (1980) often shows that this effect can be largely eliminated by subjecting the sample to a programme of strain.
conditioning or 'scragging'. Thus in many cases, effects associated with an independent carbon black network need not constitute an overwhelming practical consideration.

At higher loadings however, a carbon black network, such as that described by the Frankel Acrivos equation, may dominate the material response in infinitesimal deformation, and impose a constraint upon the application of a viscoelastic constitutive equation. In this case a composite network theory (see also §6.2.2) as reviewed by Chang, Bloch and Tschoegl (1977a) may offer some possibility of modeling material behaviour. The onset of a significant amount of material damage in the elastomer matrix similarly serves to limit the application of a viscoelastic constitutive equation in the case of large strains.

From the work of Chang, Wijayarathna and Salovey it would seem that simplifying properties such as time-strain separability (see §6.1.4) are limited to affine deformations corresponding to $\lambda \leq 2$, and a number of investigators have succeeded in producing results which are only valid for $\lambda \leq 1.6$. It follows therefore that $1.6 < \lambda < 2$ should constitute a probable limit to the range of deformation over which a viscoelastic constitutive equation might generally be expected to apply in the case of filled elastomers. It has been pointed out also that this is dependent upon loading and the specific composition of the filler elastomer.

2.2.5 The Role of a Constitutive Equation for Carbon Black Filled Elastomers

The formulation of a constitutive equation to model the behaviour of carbon black filled elastomers would bestow a number of important practical advantages. These advantages include:

(1) Predicting the performance of components, which is presently done using finite element analysis techniques, and can result in large errors.

(ii) Aiding in the production of improved compounds. Presently, as Rigbi (1980) comments, 'The achievement of a proper balance between ... undesirable contributions of a reinforcing filler
and even a minor improvement of abrasion resistance, for example, is one of the arts of the rubber compounder and the reason for the availability of a large number of grades of carbon black'. The existence of a constitutive equation for filled elastomers would aid in analysing the properties of specific formulations, and hence provide a basis for improved compounding.

(iii) Promoting an understanding of the microstructure of carbon black filled elastomers. In this respect Rigbi (1980) comments 'The mechanism by which carbon black reinforces elastomers is one of the most interesting problems of modern technology and still a subject of much speculation'.

The following points are of importance with regard to describing the behaviour of carbon black filled elastomers:-

(a) A distinction may be made depending upon whether the properties of the elastomer reveal the influence of an independent carbon black network (see §2.2.4). In the presence of such a network it may be necessary to express the composite nature of the material in terms of a 2-network theory, rather than adopt a continuum mechanical approach.

(b) At higher strains, effects such as cavitation may invalidate a continuum approach (see §2.2.4), and this is likely to impose a constraint on the range of deformation which may be described in terms of a continuum mechanical theory.

Thus we may conclude that the application of a constitutive equation to describe the behaviour of filled elastomers is likely to be confined to a certain class of such materials, and to be valid only within a certain range of deformation.

2.2.6 Specific Materials for Investigation

Carbon black filled elastomers exhibit diverse behaviours depending upon their formulation, processing and cure (see §2.2.1). It is often difficult to make a direct comparison between the
behaviour of one specific material and that of another. Furthermore, it is known that the mode in which an experiment is carried out, and in particular the strain pre-conditioning or "scraggling", often affects the observed behaviour [Peters, De Meersman and Devis]. These considerations indicate the desirability of relating discussion in this thesis to data from well defined experiments carried out upon materials whose exact composition, processing and cure are also well specified. In order to obtain such data, experiments have been carried out upon two formulations of a butadiene-acrylonitrile elastomer known commercially as KRYNAC 806. One of these formulations contains 50phr of the carbon black designated SRF N774. This is a furnace black. These samples were kindly supplied by RAPRA Technology Ltd in the form of moulded cylinders. The dimensions of the mould cavities (diameter x length) which were used to produce these samples were 16mm x 160mm and 25.4mm x 254mm. Details supplied by RAPRA of the compounding, processing, and cure of these samples are given in Table 2.1.

The use of filled and unfilled samples makes it possible to demonstrate by direct comparison effects of addition of carbon black upon the behaviour of the particular elastomer studied. The 50phr loading of the filled sample exemplifies the level of loading which is commonly encountered in industrial applications.

The particular butadiene-acrylonitrile base polymer KRYNAC 806, which possesses a high nitrile content, was chosen upon the advice of Dr P Howgate, who supported the initial stages of this work at RAPRA. KRYNAC 806 demonstrates a simple transition region, with no secondary transitions (see Figure 2.1). Moreover, the glass transition temperature for most elastomers is well below room temperature, but in the case of KRYNAC 806, $T_g$ is found to occur at around 0°C. This enables relative ease of experimental access to the whole of the glass transition region. Thus the dramatic temperature dependence of the material can be analysed to the fullest practical extent.

Experiments undertaken to characterise the specific materials selected (which will subsequently be referred to as the filled and unfilled materials) are described in Chapter 4 and Chapter 7. Analysis of the results of these experiments requires values for the densities of the samples. The density of the unfilled material was measured as 1.075g/cc, while that of the filled material was 1.228g/cc.
CHAPTER 3

LINEAR VISCOELASTIC THEORY AND TIME-TEMPERATURE SUPERPOSITION

INTRODUCTION

This chapter presents theory which is applicable to the analysis of temperature dependent experiments carried out at infinitesimal deformation. A series of such experiments is described in Chapter 4, and the theory presented here is used to analyse the results which are presented in Chapter 5. Since these experiments are carried out over a range of discrete temperatures, this chapter is divided into two overall sections, the first considering isothermal deformation and the second temperature dependence.

The first section reviews how stresses and strains are related in infinitesimal deformation by means of linear viscoelastic theory. The linear viscoelastic moduli and compliances which characterise material behaviour are introduced and defined, together with the relaxation spectrum and interrelationships between these quantities.

The second section reviews how temperature dependence can be accounted for by means of the time-temperature superposition principle. Published experimental evidence concerning the application of the time-temperature superposition principle to carbon black filled elastomers is presented and shown to provide a basis for the classification of these materials.

3.1 LINEAR VISCOELASTIC THEORY

3.1.1 The Linear Viscoelastic Constitutive Equation and Linear Viscoelastic Moduli

It has been stated in Chapter 2 that constitutive equations in general include dependencies on both kinematics and temperature. A simplification may be achieved by neglecting temperature dependence. This corresponds to the so-called 'isothermal' case (see §2.1.3). For infinitesimal deformations the relationship between stress and
strain history may be represented in terms of a relation between the
stress tensor $\sigma$ (Cauchy stress and engineering stress coincide for
infinitesimal deformation) and the history of the infinitesimal
strain tensor $\varepsilon$. For a homogeneous isotropic material [Ferry (1970)]

$$
\sigma_{ij} = 2 \int_{-\infty}^{t} G(t-\tau) \frac{d}{d\tau} [\varepsilon_{ij}(\tau)] d\tau + 2 \int_{-\infty}^{t} K(t-\tau) \frac{d}{d\tau} [\varepsilon_{kk}(\tau)] d\tau ,
$$

[3.01]

where $G(t)$ is the shear relaxation modulus, and $K(t)$ is a volumetric
relaxation modulus.

Consider an idealised experiment which consists of an
instantaneously imposed simple shear deformation, such that $\varepsilon_{12}$ and
and $\varepsilon_{21}$ are the only non-zero strain components, and

$$
\frac{d}{dt} [\varepsilon_{12}(t)] = \gamma \delta(t) ,
$$

where $\delta(t)$ is the Dirac delta function and $\gamma$ is the shear strain.

It follows from [3.01] that the relationship between shear stress
$\sigma_{12}$ and shear strain $\gamma$ is given by

$$
\sigma_{12}(t) = G(t) \gamma .
$$

[3.02]

Hence

$$
G(t) = \frac{\sigma_{12}(t)}{\gamma} .
$$

[3.03]

Thus $G(t)$ may be determined from a one-dimensional stress relaxation
experiment as the ratio of the time-dependent shear stress $\sigma_{12}(t)$ to
the 'instantaneously' imposed constant shear strain $\gamma$.

An equivalent experiment in simple tension consists of imposing
an instantaneous tensile strain $\varepsilon_{11}$ on a body of constant
cross-section such that

$$
\frac{d}{dt} [\varepsilon_{11}(t)] = \varepsilon \delta(t) ,
$$

[3.04]

where $\varepsilon$ is the tensile strain component in the axial direction and
where the lateral surfaces are free to contract producing corresponding lateral strains $\varepsilon_{22}$ and $\varepsilon_{33}$. Imposing the condition that the lateral stresses should be zero, it may be shown [Ferry (1970)] that

$$\sigma_{11}(t) = \varepsilon(t) G(t) \frac{[2G(t) + 3K(t)]}{G(t) + K(t)}. \quad [3.05]$$

By analogy with [3.03] the tensile relaxation modulus $E(t)$ is defined as

$$E(t) = \frac{\sigma_{11}(t)}{\varepsilon(t)}. \quad [3.06]$$

and from [3.05]

$$E(t) = G(t) \frac{[2G(t) + 3K(t)]}{G(t) + K(t)}. \quad [3.07]$$

For a constant density material, from equation [2.20] $\nabla \cdot \mathbf{v} = 0$, and thus by equation [2.11] $d_{kk} = 0$. \quad [3.08]

Now

$$\frac{d}{dt} [\varepsilon_{ij}(t)] = \frac{d}{dt} \left[ \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right] = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right).$$

For infinitesimal deformation $\mathbf{X} \rightarrow \mathbf{X}$, and thus

$$\lim_{\mathbf{X} \rightarrow \mathbf{X}} \frac{d}{dt} [\varepsilon_{ij}(t)].$$

Hence for an incompressible material in infinitesimal deformation, from [3.08]

$$\frac{d}{dt} [\varepsilon_{kk}(t)] = 0. \quad [3.09]$$

Moreover, for incompressible materials the strain history determines...
the stress to within an arbitrary isotropic pressure, and hence from [3.01] the deviatoric stress is given by

$$\sigma_{ij} = 2 \int_{-\infty}^{t} G(t-\tau) \frac{d}{d\tau} \epsilon_{ij}(\tau) d\tau.$$  \[3.10\]

The above relation is known as the linear viscoelastic constitutive equation. Its linearity consists not only in postulating a linear relationship between stress and strain for sufficiently small deformations, but also in postulating that the results of successive strain events may be added linearly. This second postulate, which precludes higher order interactions between distinct strain events, is known as the Boltzmann superposition principle. Infinitesimal deformation requires that the strain $\epsilon_{ij}$ should be small. The Boltzmann superposition principle imposes the additional restriction that the rate of strain $\frac{d}{dt} \epsilon_{ij}$ should also be small [Pipkin (1972)].

For an incompressible material,

$$K(t) \gg G(t)$$  \[3.11\]

and from [3.07] we derive the approximate relation

$$E(t) = 3G(t).$$  \[3.12\]

It should be noted that incompressibility is an idealisation, and that since the moduli $K(t)$ and $G(t)$ are time-dependent quantities, there will in general exist some timescale for which the inequality [3.11] is invalid for an otherwise 'incompressible' material [Ferry (1970)].

Consider a small amplitude oscillatory shear strain given by

$$\epsilon_{ij} = \text{Re}\{i\gamma_0 e^{i\omega t}\},$$  \[3.13\]

where $\gamma_0$ is the shear strain amplitude, and corresponding oscillatory shear stress, which is out of phase by the loss angle $\delta$. 

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where $\sigma_0$ is the stress amplitude. Then in view of (3.10) these are related by

$$\text{Re}\{\sigma_0 e^{i(\omega t+\delta)}\} = \text{Re}\{G^*(\omega)\gamma_0 e^{i\omega t}\} ,$$

(3.15)

where $G^*(\omega)$ is the complex shear modulus, related to the one-sided Fourier transform of the shear relaxation modulus by

$$G^*(\omega) = \omega \int_0^\infty [G(\tau) - G_e] e^{-i\omega \tau} d\tau + G_e ,$$

(3.16)

where $G_e$ is the equilibrium shear modulus defined in (3.26).

A complex tensile modulus $E^*(\omega)$ may be defined analogously. Thus from (3.12)

$$E^*(\omega) = 3G^*(\omega) .$$

(3.17)

From (3.15)

$$G^*(\omega) = \frac{\sigma_0 e^{i\omega \delta}}{\gamma_0} .$$

(3.18)

This enables $G^*(\omega)$ to be determined experimentally from the ratio of the amplitudes of oscillatory stress and strain and from the loss angle. The complex shear modulus may be decomposed into real and imaginary parts

$$G^*(\omega) = G'(\omega) + iG''(\omega) ,$$

(3.19)

where $G'(\omega)$ is the storage modulus - related to the amount of elastic energy stored and released per cycle - and $G''(\omega)$ is the loss modulus - related to the amount of viscous dissipation of energy per cycle [Ward (1979)]. From (3.18) we may define tan$\delta$ by

$$\tan \delta = \frac{G''}{G'} .$$

(3.20)
This quantity is much used by rubber technologists since it represents the ratio of dissipation to storage of the energy per cycle.

### 3.1.2 Inversion of the Linear Viscoelastic Constitutive Equation and Compliances

The linear viscoelastic constitutive equation for an incompressible isotropic material may be inverted to yield

\[
\epsilon_{ij}(t) = \frac{1}{2} \int_{-\infty}^{t} J(t-\tau) \frac{d}{d\tau} [\sigma_{ij}'(\tau)] d\tau ,
\]

where \( J(t) \) is the shear creep compliance.

A complex shear compliance \( J^*(\omega) \) is defined analogously to \([3.15]\) by

\[
\text{Re}\{\sigma_0 e^{i(\omega t + \delta)} J^*(\omega)\} = \text{Re}\{\gamma_0 e^{i\omega t}\} .
\]

The complex shear compliance and complex shear modulus are related by

\[
G^*(\omega) = \frac{1}{J^*(\omega)} .
\]

The complex shear compliance may be decomposed such that

\[
J^*(\omega) = J'(\omega) - iJ''(\omega) ,
\]

where \( J'(\omega) \) is the storage compliance, and \( J''(\omega) \) is the loss compliance.
shear modulus $G$. Thus the instantaneous analogue of [3.02] is

$$\sigma_{12}^0 = G\gamma$$

and

$$G = \lim_{t \to 0} G(t). \quad [3.25]$$

Similarly, at long times the equilibrium shear stress $\sigma_{12}^\infty$ and the shear strain $\gamma$ are related by the equilibrium shear modulus $G_e$, such that

$$\sigma_{12}^\infty = G_e\gamma$$

and

$$G_e = \lim_{t \to \infty} G(t). \quad [3.26]$$

The shear relaxation modulus $G(t)$ may be expressed as the sum of a transient component $\Delta G(t)$ and the equilibrium shear modulus $G_e$ such that

$$G(t) = \Delta G(t) + G_e. \quad [3.27]$$

The transient component of the shear relaxation modulus $\Delta G(t)$ is related to the (logarithmic) relaxation spectrum $H(\tau)$ by the relation

$$\Delta G(t) = \int_{-\infty}^{\infty} H(\tau)e^{-t/\tau}d\ln \tau. \quad [3.28]$$

In conclusion it should be stated that quantities corresponding to linear moduli and compliances are often determined for deformations which exceed the range of validity of the linear viscoelastic constitutive equation [3.10]. Such quantities may be referred to as non-linear moduli or compliances. It should be emphasised that although the experimental determination of these
non-linear quantities is the same as for the corresponding linear ones, they do not possess the same significance and are no longer related by the structure of linear viscoelastic theory.

3.2 TIME-TEMPERATURE SUPERPOSITION

3.2.1 The Time-temperature Superposition Principle

In seeking to account for changes in behaviour over a range of discrete temperatures, many authors have resorted to the time-temperature superposition principle [Ferry (1970)]. This is basically an empirical technique for relating isothermal measurements at different temperatures, and has been found to apply to a large class of materials.

In its simplest form the time-temperature superposition principle requires that isothermal plots of any quantity against logarithmic time or frequency should be superposable - by horizontal shifts, \( \log a_T(T) \) - with a reference isotherm corresponding to an arbitrary reference temperature \( T_0 \). This process is shown schematically in Figure 3.1. In particular, for the relaxation spectrum \( H(\tau) \) (from which all other linear viscoelastic quantities may theoretically be obtained), the time-temperature superposition principle implies that

\[
H(\tau, T) = H(\tau/a_T(T), T_0).
\]

Thus the spectrum at some temperature \( T \) may be obtained as \( H(\tau/a_T(T)) \), where \( H(\tau) \) is the spectrum at the reference temperature \( T_0 \). This is sometimes stated in terms of the temperature dependence of the relaxation times \( \tau \), cf. Duperray and Leblanc (1982), but since \( \tau \) represents an independent time variable it is better to refer to relaxation mechanisms, cf. Ferry and Fitzgerald (1982). The latter draw attention to 'the essential criterion for superposition ... the same temperature dependence for all relaxation mechanisms', i.e. the transformation \( \tau \rightarrow \tau/a_T \) is independent of \( \tau \).

Relaxation spectra may in turn be related to various molecular processes and their associated activation energies. Duperray and Leblanc (1982) refer to a classical Arrhenius activation mechanism,
and draw the conclusion that the distribution of relaxation times, ie. the distribution $H(\tau)$ plotted against $\log \tau$, must be affected by changes in temperature. This inference is inconsistent with the time-temperature superposition principle referred to above, indeed Cotten and Boonstra (1965) specifically state that temperature invariance of the activation energy must be assumed for the application of this principle. Nevertheless, Duperray and Leblanc use their conclusion to justify the introduction of a further vertical shift factor with the aim of improving superposition. Such vertical shift factors, either singly, or in combination with horizontal shifts, have in fact been used by a number of authors on a quite ad hoc basis eg. Chang, Bloch and Tschoegl (1976(b)), Fitzgerald and Ferry (1982).

Relating the time-temperature superposition principle to molecular theories of viscoelasticity suggests that superposition should also require multiplication of the shifted modulus curves by the factor $T_p/T_0 \rho_0$, where $\rho$ and $\rho_0$ are the densities at temperatures $T$ and $T_0$ respectively. Such a procedure is equivalent to a small vertical shift, but its effect is only marginally significant. 'In practice, the correction factor $[T_p/T_0 \rho_0]$ has a very small effect in the viscoelastic range of temperatures compared with the large changes in the viscoelastic behaviour. Thus it is usually adequate to apply a simple horizontal shift ...' Ward (1979).

The time-temperature superposition principle, as applied to unfilled materials, is taken to represent the temperature dependence of the viscoelastic mechanism associated with configurational motions of the polymer chain backbone [Ferry (1970)]. When other viscoelastic mechanisms make contributions of similar magnitude this places a limitation upon superposition, and for this reason superposition may not be obtained at temperatures far above the glass transition temperature $T_g$ (see §2.2.2). Below $T_g$ chain backbone mobility is lost. Thus superposition may generally be expected in the temperature range $T_g, T_g + 100^\circ C$, when 'the internal structure of the system does not change with change in temperature' [ibid].
3.2.2 Application of Time-temperature Superposition to Small Deformations of Carbon Black Filled Elastomers

Literature evidence for the application of time-temperature superposition to carbon black filled elastomers with regard to deformations at small strain is given in Table 2.1. It is apparent that in some cases superposition is achieved with horizontal shifts only, whereas in other cases vertical shifts are required. This leads Ferry and Fitzgerald (1982) to comment 'it seems impossible to generalise concerning the temperature and frequency dependencies of dynamic properties of carbon black-loaded rubbers'. Such disparities also seem to be connected with the relative magnitudes of the modulus values pertaining to the filled and corresponding unfilled elastomer. 'It appears that a small increase in modulus due to loading is associated with normal frequency-temperature superposition and frequency dependence of $G'$ and $G''$; whereas a large increase is associated with much more complicated behaviour' [ibid].

Such a large increase in modulus is observed in the case of cis-polybutadiene-styrene butadiene copolymer, of which Fitzgerald and Ferry (1982) comment 'it seems evident from these results that an independent carbon black network contributes substantially to the small-amplitude dynamic mechanical response'.

Fitzgerald (1982) suggested that the shear modulus of a carbon black network depends upon the number of aggregates per agglomeration, and that this in turn is dependent upon the temperature. This constitutes a mechanism for explaining the observation of Isono and Ferry (1984) that for some filled elastomers 'temperature dependence appears to be dominated by a change in magnitude of elastic modulus rather than a shift in relaxation times'.

Furthermore, instances of vertical superposition have yielded curves which are only partially superposable. Certain isothermal data fail to superpose, and constitute curves which differ in shape from the smooth composite curve produced by superposition. This has been taken to imply the existence of two separate temperature regimes for such materials. Plots of shift factor against temperature exhibit two regions of differing gradient, and this has been taken as further evidence to support this conclusion [Fitzgerald and Ferry (1982)]. These distinct temperature regimes may thus indicate the
effect of different viscoelastic mechanisms occurring within the structure of the carbon black network.

We thus conclude that carbon black filled elastomers appear to fall into three broad classes, depending upon their susceptibility to time-temperature superposition. This classification consists of those materials which superpose nearly or exactly upon application of horizontal shifts, those which require vertical shifts, and those for which no superposition can be obtained by any combination of horizontal and vertical shifts. This classification has important implications for modelling the behaviour of carbon black filled elastomers.

In conclusion we may state that consideration of the susceptibility of carbon black filled elastomers to time-temperature superposition strengthens the assertion of §2.2.5 that such materials may exhibit diverse behaviours, and reaffirms the need to restrict our attention to a particular class of such materials by relating our discussion to results obtained on specific materials.
CHAPTER 4

EXPERIMENTAL CHARACTERISATION OF LINEAR PROPERTIES

INTRODUCTION

This chapter presents details of infinitesimal deformation experiments conducted in order to determine the linear viscoelastic properties of the materials described in §2.2.6. The significance of such a linear characterisation, and the conditions which must be satisfied in order to achieve this are discussed, together with the relative advantages and disadvantages of experiments in particular modes of deformation. Reasons for choosing an oscillatory (or dynamic) mode of testing are discussed, and techniques and apparatus for dynamic testing are surveyed.

The apparatus used for testing - a Weissenberg rheogoniometer - is described in detail, together with the temperature control and data logging systems. The experimental procedure is described and the theory required for analysis of results is presented. Analytic solutions obtained by ignoring the mass of the sample are compared with numerical solutions which take such 'inertial effects' into account. Errors associated with resonance are considered and it is demonstrated that the magnitude of this effect depends on both temperature and frequency. Errors due to viscous heating are also discussed.

4.1 LINEAR CHARACTERISATION OF A MATERIAL

The linear viscoelastic constitutive equation [3.10] describes deformation history dependence and dependence on timescale of deformation for a viscoelastic material in infinitesimal deformation under 'isothermal' conditions and when the rate of strain is sufficiently small (see §3.1.1). It is thus a convenient point from which to commence the characterisation of a material in terms of a constitutive equation.

The range of deformation for which [3.10] adequately represents
the material response is known as the linear regime. In order to apply [3.10] to the behaviour of a given material it is necessary to determine that range of strain within which stress is found (to within a given approximation) to vary linearly with strain. As stated in §3.1.1, one-dimensional experiments suffice to determine linear viscoelastic moduli for isotropic materials – the modulus being defined as the ratio of stress to strain. Thus if the modulus determined at constant strain rate for increasing values of strain is found to be constant (to within a given approximation), it may thus be concluded that the applied strains lie within the region of stress-strain linearity for that particular mode of deformation and rate of strain.

We will now consider the significance of the rate of strain in determining the linear regime. Theoretically a stress relaxation experiment consists in subjecting a sample to a single instantaneously imposed deformation. This does not involve superposition of the effects of successively imposed strains, and hence places no restriction upon the applied rate of strain (which is assumed infinite) – see §3.1.1. In the general case however, [3.10] restricts admissible rates of strain. This is illustrated by data obtained by Bloch, Chang and Tschoegl (1978b) on a peroxide cured styrene-butadiene rubber. It was found that although stress relaxation data were consistent with [3.10], in constant rate of strain experiments the predictions of [3.10] were not satisfied. This indicates that in terms of the intrinsic timescale of the material the applied rates of strain were unacceptably large.

In the case of oscillatory experiments the applied rate of strain is not constant and depends upon frequency and amplitude. Increasing oscillatory amplitude at constant frequency thus not only produces a corresponding increase in stress, but also serves to increase the maximum strain rate. If the measured modulus is found to be independent of oscillatory amplitude it may thus be concluded that both the applied strain and rate of strain lie within limits for which the restrictions upon [3.10] are satisfied. Under these circumstances it is legitimate to equate the measured modulus value with that of the linear viscoelastic modulus.

Theoretically, any linear viscoelastic modulus may be used to calculate any other. Thus the choice of the modulus to be determined is largely a matter of experimental convenience. The most commonly
measured linear viscoelastic quantities include the relaxation modulus and the components of the complex modulus together with the corresponding compliances. In theory a single relaxation experiment is sufficient to characterise the linear behaviour of a material. Practically however, such experiments are subject to certain limitations, which will now be discussed.

Strains cannot be imposed instantaneously, and consequently results at short times are subject to errors due to 'ramp transients'. Similarly at long times the decay of the residual stress becomes so small that this may be affected by various sources of experimental error such as clamp slippage. Thus, at a given temperature, only a certain range of the time dependence is rendered experimentally accessible. In order to obtain equivalent information in terms of the complex modulus many experiments must be carried out over a corresponding frequency range.

Transient experiments such as stress relaxation generally take much longer to perform than oscillatory experiments. If a steady temperature cannot be maintained for the duration of an experiment it may need to be repeated, since for some materials, such as polymers, material behaviour is highly temperature dependent (see §2.2.2). Oscillatory experiments are more convenient to repeat (if viscous heating of the sample is negligible) than transient experiments since they require less time, and because steady temperatures are easier to maintain over shorter timescales. In conducting relaxation experiments at low temperatures, the timescale of relaxation will be diminished as the material becomes closer to a perfectly elastic solid. The time required to impose a deformation is however constant, and thus limits the extent to which relaxation data may usefully be exploited at reduced temperatures. Oscillatory experiments may therefore be regarded as possessing certain advantages over relaxation experiments when obtaining data at discrete temperatures. Conversely, oscillatory experiments are probably more susceptible to viscous heating than relaxation experiments. This is a factor which needs to be accounted for in experimental design.

Since it was desired to examine the temperature dependence of the experimental materials in addition to isothermal linear characterisation, an oscillatory (or dynamic) mode of testing was selected.
4.2 METHODS AND APPARATUS FOR DYNAMIC TESTING OVER A DISCRETE TEMPERATURE RANGE

Methods of dynamic testing may be classified according to whether the measured vibrations are free — such as in the case of the torsion pendulum — or forced (which may be taken as including wave propagation techniques). In the case of forced vibration these may be further classified into resonance and non-resonance methods. Although free vibration and resonance methods are more accurate than forced non-resonance techniques the former are somewhat restricted in their range of experimentally accessible frequencies, and moreover this range is found to be temperature dependent. Investigation of frequency dependence over a discrete temperature range is thus best carried out by means of a non-resonance forced vibration technique.

The choice of apparatus for a non-resonance forced vibration experiment depends essentially upon the frequency range which it is desired to investigate. A Weissenberg rheogoniometer linked to an appropriate gearing system (see Figure 4.1) is capable of accessing a frequency range whose upper bound corresponds to the design limit of the instrument, at around 60Hz, and whose lower bound is effectively determined by the gearing arrangement. Such a frequency range is quite adequate for investigation of the frequency dependence of polymeric materials close to their glass transition temperature (see §2.2.2).

As an idealisation, simple shear may be preferred to a deformation such as simple extension since the shear deformation (if indeed such a deformation can be imposed†) is one-dimensional, whereas simple extension also involves changes in the lateral directions. Moreover, shear produces no change in volume, whereas in simple extension volume changes may occur (see §3.1.1). The deformation produced by the Weissenberg rheogoniometer is torsional shear. This deformation does however possess the disadvantage of being inhomogeneous, and thus in seeking to determine the 'linear regime' (see §4.1) a departure from linearity may consequently

† The phenomenon known as the Poynting effect may cause the sample dimensions to change appreciably in other coordinate directions unless the applied shear is infinitesimal [Atkin & Fox (1980)].
produce only a small effect upon the measured modulus value. This is due to the fact that upon increasing oscillatory amplitude, strains and rates of strain which exceed the limits of the linear regime will first be encountered only in a vanishing small region at the perimeter of the sample, and this might have no significant effect upon the measured modulus value.

A further consideration is that of the sample dimensions. The Weissenberg rheogoniometer requires rather large samples (see §4.3), and thus care must be taken in establishing a homogeneous temperature field within the sample and in mitigating against the effects of viscous heating.

The Weissenberg rheogoniometer thus enables forced non-resonance testing of samples in shear deformation over a range of discrete temperatures and over a frequency range of experimental utility (sufficiently large to examine, for example, the applicability of time-temperature superposition - Ferry (1970)). However its disadvantages include the fact that torsional shear is not an ideal deformation for investigation of the linear regime, and also that the required sample dimensions present certain difficulties with regard to temperature control. Despite these drawbacks the Weissenberg rheogoniometer has been used successfully for similar experimentation by investigators such as Ward and Jenkins (1958) and Jones and Davies (1982). In view of this success and of the availability of the apparatus used by Jones and Davies, it was resolved to utilise this apparatus in investigating the extent of the linear regime and the frequency dependence of the experimental materials over a range of discrete temperatures. This apparatus is described in the following section.

4.3 EXPERIMENTAL APPARATUS: THE WEISSENBERG RHEOGONIOMETER, TEMPERATURE CONTROL, AND DATA LOGGING SYSTEMS

The arrangement of the Weissenberg rheogoniometer is represented in Figure 4.1. Power is supplied to the drive shafts by electric motors via an automatic gearbox. The drive shafts power the drive box via an electromagnetic clutch, and a mechanical sine wave generator drives the lower platen through a worm and gear arrangement. A transducer located near the base of the instrument
measures the horizontal displacement of the driving mechanism, and this is used to calculate the displacement of the vertically mounted lower platen. It is assumed that the worm and gear arrangement do not produce a significant distortion of the mechanically generated sine wave.

The sample is mounted between the upper and lower platens, and may be enclosed within a temperature chamber. The upper platen forms part of the measuring head. This is constrained within an air bearing and suspended from the column of the machine by a torsion bar.

The displacement conveyed to the upper platen via the sample is resisted by the restoring torque of the torsion bar, which may be interchanged in order to vary the torque. This displacement of the upper platen is detected by a transducer mounted above the air bearing. This measures the tangential displacement of a probe connected to the measuring head via a radially mounted bar.

The transducer voltages corresponding to the displacements of the upper and lower platens are amplified, digitised, and passed to a microcomputer. The interfacing of the rheogoniometer with an Apple II microcomputer was carried out by Dr J M Davies of Plymouth Polytechnic. A schematic of this computer control facility is given in Figure 4.3. The computer monitors the motor speed by means of a digital tachometer, and from the setting of the automatic gearbox is able to calculate the oscillation frequency. The amplitudes of oscillation of the upper and lower platens are calculated by integrating 100 readings taken over one cycle. Comparison of the 1st harmonics resulting from Fourier analysis of the waveforms also allows the phase difference to be determined. From this data the components of the complex modulus can be calculated and the variation of $G'$ and $G''$ with frequency logged directly onto magnetic disc. Such computer interfacing of the Weissenberg rheogoniometer also allows for continuous monitoring of the instantaneous waveforms

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† It is customary to refer to the sample as being mounted between the upper and lower platens of the instrument. In this application the usual parallel plate measuring faces were not in fact used, their place being taken by perspex mountings, countersunk by ~1mm in order to accommodate the ends of the sample (see Figure 4.2).
corresponding to the displacements of the upper and lower platens on VDU.

The temperature control system used by Jones and Davies was found to be incapable of maintaining steady low temperatures. This necessitated replacement of the original Sangamo refrigerator/heating unit by a Jencons CB-80 Cryobath refrigeration unit, and a large number of modifications to the original system. The resulting arrangement is shown in Figure 4.4:

The temperature control chamber which surrounds the sample is constructed of two half-cylinder tanks which are fed against gravity by parallel branches of the cooling system. This chamber, employed by Jones and Davies, was especially constructed to enclose the unusually large sample (1.6cm diam. and height between mountings 14.85cm and 15.9cm for the filled and unfilled samples respectively). One of the tanks also contains an air duct which may be used to achieve an even temperature distribution by inducing a circulation within the chamber. This air duct executes a number of loops within the coolant in order to avoid introducing relatively much warmer air into the chamber. At low temperatures it was found necessary to modify this arrangement by first passing the air through calcium chloride chips. This dries the incoming air, which prevents icing and subsequent loss of an even temperature distribution within the chamber. Cotton wool wadding was also used to pack between the oscillating lower shaft and the aperture of the chamber. This prevents loss of cold air and the creation of a significant temperature gradient within the chamber. The perspex mountings and tufnel shafts (see Figure 4.2) used by Jones and Davies both afford good insulation, and help prevent heat conduction into the chamber.

The temperature within the chamber was monitored by four copper nickel thermocouples as shown in Figure 4.4. Two were placed to monitor the temperature gradient in the chamber near the test sample. Two others were placed to measure the internal and external temperature of a dummy sample located near the Inner wall of the temperature chamber. The function of these is described in §4.4.

With decreasing temperature the viscosity of the coolant increases, and it was found that there was a tendency for flow to take place in one half of the cooling chamber only, while in the other half flow ceased. Air locks were formed with air bubbles from the circulating fluid becoming lodged in the outlet pipe of the
stagnating half of the cooling chamber. This necessitated ensuring that the T-junction joining the tank outlets was always inverted (as shown in Figure 4.4). Bubbles were thus forced to remain within the main circuit and the problem was overcome.

The cooling fluid used with the Sangamo unit was not suitable for use with the cryobath, since despite constant agitation it became very viscous and tended to freeze around the cooling element. The substitution of paraffin as coolant overcame this problem. Paraffin does however tend to swell and weaken rubber tubing, and this necessitated the substitution of clear plastic pipes which were found to be less susceptible to attack.

The centrifugal pump supplied with the cryobath was not capable of priming the cooling system, and thus a second pump was introduced into the circuit. This second pump was connected in parallel (see Figure 4.4) in such a way that once flow had been established, it could then be by-passed by closing valves. This was found necessary in order to minimise the heating in the system, and for the same reason the lengths of all sections of tubing were reduced to a minimum, and additional lagging placed around all pipes and the temperature chamber itself.

4.4 Setting up the instrument and experimental procedure

In order to quantify material behaviour using the rheogoniometer, the torque which is exerted by the sample upon the upper platen must be measured. The recorded torque on the measuring head, however, is affected by the torque due to the inertia of the instrument (associated essentially with the moment of inertia of the oscillating measuring head). Before the instrument is set up, this moment of inertia is obtained by determining the natural frequency for free oscillation of the measuring head which corresponds to a torsion bar of specified restoring constant $K$. A value for the moment of inertia $I$ may then be derived from the measured natural frequency $\omega_0$ via the relation

$$K = I\omega_0^2.$$  \[4.01\]

During torsion the sample experiences normal forces [Ward and Jenkins (1958)]. In order to ensure that the sample did not bend
under compression a slight extension was applied. After mounting, the deflection of the upper platen was then checked in order to ensure that no torque had been applied to the sample during its attachment. The measured height of the sample is the distance between the faces of the perspex mountings when the sample is attached to the rheogoniometer. This was 14.85cm and 15.9cm for the filled and unfilled samples respectively. The work of Jones and Davies (1982) indicates that for cylinders of 1.6cm diameter results are not significantly affected by the dimensions of the sample for heights greater than 7cm. It is assumed that the countersunk portion of the sample (see Figure 4.2) does not deform. If this assumption were invalid, and the entire length of the sample underwent deformation, this would be equivalent to an error of less than 2% in the measured height of the sample, and produce an equivalent percentage error in the measured moduli values (see §4.5).

It was generally found that the temperature chamber required several hours to attain the desired temperature. The thermocouple located in the dummy sample (see Figure 4.4) was used to indicate when a homogeneous temperature field had been achieved within the experimental sample. The variation in temperature within the chamber could be controlled to within 0.5°C, and more typically to within 0.1°C. The temperature gradient along the sample was typically of the order of 0.1°C, and did not generally exceed 0.5°C.

Experiments were carried out at 5°C intervals over the temperature range -20°C ~ 20°C and at a number of intermediate temperatures. At each temperature readings were taken for frequencies increasing from 5Hz to 60Hz by 5Hz intervals, and also at a number of intermediate frequencies in the range 0.1Hz ~ 60Hz. Readings were always taken in the order of increasing frequency, since this mitigates against the effects of viscous heating (see §4.6.2). At each frequency the sample was first 'scragged' (see §2.2.4) by cycling at the highest input amplitude available on the rheogoniometer - subject to the restrictions the output transducer places upon the displacement of the upper platen. The input

† At oscillatory amplitudes of the order of 0.02rad, the tangentially mounted probe begins to make contact with the sides of the output transducer. This effectively limits the amplitude of oscillation of the upper platen.
amplitude was then reduced, and readings taken at intervals of 0.002 rad for input amplitude increasing from 0.006 rad to 0.03 rad (subject to transducer restrictions). An input amplitude of 0.03 rad is close to the maximum available on the rheogoniometer.

Experiments were also carried out by increasing the frequency at a fixed value of input amplitude. Successive results could be taken more quickly in this mode, thus reducing the likelihood of significant viscous heating effects. This also enabled comparison to check that results were reasonably independent of the mode of experimentation (see §5.1).

Most of the data were collected using torsion bars with constants $K = 8650000$ and $K = 2202000000$ dyne cm/rad (see §4.6).

4.5 **ANALYSIS OF EXPERIMENTAL RESULTS**

The system of equations which governs the deformation of the sample is taken to consist of the equation of continuity [2.20], the equation of motion [2.21] and a rheological constitutive equation of the form of [3.15], which relates oscillatory shear stress and strain for linear deformation. The samples are also assumed to be incompressible.

With reference to cylindrical polar coordinates $(z,r,\theta)$, chosen such that the $z$-axis coincides with the axis of the sample, the displacement field $u$ within the sample is assumed to be the real part of the complex displacement $u^*$† which is written as

$$u^* = (0, rf(z)e^{i\omega t}/i\omega, 0).$$

The corresponding complex velocity field is then given by

$$v^* = (0, rf(z)e^{i\omega t}, 0). \quad [4.02]$$

The equation of continuity is then identically satisfied, and the equation of motion reduces to

† This notation will be used throughout to differentiate between corresponding real and complex variables.
The constitutive relation \[ (3.15) \] can be represented as

\[
\text{Re} \left\{ \sigma_{\theta Z}^* \right\} = \text{Re} \left\{ 2G^* \varepsilon_{\theta Z}^* \right\}.
\]

Now

\[
\varepsilon_{\theta Z}^* = \frac{1}{2} \frac{\partial u_\theta^*}{\partial z} = \frac{1}{2i\omega} r f'(z)e^{i\omega t}
\]

and hence

\[
\text{Re} \left\{ \sigma_{\theta Z}^* \right\} = \text{Re} \left\{ \frac{G^*}{i\omega} r f'(z)e^{i\omega t} \right\}.
\]

But

\[
G^* = i\omega \eta^* ,
\]

where \( \eta^* \) is the complex viscosity.

From \[ (4.04) \] together with \[ (4.02) \] and \[ (4.05) \] we obtain

\[
\text{Re} \left\{ \sigma_{\theta Z}^* \right\} = \text{Re} \left\{ \eta^* \frac{\partial u_\theta^*}{\partial z} \right\}.
\]

Substitution of the constitutive relation \[ (4.06) \] into the equation of motion \[ (4.03) \] yields

\[
\text{Re} \left\{ \rho \frac{\partial v_\theta^*}{\partial t} \right\} = \text{Re} \left\{ \eta^* \frac{\partial^2 v_\theta^*}{\partial z^2} \right\}.
\]

Following Walters (1975) an approximate solution for \( V_\theta \) in \[ (4.07) \] can be found by assuming that the term \( \rho \frac{\partial v_\theta}{\partial t} \) is small in comparison with the term on the right hand side of \[ (4.07) \] (which is often stated as neglecting sample inertia effects), and solving

\[
\text{Re} \left\{ \eta^* \frac{\partial^2 v_\theta^*}{\partial z^2} \right\} = 0
\]
subject to the boundary conditions.

The displacements of the upper and lower platens can be represented by \( \theta_1 e^{i\omega t} \) and \( \theta_2 e^{i(\omega t + c)} \), and constitute boundary conditions applicable at \( z = h \) and \( z = 0 \) respectively, where \( h \) is the sample height, \( \theta_1 \) and \( \theta_2 \) the amplitudes of oscillation of the upper and lower platens respectively, and \( c \) the measured phase lag between them.

From [4.06] the torque \( C \), which is applied to the upper platen by the sample, may be calculated in terms of the complex viscosity. If \( \theta \) represents the displacement of the upper platen, and \( I \) is the moment of inertia of the instrument (defined in [4.01]), the equation of motion for the upper platen may be expressed as

\[
C = K\theta + I\ddot{\theta}.
\]  

[4.09]

This enables the complex viscosity to be determined, and utilising [4.05], for \( \omega \neq \omega_0 \) the components of the complex modulus may be shown [Walters (1975)] to be given by

\[
G' = \frac{\chi(\cos c - \chi)2h(K-I\omega^2)/\pi a^4}{\chi^2 - 2\chi \cos c} + 1,
\]  

[4.10]

\[
G'' = \frac{-\chi \sin c2h(K-I\omega^2)/\pi a^4}{\chi^2 - 2\chi \cos c} + 1.
\]

where \( a \) is the sample radius and \( \chi = \theta_1/\theta_2 \) the amplitude ratio.

In order to determine whether the assumption of 'negligible sample interia', which leads to the approximate relations [4.10], results in significant errors for the moduli values calculated, we consider results obtained without recourse to this assumption. The boundary conditions may be applied, and [4.07] solved without assuming \( \rho \frac{\partial V_\theta}{\partial t} = 0 \). This leads to similar expressions for \( V_\theta \) and \( C \). However substitution of the resulting expression for \( C \) into [4.09] fails to produce analytic solutions for \( G' \) and \( G'' \). In this case numerical solutions may be obtained using a Newton-Raphson scheme. A comparison of analytic solutions given by [4.10] and corresponding numerical solutions is given in Table 4.1.

It may be seen from Table 4.1 that the approximate analytic results for storage and loss moduli are in good agreement with those
values obtained numerically. On the basis of results such as those of Table 4.1 it is concluded that neglecting sample inertia effects does not result in significantly large errors for the ranges of frequency and input amplitude considered.

4.6 SOURCES OF EXPERIMENTAL ERROR

In §4.5 consideration is given to errors associated with the inertia of the sample. In §4.4 errors associated with mounting the sample are discussed, and the accuracy of the temperature control system is indicated. Other sources of error include resonance effects and viscous heating of the sample. These will be considered in turn.

4.6.1 Resonance

When the frequency of oscillation of the upper platen equals the natural frequency \( \omega_0 \) defined in [4.01], by [4.09] the torque applied to the upper platen by the sample is zero. Thus [4.10] cannot be used to determine \( G' \) and \( G'' \). Moreover we may examine what happens near the natural frequency by inverting [4.10] to obtain approximate equations for amplitude ratio and phase difference:

\[
\chi = \sqrt{\frac{G'^2 + G''^2}{G'^2 + (G' + 2h(K - I\omega^2)/\pi a^4)^2}}
\]

[4.11]

\[
c = \tan^{-1} \left[ \frac{-G''2h(K - I\omega^2)/\pi a^4}{G'^2 + (G' + 2h(K - I\omega^2)/\pi a^4)^2} \right]
\]

From [4.11] it follows that

\[
\lim_{\omega \to \omega_0} \chi = 1
\]

[4.12]

\[
\lim_{\omega \to \omega_0} c = 0
\]
Now it may be seen that for the denominator in [4.10] \[\lim_{\omega \to \omega_0} (\chi^2 - 2\chi \cos \omega + 1) = 0 \] [4.13]

This is an approximate result since it depends on [4.11], but indicates that as the frequency of oscillation approaches the natural frequency \(\omega_0\), the denominator in [4.10] becomes small, and hence large relative errors are to be expected in the resulting values of \(G'\) and \(G''\). Expressions for \(\chi\) and \(c\) equivalent to [4.11] may be obtained without recourse to the approximation \(\rho \frac{\partial^2 \theta}{\partial t^2} = 0\). In this case the resulting expressions, although exact, are very complex, and for our present purposes do not appear to significantly aid our understanding of what happens at resonance.

Another practical consideration is whether the system comprising the measuring head and attached rubber sample also possesses other natural frequencies within the experimental range. An engineering treatment of this problem, which idealises the rubber sample as a perfectly elastic column [Bishop and Johnson (1979)] indicates the lowest natural frequency associated with the sample to be given by

\[\omega_{\text{nat}} = \sqrt{\frac{E}{\pi}} \sqrt{\frac{\rho}{h}}.\]

For the experimental samples \(G = 10^{10}\) dyne/cm\(^2\) and \(\rho = 1\) g/cm\(^3\), and thus \(\omega_{\text{nat}} = 10^4\) rad/sec. It may thus be concluded that such resonant frequencies are not encountered within the experimental range of investigation.

It is usual to select an appropriate torsion bar so that values of \(\chi\) and \(c\) fall in the range over which they are most accurately measured. In particular, when \(c\) is small relative errors in its measurement may be very large [Walters (1975)]. As the motion of the sample becomes closer to that of a rigid body with decreasing temperature, it becomes necessary to change the torsion bar for one with a greater restoring constant.

Figure 4.5 illustrates plots of \(G'\) against frequency taken with different torsion bars. It may be observed that the extent to which data are affected by resonance depends upon the choice of torsion
bar. The broken lines indicate the value of the natural frequency. In order to account for the data of Figure 4.5 we shall consider effects of small errors in the measurement of $\omega_0$.

From (4.10) we may write

$$G' = (K - l\omega^2).$$

Now the value of $l$ is determined from $\omega_0$ and the bar constant $K$ via (4.01), and thus

$$G' = K \left[ 1 - \frac{\omega^2}{\omega_0^2} \right].$$

Let $\delta G'$ represent the error in $G'$ resulting from an error $\delta \omega_0$ in the measurement of $\omega_0$. Then

$$\delta G' = 2K \frac{\omega^2}{\omega_0^2} \delta \omega_0.$$ 

In terms of relative errors

$$\frac{\delta G'}{G'} = \frac{2\omega^2}{\omega_0^2 - \omega^2} \frac{\delta \omega_0}{\omega_0}.$$ \hspace{1cm} [4.14]

It may be observed that

$$\lim_{\omega \to 0} \frac{\delta G'}{G'} = 0$$

whilst

$$\lim_{\omega \to \infty} \frac{\delta G'}{G'} = \kappa \frac{\delta \omega_0}{\omega_0},$$

where $\kappa$ is a constant of proportionality.

Thus for frequencies far enough below $\omega_0$, the error in $G'$ resulting from an error in the measurement of $\omega_0$ tends to zero, whereas above $\omega_0$ the absolute value of the relative error in $G'$ may remain greater than that in $\omega_0$. For this reason it is preferable to avoid taking data at frequencies greater than the natural frequency. Imposing the
ad hoc condition that the term $\omega^2/(\omega_0^2-\omega^2)$ which appears in [4.14] should not cause the relative error in $G'$ to exceed twice the relative error in $\omega_0$ leads to the constraints

$$\omega < \sqrt[3]{\omega_0}$$

$$\omega > \sqrt{\omega_0}.$$  \[4.15\]

It thus follows that the greater the value of the natural frequency $\omega_0$, the larger the range of frequencies near $\omega_0$ over which modulus values may be expected to be in error. This explains the data in Figure 4.5.

Since the range of frequencies affected by resonance was rather broad for most of the torsion bars available (around half the experimental range in the case of the $K = 96100000$ dyne cm/rad bar, see Figure 4.5), it was not found practicable to produce composite plots by superposing results taken with successive bars. These considerations have led to most of the data being gathered using bars with constants $K = 8650000$ and $K = 2202000000$ dyne cm/rad. For the former, [4.15] leads to the exclusion of frequencies in the range 11-19 Hz, and for the latter an estimated natural frequency of 224 Hz ensures that no resonance effects are encountered within the experimental range.

Figure 4.6 shows $G'$ data taken with the same torsion bar at two different temperatures. It is observed that the magnitude of the resonance effects at 0°C are much larger than at 20°C. This fact is also reflected in the raw data which are presented in Table 4.2. It may be seen that near the natural frequency (13.8 Hz) the value of the denominator of equation [4.10] is much smaller at 0°C than at 20°C and small values are encountered over a greater range of frequencies than at 20°C. This provides an explanation for the difference in the magnitude of the resonance effects in the plots of Figure 4.6. It is interesting to note that the raw data corresponding to Figure 4.5 which are contained in Table 4.3 demonstrate that the behaviour of the denominator of [4.10] near the natural frequency does not depend significantly on the choice of torsion bar. It may thus be concluded that differences in the plots of Figure 4.6 result from changes in $G'$ and $G''$ with temperature. This effect recalls the results of the
Nijenhuis (1980) for a controlled oscillatory stress experiment, where the width of the resonance curve increases with increasing tan δ.

### 4.6.2 Viscous Heating Effects

An equation for calculating the temperature distribution within the material may be obtained as follows. Taking the scalar product of the momentum balance equation [2.21] with the velocity vector yields a 'mechanical energy equation'. Subtraction of this mechanical energy equation from the energy balance equation [2.23] yields a thermal energy equation. Applying the state equation

\[
dU = -Pd\hat{V} + C_p dT
\]

where \( \hat{V} \) is the volume, and \( C_p \) the heat capacity at constant pressure, and assuming incompressibility, together with negligible body forces and radiation, and an equation of state for the heat flux \( q \) in the form of Fourier's law

\[
q = -k\nabla T
\]

where \( k \) is the thermal conductivity, we obtain

\[
\rho C_p \frac{dT}{dt} = k\nabla \cdot \nabla T + a' \cdot \nabla \nu . \tag{4.16}
\]

Then from [4.06] and [4.02]

\[
a' \cdot \nabla \nu = \sigma \Theta \zeta \frac{\partial V}{\partial z} - \text{Re} \{ \eta' f'(z) e^{i\omega t} \} \text{Re} \{ f'(z) e^{i\omega t} \}
\]

Now

\[
\text{Re} z_1, \text{Re} z_2 = \frac{1}{2} \left[ \text{Re}(z_1 \bar{z}_2) + \text{Re}(z_1 z_2) \right]
\]

† The following is based on an analysis carried out by my supervisor, Dr P W James.
Whence

\[ \mathbf{a} \cdot \nabla \mathbf{v} = \frac{1}{2} \left[ \text{Re} \left( \eta^* r^2 |f'(z)|^2 \right) + \text{Re} \left( \eta^* [r f'(z)]^2 e^{2i\omega t} \right) \right]. \] \hspace{1cm} [4.17]

Hence we may seek solutions to [4.16] of the form

\[ T(z, t) = T_0(z) + \text{Re} \left[ T_1(z) e^{2i\omega t} \right]. \] \hspace{1cm} [4.18]

Assuming that \( \rho C_p \frac{DT}{Dt} \) is small and may be neglected, we solve

\[ k \nabla \cdot \nabla T = -\sigma^* \cdot \nabla \mathbf{v}. \] \hspace{1cm} [4.19]

Substituting [4.17] and [4.18] into [4.19], and considering time independent terms only we obtain

\[ k \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_0}{\partial r} \right) + \frac{\partial^2 T_0}{\partial z^2} \right] = \text{Re} \left\{ \frac{1}{2} \eta^* r^2 |f'(z)|^2 \right\}. \]

Assuming that \( T_0 = T_0(r) \), we write

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_0}{\partial r} \right) = \kappa r^2, \] \hspace{1cm} [4.20]

where

\[ \kappa = \text{Re} \{ |f'(z)|^2 \eta^*/2k \}. \] \hspace{1cm} [4.21]

The solution to [4.20] satisfying \( T_0 \) finite at \( r = 0 \) and \( T_0 = T_s \) (constant) at \( r = a \) is given by

\[ T = T_s + \frac{\kappa}{16} [a^4 - r^4]. \]

The temperature excess over the ambient temperature \( T_s \) is thus

\[ T - T_s = \frac{\kappa}{16} [a^4 - r^4] \]

and the maximum temperature excess \( T_{\text{max}} \).
Now application of the boundary conditions

\[ V_0^s(h) = \theta_0 e^{i\omega t} \]
\[ V_0^s(0) = \theta_2 e^{i(\omega t + c)} \]

to [4.08] yields [Walters (1975)]

\[ f'(z) = \frac{i\omega}{h} (\theta_1 - \theta_2 e^{ic}) \]

and hence from [4.21] and [4.05]

\[ \kappa = \frac{C''\omega}{2kh^2} [\theta_1^2 + \theta_2^2 - 2\theta_1 \theta_2 \cos c] . \]

Now the amplitude \( \gamma_0 \) of the shear strain applied to the sample is given by

\[ \gamma_0 = \frac{a\theta_2}{h} \sqrt{\lambda^2 - 2\chi \cos c + 1} \] [4.23]

and hence, from [4.22]

\[ T_{\text{max}} = \frac{a^2 C''\omega \gamma_0^2}{32k} \] [4.24]

From [4.24] it may be seen that viscous heating effects depend upon \( C'' \). Viscous heating effects thus depend, as does \( C'' \), upon temperature and frequency of oscillation. Moreover, at a given temperature and frequency viscous heating also depends upon the amplitude of the applied shear strain, which from [4.23] is seen to be directly proportional to the input amplitude \( \theta_2 \).

The experimental procedure of taking readings in order of increasing frequency and input amplitude (see §4.4) thus seeks to minimise the effects of viscous heating. For the materials investigated (see §5.1) the value of the loss modulus is found to
Increase by an order of magnitude with decreasing temperature, and to achieve a maximum of around 0°C before subsequently decreasing. Thus, although viscous heating effects were found to be negligible at room temperature, they became important at around 0°C. Viscous heating was investigated by observing how moduli values change over time while the sample is subjected to continuous oscillation. Viscous heating was identified if a systematic change in moduli values was observed with increasing time. In order to check whether values obtained were free from viscous heating effects further readings were taken after removing the oscillations and allowing time for the sample to regain thermal equilibrium. If agreement was then obtained, the readings were taken to be independent of viscous heating. In order to avoid viscous heating effects two procedures were adopted. In severe cases the first reading obtained at each frequency was logged and the machine switched off and the sample allowed to equilibrate before another reading was taken. Otherwise readings at successive frequencies were taken in quick succession. If viscous heating effects were not detected for the reading taken at the highest of these frequencies upon subsequent checking, the data were accepted as free from viscous heating effects.
CHAPTER 5

RESULTS OF LINEAR EXPERIMENTS

INTRODUCTION

In this chapter results of the linear experiments described in Chapter 4 are presented and modelled in terms of the theory reviewed in Chapter 3. The linearity and reproducibility of the results are discussed. The time-temperature superposition principle is shown to be applicable to results for both the filled and unfilled materials and to yield the same shift factors, which are described by the WLF equation [Ferry (1970)]. The modified Spriggs model proposed by Jones and Davies (1982) is shown to represent data only over restricted ranges of temperature and frequency. Relaxation spectra are calculated and the model due to Huet [Salvia & Duperray (1983)] is shown to represent dynamic moduli for both the filled and unfilled materials. Results are discussed in relation to previous investigations, and a temperature-dependent linear viscoelastic equation proposed to model the behaviour of the experimental materials in infinitesimal deformation.

5.1 LINEARITY & REPRODUCIBILITY OF EXPERIMENTAL RESULTS

Representative results for storage and loss moduli against input amplitude are shown in Figures 5.1 and 5.2. These values were calculated via [4.10] from data obtained upon increasing input amplitude at fixed frequency, as described in §4.4. No significant input amplitude dependence is apparent except in loss modulus values for the filled sample at -10°C and -20°C and for the unfilled sample at -20°C (in which case negative loss modulus values† were obtained at input amplitudes below 0.018 rad).

† Negative loss modulus values are attributable to errors in the measurement of the phase lag c (see later).
The apparent non-linearity of the loss modulus plots in Figures 5.1 and 5.2 is attributable to small errors of the order of a few degrees which are associated with the measurement of the phase lag \( \phi \) (see §4.3). Table 5.1 shows typical phase lag values, which were measured for the unfilled sample at 20°C and -5°C. From Figure 5.1 it is observed that at 20°C the loss and storage moduli for the unfilled sample show no significant amplitude dependence. Such variation in the measured phase lag with input amplitude is thus considered to arise from experimental error associated with the measurement of the phase lag. In contrast to the measured phase lag values, those for the amplitude ratio \( \chi \) show little variation with input amplitude.

From [4.10] we have that

\[
G'' \propto \frac{\sin \phi}{\chi^2 - 2\chi \cos \phi + 1}
\]

Since for \( \phi = 0 \) we may write \( \sin \phi \approx \phi \) and \( \cos \phi = 1 \), it follows that for small phase lags at constant amplitude ratio

\[
G'' \propto \phi .
\]

Hence large relative errors may be expected in \( G'' \) when \( \phi \) is small, since the relative error in the phase lag becomes very large.

Table 5.2 illustrates the dependence of amplitude ratio and phase lag upon torsion bar constant. It may be seen that the phase lag increases with torsion bar constant. The bar with restoring constant \( K = 2202000000 \) dyne cm/rad was used at temperatures of 5°C and below. Although this bar produces the highest values of phase lag, the measured phase lags corresponding to the non-linear plots in Figures 5.1 and 5.2, which were taken with this bar, are of the order of 1° or less. These plots may thus simply reflect the error associated with the measurement of the phase lag. It is thus concluded that to within experimental accuracy the applied strains lie within the linear regime (see §4.1) for both filled and unfilled samples. The applied shear strain amplitude, as calculated from [4.23], does not exceed 0.003.

Figure 5.3 compares data taken by increasing input amplitude at fixed frequency with data taken by increasing frequency at fixed
Input amplitude. Results such as those of Figure 5.3 indicate that moduli values for both modes of experimentation are in good agreement. It is thus concluded that results are independent of the mode of experimentation. Data such as those of Figure 5.3 also demonstrate the reproducibility of experimental results.

5.2 APPLICATION OF THE TIME-TEMPERATURE SUPERPOSITION PRINCIPLE

In order to investigate the applicability of time-temperature superposition (see §3.2.1) to the experimental data for the filled and unfilled samples, at each of the temperatures investigated (see §4.4) further data were collected over the frequency range 0.1 ~ 60Hz. In the majority of cases this was done at an input amplitude of 0.01rad, but since the linear regime has been shown to extend over the entire range of input amplitudes available on the rheogoniometer (see §5.1), data at other values of input amplitude were also used.

Data over the frequency range 0.1 ~ 60Hz cover almost three decades of log frequency. This determines material behaviour over a sufficient range of frequency to enable superposition of all data with a reasonable degree of accuracy. Since the change in modulus corresponding to a given change in temperature depends both upon the type of modulus and the absolute value of the temperature (see Figures 5.1, 5.2), where necessary further data were collected at intermediate temperatures in order to provide sufficient overlap when superposing isothermal plots of the respective moduli against frequency (see Figure 3.1).

It was found that for all data above around -10°C composite curves could be formed by simple horizontal shifts. This process was carried out by manually superposing isothermal plots of dynamic moduli against frequency. (It had been anticipated that both vertical and horizontal shifts might be required to achieve superposition - see §3.2.1. Thus no multiplicative factor corresponding to $T_0 \rho_0/(T \rho)$ was used to scale data before shifting, since this would result only in a modification of vertical shift factors). Such composite curves, reduced to a reference temperature of 2.5°C are shown in Figures 5.4 and 5.5. These curves extend over a range of approximately ten decades of log frequency, and are in
good qualitative agreement with literature studies, such as that of Payne (1958). The results shown in Figures 5.4 and 5.5 for the unfilled and filled materials demonstrate broadly similar behaviour.

At low temperatures $C'$ shows little frequency dependence, and thus the manually determined shift factors must be obtained from $C''$ data alone. For higher frequencies, the gradient of the composite $C''$ curve (see Figures 5.4, 5.5) is negative. This region of negative gradient corresponds to low temperature isotherms. These low temperature isotherms demonstrate a tendency for the negative gradient to become less so, or even positive, with increasing frequency. Only partial superposition can be achieved for such $C''$ isotherms using horizontal shifts but it is apparent from the almost constant value of the $C'$ isotherms at these temperatures, that no vertical shift factor can be applied. At temperatures below around -10°C it is difficult to discern a definite trend in $C''$ values with increasing frequency and thus no shift factors can be ascertained for data at these temperatures.

Upturns in low temperature $C''$ isotherms might be explained by viscous heating. Repeated readings however, having allowed time for the sample to regain thermal equilibrium, do not indicate a substantial decrease in this behaviour. It should be noted from the composite $C''$ curve of Figure 5.5, that for the filled sample the magnitude of the loss modulus at around -10°C (corresponding to the extreme right of the plot) is comparable to values encountered at room temperature (extreme left of plot). Since the temperature dependence of the loss modulus - represented by the gradient of the curve in Figure 5.5 - is greater at room temperature than at around -10°C, it might be expected that greater aberrations due to viscous heating are to be observed at room temperature than at around -10°C. This is not however the case. Departures from the composite $C''$ curve in the region of positive gradient (i.e. left hand side of plot) correspond largely to resonance effects (see §4.6.1). This indicates that for the filled sample at least, the apparent upturn in low temperature $C''$ isotherms is not due to viscous heating.

Another possible explanation for the trend towards a positive gradient with increasing frequency for low temperature $C''$ isotherms lies in errors in the measurement of the phase lag, similar to those discussed in §5.1. The phase lag can only be measured accurately to within a few degrees, and at low temperatures is found to decrease
with increasing frequency (see Table 5.3). Thus at low temperatures, and especially at higher frequencies, the uncertainty in the measurement of the phase lag becomes significant, and may lead to large relative errors in the measurement of $G'$. The applied strain amplitude given by \([4.23]\) and indeed the applied strain rate, are both frequency dependent. Thus it may also be conjectured that the trend towards a positive gradient with increasing frequency for low temperature $G''$ isotherms might represent a non-linear effect, with the applied deformation exceeding the bounds of the linear regime (see §4.1). This possibility cannot be excluded, but it appears that in the present experiment the phase lag cannot be measured with sufficient accuracy to determine whether this is the case.

It may be concluded that despite lack of complete superposition, satisfactory - if indeed only partially superposed - composite curves may be constructed from dynamic data for the filled and unfilled samples for all temperatures investigated above around $-10^\circ C$. To within experimental accuracy it is not possible to determine whether lack of superposition simply reflects experimental error or a non-linear effect.

5.3 APPLICATION OF THE WLF EQUATION

It is found that the horizontal shift factor $a_T$ of the time temperature-superposition principle (see §3.2.1) may often be represented empirically by the equation known as the Williams-Landel-Ferry (WLF) equation,

$$\log a_T = \frac{-C_1(T-T_0)}{C_2+T-T_0}, \quad [5.02]$$

where $T_0$ is a reference temperature, and $C_1$ and $C_2$ are constants.

Shift factors for the unfilled sample were calculated with respect to a reference isotherm at $2.5^\circ C$, while those for the filled sample were calculated for a reference temperature of $2^\circ C$. The manually obtained shift factors were then fitted by a WLF equation following a graphical method given by Ferry (1970). For the unfilled sample the WLF coefficients $C_1$ and $C_2$ were 9.00 and 32.40, and for
the filled sample 9.25 and 32.14 respectively. The WLF fits to the manually obtained shift factors for the unfilled and filled materials are shown in Figures 5.6 and 5.7 respectively. The WLF coefficients for the filled sample applicable at a reference temperature of 2.5°C were then calculated from those at 2°C using a formula given by Ferry (1970). This yields values of 9.11 and 32.64 for $C_1$ and $C_2$ respectively.

The agreement between the WLF coefficients for the filled and unfilled samples is extremely good. Similar agreement of shift factors for a butyl rubber black stock and butyl rubber gum stock was reported by Ferry and Fitzgerald (1982) and similar findings have been reported by a number of other investigators (see §5.9).

Essentially identical shift factors are found to be applicable to both the filled and unfilled materials, and these are well fitted by the WLF equation. Accordingly [5.02] with $C_1 = 9.00$ and $C_2 = 32.40$ was used to obtain the composite curves reduced to a reference temperature of 2.5°C which are shown in Figures 5.4 and 5.5.

5.4 MODELLING FREQUENCY DEPENDENCE BY MEANS OF A MODIFIED SPRIGGS MODEL

Jones and Davies (1982) carried out dynamic testing of a material identical to the unfilled material specified in §2.2.6. They proposed that the frequency dependence of storage and loss moduli can be modelled by a modification of the model due to Spriggs (1965). This modified Spriggs model is given by

$$G' = G + \frac{m \omega^{1/\alpha}}{\tan \left( \frac{\pi}{2\alpha} \right)}$$

$$G'' = m \omega^{1/\alpha}$$

where $m$ and $\alpha$ are constants satisfying

$$\alpha > 1$$
\[
m = \frac{\eta_0 \pi (1+1/\alpha)}{\zeta(\alpha) 2\alpha \cos \left( \frac{\pi}{2\alpha} \right)}, \quad \tau \omega \gg 1,
\]
and \(\eta_0\) is the zero shear viscosity, \(\tau\) a relaxation time, and \(\zeta(\alpha)\)
the Riemann zeta function.

For the purposes of data fitting, \(G, m\) and \(\alpha\) are treated as
model parameters. From [5.03] it may be seen that \(m\) and \(\alpha\) can be
determined either from \(G'\) or from \(G''\) data. Parameter values obtained
from one component of the complex modulus do not however generally
produce a good fit to the other component. Fitting simultaneously to
both \(G'\) and \(G''\) data was also found to present difficulties, since for
lower temperatures, aberrations due to resonance (see §4.6.1) and
errors due to small phase lag (see §5.1) are found to effect \(G'\) and
\(G''\) data unequally. Each of these two data sets is thus generally
found to be subject to differing degrees of experimental scatter.

This problem was overcome by applying a Newton-Raphson
 technique to the weighted sum of the standard deviations

\[
S' + S'' W,
\]

with respect to the theoretical predictions of [5.03], such that

\[
S' = \sum_{i=1}^{N} \left[ G'_i - G - \frac{\omega_1^{1/\alpha}}{\tan \left( \frac{\pi}{2\alpha} \right)} \right]^2
\]

\[
S'' = \sum_{i=1}^{N} \left[ G''_i - \omega_1^{1/\alpha} \right]^2
\]

where \(G'_i\) and \(G''_i\) are the experimental moduli values measured at
frequency \(\omega_1\), \(n\) is the number of readings, and \(w\) is the weighting
term given by

\[
w = \sqrt{\frac{S'}{S''}},
\]

which is the ratio of the variance of the storage modulus data to
that for the loss modulus.

Figures 5.8 and 5.9 show the fit which the modified Spriggs
model provides to experimental data for the unfilled and filled
samples respectively. The agreement between model and data is excellent over the temperature ranges indicated, ie. 10 ~ 20°C for the unfilled sample and 15 ~ 20°C for the filled sample. With decreasing temperature below the cited temperature ranges, however, the fit provided by the modified Spriggs model to the experimental data becomes progressively less satisfactory. As stated in §5.2, at lower temperatures G" is found to decrease with increasing frequency. From [5.03] it is seen that G" is predicted to be a monotonic increasing function of frequency under the restriction \( \alpha > 1 \). Hence the modified Spriggs model cannot account for the observed frequency dependencies of loss and storage moduli over the entire experimental temperature range, its application being confined to those temperature and frequency ranges where G" is a monotonic increasing function of frequency.

5.5 OBTAINING RELAXATION SPECTRA

Since models for the frequency dependence of linear viscoelastic moduli correspond basically to a prescription of the distribution of relaxation times (see §3.1.3), relaxation spectra were obtained from the composite G' and G" curves in order to facilitate the search for a linear viscoelastic model. Values for the relaxation spectrum were obtained separately from the G' and G" data of Figures 5.4 and 5.5 using the approximate methods of Williams and Ferry [Ferry (1970)] - see Table 6.2.

The Williams and Ferry method requires values for the gradients of log-log plots of modulus against frequency. In order to obtain these values the composite curve data were fitted with Chebyshev polynomials, and the derivative of these polynomials obtained. The agreement of values calculated from G' and G" data was generally good, except at small relaxation times, where values corresponding to G' data diverged markedly from those calculated from G". This divergence was interpreted as a fitting artefact since small relaxation times correspond to high frequency and at such frequencies G' values are almost constant (see Figures 5.4 and 5.5) and are not well suited to representation in terms of a polynomial approximation. The G' data were subsequently fitted by two Chebyshev polynomials...
corresponding to the glassy plateau and transition regions (see Figure 2.1), and having a continuous first derivative. The Chebyshev polynomial fit to the data of Figures 5.4 and 5.5 is shown in Figures 5.10 and 5.11 respectively. The resulting spectra for the unfilled and filled materials are shown in Figures 5.12 and 5.13 respectively. These values exhibit much improved agreement, although fitting artefacts are still observable at the ends of the ranges of relaxation times over which the relaxation spectra are calculated. The agreement between the spectrum values produced from $G'$ and $G''$ data is not as good for the filled as for the unfilled sample.

Relaxation spectrum data generated from $G''$ curves appear to be much freer from fitting artefacts than the corresponding $G'$ results. This seems to reflect the fact that the maximum of the $G''$ composite curve is more amenable to polynomial fitting than the sigmoidal $G'$ curve. In view of this, the relaxation spectra generated from $G''$ data are to be regarded as the most reliable values.

5.6 EMPIRICAL REPRESENTATIONS OF THE RELAXATION SPECTRUM

The relaxation spectrum is a useful theoretical concept in that it attempts to relate observed moduli values pertaining to a particular mode of deformation to the structure of the material. It should however be born in mind that there is no guarantee that the relaxation spectrum does in fact possess a physical analogue within the material. Also, theoretically, in order to calculate exact modulus values, the spectrum must be evaluated over an infinite range of relaxation times, which in general is not possible unless the viscoelastic processes of the material are restricted to a limited range of relaxation times and thus non-zero values of relaxation spectrum only occur within such a limited range.

Given these reservations, it has often been considered preferable to seek an analytic expression for one of the viscoelastic moduli, and calculate modulus values by exploitation of exact

\[ \text{Near the ends of the range the gradients required to obtain relaxation spectrum values cannot be accurately calculated. This gives rise to the observed fitting artefacts.} \]
theoretical relationships between the viscoelastic moduli. This approach is however of limited practical application, since as observed by Vinogradov and Malkin (1980) 'It should be noted in general that no sufficiently simple analytic expressions can be obtained for the entire set of viscoelastic characteristics of the material. Therefore, the following situation is typical here: the comparative simplicity and vividness of the analytical representation of any one of the viscoelastic functions chosen for the treatment of the experimental data turn into an extremely unwieldy and complicated procedure and sometimes it becomes even impossible to obtain analytic expressions for the function ...'.

Despite this difficulty a number of forms for the relaxation spectrum may be derived by taking inverse Laplace transforms of analytical expressions for the relaxation modulus, i.e. inverting \[3.28\]. Some of these are listed in Table 5.4.

An additional form quoted by Bird, Armstrong and Hassager (1977) as a useful empiricism for the relaxation modulus is

$$G(t) = \frac{2\eta_0}{\sqrt{\pi} \tau} \left[ \frac{2\tau}{t} \right]^{n/2} \frac{1}{\Gamma\left(\frac{1}{2}(1-n)\right)} K_{-n/2} \left[ \frac{t}{\tau} \right]$$  \hspace{1cm} [5.04]

where \(n\) is a model parameter, \(K_{-n/2}\) is a modified Bessel function of the 2nd kind, and \(\Gamma\) is the gamma function.

Equation [5.04] is not readily amenable to inverse Laplace transform, but is known to give rise to the Carreau viscosity function, and satisfies

$$\int_0^\infty G(s)\cos\gamma ds = \frac{\eta_0}{(1+\gamma^2)^{1-n/2}}.$$  \hspace{1cm} [5.05]

Taking the imaginary part of [3.16] we obtain

$$G''(\omega) = \omega \int_0^\infty G(t) \cos \omega t \, dt.$$  \hspace{1cm} [5.06]
Hence from \([5.05]\)

\[
G'' = \frac{n_\omega}{[1+(\lambda \omega^2)]^{1-n/2}} \tag{5.07}
\]

and

\[
\frac{dG''(\omega)}{d\omega} = \frac{n_\omega[1+n(\omega\lambda)^2]}{[1+(\lambda \omega)^2]^{(3-n)/2}} \tag{5.08}
\]

Physically, in \([5.04]\) we must have \(n > 0\), and hence from \([5.08]\) \(G''\) is predicted to be a monotonic increasing function of frequency. To a first approximation we may write [Jouandeau and Duperray (1984)]

\[
H(\tau) = G''(\omega) \bigg|_{\omega = 1/\tau} \tag{5.09}
\]

and thus we may see that \([5.04]\) predicts \(H(\tau)\) to be a monotonic decreasing function of \(\tau\).

With regard to the relaxation spectrum data of Figures 5.12 and 5.13 it may be seen that an important criterion for a suitable linear viscoelastic model is that it should predict the observed form of the maximum in the spectrum data. In view of \([5.09]\) it is also required that the proposed function predicts the maximum in the plot of the composite \(G''\) curves against frequency in Figures 5.4 and 5.5.

From \([5.03]\) it may be seen that the modified Spriggs model fails in the above respect. In fact neither \([5.04]\) nor any of the relaxation moduli or spectra of Table 5.4 afford a suitable representation of the data of Figures 5.12 and 5.13. It is shown in the following section that a linear viscoelastic model which is capable of representing the data of Figures 5.4 and 5.5 is the bi-parabolic element model due to Huet [Salvia and Duperray (1983)].

### 5.7 THE HUET MODEL

The Huet model can be related to a mechanical model which is not composed exclusively of springs and dashpots but contains 'parabolic elements'. A parabolic element is defined in terms of its
creep behaviour (i.e., its response to an instantaneously imposed constant stress) which is given by

$$\epsilon(t) = A \tau^h \sigma, \quad 0 < h < 1 \quad [5.10]$$

where $\epsilon$ and $\sigma$ are components of the infinitesimal strain tensor and Cauchy stress tensor respectively, and $A$ and $h$ are constants.

The response of a spring or dashpot to a creep experiment is represented by the limiting cases of $h = 0$ and $h = 1$ respectively. The mechanical representation of the Huet model is given in Figure 5.14. Analogously to [3.16], Fourier transformation of the creep compliance $A^h$ associated with a single parabolic element yields an expression for the complex compliance, which in turn may be inverted via [3.23] to obtain the complex modulus. It thus follows that the Huet model may be expressed exactly in terms of any one of the above quantities. The simplest of these representations is that for the complex modulus

$$G^*(\omega) = G_e + \frac{C-C_e}{1+\delta(1+\omega^\tau)^{-1}+\omega^{-k}}, \quad [5.11]$$

where

$$\tau = [\frac{(C-C_e)B\Gamma(k+1)}{A\Gamma(k+1)}]^{-1/k},$$

$$\delta = [\frac{(C-C_e)A\Gamma(h+1)}{(C-C_e)B\Gamma(k+1)}]^{-h/k},$$

and $\Gamma$ is the gamma function, and $A$, $B$, $h$ and $k$ are constants associated with the parabolic elements shown in Figure 5.14.

An approximate form for the relaxation modulus can be obtained using the relation [Jouandeau and Duperray (1984)]

$$G(t) = G^*(\omega) \bigg|_{\omega = -i/t} \quad [5.12]$$

and similarly for the relaxation spectrum (ibid)

$$H(\tau) = \text{Im} \ G^*(\omega) \bigg|_{\omega = 1/\tau} \quad [5.13]$$

It may thus be seen that [5.11] not only represents an empiricism
containing a sufficient degree of flexibility to model the data of Figures 5.4 and 5.5 but also affords approximate representations of linear viscoelastic quantities for which simple analytic expressions might otherwise be unavailable.

5.8 MODELLING DYNAMIC DATA BY MEANS OF THE HUET MODEL

Since the composite curves of Figures 5.4 and 5.5 consist of hundreds of data points, the Chebyshev polynomial values shown in Figures 5.10 and 5.11 were used to represent these data. A Newton-Raphson method was then used to obtain a least squares fit between these composite curve data and the predictions of [5.11]. Although in principle it is possible to measure $G$ and $G_e$ as the limiting values of $G'(\omega)$ corresponding to high and low frequency respectively, these quantities were treated as model parameters, the high and low frequency results being used to provide initial estimates. Since the above moduli enter into the expression for $G''$ only in terms of a multiplicative factor $G-G_e$ this quantity may accordingly be regarded as a single parameter. Fitting the Huet model to the $G''$ composite curves thus requires the determination of five parameters, $G-G_e$, $h$, $k$, $\tau$, $\delta$. An initial fit was attempted using $G''$ data only.

For the unfilled sample, the parameters derived from the $G''$ data provided a good fit, and when supplemented by a suitable $G_e$ value, a good fit was also obtained to the $G'$ data. In the case of the filled sample an excellent fit was obtained to the $G''$ data, but the resulting fit to the $G'$ data did not produce sufficiently large values at high frequencies. A fit was then performed using $G'$ data only. The values of the parameters obtained by fitting to $G'$ data were quite different from those obtained for the $G''$ data. In the case of the filled sample the corresponding fit to $G''$ data was much inferior, and the values obtained for $G-G_e$ appeared to be unphysically large.

A simultaneous least squares fit to both $G'$ and $G''$ data was then performed, giving each equal weighting. For the unfilled sample the resulting fit to both $G'$ and $G''$ data was generally good, although there is some indication of the influence of the fitting artefacts present in the Chebyshev polynomial values in Figures 5.10 and 5.11.
For the filled sample $G'$ values at high frequencies were still underestimated, while $G''$ values for the extremes of high and low frequency were overestimated. Since the fitting artefacts in the Chebyshev polynomial are present only at the extreme ends of the frequency range, these values were subsequently disregarded, and the fitting procedure repeated. The resulting fits to both components of the complex modulus for the unfilled and filled samples are shown in Figures 5.15 and 5.16 respectively, and values of the parameters are listed in Table 5.5.

5.9 DISCUSSION OF RESULTS

To within experimental accuracy it has been shown that the deformation remains within the linear regime for both experimental materials under all conditions investigated (see §5.1). At 20°C the observed increase in storage modulus of the filled over the unfilled material is approximately sixfold. This agrees well with the increase in tensile modulus reported by Chang, Wijayarathna and Salovey (1984) for a nitrile rubber (Krymac-800) containing a similar loading of high structure furnace (HAF) black N330. This increase in modulus, together with those observed at higher loadings, was modelled by the Frankel Acrivos equation [2.29], and this indicates that an independent carbon black network makes a significant contribution to the response of the filled material. The observed increase in the modulus of the filled over the unfilled material is larger than can be predicted by the Guth-Gold equation [2.30].

Figure 5.17 compares data for the unfilled sample with the corresponding data of Jones and Davies (1982). These data are not in agreement. At least one of the samples used by Jones and Davies was subsequently discovered to contain a large air pocket. It is thought that this might explain the discrepancy between the data which is apparent from Figure 5.17.

With regard to time-temperature superposition, no attempt was made - such as in the study by Duperray and Leblanc (1982) - to apply separate shift factors to storage and loss moduli. This is not in accordance with the time-temperature superposition principle as stated by Ferry (1970), where it is observed that 'the same values of $\tau$ must superpose all the viscoelastic functions'.
In §§5.2 and 5.3 it was demonstrated that isothermal plots of $G'$ and $G''$ against frequency are superposable by horizontal shifts only, and that the same shift factors are applicable to both the filled and unfilled materials. Superposition by means of horizontal shifts indicates that although an independent carbon black network dominates the frequency response of the filled material, for small deformations the thermal behaviour of the filled material is identical to that of the unfilled material. This implies that structural changes due to change in temperature are associated primarily with changes in the elastomer matrix. This contrasts with the thermal behaviour of some other carbon black filled elastomers which also exhibit relatively large increases in modulus for the filled over the unfilled material (see §3.2.2).

Medalla (1978) cites a number of studies for which essentially the same shift factors were found to apply to both filled and unfilled elastomers. These studies include an investigation by Payne of SBR 1500 for various loadings up to 50phr N330 black. Ecker (1968) - who's work assumed the validity of time temperature superposition - also found that for SBR 1500 with loadings up to 50phr HAF, the shift factors obtained were hardly dependent upon loading. The present results thus agree with a number of literature reports which indicate that time-temperature superposition is unaffected by carbon black loading for a restricted class of elastomers. The preservation of time-temperature superposition upon addition of carbon black does not hold universally, since there are some filled elastomers for which this property is destroyed upon addition of carbon black (see §2.2.2). In the light of the work of Payne and Ecker, it might be expected that for the nitrile rubber in the present study similar shift factors would apply also to intermediate carbon black loadings. With regard to the Huet model parameter values listed in Table 5.5, it is interesting to note that the $k$ value which corresponds to the creep rate of one of the parabolic elements is almost identical for both the filled and unfilled samples. We may speculate that this perhaps represents the creep behaviour of the elastomer matrix, while the other parabolic element of the model is associated with the black filler. In order to test this hypothesis it would be necessary to fit the model to data for samples containing varying amounts of filler.

Comparison of the relaxation spectra for the filled and
unfilled samples given in Figures 5.13 and 5.12 respectively shows that for short relaxation times there is relatively little change in the value of the spectrum. For long relaxation times however, the spectrum for the filled material demonstrates an increase over the corresponding values for the spectrum of the unfilled material. This is consistent with a broadening of the spectrum upon addition of carbon black [Medalla (1978)].

The overall objective of the linear experimental programme was to enable the proposal of a linear constitutive equation capable of modelling the observed frequency and temperature dependencies of the experimental materials. In §5.8 it is shown that the Huet model successfully describes the frequency dependence of the storage and loss moduli for the filled and unfilled materials. In order to describe general infinitesimal deformation we require a constitutive equation of a form such as [3.10]. Since data are available only over a finite frequency range, use cannot be made of the exact relationships between the viscoelastic functions. Hence an approximation is required for the relaxation modulus. One such approximation is that given by [5.13], which yields

\[ G(t) = G_e + \frac{G-G_e}{1+\delta(t/\tau)\eta(t/\tau)^k}. \]  \[5.14\]

Substituting into [3.10] we obtain

\[ \sigma_{ij} = 2G_e \varepsilon_{ij} + 2 \left[ \frac{G-G_e}{1+\delta[(t-u)/\tau]\eta[(t-u)/\tau]^k} \right] \frac{d}{du} \left[ \varepsilon_{ij}(u) \right] du \]  \[5.15\]

With regard to temperature dependence, the molecular theories of rubber elasticity predict that shear moduli should increase in direct proportion to the absolute temperature. Such ideal rubber behaviour is observed for lightly filled elastomers over certain ranges of temperature. Conversely the WLF equation [5.02] predicts a decrease in storage modulus with increasing temperature. Hsich, Yanyo and Ambrose (1984) have proposed a hybrid model which combines these behaviours. This model has been used to describe the temperature dependence of the storage modulus for samples of natural [natural text continues...].
rubber containing various loadings up to 50phr carbon black.

Compared to the very large changes in modulus which we observed within the range of experimental temperatures - these changes being described by the WLF equation (see §5.3) - the temperature dependence of shear moduli represents only a small correction. It is thus reasonable to assume that shear moduli values are independent of temperature. Combining [5.11] and [5.02] then yields

\[ G^*(\omega, T) = G_e + \frac{G-C_e}{1+\delta(1\omega\tau)^h+(1\omega\tau)^k} \]

where \[ \log\alpha_T = \frac{-C_1(T-T_0)}{C_2+T-T_0} \]

Equation [5.16] thus predicts the observed frequency and temperature dependencies of the experimental data.

In order to arrive at a temperature dependent linear constitutive equation similar to [5.15] we have recourse not only to an approximation such as [5.13], but also to the assumption that the time-temperature superposition principle is valid for transient temperatures [Lockett (1972)]. This assumption allows us to define a 'reduced time'

\[ du' = \frac{du}{a_T(T(u))} \]

whence

\[ u' = \int_{\infty}^{u} \frac{d\xi}{a_T(T(\xi))} \]

The temperature dependent analogue of [5.15] then becomes

\[ \sigma'_{ij} = 2G_e\varepsilon_{ij} + 2 \int_{-\infty}^{t} \frac{G-C_e}{1+\delta[(t'-u')/\tau]^h+(t'-u')/\tau} \cdot \frac{d}{du'} [\varepsilon_{ij}(u')] du' \]

where \( t' \) is defined analogously to \( u' \) in [5.17].
The question of whether [5.18] proves useful for the quantitative modelling of results depends upon the validity of the assumptions and approximations which have been used in its derivation. In particular it is reasonable to suppose that the accuracy of the approximation [5.13] will depend upon the range of frequencies considered. This implies that the accuracy of [5.18] will depend upon the timescale of the applied deformation. A systematic investigation of [5.18] in this respect remains as further work to be carried out. It is however hoped that [5.18] characterises the experimental materials sufficiently well to be of at least qualitative use in the modelling of results.

5.10 CONCLUSIONS

The main conclusions of this chapter may be summarised as follows:-

(1) All data collected upon the rheogoniometer indicate that to within experimental accuracy the applied deformation lies within the linear regime of the experimental materials.

(2) The observed increase in storage modulus values of the filled over the unfilled material indicates that an independent carbon black network plays an important rôle in determining the behaviour of the filled sample for small deformations.

(3) The filled material belongs to that class of carbon black filled elastomers for which time-temperature superposition is applicable.

(4) For both the filled and unfilled material time-temperature superposition is achieved by application of identical horizontal shift factors which are modelled by the WLF equation.

(5) The modified Spriggs model is capable of representing the frequency dependence of dynamic data only over certain ranges of temperature and frequency where the loss modulus is found to
be a monotonic increasing function of frequency.

(6) The Huet model affords a representation of dynamic data over the entire frequency range examined.

(7) The predictions of the Huet model and time-temperature superposition may be combined in a constitutive equation which is proposed to model the observed frequency and temperature dependencies of the experimental materials for general infinitesimal deformation.
CHAPTER 6

ASPECTS OF NON-LINEAR VISCOELASTIC THEORY & REPORTED EXPERIMENTAL EVIDENCE REGARDING ITS APPLICATION

INTRODUCTION

The aim of this chapter is to highlight constitutive equations capable of describing the non-linear deformation of carbon black filled and unfilled elastomers, and also to establish the mode of experimentation best suited as a means of evaluating these theories.

The chapter is divided into three main sections. The first section deals with aspects of non-linear viscoelastic constitutive equations chiefly from a theoretical viewpoint. Equations are presented which may be used to model the deformation of both unfilled and carbon black filled elastomers and theoretical quantities are defined which aid in the selection of suitable constitutive relations.

The second section considers reported experimental evidence for carbon black filled elastomers from which the applicability of the concepts of the modified Boltzmann superposition principle, separability, incremental dynamic moduli, and time-temperature superposition can be determined, these being features of the non-linear constitutive equations presented in the first section.

The main conclusions of the chapter are summarised in the third section.

6.1 ASPECTS OF NON-LINEAR VISCOELASTIC THEORY

In contrast to the linear viscoelastic theory discussed in Chapter 3, there exists no unique formulation of constitutive equation to characterise non-linear viscoelastic deformation. This relates essentially to the choice of suitable objective tensorial strain measures to replace the non-objective infinitesimal strain tensor of the linear theory. Having selected such a strain measure (or measures), a constitutive relation can then be obtained, where
the stress tensor is specified as a functional over the strain history or vice versa. Various constitutive equations may then be proposed which correspond to particular choices of the form of this functional. A number of single integral constitutive equations are considered which appear to be of practical utility.

In order to evaluate the material functions and parameters contained in such non-linear constitutive equations, it is most convenient to restrict our attention to uniaxial deformation. The choice of non-linear constitutive equations is further aided by comparison of model predictions with regard to criteria such as separability, incremental moduli and spectra functions, with experimental results. These criteria are accordingly discussed, and predictions of the non-linear models are presented.

6.1.1 Strain Dependent Non-Linear Constitutive Equations for Multiaxial Deformation

Linear viscoelastic theory, as described in §3.1, is based upon a number of simplifying axioms. Amongst these is the assumption that infinitesimal deformation can be described explicitly in terms of the position vector \( \vec{X} \). This assumption entails dropping the distinction between the reference state and other states of deformation. For the case of finite deformation however, a clear distinction must be made between an instantaneous state of deformation denoted by \( \vec{X} \) and the reference configuration denoted by \( \vec{X} \).

In further formulating a finite viscoelastic theory, it is important to distinguish between those materials which may be considered to possess a natural reference configuration, and those for which this is absent (see §2.1.4). In the latter case past deformation may be considered to be relative to the configuration at the present time \( t \). In this case the state of deformation \( \vec{X} \) at some instant of time \( r \) may be related to the current reference configuration \( \vec{X}(t) \) via the relative deformation gradient \( F_{\vec{X}}(t) \), which is defined analogously to [2.13], such that

\[
\frac{d\vec{X}(r)}{dt} = F_{\vec{X}}(r) \cdot d\vec{X}(t) \quad \text{[6.01]}
\]
By analogy to [2.14] we may define the right Cauchy-Green relative deformation tensor by

$$C_t = F_t^T F_t$$  \[6.02\]

while the left Cauchy-Green deformation tensor is defined in terms of the deformation gradient $F$ such that

$$B = F F^T.$$  \[6.03\]

The deformation tensors $C_t$ and $B$ are frame indifferent [Chang, Bloch and Tschoegl (1976a)]. A frame indifferent constitutive equation for an isotropic material possessing a natural reference configuration may then be expressed as [Lockett (1972)]

$$\sigma(t) = \frac{1}{\tau} \left[ C_t(\tau); B(t) \right],$$  \[6.04\]


We now consider a restriction which the 2nd law of thermodynamics places upon the constitutive functional given in [6.04]. In §2.1.3 it was stated that for simple fluids, in order to satisfy the 2nd law of thermodynamics, stresses and strains must be related via a strain energy function. The argument leading to this conclusion is based upon sudden cyclic deformations. Although [6.04] is a constitutive functional relationship for a material possessing a natural reference state i.e. a solid, a similar argument to that for simple fluids can be applied with regard to sudden cyclic deformation (see §2.1.3). Thus it is required that constitutive equations corresponding to particular forms of [6.04] are such that in the limit of elastic deformation stresses and strains are related via a strain energy function.

A strain energy function may be expressed in terms of

---

† The names of the various deformation tensors used in continuum mechanics are not definitively settled, and $B$ and $C_t$ are sometimes referred to as Finger's and Green's deformation tensors respectively.
principal extension ratios and these will now be defined. The deformation gradient tensor $\mathbf{F}$ defined in [2.12] may be uniquely decomposed such that

$$\mathbf{F} = \mathbf{R} \mathbf{U},$$

[6.05]

where $\mathbf{U}$ is the right stretch tensor and $\mathbf{R}$ is the rotation tensor. The right stretch tensor is a positive-definite symmetric tensor, and can be diagonalized when referred to the principal axes given by its eigenvectors. The corresponding principal values $\lambda_1, \lambda_2, \lambda_3$ are the principle extension ratios.

The strain energy function proposed by Blatz, Sharda and Tschoegl (1974) to describe moderate elastic deformations of incompressible materials has been shown by Sullivan (1986b) to describe biaxial tension data on a carbon black filled elastomer for principal extension ratios up to about 1.9. This strain energy function is given by

$$w = \frac{2G}{n^2} \left[ \lambda_1^n + \lambda_2^n + \lambda_3^n - 3 \right],$$

[6.06]

where $G$ is the shear modulus, and $n$ a material parameter.

The Cauchy principal stress is related to the strain energy function by

$$\sigma_\alpha = -p + \lambda_\alpha \frac{\partial w}{\partial \lambda_\alpha}, \quad \alpha = 1, 2, 3$$

[6.07]

where $p$ is an arbitrary isotropic mechanical pressure.

Applying [6.07] to [6.06] we obtain

$$\sigma_\alpha = -p + \frac{2G}{n} \lambda_\alpha^n, \quad \alpha = 1, 2, 3.$$  

[6.08]

The Constitutive Equations of Chang, Bloch & Tschoegl

Chang, Bloch and Tschoegl (1976a) have proposed constitutive equations for solids and liquids which extend [6.08] to general
viscoelastic deformation. The Chang, Bloch and Tschoegl (CBT) solid model is a particular form of [6.04] which has been successfully employed to characterise non-linear viscoelastic solids in a number of strain fields. This model is given by

\[
\sigma(t) = -p_l + \frac{1}{3n} \left[ E(t-u) \left( \frac{d}{du} C_t^{n/2}(u) + \frac{d}{du} C_t^{n/2}(u) B_t^{n/2}(t) \right) \right]_{-\infty}^t
\]

[6.09]

The CBT liquid model does not depend upon \( B(t) \). It thus corresponds to a particular case of a restricted form of the constitutive functional [6.04], where the \( B(t) \) dependence is omitted. This model can be written as

\[
\sigma(t) = -p_l - \frac{2}{3n} \left( E(t-u) \frac{d}{du} C_t^{-n/2}(u) \right)_{-\infty}^t
\]

[6.10]

It should be noted that in the limit of sudden elastic deformation [6.09] and [6.10] reduce to [6.08].

Other Constitutive Equations

Another constitutive equation which is a particular case of [6.04] is that proposed by Sullivan (1986a). This is written as

\[
\sigma(t) = -p_l + \frac{2}{3n} E_e B_t^{n/2}(t) - \frac{2}{3m} \left( \Delta E(t-u) \frac{d}{du} C_t^{-m/2}(u) \right)_{-\infty}^t
\]

[6.11]

where \( m \) and \( n \) are material parameters, and \( E_e \) and \( \Delta E(t) \) are the equilibrium and transient components of the tensile relaxation modulus, defined analogously to [3.27].

In the limit of elastic deformation from [6.11] we obtain
\[
\sigma_\alpha = -p + \frac{2}{3_n} E_e \lambda^n_\alpha + \frac{2}{3_m} [E-E_e] \lambda^m_\alpha , \quad \alpha=1,2,3. \tag{6.12}
\]

Equation [6.12] can be written in the form

\[
\sigma_\alpha = -p + \sigma^E_\alpha + \sigma^{\text{VE}}_\alpha , \quad \alpha=1,2,3, \tag{6.13}
\]

where \(\sigma^E_\alpha\) and \(\sigma^{\text{VE}}_\alpha\) are the components of the principal stress associated with the purely elastic and viscoelastic terms of [6.11] respectively. Now \(\sigma^E_\alpha\) can be derived from a strain energy function \(w^E\) given by

\[
w^E = \frac{2E_e}{3n^2} [\lambda_1^n + \lambda_2^n + \lambda_3^n - 3] \tag{6.14}
\]

while \(\sigma^{\text{VE}}_\alpha\) can be derived from a strain energy function \(w^{\text{VE}}\) given by

\[
w^{\text{VE}} = \frac{2}{3m^2} [E-E_e] [\lambda_1^m + \lambda_2^m + \lambda_3^m - 3]. \tag{6.15}
\]

From [6.07] we have that

\[
\sigma^E_\alpha = -p + \lambda_\alpha \frac{\partial w^E}{\partial \lambda_\alpha}, \quad \alpha=1,2,3. \tag{6.16}
\]

\[
\sigma^{\text{VE}}_\alpha = -p + \lambda_\alpha \frac{\partial w^{\text{VE}}}{\partial \lambda_\alpha}
\]


\[
\sigma_\alpha = -p' + \lambda_\alpha \left[ \frac{\partial w^E}{\partial \lambda_\alpha} + \frac{\partial w^{\text{VE}}}{\partial \lambda_\alpha} \right], \quad \alpha=1,2,3 \tag{6.17}
\]

where \(p'\) is an arbitrary isotropic mechanical pressure.

From [6.17] we observe that we may define a strain energy function \(W\) such that

\[
W = w^E + w^{\text{VE}} = \frac{2E_e}{3n^2} [\lambda_1^n + \lambda_2^n + \lambda_3^n - 3] + \frac{2}{3m^2} [E-E_e] [\lambda_1^m + \lambda_2^m + \lambda_3^m - 3]. \tag{6.18}
\]

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Substitution of [6.18] into [6.07] yields [6.12], and thus we see that $W$ describes the instantaneous elastic deformation given by [6.11].

We may propose a further constitutive equation based on [6.04], differing from [6.11] in that the deformational dependence of the integral term is that of the CBT solid model [6.09]. This model may be expressed as

$$
\sigma(t) = -pI + \frac{2}{3n} E_0 B^{n/2}(t) + \frac{1}{3m} \int_{-\infty}^{t} \Delta\epsilon(t-u) \left[ B^{m/2}(t) \frac{d}{du} \epsilon^{m/2}(u) + \frac{d}{du} \delta^{m/2}(u) B^{m/2}(t) \right] du .
$$

[6.19]

A similar argument to the foregoing shows that the associated strain energy function is also given by [6.18].

The Modified Boltzmann Superposition Principle

The Fréchet Theorem allows a functional to be expressed as a series of integral terms of increasing order. The first such term is a single integral, and may be regarded as a first order approximation to the functional. The single integral term of linear viscoelastic theory (see §3.1) implies that distinct events in the deformation history of the material do not interact with each other, i.e., they obey the Boltzmann superposition principle. In non-linear viscoelastic theory, single integral terms such as those in [6.09] and [6.10] correspond to a modified Boltzmann superposition principle. In this case previous deformation effects the magnitude of the response to a particular event in the deformation history, but the time dependence associated with this event is unaffected. If the time dependence of the response to an event in the deformation

† Other superposition principles are applicable to single integral constitutive equations e.g. Stafford's superposition theory [Lockett (1972)].
history is influenced by previous deformation, then no form of the Boltzmann superposition principle is applicable. This in general is the case for \([6.25]\) and for higher order approximations to the constitutive functional, which comprise multiple integral terms.

6.1.2 Strain Dependent Non-Linear Constitutive Equations for Uniaxial Deformation

The constitutive equations of \(\S 6.1.1\) are in principle applicable to any general deformation. In order to determine material parameters however, it is most convenient to restrict the deformation to uniaxial cases, such as for example, uniaxial extension or pure shear. In these cases the principal axes are unaffected by the deformation, which can accordingly be characterised in terms of extension ratios \(\lambda_\alpha\), defined by

\[
\lambda_\alpha = \frac{\ell}{\ell_0},
\]

where \(\ell\) and \(\ell_0\) are the distances between two points on the principal axis, \(\alpha\), in the deformed and undeformed states respectively.

In uniaxial extension, let the principal stress component along the axis of extension be \(\sigma\), and the corresponding extension ratio \(\lambda\). For an incompressible material, the extension ratio in the transverse direction is consequently \(\lambda^{-1}\). Eliminating \(p\) from \([6.09]\), we obtain

\[
\sigma(t) = \frac{2}{3n} \int_{-\infty}^{t} E(t-u) \frac{d}{du} \left[ \lambda^n(u) - \lambda^{-n/2}(u) \right] du.
\]

Similarly from \([6.11]\) we obtain

\[
\sigma(t) = \frac{2}{3n} E \left[ \lambda^n(t) - \lambda^{-n/2}(t) \right] - \frac{2}{3m} \int_{-\infty}^{t} \Delta E(t-u) \frac{d}{du} \left[ \lambda^m(u) - \lambda^{-m/2}(u) \right] du
\]

whilst \([6.19]\) yields

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\[
\sigma(t) = \frac{2}{3n} E_e [\lambda^n(t) - \lambda^{-n/2}(t)] - \frac{2}{3m} \int_{-\infty}^{t} \Delta E(t-u) \frac{d}{du} [\lambda^m(u) - \lambda^{-m/2}(u)] \, du
\]  

[6.23]

Schapery (1969) has developed a uniaxial theory of temperature dependent non-linear viscoelasticity based upon thermodynamic arguments. This theory is couched in terms of the nominal stress component \( \sigma_n \) (see §2.1.1), while the corresponding strain component \( \epsilon \) is calculated relative to the undeformed configuration, and is given by

\[
\epsilon = \lambda - 1.
\]  

[6.24]

The Schapery constitutive equation for stress can be expressed as

\[
\sigma_n(t) = h_e[\epsilon(t) - \epsilon_0] E_e \epsilon(t) + h_1[\epsilon(t)] \int_{0}^{t} \Delta E(\rho-\rho') \frac{d}{d\tau} [h_2(\epsilon(\tau)) \cdot \epsilon(\tau)] \, d\tau,
\]  

[6.25]

where \( h_e, h_1, \) and \( h_2 \) are material functions, and the reduced times \( \rho \) and \( \rho' \) are defined similarly to those of [5.18], such that

\[
\rho = \int_{0}^{t} \frac{d\xi}{a_\epsilon[\epsilon(\xi), T(\xi)]},
\]  

[6.26]

\[
\rho' = \int_{0}^{t} \frac{d\xi}{a_\epsilon[\epsilon(\xi), T(\xi)]}.
\]  

The reduction factor \( a_\epsilon \) may however depend on the strain component \( \epsilon \) in addition to temperature.

We may note that [6.21] and [6.23] may be regarded as particular cases of the more general one-dimensional form [6.25]. This however is not true of [6.22], since the strain dependent function under the integral sign is not generally a separable function of the deformation at past and present times.

Schapery also proposes a non-linear constitutive equation analogous to [6.25] which determines the strain component \( \epsilon \) as a
function of the nominal stress component $\sigma_n$. It is however shown in Schapery (1969) that unlike the case of linear viscoelasticity, such a non-linear equation for $\epsilon$ is in general not equivalent to the expression which results from inversion of [6.25]. Thus a material for which the strain component $\epsilon$ is determined as a function of $\sigma_n$ by the analogue of [6.25], will not generally allow $\sigma_n$ to be expressed as a function of $\epsilon$ according to the form [6.25]. The question of whether constitutive equations are explicit in stress or in strain is thus of fundamental importance in the case of non-linear viscoelasticity. In most of the subsequent treatment, as in the foregoing, stress will be considered primarily as a function of strain. This choice is however quite arbitrary, and does not preclude the possibility that the converse approach might prove at least equally successful.

6.1.3 A stress Dependent Non-Linear Constitutive Equation for Multiaxial Deformation

A particular constitutive equation for strain, which has given rise to some interesting work regarding temperature dependence, is the form considered by Talybly (1978). This can be written as

$$2\epsilon^{ij}(t) = f_1(\sigma_u, T)\sigma^{ij}_t(t) + \int_0^t J(t-\tau, T)f_2(\sigma_u, T)\sigma^{ij}_t(\tau)d\tau , \quad [6.27]$$

where $\epsilon^{ij}$ is a component of the deviatoric part of the infinitesimal strain tensor, defined analogously to the deviatoric stress $\sigma^{ij}_t$ in [2.04], and $f_1$ and $f_2$ are material functions of the 'stress intensity' $\sigma_u$ which is defined by

$$\sigma_u(t) = \sqrt{\frac{2}{3} \frac{\sigma'(t) : \sigma'(t)}{\sigma'(t)}} . \quad [6.28]$$

Schapery (1969) states that if the free energy depends strongly on temperature, then all the strain dependent functions of [6.25], excepting $h^2$, together with all the stress dependent functions of its analogue, may depend on temperature. Thus the stress dependent
analogue of [6.25] corresponds to a one-dimensional extension of [6.27].

Equation [6.27] is based on the 'quasi-linear' theory of Ilyushin and Ogibalov (1966), which seeks to account for third order stress effects by considering products of the form $\sigma'_i j (\tau) \sigma'_i (u) \sigma'_j (u)$. This theory is couched in terms of the infinitesimal strain tensor $\varepsilon'_i j$, and is thus valid only in the region of small strains.

Talybly (1978) has shown that taking into account the temperature dependencies of the non-linear functions $f_1$ and $f_2$ appearing in [6.27] can lead to greater accuracy in the calculated strain than is the case when the temperature dependence of the constitutive equation is expressed solely in terms of 'reduced time' (see §§5.9 and 6.1.2). Moreover, for certain materials isothermal plots of the non-linear functions $f_1$ and $f_2$ against $\log \sigma_u$ are horizontally superposable, as is the analogous case of time-temperature superposition (see §3.2.1). These experimental observations indicate that $f_1$ and $f_2$ can be written as functions of a reduced stress intensity, analogous to reduced time. In particular, for the case of high density polyethylene Talybly (1983) has shown that the temperature dependence of non-linear creep curves can be adequately expressed entirely in terms of such a reduced stress intensity.

Bloch, Chang and Tschoegl (1978a) analysed the temperature dependence of stress relaxation in styrene-butadiene rubber in terms of the prediction of the CBT solid and liquid models [6.09] and [6.10]. It was found that time-temperature superposition did not completely characterise the observed temperature dependence, and that the form of the stress-strain relationship also depended upon temperature. This temperature dependence was modelled by allowing the material parameter $n$ to depend on temperature.

These results demonstrate that although reduced time has been used almost exclusively to describe temperature dependence in the linear regime, for non-infinitesimal deformation temperature dependence can be expressed in a number of ways. In particular, in the case of materials characterised by constitutive equations involving strongly temperature dependent non-linear functions which are independent of time (such as the function which for some materials characterises the stress-strain relationship at equilibrium), the temperature dependence cannot be adequately
represented solely by means of reduced time.

6.1.4 Separability

A material exhibits time-strain separability if, following a sudden deformation, the stress relaxation can be expressed as a product of a time dependent and strain dependent function. This property implies that functions of time and strain in the viscoelastic term of the constitutive equation should be factorisable, as is the case if the material obeys a form of the Boltzmann superposition principle (see §6.1.1). The converse however does not generally hold. This is demonstrated by [6.11] and [6.19], which although obeying the modified Boltzmann superposition principle, do not exhibit separability except in the case when \( m = n \).

6.1.5 Incremental Dynamic Moduli

In the case of non-linear deformation the application of a sinusoidally oscillating strain does not produce a sinusoidally oscillating stress. This means that dynamic moduli such as those defined in §3.1.1 cannot be determined. However, for the case of small sinusoidal oscillations superimposed upon a static deformation the resulting perturbation is sinusoidal, provided that the amplitude of oscillation is sufficiently small. This enables us to determine non-linear dynamic moduli which are known as incremental, or differential, dynamic moduli.

For pure deformation characterised by the extension ratio \( \lambda \), it is convenient to define the superimposed oscillatory strain relative to the deformed configuration, such that

\[
\lambda(t) = \lambda(1 + \varepsilon_0 \cos \omega t), \tag{6.29}
\]

where \( \varepsilon_0 \) is the strain amplitude relative to the deformed sample dimensions and \( \omega \) is the frequency of oscillation.

Equation [6.21] may be expressed in the form
\[ \sigma(t) = 2 \frac{E_0}{3n} \left( \lambda^n(t) - \lambda^{-n/2}(t) \right) + 2 \frac{E_0}{3n} \int_{-\infty}^{t} \Delta E(t-u) \frac{d}{du} \left[ \lambda^n(u) - \lambda^{-n/2}(u) \right] du. \] [6.30]

Using the approximation

\[ \lambda^n(u) = \lambda^n + n \lambda^n \epsilon_0 \cos \omega u + O(\epsilon_0^2) \] [6.31]

we obtain

\[ \sigma = 2 \frac{E_0}{3n} \left[ \lambda^n - \lambda^{-n/2} \right] + 2 \frac{E_0}{3n} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \epsilon_0 \cos \omega t \]

\[ + 2 \frac{E_0}{3n} \int_{-\infty}^{t} \Delta E(t-u) \frac{d}{du} \left[ n \lambda^n \epsilon_0 \cos \omega u + \frac{n}{2} \lambda^{-n/2} \epsilon_0 \cos \omega u \right] du \] [6.32]

Also from [6.30] we see that at long times the stress relaxes towards an equilibrium value \( \sigma_e \), given by

\[ \sigma_e = 2 \frac{E_0}{3n} \left[ \lambda^n - \lambda^{-n/2} \right]. \] [6.33]

Thus from [6.32] and [6.33] we obtain

\[ \sigma - \sigma_e = 2 \frac{E_0}{3n} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \epsilon_0 \cos \omega t + \]

\[ + 2 \frac{E_0}{3n} \int_{-\infty}^{t} \Delta E(t-u) \frac{d}{du} \left[ n \lambda^n \epsilon_0 \cos \omega u + \frac{n}{2} \lambda^{-n/2} \epsilon_0 \cos \omega u \right] du. \] [6.34]

or

\[ \sigma - \sigma_e = 2 \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \left\{ E_0 \epsilon_0 \cos \omega t + \int_{-\infty}^{t} \Delta E(t-u) \frac{d}{du} \epsilon_0 \cos \omega u du \right\}. \] [6.35]

From [3.27] and [3.16] we obtain
\[ G^*(w) = i\omega \int_0^\infty \Delta G(\tau) e^{-i\omega \tau} d\tau + G_e. \quad [6.36] \]

Now from [6.35], letting \( t = u - \tau \)

\[
\begin{align*}
\sigma - \sigma_e &= \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \left\{ E_e \epsilon_0 \cos \omega t - \int_0^\infty \Delta E(\tau) \frac{d}{du} \epsilon_0 \cos \omega (t - \tau) d\tau \right\} \\
\sigma - \sigma_e &= \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \left\{ E_e \epsilon_0 \cos \omega t + \epsilon_0 \cos \omega t \right\} \int_0^\infty \Delta E(\tau) \sin \omega \tau d\tau \\
&\quad - \epsilon_0 \sin \omega t \int_0^\infty \Delta E(\tau) \cos \omega \tau d\tau \right\}.
\end{align*}
\]

And by the tensile analogue of [6.36]

\[
\begin{align*}
\sigma - \sigma_e &= \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \left\{ E_e \epsilon_0 \cos \omega t + \epsilon_0 \cos \omega t \cdot \text{Re}\{E^*(\omega) - E_e \} \\
&\quad - \epsilon_0 \sin \omega t \cdot \text{Im}\{E^*(\omega) - E_e \} \right\} \\
\sigma - \sigma_e &= \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] \left\{ \text{Re}\{E_e \epsilon_0 e^{i\omega t} \} + \text{Re}\{E^*(\omega) - E_e \} \epsilon_0 e^{i\omega t} \right\} \\
\sigma - \sigma_e &= \text{Re} \left\{ \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] E^*(\omega) \epsilon_0 e^{i\omega t} \right\}. \quad [6.37]
\end{align*}
\]

Equation [6.37] is of equivalent form to [3.15]. Denoting incremental tensile dynamic moduli by \( E'(\omega,\lambda) \) and \( E''(\omega,\lambda) \), from [6.37] we obtain

\[
E'(\omega,\lambda) = \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] E'(\omega) \quad [6.38]
\]

\[
E''(\omega,\lambda) = \frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] E''(\omega)
\]

Consider a small time dependent deformation \( \epsilon(t) \) imposed at \( t = 0 \) upon a steady deformation with extension ratio \( \lambda \). For such a deformation history we may write
\[
\lambda(t) = \begin{cases} 
\lambda(t) & t < 0 \\
\lambda(1+\varepsilon(t)) & t > 0 
\end{cases}
\]

For the quantity \( \frac{\lambda(t)}{\lambda(u)} \), which appears in [6.22] we observe that

\[
\frac{\lambda(t)}{\lambda(u)} = \begin{cases} 
\left( \frac{\lambda(1+\varepsilon(t))}{\lambda} \right)^m - 1+m\varepsilon(t)+O(\varepsilon^2) & , u < 0 \\
\left( \frac{\lambda(1+\varepsilon(t))}{\lambda(1+\varepsilon(u))} \right)^m - 1+m\varepsilon(t)-m\varepsilon(u)+O(\varepsilon^2) & , u > 0 
\end{cases}
\]

Equation [6.39] can be written more concisely in the form

\[
\frac{\lambda(t)}{\lambda(u)} = 1 + m\varepsilon(t) - m\varepsilon(u)\delta(u) + O(\varepsilon^2). \tag{6.40}
\]

Substituting [6.40] into [6.22] and disregarding transients associated with taking derivatives of the Heavyside function, we obtain

\[
\sigma(t) = \frac{2}{3n} E\varepsilon \left[ \lambda^n [1+n\varepsilon(t)] - \lambda^{-n/2} [1-n\varepsilon(t)] \right] + \int_0^t \Delta E(t-u) \frac{d}{du} [\varepsilon(u)] du. \tag{6.41}
\]

Thus for a small time dependent deformation superimposed on a steady deformation [6.22] reduces to [6.41]. We observe that [6.41] corresponds to a particular case of the Schapery equation [6.25].


\[
E'(\omega,\lambda) = \frac{2E\varepsilon}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] + E'(\omega) - E_e
\]

\[
E''(\omega,\lambda) = E''(\omega). \tag{6.42}
\]

Incremental moduli resulting from the constitutive equation proposed in [6.19] are of the form
\[ E'(\omega, \lambda) = \frac{2E_\infty}{3} \left[ \lambda^n + \frac{\lambda^m}{2} \right] + \frac{2}{3} \left[ \lambda^m + \frac{\lambda^{-m/2}}{2} \right] (E'(\omega) - E_\infty) \]  
\[ E''(\omega, \lambda) = \frac{2}{3} \left[ \lambda^m + \frac{\lambda^{-m/2}}{2} \right] E''(\omega). \]

We also consider the form of the incremental moduli corresponding to [6.25]. For an incompressible material the Cauchy stress and nominal stress components are related by

\[ \sigma = \lambda \sigma_n \]  

and hence from [6.24]

\[ \sigma = (\varepsilon + 1)\sigma_n. \]  

Equation [6.25] can thus be expressed in terms of the Cauchy stress component as

\[ \sigma = h_0(\varepsilon) E_e. [1+\varepsilon]. \varepsilon + [1+\varepsilon]. h_1(\varepsilon) \int_0^t \Delta E(\rho - \rho') \frac{d}{d\tau} \left[ h_2(\varepsilon) . \varepsilon \right] d\tau. \]  

Let the applied strain be decomposed into steady and time dependent components such that

\[ \varepsilon(t) = \varepsilon_S + \Delta \varepsilon(t). \]  


\[ \sigma = h_0(\varepsilon_S + \Delta \varepsilon) E_e. [1+\varepsilon_S + \Delta \varepsilon]. [\varepsilon_S + \Delta \varepsilon] + \]

\[ [1+\varepsilon_S + \Delta \varepsilon] h_1(\varepsilon_S + \Delta \varepsilon) \int_0^t \Delta E(\rho - \rho') \frac{d}{d\tau} \left[ h_2(\varepsilon_S + \Delta \varepsilon) . [\varepsilon_S + \Delta \varepsilon] \right] d\tau. \]

Assuming that the functions \( h_0, h_1, \) and \( h_2 \) may be expanded as Taylor series, we obtain
\[
\sigma = \left[ h_e(\epsilon_s) + \Delta \epsilon \frac{dh_e}{d\epsilon} (\epsilon_s) + \ldots \right] E_e [1+\epsilon_s+\Delta \epsilon] [\epsilon_s+\Delta \epsilon] + \\
[1+\epsilon_s+\Delta \epsilon] \left[ h_1(\epsilon_s)+\Delta \epsilon \frac{dh_1}{d\epsilon} (\epsilon_s)+\ldots \right] \times \\
\int_0^t \Delta E(\rho-\rho') \frac{d}{d\tau} \left\{ [h_2(\epsilon_s)+\epsilon_s \frac{dh_2}{d\epsilon} (\epsilon_s)+\ldots] [\epsilon_s+\Delta \epsilon] \right\} \, d\tau. \tag{6.48}
\]

Now from (6.46)

\[
\sigma_e = h_e(\epsilon_s) E_e [1+\epsilon_s] \cdot \epsilon_s \tag{6.49}
\]

Subtracting (6.49) from (6.48) we obtain

\[
\sigma - \sigma_e = \left\{ h_e(\epsilon_s) \cdot E_e \cdot [1+\epsilon_s] + h_e(\epsilon_s) \cdot E_e \cdot \epsilon_s + \frac{dh_e}{d\epsilon} (\epsilon_s) \cdot E_e \cdot [1+\epsilon_s] \cdot \epsilon_s \right\} \Delta \epsilon + \\
[1+\epsilon_s] \cdot h_1(\epsilon_s) \cdot \int_0^t \Delta E(\rho-\rho') \frac{d}{d\tau} \left\{ [h_2(\epsilon_s)+\epsilon_s \frac{dh_2}{d\epsilon} (\epsilon_s)] \Delta \epsilon \right\} d\tau + O(\Delta \epsilon)^2.
\]

Therefore

\[
\sigma - \sigma_e = \left[ \frac{d}{d\epsilon} \left\{ h_e(\epsilon) \cdot E_e \cdot [1+\epsilon] \cdot \epsilon \right\} \right] \cdot \Delta \epsilon + \\
[1+\epsilon] \cdot h_1(\epsilon) \cdot \frac{d}{d\epsilon} \left\{ h_2(\epsilon) \cdot \epsilon \right\} \int_0^t \Delta E(\rho-\rho') \frac{d}{d\tau} \Delta \epsilon \, d\tau \bigg|_{\epsilon=\epsilon_s} + O(\Delta \epsilon)^2. \tag{6.50}
\]

In the case of a small superimposed sinusoidal oscillation, we may write

\[
\Delta \epsilon(t) = \lambda \epsilon_0 \cos \omega t. \tag{6.51}
\]

For isothermal conditions, from (6.26) we have the (approximate) relations

\[
\rho = t/a_\epsilon(\epsilon_s) \tag{6.52}
\]

\[
\rho' = t'/a_\epsilon(\epsilon_s).
\]

\[ E'(\omega, \lambda) = \left[ \lambda \frac{d}{d\varepsilon} \left\{ h_0(\varepsilon) \cdot E_e \cdot (1+\varepsilon) \cdot \varepsilon \right\} + \right. \]

\[ \left. \lambda \cdot (1+\varepsilon) \cdot h_1(\varepsilon) \cdot \frac{d}{d\varepsilon} \left\{ h_2(\varepsilon) \cdot \varepsilon \right\} \cdot \left[ E'(\omega a_\varepsilon - E_e) \right] \right|_{\varepsilon = \varepsilon_s} \]

[6.53]

\[ E''(\omega, \lambda) = \left[ \lambda \cdot (1+\varepsilon) \cdot h_1(\varepsilon) \cdot \frac{d}{d\varepsilon} \left\{ h_2(\varepsilon) \cdot \varepsilon \right\} \cdot E''(\omega a_\varepsilon) \right] \right|_{\varepsilon = \varepsilon_s} \]

From [6.24] and [6.49] we may write

\[ E'(\omega, \lambda) = \lambda \frac{d\varepsilon}{d\lambda} \cdot \frac{d\varepsilon}{d\lambda} + \lambda^2 h_1(\lambda-1) \cdot \frac{d}{d\lambda} \left\{ h_2(\lambda-1) \cdot (\lambda-1) \right\} \cdot \left[ E'(\omega a_\varepsilon - E_e) \right] \]

[6.54]

\[ E''(\omega, \lambda) = \lambda^2 h_1(\lambda-1) \cdot \frac{d}{d\lambda} \left\{ h_2(\lambda-1) \cdot (\lambda-1) \right\} \cdot E''(\omega a_\varepsilon) \]

Equations [6.38], [6.42], [6.43] are thus seen to be particular forms of [6.54], corresponding to the case \( a_\varepsilon = 1 \).

The incremental dynamic moduli predictions in simple tension for the non-linear constitutive equations which have been given in this section will be referred to frequently throughout the remainder of this thesis. For ease of reference these are presented together in Table 6.1.

6.1.6 Relaxation Spectrum Functions

The relaxation spectrum of linear viscoelastic theory is defined in [3.28], and in §5.5 the methods of Williams and Ferry are used to obtain approximate spectrum values from linear loss and storage modulus data. There exists no unique extension of [3.28] for non-linear deformation. However, Sullivan (1986a) has proposed modifications to the Williams and Ferry relations which serve to define 'relaxation spectrum functions'. These are given in Table 6.2.

These relaxation spectrum functions are related to the linear relaxation spectrum via non-linear constitutive equations such as
those of §6.1.1 and [6.25]. The predictions of these constitutive equations with regard to the relaxation spectrum functions are listed in Table 6.3.

6.2 **SIGNIFICANT FEATURES OF THE NON-LINEAR BEHAVIOUR OF CARBON BLACK FILLED ELASTOMERS WITH REGARD TO MODELLING**

The constitutive equations of Chang, Bloch and Tschoegl (see §6.1.1) have enjoyed considerable success in modelling the non-linear viscoelastic behaviour of unfilled elastomers - Bloch, Chang, Tschoegl (1978). Sullivan and Demery (1982) attempted to apply the CBT solid equation to model the non-linear deformation of natural rubber loaded with N351 carbon black, but this did not prove successful. This section is concerned with discussing features of the non-linear deformation of carbon black filled elastomers which are significant from a modelling perspective. These features comprise cyclic deformation, separability, incremental dynamic moduli and time-temperature superposition, and will be discussed in turn.

6.2.1 **Cyclic Deformation**

In §6.1.1 it is stated that constitutive equations which do not obey a form of the Boltzmann superposition principle may involve multiple integral terms. These terms account for higher order interactions between distinct events in the deformation history of the material. Lockett (1972) states that 'if triple and higher order integral terms are necessary in constitutive relations ... their contributions will be evident in the analysis of multiple-step experiments'. An example of such a multiple-step experiment is cyclic deformation (see Figure 6.1).

The applicability of the (modified) Boltzmann superposition principle can be examined with the aid of the following analysis. Let $G(t,\lambda)$ represent the relaxation of the stress component corresponding to a uniaxial extension $\lambda$ imposed at $t = 0$. Thus for this single step deformation we write

$$\sigma(t,\lambda) = G(t,\lambda) . \quad [6.55]$$
The stress relaxation response \( \sigma_C(t, \lambda) \) of any single-integral constitutive equation obeying the modified Boltzmann superposition principle when subjected to a cyclic deformation history such as indicated in Figure 6.1 is then given by

\[
\sigma_C(t, \lambda) = G(t, \lambda) - G(t-t_1, \lambda) + G(t-t_2, \lambda) - \ldots - G(t-t_{n-1}, \lambda) + G(t-t_n, \lambda).
\]  

[6.56]

Since stress relaxation is a monotonic decreasing function of time

\[
G(t-t_r, \lambda) - G(t-t_{r-1}, \lambda) > 0 \quad \text{for } t_r > t_{r-1}
\]  

[6.57]

and hence from [6.56]

\[
\sigma_C(t, \lambda) \geq G(t, \lambda).
\]  

[6.58]

Equation [6.58] shows that the single step stress relaxation response is predicted to be a lower bound for the stress in cyclic deformation histories for materials obeying the modified Boltzmann superposition principle. McKenna and Zapas (1981) found that for NBS 388j butyl rubber filled with 50phr NBS 387b HAF carbon black the inequality [6.58] was not satisfied. They concluded that the material softens slightly under cyclic deformation. Much greater softening was however observed under cyclic loading.

These observations can be interpreted in terms of the progressive breakdown of a carbon black network structure. In rubber technology this is known as the 'Mullins effect', and can be removed by 'scragging' (see §2.2.4). Such an explanation accounts for the difference in the observed 'softening' under cyclic deformation and cyclic loading. In the former case imposition of a few initial cycles of deformation will cause a certain degree of disruption to the carbon black network, and subsequent cycling may produce comparatively little effect. In the latter case however, successive loading can cause progressive disruption of the carbon black network until it is completely destroyed.

The results of McKenna and Zapas do not thus necessarily invalidate the modelling of filled elastomers in terms of a single integral constitutive equation, since it is likely that scragging would reduce much of the apparent softening. A single integral
constitutive equation requires a substantially simpler experimental programme to evaluate material functions and parameters than is the case for multiple integral equations, see for example Lockett (1972). For this reason it is preferable to seek a description of material behaviour in terms of a single integral equation and all further discussion will be restricted to such forms.

6.2.2 Experimental Observation of Separability

The criterion of separability is defined in §6.1.4. Experimental evidence for separability in carbon black filled elastomers reported in the literature is cited in Table 6.4. It is apparent that this evidence is rather mixed. Table 6.4 shows that for certain investigations where a lack of separability is demonstrated for filled elastomers, the corresponding unfilled elastomer does indeed exhibit separability. Thus in some cases the property of separability is destroyed by the presence of carbon black filler. Indeed, the results of Gent (1963) imply the existence of an independent carbon black network (see §2.2.4) and separability is only exhibited when this is destroyed by application of a momentary pre-strain.

Chang, Wijayarathna and Salovey (1984) propose that separability is only possible below a certain critical extension ratio which depends upon the type and loading of carbon black. They base this upon the proposition that geometrical factors concerned with particle size and separation make affine deformation of filler particles impossible above certain extension ratios and believe this to affect separability. This proposition can be interpreted in terms of a 2-network theory, which will now be considered.

One idealisation of the structure of a filled elastomer is in terms of a 2-network theory [Chang, Bloch and Tschoegl (1977a)] where one network represents the elastomer matrix, and the other the structure due to the carbon black filler. Each of these networks is taken to be independent of the other and to conform to the Gaussian statistical (molecular) theory of rubber-like materials, see for example Ward (1979). A basic assumption of this statistical theory is that of affine deformation. Smith and Gaylord (1972) have shown that an independent network hypothesis is only valid for Gaussian
systems. (The behaviour of the unfilled elastomer matrix does not generally correlate well with Gaussian statistical theory but better agreement is obtained for small deformations). The proposition of Chang et al which limits affine deformation of the filler network, thus also limits the application of an independent network theory. Above a certain extension ratio we thus expect an interaction between the filler and elastomer networks, and this might well account for a loss of separability.

In unfilled elastomers, such as the natural rubber studied by Sullivan, Morman and Pett (1980), separability is sometimes only demonstrated below a certain extension ratio. Here the effect was attributed to strain induced crystallisation. For other elastomers however, strain induced crystallisation is only important at quite large deformations. For instance Gent (1963) comments that 'vulcanisates of butyl rubber do not show significant amounts of crystallinity until the extension reaches 500 to 700%'.

Separability also depends upon time and temperature. Bloch, Chang and Tschoegl (1978a) comment that '... published data indicate that the effects of time and strain are separable ... in regions of the response which are not too close to the glassy region' (see §2.2.2).

In conclusion it should be stated that often it appears difficult to obtain conclusive experimental evidence with regard to separability. This is demonstrated by the investigations of Sullivan, Morman and Pett (1980) and Sullivan (1986a) where stress relaxation data on the same material are used to attest both separability and lack of separability respectively. Sullivan and Demery (1982) also demonstrated separability for stress relaxation data, but concluded in the light of incremental dynamic modulus data that this separability was only apparent. For some materials characterised by a separable constitutive equation, separability is also observed in modes of deformation for which separability is not predicted by the constitutive equation. This is instanced by Bloch, Chang and Tschoegl (1978a) who comment that '... these effects [i.e. time and strain] should not uncouple in the response to a ramp of strain. Experimental evidence, particularly the work of Smith, shows however, that in such experiments the effects of strain and time appear to be separable'.

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6.2.3 Experimental Results on Incremental Dynamic Moduli

Various incremental dynamic moduli have been measured for carbon black filled elastomers by Meinecke and Maksin (1980), Sullivan and Demery (1982), Isono and Ferry (1984) and Arai and Ferry (1986a, 1986c). The investigations of Isono and Ferry and of Arai and Ferry are primarily concerned with investigating structural changes during the course of relaxation, while those of Meinecke and Maksin and of Sullivan and Demery are concerned with characterising materials close to equilibrium under varying degrees of strain.

In order to measure incremental dynamic moduli close to equilibrium, a uniaxial strain is imposed corresponding to an extension ratio \( \lambda \), and the quasi-equilibrium value of the resulting force \( F_e \) is measured when sufficient time has elapsed for the residual stress relaxation to become small. A sinusoidally oscillating strain is then imposed, such that the extension ratio \( \lambda(t) \) is given by [6.29], and the resulting force \( F(t) \) is decomposed into steady and time dependent components \( F_e \) and \( F'(t) \) such that

\[
F(t) = F_e + F'(t) . \tag{6.59}
\]

The amplitude \( \delta F \) of the oscillatory component of the force is measured, together with the phase angle \( \phi \) between oscillatory components of force and displacement.

The calculation of incremental dynamic moduli from the observed experimental quantities is performed in different ways by different authors. The theory of Goldberg and Liapis (1968) appears to give the most satisfactory definition of incremental dynamic moduli viz.

\[
E'(\omega, \lambda) = \frac{\lambda \delta F}{A_0 \varepsilon_0} \cos c + \sigma_e ,
\]

\[
E''(\omega, \lambda) = \frac{\lambda \delta F}{A_0 \varepsilon_0} \sin c
\]

where \( A_0 \) is the undeformed cross-sectional area of the sample, and \( \sigma_e \) is the quasi-equilibrium stress given by

\[
\sigma_e = \frac{\lambda F_e}{A_0} . \tag{6.61}
\]
A more simplistic approach to the definition of incremental dynamic moduli has been adopted by Meinecke and Maksin, Isono and Ferry, and Arai and Ferry. This omits the term $\sigma_e$ from the definition given in [6.60]. It then follows from the extension of [3.20] to incremental tensile dynamic moduli that the phase difference $\phi$ appearing in [6.60] is identical with the loss angle $\delta$.

In order to determine incremental dynamic moduli, use is often made of elliptical plots of oscillatory force against displacement. The theory of such plots is contained in Appendix I.

The results of Sullivan and Demery are based upon equation [6.60]. Those of Meinecke and Maksin however are based upon measurements of elliptical plots such as Figure A1.1 and include approximations which strictly are only valid for $\lambda = 1$ and $\phi = 0$. Moreover the moduli determined by Meinecke and Maksin relate nominal stress to strain relative to the undeformed configuration, whereas those determined by Sullivan and Demery relate Cauchy stress to strain relative to the deformed configuration.

Sullivan and Demery have shown that for a natural rubber containing 46phr N351 carbon black the incremental dynamic moduli do not possess the same $\lambda$-dependence. Although the results of Meinecke and Maksin on a styrene butadiene copolymer containing loadings up to 50phr HAF are based upon questionable approximations, and are based upon different definitions of modulus (which strictly invalidates a direct comparison with the results of Sullivan and Demery), their results show broadly the same features.

Equation [6.38] shows that the CBT solid equation [6.09] predicts the $\lambda$-dependencies of incremental loss and storage moduli to be identical. It is thus concluded that [6.09] cannot model the results of Sullivan and Demery or of Meinecke and Maksin. Indeed Sullivan and Demery examined the fit of the CBT solid model to their incremental moduli data and noted the poor agreement.

6.2.4 Application of Time-temperature Superposition to Non-infinitesimal Deformation

Experimental evidence reported for the application of time-temperature superposition to carbon black filled elastomers in non-infinitesimal deformation is given in Table 6.5.
The results of Isono and Ferry, and Martin and Malguarnera (see Table 6.5) indicate that the shift factor \( a_T \) (see §3.2.1) is independent of strain. There exists no a priori reason to assume that such shift factors should be strain independent. Indeed, the non-linear viscoelastic theory of Schapery (see §6.1.2) assumes that shift factors of this type do generally depend also upon strain.

The discussion of §6.1.3 shows that for non-linear deformation time-temperature superposition is not the only means of modelling temperature dependence, and may indeed not be the most satisfactory means of doing so. The results of Table 6.5 however indicate that there exists at least a restricted class of carbon black filled elastomers for which an isothermal non-linear constitutive equation could be extended to include temperature dependence by the use of 'reduced time' (see §§5.9 and 6.1.2).

6.3 CONCLUSIONS

The main conclusions of this chapter can be summarised as follows:-

(1) No strong experimental evidence has been found to preclude the modelling of carbon black filled elastomers in terms of a single integral constitutive equation obeying the modified Boltzmann superposition principle.

(2) Not all carbon black filled elastomers demonstrate separability.

(3) Although lack of separability can be established experimentally, verification of this property by experimental means cannot be readily achieved, especially when relying on stress relaxation data alone.

(4) Examination of the strain dependence of incremental dynamic moduli, in certain cases at least, proves a more critical criterion for separability than consideration of stress relaxation.
(5) Examination of the strain dependence of incremental dynamic moduli provides a test for whether a constitutive equation consisting solely of a viscoelastic term is sufficient to model deformation.

(6) Examination of the frequency dependence of the incremental loss modulus for various static strains affords a criterion for factorisation of time and strain in the viscoelastic term of the constitutive equation, i.e. a test for consistency with the modified Boltzmann superposition principle.

(7) Comparison of the observed strain dependence of incremental dynamic moduli with the predictions of the Schapery theory (given in [6.54]) provides a test for whether a constitutive equation consisting of the sum of a purely elastic and viscoelastic component is sufficient to model deformation.

(8) Determination of relaxation spectrum functions provides further evidence with regard to factorisation of time and strain effects in the viscoelastic term of the constitutive equation, i.e. a test for consistency with the modified Boltzmann superposition principle.

(9) Application of time-temperature superposition by means of the introduction of 'reduced time' into non-linear constitutive equations does not represent the only, nor necessarily the best method of describing temperature dependence in non-linear deformation.

(10) Experimental evidence suggests that for at least a restricted class of carbon black filled elastomers temperature dependence in non-linear deformation may be described by application of time-temperature superposition.
CHAPTER 7

EXPERIMENTAL CHARACTERISATION OF NON-LINEAR DEFORMATION

INTRODUCTION

The linear properties of the experimental materials whose compositions are given in §2.2.6 have been investigated and are reported in Chapter 5. The present chapter describes an investigation of the non-linear properties of these materials and is divided into four sections.

The first section discusses experiments designed to measure incremental dynamic moduli (see §6.1.5). Consideration is given to the various types of experimental apparatus used in reported investigations, and the particular apparatus and procedures used for testing the experimental materials are described in detail. In the second and third sections results obtained from experiments on the unfilled and filled materials respectively are presented, discussed, and modelled in terms of the non-linear theories presented in Chapter 6. The fourth section highlights some of the differences in the behaviours of the filled and unfilled materials, and shows that a single constitutive equation could in principle be used to model the behaviour of vulcanised elastomers containing variable amounts of carbon black.

7.1 EXPERIMENTAL INVESTIGATION OF NON-LINEAR DEFORMATION

From the conclusions presented in §6.3 it can be seen that a useful starting point for investigation of non-linear properties is the measurement of incremental dynamic moduli. As in the case of the methods for dynamic testing described in §4.2, methods used in determining incremental dynamic moduli involve either free or forced vibration. A free vibration method using a modified torsion pendulum was employed by Isono and Ferry (1984) and by Aral and Ferry (1986a, 1986c). Forced vibration methods were used by Meinecke and Maksin (1980) and by Sullivan and Demery (1982).
The apparatus of Meinecke and Maksin exploited a cranking mechanism to apply a sinusoidal displacement to the sample. The crank was of fixed eccentricity, and thus the applied strain relative to the dimensions of the pre-strained sample varied with the value of the pre-strain. Sullivan and Demery made use of a servohydraulic testing machine capable of imposing sinusoidal deformations of variable amplitude. They measured incremental dynamic moduli both in simple tension and in pure shear. However, for pure shear measurements, specialised clamping fixtures and especially moulded samples were required.

With regard to carrying out similar investigations for the experimental materials considered here, it was found that of the types of apparatus mentioned above, the servohydraulic testing machine was the most readily available. In view of the comparative difficulty of clamping samples in pure shear, as opposed to simple extension experiments, the present investigations were confined to the latter mode of deformation. The experiments were performed initially at the laboratories of RAPRA Technology Ltd and subsequently, in order to examine an anomaly in some of the data, a limited number were repeated in the Department of Mechanical Engineering at Plymouth Polytechnic. The basic mode of experimentation was the same in both cases and thus only the apparatus and testing procedures employed at RAPRA will be described in detail.

7.1.1 Experimental Apparatus: The Servohydraulic Testing Machine and Data Logging System

The experimental apparatus used at RAPRA was the +/-250kN servohydraulic testing machine manufactured by ESH Testing Ltd. This is shown schematically in Figure 7.1. The actuator rod is driven by a piston powered by a hydraulic pump. Displacement of the actuator rod is measured by means of a transducer. In extension the maximum velocity attainable on the machine is 2.9m per minute. Sinusoidal oscillations are achieved by means of a dynamic function generator (ESH DFG600). Forces are measured by means of the load cell (see Figure 7.1). Two series U-4000 load cells manufactured by Maywood Instruments Ltd were used. These were calibrated to measure forces
in the ranges 0~250N and 0~2500N respectively. The signals from the load cell and transducer are amplified to give earthed outputs in the range 0~10V.

In order to record stress relaxation data the output from the load amplifier was passed to an 8 bit A/D converter, and the digitised signal logged onto disc (see Figure 7.2). The computer program used for data acquisition was written in machine code†. Data logging is initiated when the stroke voltage level (corresponding to the actuator rod displacement) reaches a certain pre-set value - the trip voltage. The trip voltage thus corresponds to a given displacement of the actuator and, since its velocity is known, the time lag between initiation of the experiment and the logging of data can be estimated. This enables an accurate time-base to be established for the relaxation data, which is important with regard to examining separability and the applicability of the modified Boltzmann superposition principle (see §6.3). Since the data logging program is written in machine code, this is not expected to induce a significant time lag in recording data. Stress relaxation data were simultaneously charted on a pen plotter (see Figure 7.2), which enables continuous visual monitoring of the rate of stress relaxation during the experiment.

Stress relaxation is followed by the imposition of a small sinusoidal displacement. The oscillatory strain amplitude relative to the deformed sample dimensions is of the order of 0.01 or less (see §7.1.3). This constitutes a relatively small perturbation of the signal associated with the imposed static extension and is of the order of 10mv or less. Thus for purposes of data acquisition it is desirable to suppress the component of the signal associated with the extension, in order that the remaining (essentially oscillatory) signal component can be amplified independently. Suppression of the static - or in the case of the load, quasi-static - signal components (see Figure 7.3) was accomplished by means of a system of comparators. A 2-channel comparator box‡ was specially constructed for this purpose.

† This program was kindly written by my joint second supervisor Dr J M Davies.

‡ This was constructed to specification by Technical Services at Plymouth Polytechnic.
The oscillatory signals output from the comparator box were found to be quite noisy. Sullivan, Morman and Pett (1980) encountered similar noise problems - which they attributed to actuator and hydraulic pump vibrations - and used RC Filtering\textsuperscript{†} to overcome this difficulty. Tracing elliptical plots of oscillatory force against displacement (see Appendix 1) using a pen plotter suppresses much of the noise, since the pen plotter does not respond to high frequency signals and thus acts as a crude filter. (It is assumed that plotting in such a manner does not affect the phase lag between oscillatory components of force and displacement.) This method was accordingly used for recording results for oscillations imposed upon a static pre-strain.

7.1.2 Sample Preparation and Mounting

The simple extension samples used in the non-linear experiments were rectangular laminae cut from moulded cylindrical samples. These laminae were of the following approximate dimensions: thickness 0.2cm, width 2cm, length 10cm and 12cm (for the unfilled and filled samples respectively). In order to calculate incremental dynamic moduli using [6.60] and [6.61] it is necessary to obtain a value for the undeformed cross-sectional area of the sample. It is assumed that each of the samples is of uniform cross-section. The density of each of the experimental materials was calculated. The volume of each sample was calculated from its mass, and a mean cross-sectional area determined by dividing the volume by the measured length of the sample. The cross-sectional areas of five filled and five unfilled samples were calculated in this way, and fiducial marks drawn approximately 2cm apart near the centre of each sample.

Initially Gavin grips (see Figure 7.4) were used to clamp the samples. It was found that the sample extension calculated from the grip separation was in poor agreement with the extension calculated from the fiducial marks, and necking of the sample was also apparent.

\textsuperscript{†} RC Filtering: filtering accomplished by means of a system of resistors and capacitors.
Cross-hatched eccentric roller grips (see Figure 7.4) were substituted, and these largely eliminated necking, although lack of agreement between extensions calculated from fiducial marks and grip separation persisted.

As may be appreciated from Figure 7.4, it is difficult to determine the exact sample length between the grips. The point at which the sample is gripped also changes slightly as the sample deforms and the grips tighten. The lack of agreement between fiducial marks and grip separation, however, exceeded the error attributable in such sources. It is therefore assumed that slippage of the sample occurred in the grips during the imposition of the static pre-strain. Sample extensions were thus calculated from fiducial marks.

The samples were subjected to a programme of strain conditioning or scraggling (see §§2.2.4 and 4.4). For the unfilled samples this consisted of extending them five times to the desired extension ratio immediately before conducting the experiment. The preconditioning applied to the filled samples was subsequently modified, and consisted of straining the samples five times to an extension ratio $\lambda = 2$, and then leaving them to recover for at least 24 hours before the initiation of the experiment. The aim of preconditioning is to ensure experimental repeatability.

### 7.1.3 Experimental Procedure

The strain history (in simple tension) imposed upon the samples is illustrated schematically in Figure 7.3. All non-linear experiments were carried out at room temperature, which for our present purposes will be taken as 23°C. The samples were mounted so that the undeformed length between the grips was 8cm - subject to the limitations on accuracy due to the construction of the grips, see §7.1.2. The initial part of the experiment consists of imposing a static pre-strain.

Since sample extension cannot be predicted from grip separation (see §7.1.2) a dummy sample was used to enable a given pre-strain to be imposed on the experimental samples. The dummy sample was mounted in the grips, and the grip separation increased until the fiducial marks indicated that the desired extension had been achieved. The
grip separation was then noted and subsequently applied to the experimental sample. Various static pre-strains were imposed, giving values of extension ratio of up to about $\lambda = 2$. When a particular sample was used in more than one experiment, care was taken to ensure that the imposed extension ratios were substantially different, that the smaller strain experiment was conducted first, and that the sample was left overnight to recover between experiments. The experimental sample is extended to the required extension ratio using the maximum velocity attainable on the machine (see §7.1.1). the load voltage registering the decay of the force is simultaneously recorded on magnetic disc and on a chart recorder (see §7.1.1). Relaxation data were recorded in this way for approximately one hour - except for relatively small pre-strains, where a quasi-equilibrium state appeared to have been reached after approximately 30 minutes.

The second stage of the experiment consists of superposing a small sinusoidal displacement upon the pre-strained sample in quasi-equilibrium (see Figure 7.3). The strain amplitude relative to the extended length of the sample between the grips was 0.01 for the unfilled material. Plots for the determination of incremental dynamic moduli (see Appendix I) obtained for the filled material at higher extensions, using a strain amplitude of 0.01, were very obviously non-elliptical. This indicates that the applied strain amplitude exceeded that for which incremental dynamic moduli could be determined (see §6.1.5). A displacement amplitude of approximately 0.3mm - corresponding to the smallest setting available on the machine - was then applied, and found to produce elliptical plots. For the case $\lambda = 2$, a displacement amplitude of 0.3mm corresponds to a strain (relative to the extended sample length) of approximately 0.002. A value of ~0.3mm for the displacement amplitude was used for all measurements on the filled material at extension ratios of 1.73 and above, otherwise the strain amplitude was 0.01.

For each experiment elliptical plots (as described in Appendix I) were obtained at 9 frequencies in the range 0.01~1Hz. This is the most extensive frequency range available on the apparatus. Above

† quasi-equilibrium indicates that the observed rate of stress relaxation is small compared with that encountered immediately following deformation.
kHz the plots obtained are seen to be distinctly non-elliptical. This occurs because the imposed deformation is non-sinusoidal, and is the result of inertial effects due principally to the inertia of the actuator arm. (Effects due to the mass of the sample are considered in §7.1.4). The frequency was increased from 0.01 kHz and at each frequency at least 5-10 cycles were allowed to pass before recording the data. This mitigates against the effect of transients. The observed ellipticity of the plots obtained was taken to validate the assumption that the applied strain amplitude was sufficiently small to justify the measurement of incremental dynamic moduli (see Appendix I and §6.1.5). We will now consider the analysis of the data obtained.

7.1.4 Data Analysis

The deformation of the sample is governed by the equation of continuity [2.20], the equation of motion [2.21], and a constitutive equation which represents a non-linear extension of [3.15]. The experimental materials are assumed to be incompressible, and it is assumed that the lateral deformation is such that [2.20] is satisfied. We first consider the effect of the mass of the sample, and then how incremental dynamic moduli and relaxation spectrum function values are obtained from the recorded data.

(i) Effect of the Mass of the Sample

Let the x-axis coincide with that of the sample. The reference configuration \( X \) is that of the extended sample before the imposition of the oscillations. The positions of the grips are given by \( X = 0 \) and \( X = \ell \). For a particle at \( X \) in the reference configuration, the displacement \( u(X,t) \) in the x-direction is assumed to be the real part of the complex displacement \( u^*(X,t) \) given by

\[
u^*(X,t) = f(X) \epsilon_0 e^{i\omega t}, \tag{7.01}\]

where \( \epsilon_0 \) is the strain amplitude relative to \( \ell \), \( \omega \) is the frequency, and \( f \) is a complex valued function satisfying the boundary conditions.
\[ f(0) = 0 \]
\[ f(\ell) = \ell . \]

The corresponding complex velocity \( V^*(X,t) \) for the particle is given by

\[ V^*(X,t) = \frac{\partial u^*(X,t)}{\partial t} \]
\[ = if(X)\omega \epsilon_0 e^{i\omega t} . \]

It is assumed that the principal stress component in the \( x \)-direction \( \sigma \) can be decomposed into a steady and oscillatory component such that

\[ \sigma(x,t) = \sigma_e + \sigma'(x,t) , \]

where \( \sigma_e \) is the equilibrium stress defined in [6.61].

In the absence of body forces, and dropping the distinction between current and reference coordinates (i.e. replacing \( X \) by \( x \)), from [2.21] the equation of motion in the \( x \)-direction can be expressed in the form

\[ \frac{\partial \sigma(x,t)}{\partial x} - \frac{\partial \sigma'(x,t)}{\partial x} = \rho \frac{\partial V(x,t)}{\partial t} + O(\epsilon_0^2) \]

and hence

\[ \frac{\partial}{\partial x} [\sigma - \sigma_e] = \rho \frac{\partial V}{\partial t} + O(\epsilon_0^2) . \]

The constitutive equation [3.15] can be extended for the case of small sinusoidal oscillations superposed on a tensile pre-strain with extension ratio \( \lambda \), and written in the form

\[ \sigma - \sigma_e = \text{Re}\{E^*(\omega,\lambda)\epsilon_{xX}^*\} . \]

Now from [7.01]
\[ \epsilon^{* \omega} = f'(x) \epsilon_0 e^{i \omega t} \quad [7.07] \]

and substituting into [7.06] we obtain

\[ \sigma - \sigma_e = \Re \{ E^*(\omega, \lambda) f'(x) \epsilon_0 e^{i \omega t} \} . \quad [7.08] \]

From [7.05], [7.03] and [7.08] we obtain

\[ E^*(\omega, \lambda) f''(x) \epsilon_0 e^{i \omega t} = - \rho \omega^2 f(x) \epsilon_0 e^{i \omega t} \]

and hence

\[ f''(x) + \frac{\rho \omega^2}{E^*(\omega, \lambda)} f(x) = 0 . \quad [7.09] \]

Making the substitution

\[ \alpha^2 = \frac{\rho \omega^2}{E^*(\omega, \lambda)} . \quad [7.10] \]

From [7.09]

\[ f'' + \alpha^2 f = 0 . \quad [7.11] \]

Equation [7.11] has solutions of the form

\[ f = A \sin \alpha x + B \cos \alpha x , \quad [7.12] \]

where A and B are complex-valued constants.

Applying the boundary conditions [7.02] yields

\[ f = \frac{\theta}{\sin \alpha x} \sin \alpha x . \quad [7.13] \]

Substituting [7.13] into [7.08] we obtain

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Equation [7.14] shows that the quantity \( \sigma - \sigma_e \) depends upon the value of the coordinate \( x \). The value of \( \sigma - \sigma_e \) measured by the load cell at \( X = 2 \) is thus given by

\[
\sigma - \sigma_e = \text{Re} \left\{ E^*(\omega, \lambda) \frac{\alpha \ell}{\sin \alpha \ell} \cos \alpha \ell \cdot \epsilon_0 e^{i \omega t} \right\}. \quad [7.15]
\]

Since \( E^*(\omega, \lambda) \) is typically of the order of at least \( 10^7 \text{dyne/cm}^2 \) (see §§7.2.3, 7.3.3), while \( \rho = 1 \text{g/cm}^3 \) (see §2.2.6) and \( 0.01 \leq \omega \leq 1 \text{Hz} \), from [7.10] \( \alpha < 1 \times 10^{-7} \). Thus we may write

\[
\frac{\alpha \ell}{\sin \alpha \ell} \cos \alpha \ell = \frac{\alpha \ell \left[ 1 - \frac{(\alpha \ell)^2}{2} + \frac{(\alpha \ell)^4}{4!} \ldots \right]}{\alpha \ell \left[ \frac{(\alpha \ell)^3}{3!} + \frac{(\alpha \ell)^5}{5!} \ldots \right]}
\]

\[
= 1 - \frac{(\alpha \ell)^2}{3} + O(\alpha \ell)^4 + O(\epsilon_0^2). \quad [7.16]
\]

Substituting [7.16] into [7.15] we obtain

\[
\sigma - \sigma_e = \text{Re} \left\{ E^*(\omega, \lambda) \left[ 1 - \frac{(\alpha \ell)^2}{3} \right] \epsilon_0 e^{i \omega t} \right\} + O(\alpha \ell)^4 + O(\epsilon_0^2). \]

And from [7.10]

\[
\sigma - \sigma_e = \text{Re} \left\{ E^*(\omega, \lambda) \left[ 1 - \frac{\rho \omega^2 \ell^2}{E^*(\omega, \lambda)} \right] \epsilon_0 e^{i \omega t} \right\} + O(\alpha \ell)^4 + O(\epsilon_0^2). \]

\[
- \text{Re} \left\{ E^*(\omega, \lambda) \epsilon_0 e^{i \omega t} \right\} - \text{Re} \left\{ \rho \omega^2 \ell^2 \epsilon_0 e^{i \omega t} \right\} + \ldots \quad [7.17]
\]

From [7.17] it can be seen that a first order approximation in \( \epsilon_0 \) for the effect of the mass of the sample is given by the term \( \rho \omega^2 \ell^2 \epsilon_0 e^{i \omega t} \). The dependence of this term on \( \omega^2 \) implies that effects associated with the mass of the sample may be ignored at sufficiently low frequencies. It is concluded that in the present experiments such effects are negligible.
(II) **Incremental Dynamic Moduli Values**

Incremental dynamic moduli values were calculated from the formulae given in [6.60] and [6.61], viz

\[
E'(\omega, \lambda) = \frac{\lambda \delta F}{A_0 \varepsilon_0} \cos \varepsilon + \sigma_e
\]

\[
E''(\omega, \lambda) = \frac{\lambda \delta F}{A_0 \varepsilon_0} \sin \varepsilon
\]

\[
\sigma_e = \frac{\lambda F_e}{A_0}
\]

Values for the quasi-equilibrium force \( F_e \) were obtained by direct measurement of the plots of stress relaxation. Since the extension ratio and undeformed cross-sectional area of the sample are known (see §7.1.2), the quasi-equilibrium stress \( \sigma_e \) can be calculated from [6.61].

Direct measurement of elliptical plots such as Figure A1.1 was used to determine the phase lag \( \varepsilon \). If the measured lengths of the axes of the ellipse are \( a \) and \( b \), and the measured lengths of the sides of the enclosing rectangle \( x \) and \( y \), then from [A1.9] we have

\[
sinc = \frac{ab}{xy}
\]

[7.18]

The amplitude of the oscillatory force \( \delta F \) was also calculated from direct measurement of the elliptical plots. All quantities appearing on the right hand side of [6.60] having thus been determined, values for the incremental dynamic moduli were calculated.

(iii) **Relaxation Spectrum Function Values**

The relaxation spectrum functions \( F_1(\tau, \lambda) \), \( F_2(\tau, \lambda) \) and \( F_{sr}(\tau, \lambda) \) are defined in Table 6.2. Evaluation of these formulae requires values for gradients of log-log plots of \( H(\tau) \) against \( \tau \). Inspection of the predicted forms for the relaxation spectrum functions given in Table 6.3 shows that for the constitutive equations [6.09], [6.11],
\[ \frac{\partial \ln F_1}{\partial \ln r} = \frac{\partial \ln F_2}{\partial \ln r} - \frac{\partial \ln F_{sr}}{\partial \ln r} - \frac{\partial \ln H}{\partial \ln r} = -m. \]  \[7.19\]

An iterative procedure requiring successive evaluations of \( m \) [Ferry (1970)] is used to determine the relaxation spectrum \( H(r) \) from the formulae of Table 6.2, and thus in view of [7.19] the same procedure can also be used to evaluate the relaxation spectrum functions by using \( m = \frac{\partial \ln F_1}{\partial \ln r} \) etc. In order to minimise the number of iterations required, the initial estimate for \( m \) must be as accurate as possible. (The standard method uses \( A(m) - B(m) - M(m) - 1 \) as starting values - see Ferry (1970)).

The Williams and Ferry formulae chosen by Sullivan (1987) to define the relaxation spectrum functions are approximate first order formulae\(^\dagger\) which feature amongst a number of approximate first and higher order formulae used to evaluate the relaxation spectrum \( H(r) \). In particular Ferry (1970) quotes two alternative second order formulae for obtaining the relaxation spectrum from relaxation modulus data, viz.

\[ H(r) - \left[ - \frac{dG(t)}{d\ln t} + \frac{d^2G(t)}{d(\ln t)^2} \right] \bigg|_{t=2r} \]  \[7.20\]

and

\[ H(r) - \left[ - \frac{dG(t)}{d\ln t} + \frac{1}{3} \frac{d^2G(t)}{d(\ln t)^2} \right] \bigg|_{t=r/f^2} \]  \[7.21\]

Equations [7.20] and [7.21] are of interest because they are second order approximations, which taken together determine \( H(r) \) over a wider range of relaxation times than the first order Williams and Ferry equation of Table 6.2. By applying [7.20] and [7.21] together we may thus hope to obtain a reasonably accurate initial estimate of \( m \). This is the method used in the program which calculates values

\( \dagger \) 'First order' in the sense used by Ferry (1970), i.e. containing terms up to the first derivative of the modulus.
With regard to calculating $H(\tau)$ from storage modulus data, the second order formula quoted by Ferry (1970) does not provide values over the same range of relaxation times as the formula in Table 6.2. Thus the program which calculates values of $F_1(\tau,\lambda)$ uses the initial assumption $A(m) = 1$. The program which calculates values of $F_2(\tau,\lambda)$ similarly uses the initial assumption $B(m) = 1$. At each iteration the formulae appearing in Table 6.2 must be evaluated, and we now consider how this is achieved.

In order to evaluate the gradients appearing in the formulae [7.20], [7.21], or in Table 6.2 it is necessary to interpolate the experimental data with some empirical function. Thus log-log plots were fitted with cubic splines, which give a least squares fit to the experimental data, and their first and second derivatives were evaluated. Values of $F_1(\tau,\lambda)$ and $F_2(\tau,\lambda)$ were thus obtained by applying the above procedures to incremental dynamic modulus data (see §7.1.4), while values of $F_{sr}(\tau,\lambda)$ were similarly obtained using stress relaxation data (see §7.1.3).

Since a finite time is required to impose a given extension, stress relaxation data corresponding to times less than ten times that required to impose the deformation are disregarded. This procedure aims to avoid the effects of 'ramp transients'. The velocity of the actuator arm is known (see §7.1.3), and thus the time required to achieve a given displacement can be calculated. For an extension ratio of $\lambda = 2$ the time required to impose the deformation is of the order of 2 sec, and thus stress relaxation data corresponding to times less than 20 sec are disregarded.

7.2 RESULTS OF NON-LINEAR EXPERIMENTS ON THE UNFILLED MATERIAL

7.2.1 Quasi-equilibrium Stress Results

The quasi-equilibrium stress $\sigma_e$ defined in [6.61] is calculated from stress relaxation data as described in §7.1.4. Figure 7.5 shows $\sigma_e$ plotted against extension ratio $\lambda$.

From equations [6.30], [6.22] and [6.23] - which give the uniaxial extension forms of the constitutive equations [6.09], [6.11] and [6.19] respectively - it can be seen that each predicts the form
of the equilibrium stress to be that given by [6.33], where \( E_e \) and \( n \) may be treated as fitting parameters. Figure 7.5 also shows the function given in [6.33] plotted for \( E_e = 2.1 \times 10^7 \text{dyne/cm}^2 \) and \( n = 1.44 \). These values are derived in §7.2.3.

7.2.2 Phase Angle Results

The phase angle \( \phi \) between the oscillatory components of force and displacement is introduced in §7.2.3. This quantity was determined from elliptical plots as described in §7.1.4. Figure 7.6 shows \( \sin \phi \) plotted against frequency for various extension ratios. The data above 0.1 Hz exhibit greater scatter than those at lower frequencies, but for the lower frequencies at least, \( \sin \phi \) is largely independent of \( \lambda \).

7.2.3 Incremental Dynamic Moduli Results

(1) Results & Data Analysis

Incremental dynamic moduli values were calculated as described in §7.1.4. Log-log plots of \( E''(\omega, \lambda) \) and \( E'(\omega, \lambda) \) against frequency for various extension ratios are shown in Figures 7.7 and 7.8 respectively. \( E'(\omega, \lambda) \) values demonstrate a much greater \( \lambda \)-dependence than do the corresponding \( E''(\omega, \lambda) \) values. Indeed, disregarding the anomalously low \( E''(\omega, \lambda) \) values corresponding to \( \lambda = 1.33 \), incremental loss moduli demonstrate only a weak dependence upon \( \lambda \) compared with that of the \( E'(\omega, \lambda) \) results (see Figure 7.9). The \( \lambda \)-dependence of the \( E'(\omega, \lambda) \) data was found to be due almost entirely to the \( \lambda \)-dependence of the \( \sigma_e \) term (see Figure 7.5) appearing in [6.60]. This demonstrates that the choice of formula for the calculation of incremental dynamic moduli from experimental data is crucial, since the data analysis employed by Meinecke and Maksin (1980), for example, would have resulted in \( E'(\omega, \lambda) \) being largely independent of \( \lambda \) (see §6.2.3). The observed incremental dynamic modulus behaviour is in qualitative agreement with that reported by Sullivan (1987) for an unfilled elastomer.
Comparison with Dynamic Moduli Results of Linear Experiments

Figure 7.9 shows the dependencies of the incremental dynamic moduli on extension ratio at 1Hz. $E'(\omega, \lambda)$ is observed to increase with increasing $\lambda$, while $E''(\omega, \lambda)$ data exhibit no clear $\lambda$-dependence. Incremental dynamic moduli are related to dynamic moduli via the relations

\[
\lim_{\lambda \to 1} E'(\omega, \lambda) = E'(\omega) \quad [7.22]
\]

\[
\lim_{\lambda \to 1} E''(\omega, \lambda) = E''(\omega) \quad [7.23]
\]

and thus from Figure 7.9 we have

\[
E'(\omega) = E'(\omega, \lambda) \bigg|_{\lambda=1.08}
\]

\[
E''(\omega) = E''(\omega, \lambda) \bigg|_{\lambda=1.08}
\]

In view of [3.17] we may express [7.22] in terms of the dynamic shear moduli, as follows

\[
\lim_{\lambda \to 1} E'(\omega, \lambda) = 3G'(\omega) \quad [7.24]
\]

\[
\lim_{\lambda \to 1} E''(\omega, \lambda) = 3G''(\omega)
\]

Thus [7.24] enables values for the dynamic shear moduli to be estimated from tensile incremental dynamic moduli. Table 7.1 compares estimates of dynamic shear moduli with similar data obtained on the rheogoniometer at room temperature and a frequency of 1Hz.

Table 7.1 shows that modulus values obtained with the rheogoniometer are higher than those taken with the servohydraulic machine. This disparity is greater than that attributable to sample to sample variation, and is likely to be connected with the preconditioning of the samples. The samples mounted in the rheogoniometer are subjected to strain amplitudes of less than 0.003
(see §5.1). Samples mounted in the servohydraulic testing machine
are however subjected to much larger strains during preconditioning
(see §7.1.2).

In order to test this hypothesis the sample used in the linear
experiments (see §4.4) was subjected to 100% extension at a rate of
0.5m/min using a servohydraulic test machine and then retested on the
rheogoniometer after relaxing for approximately 30min. This
procedure is not entirely satisfactory since large portions of the
sample are held in the grips of the servohydraulic machine, which
leads to the imposed strain being non-uniform along the length of the
sample. The extension was measured by fiducial marks near the centre
of the sample. The preconditioning of the samples in the non-linear
experiments consists of five successive cycles imposed at a strain
rate of 2.9m/min, and is thus rather different from that described
above. For the rheogoniometer samples, preconditioning is in a
direction normal to that of the strain imposed during testing, while
for the tensile samples these directions are the same. Despite these
limitations the results obtained on the rheogoniometer with a
previously extended sample (see Table 7.1) support the hypothesis
that the disparity in the results of Table 7.1 is connected with the
preconditioning of the samples. These results demonstrate that
sample preconditioning is important even for the unfilled material,
and affects the agreement of linear and non-linear data.

(III) Choice of Constitutive Equation to Model Data

In §6.1.5 the incremental dynamic moduli predictions of the
constitutive equations [6.09], [6.11], [6.19] and [6.25] were
presented. For ease of reference these are displayed in Table 6.1.
It has been shown that the predictions of [6.09], [6.11] and [6.19]
correspond to special cases of equation [6.54], which gives the forms
of the incremental dynamic moduli associated with the Schapery
constitutive equation [6.25]. The validity of [6.54] may be tested
by examining the dependencies of $E''(\omega, \lambda)$ and $E'(\omega, \lambda) - \frac{\lambda dE}{d\lambda}$ upon the
extension ratio \( \lambda \). These quantities are plotted in Figure 7.10, and
although subject to much scatter, demonstrate no significant
difference in their \( \lambda \)-dependencies. This indicates that the
incremental dynamic moduli may indeed be modelled by at least one of
Table 6.1 shows that the Chang, Bloch and Tschoegl solid model \[6.09\] predicts the $\lambda$-dependencies of the incremental loss and storage moduli to be identical. The data of Figure 7.9 thus indicate that \[6.09\] is unsuitable for representing the present data. Both \[6.11\] and \[6.19\] predict distinct $\lambda$-dependencies for $E'(\omega, \lambda)$ and $E''(\omega, \lambda)$.

The forms for the incremental dynamic moduli predicted by \[6.19\] are given in Table 6.1. The function $\frac{3}{2} \left[ \lambda^m + \frac{\lambda - m/2}{2} \right] E''(\omega)$ was fitted to $E''(\omega, \lambda)$ data at 0.1Hz, treating $E''(\omega)|_{\omega=0.1Hz}$ and $m$ as fitting parameters. The resulting values were $E''(\omega)|_{\omega=0.1Hz} = 4.3 \times 10^6$ dyne/cm$^2$ and $m = 0.28$. Utilising the values $E_e = 2.44 \times 10^7$ dyne/cm$^2$ and $n = 1.00$ (which were obtained from fitting the functional form given in \[6.33\]) to the data of Figure 7.5 the 'elastic' component $\frac{3}{2} \left[ \lambda^n + \frac{\lambda - n/2}{2} \right] E_e$ of the incremental storage modulus was calculated and subtracted from the $E'(\omega, \lambda)$ data. The resulting values for the 'viscoelastic' component were fitted by the function $\frac{3}{2} \left[ \lambda^m + \frac{\lambda - m/2}{2} \right] (E'(\omega) - E_e)$, while constraining the value of $m$ to that obtained from the $E''(\omega, \lambda)$ data. This yields a value for $(E'(\omega) - E_e)|_{\omega=0.1Hz}$. Utilising the values of $m$ and $(E'(\omega) - E_e)|_{\omega=0.1Hz}$ thus obtained, the viscoelastic component was subtracted from $E'(\omega, \lambda)$ to give a further estimate for the elastic component. Fitting the function $\frac{3}{2} \left[ \lambda^n + \frac{\lambda - n/2}{2} \right] E_e$ then yields further values for $n$ and $E_e$, and the process may be repeated iteratively.

Applying this technique to $E'(\omega, \lambda)$ data at 0.1Hz yields $E_e = 2.10 \times 10^7$ dyne/cm$^2$, $(E'(\omega) - E_e)|_{\omega=0.1Hz} = 1.03 \times 10^7$ dyne/cm$^2$, and $n = 1.44$. The resulting fit to quasi-equilibrium stress data is quite satisfactory, and is shown in Figure 7.5. The fit provided to $E'(\omega, \lambda)$ and $E''(\omega, \lambda)$ data at 0.1Hz is shown in Figure 7.11.

The forms for the incremental dynamic moduli predicted by Sullivan's constitutive equation \[6.11\] are given in Table 6.1. Utilising the values of $n$ and $E_e$ determined above and setting $(E'(\omega) - E_e)|_{\omega=0.1Hz} = 1.10 \times 10^7$ dyne/cm$^2$ and $E''(\omega)|_{\omega=0.1Hz} = 4.6 \times 10^6$ dyne/cm$^2$ the resulting fit to incremental dynamic moduli data at 0.1Hz is virtually identical to that obtained from the constitutive equation \[6.19\] in Figure 7.11.

It is concluded that incremental dynamic moduli data such as those of Figure 7.11 show the Chang, Bloch and Tschoegl solid model to be unsuitable for representing the present data. From the
evidence of Figure 7.10 however, it appears that a constitutive equation of the Schapery type is capable of describing the incremental dynamic moduli and quasi-equilibrium stress data. Both equation [6.19] and the Sullivan constitutive equation afford a satisfactory description of quasi-equilibrium stress and incremental dynamic moduli, as shown by Figures 7.5 and 7.11 respectively.

7.2.4 Relaxation Spectrum Function Results

Relaxation spectrum function values were calculated as described in §7.1.4. The relaxation spectrum function values obtained from incremental storage and loss moduli are shown in Figures 7.12 and 7.13 respectively. The \( F_1(\tau, \lambda) \) data of Figure 7.12 are very much affected by fitting artefacts† and indeed it is difficult to draw any firm conclusions on the basis of these data. The \( F_2(\tau, \lambda) \) data of Figure 7.13 however appear to be less affected by artefacts, and apart from the anomalously low values corresponding to \( \lambda = 1.33 \), exhibit a weak \( \lambda \)-dependence. These features of the \( F_2(\tau, \lambda) \) plot thus reflect the behaviour of the \( E''(\omega, \lambda) \) data in Figure 7.7. In the light of the \( F_2(\tau, \lambda) \) data we might conclude that \( F_1(\tau, \lambda) \) data shows broadly similar behaviour. The constitutive equations of Table 6.3 predict that \( F_1(\tau, \lambda) \) and \( F_2(\tau, \lambda) \) should be the same. The Sullivan constitutive equation [6.11] predicts that \( F_1(\tau, \lambda) \) and \( F_2(\tau, \lambda) \) should be independent of \( \lambda \) (see Table 6.3). The constitutive equation [6.19] however predicts that the \( \lambda \)-dependence of \( F_1(\tau, \lambda) \) and \( F_2(\tau, \lambda) \) is identical to that of \( E''(\omega, \lambda) \) as given in [6.43]. From Figure 7.11 we observe that this \( \lambda \)-dependence is quite weak, and thus the constitutive equations [6.11] and [6.19] cannot be distinguished on the basis of the \( \lambda \)-dependence of the present \( F_1(\tau, \lambda) \) and \( F_2(\tau, \lambda) \) data.

The relaxation spectrum function values obtained from stress relaxation data are shown in Figure 7.14. The \( F_{SR}(\tau, \lambda) \) data of figure 7.14 are rather incomplete. Technical difficulties

† Near the ends of the range the gradients required to obtain relaxation spectrum function values cannot be accurately calculated. The resulting aberrations are termed fitting artefacts.
associated with data logging (see §7.1.3) resulted in incomplete records of stress relaxation data at certain extension ratios, and in certain cases the remaining data could not be distinguished from a straight line when plotted against log t. From the formula given in Table 6.2 it may be seen that such straight line plots yield constant values for $F_{SR}(\tau, \lambda)$. Relaxation spectrum functions generated from more complete data however indicate that $F_{SR}(\tau, \lambda)$ is not a constant. Values generated from straight line plots cannot thus be regarded as valid, and were accordingly discarded. The remaining data, excluding those corresponding to $\lambda = 1.15$, are approximately parallel. This parallelism is predicted by the constitutive equations of Table 6.3 (but only in the case $\alpha_{\epsilon} = 1$ for equation [6.25]), and supports the assumption that the time and strain dependencies in the viscoelastic terms of these constitutive equations can be factored.

In view of [7.24] and the definitions of Table 6.2, we observe that for the relaxation spectrum functions $F_1(\tau, \lambda)$ and $F_2(\tau, \lambda)$ we may write

$$\lim_{\lambda \to 1} F_1(\tau, \lambda) = 3H(\tau)$$
$$\lim_{\lambda \to 1} F_2(\tau, \lambda) = 3H(\tau)$$

Since the $F_1(\tau, \lambda)$ and $F_2(\tau, \lambda)$ data of Figures 7.12 and 7.13 show little coherent dependence upon $\lambda$, they can be used to estimate values for the relaxation spectrum (see later).

The constitutive equations [6.11] and [6.19] predict the same form for the $\lambda$-dependence of the relaxation spectrum function $F_{SR}(\tau, \lambda)$ (see Table 6.3). In order to test this prediction however, we require an estimate of the value of the relaxation spectrum $H(\tau)$. By analogy with the relations [7.25], for $F_{SR}(\tau, \lambda)$ we have

$$\lim_{\lambda \to 1} F_{SR}(\tau, \lambda) = 3\epsilon H(\tau),$$

where $\epsilon$ is the axial component of the infinitesimal strain tensor. Thus the $F_{SR}(\tau, \lambda)$ data of Figure [7.14] cannot be used to estimate $H(\tau)$ directly, since $\epsilon$ is not defined for the large extensions corresponding to $\lambda > 1.15$. We proceed to evaluate $H(\tau)$ by exploiting
all the available relaxation spectrum function data. From Figure 7.14 we observe that the plot of \( \log F_{sr} \) against \( \log r \) is approximately linear in the range \( 1 < \log r < 3 \), and thus in view of [7.19]

\[
\frac{d \log H}{d \log r} \approx -0.15, \quad 1 < \log r < 3. \quad [7.27]
\]

From Figures 7.12 and 7.13

\[
\log F_1 \bigg|_{\log r=0.9} \approx \log F_2 \bigg|_{\log r=0.9} = 7.3
\]

whence from [7.25]

\[
\log H(\tau) \bigg|_{\log r=0.9} = 6.8.
\]

Applying [7.27], we write

\[
\log H(\tau) \bigg|_{\log r=2.1} \approx 6.8 - 0.25 \times (2.1 - 0.9)
\]

\[
\text{i.e. } \log H(\tau) \bigg|_{\log r=2.1} = 6.5
\]

and hence

\[
H(\tau) \bigg|_{\log r=2.1} \approx 3.2 \times 10^6 \text{dyne/cm}^2. \quad [7.28]
\]

The \( F_{sr}(\tau, \lambda) \) prediction of equations [6.11] and [6.19] given in Table 6.3 is plotted in Figure 7.15 for \( \log r = 2.1 \), utilising the value of \( H(\tau) \big|_{\log r=2.1} \) given in [7.28] and the value of \( m \) obtained in §7.2.3. Although these data are insufficient to reach firm conclusions, it appears that the \( F_{sr}(\tau, \lambda) \) values corresponding to \( \lambda = 1.83 \) are subject to an unidentified source of error. This could possibly be accounted for by slippage in the grips during relaxation.

Table 7.2 compares estimates of \( H(\tau) \) calculated from \( F_1(\tau, \lambda) \) and \( F_2(\tau, \lambda) \) with values of \( H(\tau) \) obtained from dynamic modulus data reduced to 2.5°C (see §5.5) and shifted according to the WLF equation.
Since these data do not refer to exactly the same relaxation time $\tau$, values obtained from the Huet model [5.16] using the approximation [5.13] are also presented in order to facilitate comparison. Such model predictions do not agree well with the experimental values. This lack of agreement can be attributed to the fairly crude approximation [5.13]. The model predictions are thus only included as a rough guide to the likely change in the value of $\log H(\tau)$ between the given values of $\log \tau$.

As for the dynamic moduli values compared in Table 7.1, Table 7.2 shows that estimates for the value of the relaxation spectrum obtained from non-linear data are lower than those obtained from linear data. Although Table 7.1 shows better agreement between loss modulus than between storage modulus data, it is interesting to note that there is little difference between the relaxation modulus values obtained from either of these sets of data. This further supports the conclusion that the preconditioning of samples in the non-linear experiments produces a change in the properties measured at infinitesimal deformation (see §7.2.3). This phenomenon is known as stress softening, and has been observed in other unfilled vulcanised elastomers, such as sulphur cross linked natural rubber [McKenna and Zapas (1981)].

7.2.5 Conclusions

(1) The phase angle between oscillatory components of force and displacement is found to be largely independent of extension ratio, at least for frequencies between 0.01 and 0.1Hz.

(2) Lack of agreement is noted between dynamic moduli values and relaxation spectrum values estimated from experimental data at infinitesimal and non-infinitesimal deformation. This observation is regarded as evidence of stress softening.

(3) The weak extension ratio dependence of incremental loss modulus and of relaxation spectrum function data calculated from incremental dynamic moduli, together with the approximate parallelism of relaxation spectrum function values calculated from stress relaxation data indicate that material behaviour is consistent with the modified Boltzmann superposition principle.
(see §§6.1.1 and 6.3).

(5) The observed dependencies of quasi-equilibrium stress and incremental dynamic moduli upon extension ratio indicate that these quantities can be modelled in terms of at least one of the constitutive equations presented in Chapter 6.

(6) The difference in dependencies upon extension ratio noted for incremental storage and loss moduli indicates that these cannot be represented by the Chang, Bloch and Tschoegl solid model.

(7) The Sullivan constitutive equation [6.11] and equation [6.19] are both found to provide a satisfactory description of quasi-equilibrium stress, incremental dynamic moduli, and relaxation spectrum function data.

7.3 RESULTS OF NON-LINEAR EXPERIMENTS ON THE FILLED MATERIAL

7.3.1 Quasi-equilibrium Stress Results

The quasi-equilibrium stress $\sigma_e$, defined in [6.61], is calculated from stress relaxation data as described in §7.1.4. Figure 7.16 shows $\sigma_e$ plotted against extension ratio $\lambda$. This figure contains data subsequently obtained at Plymouth Polytechnic in addition to those originally obtained at RAPRA. Except for $\lambda = 1.08$ good agreement is observed between both sets of results.

A slight upturn is observed in the data for higher values of $\lambda$. This would be expected if insufficient time had been allowed for a quasi-equilibrium state to be achieved (see §7.1.3). Such an upturn is however also observed in the data of Sullivan and Demery (1982) and Meinecke and Maksin (1980) and is shown by the latter to be present also in data for an unfilled elastomer at sufficiently large $\lambda$. It is thus concluded that the observed upturn represents a real trend in the data.

Figure 7.16 also shows the function given in [6.33] (see §7.2.1) plotted for $E_e = 5.10 \times 10^7$dyne/cm$^2$ and $n = 2.22$, these values being obtained from a least squares fit to the quasi-equilibrium stress data.
7.3.2 Phase Angle Results

The phase angle \( \phi \) between oscillatory components of force and displacement is introduced in §6.2.3, and was determined from elliptical plots as described in §7.1.4. Figure 7.17 shows sinc plotted against frequency for various extension ratios \( \lambda \). It can be seen that sinc remains largely independent of \( \lambda \) for extension ratios up to \( \lambda = 1.45 \), but depends on \( \lambda \) at extension ratios of 1.61 and above. This behaviour differs from that of the unfilled material described in §7.2.2.

7.3.3 Incremental Dynamic Moduli Results

(1) Results & Interpretation

Incremental dynamic moduli values were calculated as described in §7.1.4. log-log plots of \( E''(\omega,\lambda) \) and \( E'(\omega,\lambda) \) against frequency for various extension ratios \( \lambda \) are shown in Figures 7.18 and 7.19 respectively. Both incremental dynamic moduli exhibit a clear dependence upon \( \lambda \). This is in qualitative agreement with data reported by Sullivan and Demery (1982) and Meinecke and Maksin (1980). It is however apparent that the data fall into two distinct bands corresponding to \( \lambda < 1.73 \) and \( \lambda > 1.73 \). The data at \( \lambda > 1.73 \) were obtained with a 2500N load cell, whereas all other data collected at RAPRA were obtained using a 250N load cell.

In order to investigate the apparent disparity in the results obtained at RAPRA for \( \lambda < 1.73 \) and \( \lambda > 1.73 \) additional data were subsequently obtained at Plymouth Polytechnic. These additional data were collected at a frequency of 0.3Hz using an oscillatory strain amplitude of approximately 0.003 relative to the extended length of the sample\(^\dagger\). Figure 7.20 shows incremental dynamic moduli data from Plymouth and RAPRA plotted against \( \lambda \) at a frequency of 0.3Hz. The additional Plymouth data appear to confirm that the RAPRA data do indeed lie in two distinct bands, and on the basis of incremental

\[^\dagger\] The strain amplitude of 0.003 was chosen because this approximates to the smallest strain amplitude applied to the samples at RAPRA. The apparatus used at Plymouth produced rather noisey results, and 0.3Hz was found to be the optimum frequency for producing plots.
storage modulus data at least, they agree with RAPRA data for \( \lambda \geq 1.73 \).

The reason for the disparity in the RAPRA results is not clear. Possible causes include the effect of scragging, amplitude effects, or some unidentified factor connected with changing the load cell. All samples at RAPRA were initially scragged as described in §7.1.3, and subsequently allowed to relax for periods ranging from approximately 12~24 hours before being tested. Varying the scragging procedure at Plymouth has however failed to produce any agreement with RAPRA results for \( \lambda < 1.73 \). The datapoints for \( \lambda = 1.07 \) which were collected at RAPRA correspond to a strain amplitude of approximately 0.005. From Figure 7.20 there is some suggestion that other datapoints for \( \lambda < 1.73 \) may be affected as a result of the higher strain amplitudes imposed (see §7.1.3) - Sullivan and Demery (1982) demonstrate that increasing strain amplitude decreases the apparent value of the incremental storage modulus†. At Plymouth experiments for \( \lambda = 1.07 \) were conducted with strain amplitudes of 0.003 and 0.005. The resulting values for the incremental storage modulus agreed to within about 2%. This indicates that amplitude effects are not responsible for the observed disparity in the RAPRA data. It is concluded that this is most likely to be connected with changing the load cell.

(ii) **Comparison with Dynamic Moduli Results of Linear Experiments**

The agreement of the results of the linear and non-linear experiments is indicated by the data of Table 7.3. Since incremental dynamic moduli values were obtained at Plymouth Polytechnic for a frequency of 0.3Hz only, their values at 1Hz have been estimated using the data of Figures 7.18 and 7.19. In these figures \( E''(\omega,\lambda) \) and \( E'(\omega,\lambda) \) plots are approximately parallel. Thus comparing Plymouth and RAPRA results at 0.3Hz enables an estimate to be made for Plymouth results at 0.1Hz, since Figures 7.18 and 7.19 imply that RAPRA and Plymouth results should bear an approximately constant ratio to each other.

† In fact incremental dynamic moduli cannot depend upon strain amplitude. Measurement of an amplitude effect indicates that the applied value exceeds that for which the determination of incremental dynamic moduli is theoretically justified.
It is significant that although both loss and storage moduli, as measured on the rheogoniometer, are decreased as a result of scragging at 100% extension (which agrees with results for the unfilled material, see Table 7.1), values calculated from incremental dynamic moduli are higher than those measured on the rheogoniometer. Since samples of the filled material were not scragged immediately prior to testing, but were first allowed to relax for at least 12 hours (see §7.1.3), the scragging procedure does not appear to have such a profound influence on the material under testing as is the case for the procedure adopted with the unfilled material (see §7.2.3). Although the scragging procedure does not appear to influence the results for the filled material as it does for the unfilled, there remains a distinct lack of agreement between loss modulus values obtained on the rheogoniometer and servohydraulic testing machine in the case of the filled material. The high value of the incremental loss modulus measured on the servohydraulic testing machine in Plymouth may be attributable to the grips used in these experiments. These grips tended to cut into the sample and it is possible that energy dissipated in rupturing the sample between the grips contributed to the magnitude of the measured incremental loss modulus. This might also explain the negative gradient of incremental loss modulus against extension ratio which is observed for the Plymouth data in Figure 7.20. Data taken at RAPRA, and also the results of Sullivan and Demery (1982) and Neinecke and Maksin (1980) indicate that this plot should pass through a minimum.

(III) Choice of Constitutive Equation to Model Data

In order to test whether the present data can be modelled by any of the constitutive equations presented in Chapter 6, we investigate the validity of equation [6.54] by examining the dependencies of $E''(\omega, \lambda)$ and $E'(\omega, \lambda) \cdot \frac{\lambda d\sigma}{d\lambda}$ upon the extension ratio. Since RAPRA data for $\lambda < 1.70$ are likely to be in error, these have been neglected, and the Plymouth Polytechnic data shown in Figure 7.20 have been used for $\lambda < 1.70$. Plots of $E''(\omega, \lambda)$ and $E'(\omega, \lambda) \cdot \frac{\lambda d\sigma}{d\lambda}$ based on this composite data set are shown in Figure 7.21. Although these data are subject to a certain amount of experimental scatter (which is also the case for the similar plot obtained for the unfilled material, see figure 7.10), it appears that the
dependence on $E'(w, \lambda)$ and $E''(w, \lambda) - \lambda \frac{d\sigma_e}{d\lambda}$ are identical to within experimental error. The prediction of equation [6.54] is thus satisfied, and the observed behaviour can therefore be modelled by at least one of the constitutive equations presented in Chapter 6.

The incremental dynamic moduli predictions of the Chang, Bloch and Tschoegl solid model are presented in Table 6.1. Utilising the value of $n$ determined from the $\sigma_e$ data of Figure 7.16 and treating $E'(w)|_{\omega=0.3\text{Hz}}$ as a fitting parameter results in a very unsatisfactory fit to incremental storage modulus data. Sullivan and Demery (1982) also found that the Chang, Bloch and Tschoegl solid model gave a poor representation of their results. The observed $\lambda$-dependence of the $E''(w, \lambda)$ data fails to accord with the prediction of the Sullivan constitutive equation [6.11] given in Table 6.1, and perhaps more significantly this is also the case for $E'(w, \lambda) - \lambda \frac{d\sigma_e}{d\lambda}$ data (see Figure 7.21). The forms of the incremental dynamic moduli predicted by the constitutive equation [6.19] are also given in Table 6.1. According to [6.19] the $\lambda$-dependence of the plots in Figure 7.21 should be given by the function

$$f(\lambda) = \lambda^m + \frac{\lambda^{m/2}}{2}.$$  \[7.29\]

The condition that $f'(\lambda) = 0$ at $\lambda = \lambda_0$ yields the result

$$m = -\frac{2 \log_4}{3 \log_\lambda_0}.$$  \[7.30\]

It is significant that the plots of $E'(w, \lambda) - \lambda \frac{d\sigma_e}{d\lambda}$ and $E''(w, \lambda)$ against $\lambda$ in Figure 7.21 show a negative gradient for small extension ratios. This indicates that these quantities pass through a minimum. From [7.30] we observe that in the range $\lambda > 1$ a minimum can only be obtained if the parameter $m$ is allowed to take a negative value. Fitting the function $\frac{3}{3}[\lambda^m + \frac{\lambda^{-m/2}}{2}](E'(w)-E_e)|_{\omega=0.3\text{Hz}}$ to the data set shown in Figure 7.21, treating $m$ and $(E'(w)-E_e)|_{\omega=0.3\text{Hz}}$ as fitting parameters yields $m = -5.83$ and $(E'(w)-E_e)|_{\omega=0.3\text{Hz}} = 4.75 \times 10^8$ dyne/cm². Utilising the value of $m$ thus obtained, and treating $E''(w)|_{\omega=0.3\text{Hz}}$ as a fitting parameter, the $E''(w, \lambda)$ data of Figure 7.21 were fitted by the function predicted by [6.19] in Table 6.1.
yielding \( E''(\omega)_{\omega=0.3\text{Hz}} = 1.29 \times 10^8 \text{dyne/cm}^2 \). Utilising these values of \( m \), \( (E'(\omega)-E_e)_{\omega=0.3\text{Hz}} \) and \( E''(\omega)_{\omega=0.3\text{Hz}} \) together with the values of \( n \) and \( E_e \) obtained in §7.3.1, the incremental dynamic moduli predictions of [6.19] are plotted in Figure 7.20. Considering the scatter apparent in these data, the resulting fit is quite satisfactory. It is concluded that the constitutive equation [6.19] affords a satisfactory representation of incremental dynamic moduli data.

7.3.4 Relaxation Spectrum Function Results

Relaxation spectrum function values were calculated as described in §7.1.4. The relaxation spectrum function values obtained from the incremental storage and loss moduli of Figures 7.19 and 7.18 are shown in Figures 7.22 and 7.23 respectively. The \( F_1(\tau,\lambda) \) values of Figure 7.22 are smaller than the corresponding \( F_2(\tau,\lambda) \) values of Figure 7.23. As with the unfilled material, \( F_1(\tau,\lambda) \) plots appear to be more susceptible to fitting artefacts than the corresponding \( F_2(\tau,\lambda) \) plots (see §7.2.4). Both Figures 7.22 and 7.23 demonstrate a lack of parallelism between plots at different extension ratios \( \lambda \). Considering these plots together the observed trend is for the gradient to become more negative with increasing \( \lambda \).

Incremental dynamic modulus data obtained at RAPRA have been used to generate the data of Figures 7.22 and 7.23, even though values obtained for \( \lambda < 1.73 \) are thought to be in error (see §7.3.3). From Figures 7.18 and 7.19 we observe that although there is a marked difference in the moduli values obtained for \( \lambda < 1.73 \) and \( \lambda > 1.73 \), the same trend is exhibited in the frequency dependence for all data. Thus although the absolute values of the relaxation spectrum functions generated from data at \( \lambda < 1.73 \) are unlikely to be correct, the observed time dependencies may still be meaningful.

Table 7.4 compares estimates of \( H(\tau) \) calculated from \( F_1(\tau,\lambda) \) and \( F_2(\tau,\lambda) \) data with values of \( H(\tau) \) obtained from dynamic modulus data reduced to 2.5°C and shifted according to the WLF equation. Table 7.2 contains similar information with regard to the unfilled material and the significance of the quantities listed is discussed in §7.2.4. Since the values of \( F_1(\tau,\lambda) \) and \( F_2(\tau,\lambda) \) derived from RAPRA data for \( \lambda < 1.73 \) are thought to be in error, a correction was
sought by comparing values of the dynamic data taken at RAPRA and at Plymouth. From Figure 7.20 we observe that for $\lambda = 1.07$ the ratios of the incremental storage and of the loss moduli taken at RAPRA to those at Plymouth are approximately equal. This enables us to determine a multiplicative factor to correct the RAPRA results. In view of the formulae of Table 6.2, multiplying incremental dynamic moduli by such a correction factor results in a vertical shift for the $F_1(\tau, \lambda)$ and $F_2(\tau, \lambda)$ plots of Figures 7.22 and 7.23. The value of this shift is approximately 0.35 on the log scale. We note that the $F_1(\tau, \lambda)$ plot for $\lambda = 1.07$ shown in Figure 7.22 is very much affected by fitting artefacts, and this accounts for the poor agreement of the $H(\tau)$ value calculated from these data in Table 7.4. The corresponding $F_2(\tau, \lambda)$ data in Figure 7.23 are less affected by artefacts and the agreement shown in Table 7.4 is comparatively much better. The resulting $H(\tau)$ value is greater than those obtained from linear experiments. This agrees with the dynamic moduli results compared in Table 7.3, and contrasts with the corresponding results for the unfilled material shown in Table 7.2. As with the unfilled material, the Huet model predictions appear to give an overestimate of the observed values (see §7.2.4).

Since the results of Table 7.4 are based on extreme values (the domain of the shifted relaxation spectrum does not overlap with that of the relaxation spectrum functions $F_1(\tau, \lambda)$ and $F_2(\tau, \lambda)$ - hence the choice of $\log r = -1.15$ and $\log r = -0.80$), which are most susceptible to fitting artefacts, it is difficult to reach any firm conclusions on the basis of these data.

The relaxation spectrum function values obtained from stress relaxation data are shown in Figure 7.24. These plots are distinctly non-parallel and exhibit the same trend as $F_1(\tau, \lambda)$ and $F_2(\tau, \lambda)$ data i.e. an increasingly negative gradient with increasing $\lambda$. The non-parallelism of the relaxation spectrum functions indicates that constitutive equations such as those of Table 6.3, which feature a viscoelastic term with factored time and strain dependencies, are not strictly applicable for the case of the filled material. This means that the filled material does not obey the modified Boltzmann superposition principle. The Schapery constitutive equation [6.25] does not satisfy the modified Boltzmann superposition principle in general, but requires that plots obtained at different extension ratios should superpose to form a composite curve similar to that
obtained by time-temperature superposition (see §3.2.1). Such superposition involves both horizontal and vertical shifts.

From Figure 7.24, comparing plots for $\lambda = 1.07$ and $\lambda = 2.13$, we observe that a horizontal shift in excess of 2 decades in log $\omega$ would be required to bring about superposition, irrespective of any vertical shift. The parallelism of the incremental loss modulus data of Figure 7.18 however indicates that the filled material does obey the modified Boltzmann superposition principle to a good approximation. Moreover, these data clearly show that a continuous composite curve could not be formed from $E''(\omega, \lambda)$ data by shifting data at $\lambda = 2.13$ by 2 decades in log $\omega$ relative to the $\lambda = 1.07$ plot.

We conclude that although the intrinsic timescale of the filled material, as reflected in the relaxation spectrum functions, may be affected by the applied strain, this does not necessarily produce a significant effect on the more immediately observable experimental quantities, such as $E''(\omega, \lambda)$. From the point of view of modelling such quantities, recourse to constitutive equations which conform with the modified Boltzmann superposition principle is thus justifiable.

Since relaxation spectrum function plots are non-parallel, their $\lambda$-dependencies must vary with relaxation time $\tau$. The $\lambda$-dependencies of these quantities will not therefore be compared with model prediction, since such predictions can only account for $\lambda$-dependencies which are identical to within a multiplicative constant for each value of $\tau$, and lead to parallel relaxation spectrum function plots.

7.3.5 Conclusions

(1) The phase angle between oscillatory components of force and displacement is found to depend upon the extension ratio for $\lambda \geq 1.61$.

(2) The strain conditioning programme applied to the filled samples does not significantly affect agreement with the results of linear experiments.
(3) The evidence of relaxation spectrum function results indicates that the intrinsic timescale of the material is affected by straining. However, incremental loss modulus data demonstrate that the modified Boltzmann superposition principle can still represent the observed behaviour to a good approximation.

(4) The observed dependencies of quasi-equilibrium stress and incremental dynamic moduli upon extension ratio indicate that these quantities can be modelled in terms of at least one of the constitutive equations presented in chapter 6.

(5) The dependencies upon extension ratio noted for incremental storage moduli and quasi-equilibrium stress data indicate that these quantities cannot be represented by the Chang, Bloch and Tschoegl solid model.

(6) The dependence of incremental loss moduli upon extension ratio indicates that these cannot be represented in terms of the Sullivan constitutive equation.

(7) A satisfactory fit has been produced for quasi-equilibrium stress and incremental dynamic moduli data using the constitutive equation [6.19].

7.4 COMPARISON OF THE PROPERTIES OF THE FILLED AND UNFILLED MATERIALS IN NON-LINEAR DEFORMATION

From the results obtained in §§7.2 and 7.3 we may draw the following conclusions regarding the behaviour of the unfilled and filled materials in non-linear deformation:

(1) For the unfilled material the phase angle between the oscillatory components of force and displacement is found to be independent of extension ratio, at least over a certain range of frequencies, while for the filled material beyond a critical extension this quantity depends upon extension ratio.
(2) The frequency dependencies of the incremental loss moduli measured for the unfilled and filled materials show little dependence on extension ratio. These results are thus theoretically consistent with the modified Boltzmann superposition principle. Examination of relaxation spectrum functions for the unfilled and filled materials however indicates that although the intrinsic timescale of the unfilled material can be regarded as independent of extension ratio under the conditions studied, for the filled material this is not the case. Thus although the modified Boltzmann superposition principle may be usefully applied to both materials, nevertheless with regard to the theory whereby this principle is expressed, the assumption that the intrinsic timescale of the material is unaffected by strain is more valid in the case of the unfilled material than in that of the filled.

(3) It has been shown that the solid model of Chang, Bloch and Tschoegl fails to predict the behaviour of the unfilled material. Both the constitutive equation of Sullivan and equation [6.19] model the observed behaviour for the unfilled material, but only the latter is suitable for representing the filled material also. Thus varying the parameters of equation [6.19] may facilitate modelling of the non-linear deformation of vulcanised elastomers containing variable loadings of carbon black.
CHAPTER 8

DISCUSSION AND FURTHER WORK

Schau zurück auf Gottes Wege,
Wie er dich bisher geführt,
Als denn kluglig überlege,
Was dir ießt zu thun gebührt.

INTRODUCTION

In this chapter the results of Chapter 7 are discussed. This discussion consists firstly of considering the application of these results to published data on carbon black filled elastomers and secondly of assessing the implications of these results in terms of the work necessary to further the development of a suitable constitutive equation for these materials.

8.1 APPLICATION TO PUBLISHED DATA

As stated in §6.3, incremental dynamic moduli represent a useful starting point for the characterisation of non-linear deformational properties, and thus it is published data of this type which will be considered. As reviewed in §6.2.3, incremental dynamic moduli have been used as a means of investigating deformational dependence by both Meinecke and Maksin (1980) and Sullivan and Demery (1982). The data of each of these investigations will be considered in turn.

8.1.1 The Results of Meinecke and Maksin

The simple tension experiments of Meinecke and Maksin were carried out on a series of styrene-butadiene copolymers, both unfilled and containing loadings of up to 50phr HAF carbon black. As stated in §6.2.3 the methods by which Meinecke and Maksin analyse their data differ significantly from those adopted in this thesis. In order to evaluate their reported data correctly these differences
must therefore be considered in greater detail.

The data of Meinecke and Maksin were obtained by measuring ellipses in a similar fashion to that described in Appendix 1. Meinecke and Maksin however take [A1.9] to determine tanc instead of sinc. This is a consequence of the small angle approximation sinc = tanc and does not produce a significant effect on results for small values of the phase angle c. (Meinecke and Maksin further equate the phase angle c with the loss angle δ, which is only valid in the case of zero prestrain - see §6.2.3). In view of the above approximation, the true phase angle c can be calculated from the incremental dynamic modulus data reported by Meinecke and Maksin.

Another quantity which must be determined in order to calculate incremental dynamic moduli of the form of [6.60] is the ratio of the amplitudes of oscillatory stress and strain. This appears in [6.60] as the quantity $\lambda \delta F/A_0 \epsilon_0$. We note that this quantity is proportional by a factor of $\lambda^2/A_0$ to the positive gradient of the diagonal of the rectangle in Figure A1.1. This gradient has a value of $\delta F/\lambda \epsilon_0$ and can be determined by direct measurement. The moduli determined by Meinecke and Maksin are based upon nominal stress and strain relative to the undeformed sample length. The ratio of oscillatory stress and strain amplitudes they determine thus differs by a factor of $\lambda^2$ from that appearing in [6.60]. The principle by which this ratio is determined should however be the same. The measurements of Meinecke and Maksin nevertheless are based upon the 'slope of the major ellipse axis' rather than the gradient of the diagonal of the rectangle. As can be seen from Figure A1.1 the gradient of the major axis of the ellipse is not the same as the gradient of the diagonal of the rectangle, and this represents another approximation. It can be shown (Geary, Lowry and Hayden, 1963) that the gradient of the major axis of the ellipse $g$ is in fact given by

$$g = \frac{1}{2\epsilon_0 \lambda \delta F \cos \delta} \left[ \frac{\delta F^2 - \lambda^2 \epsilon_0^2}{\sqrt{(\delta F^2 + \lambda^2 \epsilon_0^2)^2 - (2\delta F \epsilon_0 \lambda \text{sinc})^2}} \right]$$

[8.01]

which only reduces to $\delta F/\lambda \epsilon_0$ in the case $c = 0$. This represents another small angle approximation. It is possible to calculate $g$ from the results of Meinecke and Maksin and invert [8.01] to yield an expression for $\delta F/\lambda \epsilon_0$. Thus we obtain

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Finally quasi-equilibrium stress data must be used to obtain a value for the \( \sigma_e \) term appearing in [6.60], thus enabling incremental dynamic moduli of the form given in [6.60] to be determined.

Having determined values for the incremental dynamic moduli in the form of [6.60], these data were examined in the same way as the experimental data presented in Chapter 7. Figure 8.1 shows plots of \( \log[E'(\omega,\lambda)-\lambda d\sigma_e/d\lambda] \) and \( \log[E''(\omega,\lambda)] \) against \( \lambda \) for the material containing 50phr HAF black. These quantities exhibit different \( \lambda \)-dependencies, which demonstrates that the incremental dynamic modulus and quasi-equilibrium stress behaviour of the material is not in agreement with the predictions of [6.54]. This implies that neither the Schapery constitutive equation, nor indeed any of the other constitutive equations presented in Chapter 6, is suitable for representing these results (see §7.2.3). Figure 8.2 shows a similar plot derived from Meinecke and Maksin's data for the unfilled material. This reveals the same qualitative features as the data for the filled material and hence we conclude that the difficulty in representing the data of Meinecke and Maksin in terms of a constitutive equation stems primarily from the behaviour of the unfilled styrene-butadiene copolymer, rather than being a result of carbon black loading.

We observe that agreement with [6.54] provides a powerful means of testing whether a wide class of constitutive equations is suitable for modelling material behaviour. This class of constitutive equations is not restricted solely to those presented in Chapter 6. Morman (1988), for example, has recently proposed a generalised constitutive equation for viscoelastic rubber-like solids derived in a similar fashion to the finite linear viscoelasticity theory of Coleman and Noll (1961). One particular form of this theory, which features the 'n' strain measure, reduces to the same expression as the Chang, Bloch and Tschoegel solid model in the case of homogeneous uniaxial and biaxial deformations, and thus agreement with [6.54] provides a critical test of its validity with regard to a particular material. Further evidence on the utility of the 'n' strain measure with regard to modelling the behaviour of carbon black filled elastomers is afforded by consideration of the results of Sullivan.
8.1.2 The Results of Sullivan & Demery

Sullivan and Demery (1982) conducted simple tension and pure shear experiments on a natural rubber compound containing a loading of N351 carbon black variously reported as 34.5phr and 46phr (see Table 6.4). The incremental dynamic moduli values measured by Sullivan and Demery were of the form given in [6.60] but are reported as being dependent upon strain amplitude (measured relative to the extended sample length). Such an amplitude effect strictly invalidates the measurement of incremental dynamic moduli (see §6.1.5). Upon increasing strain amplitude from 0.005 to 0.04 the apparent drop in incremental storage modulus is of the order of 10%, while the corresponding increase in incremental loss modulus can be as high as 100%. The deformational dependence of the measured incremental dynamic moduli is reported most extensively at a strain amplitude of 0.02, but as pointed out above, such values cannot be regarded as true incremental dynamic moduli. From the data of Sullivan and Demery it appears however that the plots obtained at different strain amplitudes for log$E'(\omega, \lambda)$ against $\lambda$ are parallel, and that this is also the case for log$E''(\omega, \lambda)$. This implies that although the actual values of the moduli measured at $\epsilon_0 = 0.02$ are questionable, their deformational dependencies should be relatively unaffected by strain amplitude.

Sullivan and Demery present incremental dynamic modulus data in both simple tension and pure shear for temperatures of 55°C and 30°C. Plots of log$[E'(\omega, \lambda)-\lambda d\sigma_\phi/d\lambda]$ and log$E''(\omega, \lambda)$ against $\lambda$ derived from the simple tension data of Sullivan and Demery at 55°C and 30°C are shown in Figures 8.3 and 8.4 respectively. We observe that the data of neither of these figures agrees with the predictions of [6.54] and conclude that none of the constitutive equations presented in Chapter 6 is capable of characterising these data over the full range of $\lambda$ shown. It is however of interest to examine to what extent the data of Sullivan and Demery can be represented in terms of these constitutive equations.

Sullivan and Demery have shown that the Chang, Bloch and Tschoegi solid model [6.09] gives a reasonable fit to incremental
storage modulus data up to an extension ratio of $\lambda = 1.6$ but fails to represent incremental loss modulus data at all. Figure 8.5 compares fits obtained to incremental dynamic moduli measured in simple tension at 55°C using the Sullivan constitutive equation [6.11] and equation [6.19]. The fit obtained using equation [6.19] is slightly more satisfactory than that of the Sullivan model and affords a crude representation of incremental storage modulus data up to an extension ratio of $\lambda = 1.9$. Such a fit is perhaps surprising in view of the data of Figure 8.3 and encourages examination of the agreement attainable for similar data at 30°C. This is shown in Figure 8.6. Comparison of Figures 8.5 and 8.6 reveals that the fit obtained at 30°C is inferior to that at 55°C. This suggests that the suitability of a particular constitutive equation, such as [6.19], for modelling material behaviour depends upon the temperature range considered. These results also demonstrate that deformational dependence is affected by temperature. This supports the observation of §6.1.3 that temperature dependence in finite deformation cannot necessarily be accounted for exclusively by means of reduced time.

In view of the comparatively good fit obtained for the simple tension data of Figure 8.5, we also examine the fit obtained for similar data in pure shear. The pure shear analogue of [6.43] is given by

$$E'(\omega, \lambda) = \frac{2}{3} E_0 \left[ \lambda^{n-\lambda^{-n}} \right] + \frac{2}{3} \left[ \lambda^{m+\lambda^{-m}} \right] (E'(\omega) - E_0)$$

$$E''(\omega, \lambda) = \frac{2}{3} \left[ \lambda^{m+\lambda^{-m}} \right] E''(\omega).$$

The fit obtained to pure shear data at 55°C using [8.03] and exploiting parameter values obtained from simple tension data at the same temperature is shown in Figure 8.7. Although incremental storage modulus values are represented fairly well, [8.03] fails to represent incremental loss modulus data. The prediction of an unrealistically strong $\lambda$-dependence for incremental loss moduli is a consequence of allowing the parameter $m$ to take relatively large negative values (see §6.3.3(iii)). Such negative values are necessary in order to represent the very weak $\lambda$-dependence or slight minimum which is observed for $E''(\omega, \lambda)$ results at small $\lambda$ in simple
tension. Similar behaviour is observed in experimental data in pure shear (see Figure 8.7) but the deformatonal dependence for $E''(\omega, \lambda)$ data predicted by [8.03] can only give a minimum at $\lambda = 1$.

These results indicate that the deformatonal dependence of the Chang, Bloch and Tschoegl solid model [6.09], which is assumed for the viscoelastic term in [6.19], is not necessarily well-suited to representing the deformatonal dependence of the viscoelastic processes of filled elastomers. This is perhaps to be expected, since this non-linear strain measure was originally developed in conjunction with the strain energy function of Blatz, Sharda and Tschoegl (1974) to describe the deformatonal dependencies of unfilled elastomers. The viscoelastic processes modelled by this strain measure are thus those associated with the chains of the polymer matrix. In filled elastomers however, viscoelastic behaviour may be dominated by processes associated primarily with the carbon black filler. Deformatonal dependencies, such as that of $E''(\omega, \lambda)$ in Figure 8.7, which include a region of weak $\lambda$-dependence or a slight minimum for small $\lambda$ are not characteristic of the deformatonal dependencies of unfilled elastomers, but may be characteristic of behaviour associated with the carbon black filler. This is a point which merits further investigation.

8.2 FURTHER WORK

Rubber technologists seeks easily applicable principles with which to work. The differences in relaxation spectrum noted for the filled and unfilled materials in §5.5 indicate that generally no simple relationship exists between the properties of the filled and unfilled materials, even in infinitesimal deformation. Despite this fact, as reviewed in §2.2.4, relations such as the Frankel Acrivos equation or the Guth-Gold equation, which relate the (instantaneous) moduli of the filled and unfilled materials in infinitesimal deformation, may still represent useful tools for technological applications.

In non-linear deformation, as indicated by the results of Chapter 7, the relationship between moduli measured for a filled and corresponding unfilled elastomer is likely to be extremely complex. This does not however preclude the possibility of developing some
simple practical relationships applicable to non-linear deformation. One means of doing so might be through the development of non-linear constitutive equations to describe material behaviour in non-linear deformation.

Constitutive equations have been presented in Chapter 6 which can be used to represent the non-linear behaviour of elastomers. It has been shown in Chapter 7 that, to within the accuracy of the experimental data available, one of these constitutive equations models the behaviours of both the filled and unfilled elastomers studied. Analysis of the data of Meinecke and Maksin (1980) however indicates that their results cannot be modelled by any of the constitutive equations presented in Chapter 6. This appears to be due not primarily to the effect of carbon black filler, but to the behaviour of the elastomer matrix. The results of Sullivan and Demery (1982) similarly fail to satisfy the criterion imposed by the constitutive equations of Chapter 6, although this may be due to the fact that these results were not measured at sufficiently small strain amplitude to represent true incremental dynamic moduli.

In order to further the work of this thesis it would be desirable to obtain more accurate data (possibly by using a cam mechanism to oscillate the sample) and to measure incremental dynamic moduli for a number of strain amplitudes in order to establish the validity of the measured values. Applying the criterion represented by [6.54] would then establish whether these data could be characterised by constitutive equations such as those presented in Chapter 6. If this were found to be the case, further experiments in a variety of strain fields would be required in order to investigate the strain dependence associated with the viscoelastic term of the constitutive equation. This is equivalent to seeking a strain-energy function to express the deformational dependence of the viscoelastic processes within the filled elastomer. The results of Sullivan and Demery (1982) indicate that such a strain energy function is likely to be temperature dependent and this could also be investigated experimentally.

Having developed a suitable constitutive equation, this could then be used to predict the non-linear response of the material when subjected to large amplitude oscillations. This response could be interpreted in terms of apparent dynamic moduli (although such moduli are not actually defined for large amplitude oscillation), and thus
it might be hoped to model the dependence of 'modulus' on oscillatory strain amplitude which has been noted by many workers in the field of rubber technology. The degree of sophistication required of a constitutive equation in order to model this behaviour is also a topic for further investigation.
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Wool R.P.
### Symbols

- **A** | Helmholtz free energy
- **A_0** | undeformed cross-sectional area of sample
- **A(m)** | term appearing in Williams & Ferry relaxation spectrum formula
- **A_T** | rate of accumulation of elastic energy
- **B** | left Cauchy-Green deformation tensor
- **B(m)** | term appearing in Williams & Ferry relaxation spectrum formula
- **C** | torque on upper platen
- **C_r** | right Cauchy-Green deformation tensor
- **C_p** | heat capacity at constant pressure
- **C^r_t** | right Cauchy-Green relative deformation tensor
- **D** | rate of energy dissipation
- **D_M** | mechanical dissipation rate
- **D_T** | thermal dissipation rate
- **E** | Lagrangian strain tensor
- **E(t)** | tensile relaxation modulus
- **E_e** | tensile equilibrium modulus
- **E^*(w)** | complex tensile modulus
- **E^*(w,λ)** | complex incremental tensile modulus
- **E'(w)** | tensile storage modulus
- **E''(w)** | tensile loss modulus
- **E'(w,λ)** | incremental tensile storage modulus
- **E''(w,λ)** | incremental tensile loss modulus
- **E_0^r** | relative (instantaneous) tensile modulus
- **F** | deformation gradient tensor
- **F_e** | quasi-equilibrium force
- **F_{SR}(τ,λ)** | relaxation spectrum function calculated from stress relaxation data
- **F_{dT}(τ,λ)** | relative deformation gradient tensor
- **F_1(τ,λ)** | relaxation spectrum function calculated from incremental storage modulus data
- **F_2(τ,λ)** | relaxation spectrum function calculated from incremental loss modulus data
- **G** | (instantaneous) shear modulus
- **G(t)** | shear relaxation modulus
$G_e$ shear equilibrium modulus
$G^*(\omega)$ complex shear modulus
$G'(\omega)$ shear storage modulus
$G''(\omega)$ shear loss modulus
$H(u)$ Heavyside function
$H(\tau)$ (logarithmic) relaxation spectrum
$I$ moment of inertia of measuring head
$I$ 2nd order unit tensor
$J(t)$ shear creep compliance
$J^*(\omega)$ complex shear compliance
$J'(\omega)$ storage compliance
$J''(\omega)$ loss compliance
$K$ torsion bar restoring constant
$K(t)$ volumetric relaxation modulus
$M(m)$ term appearing in Williams & Ferry relaxation spectrum formula
$P$ thermodynamic pressure
$Q$ energy influx per unit volume due to radiation
$R$ rotation tensor
$S$ entropy
$T$ absolute temperature
$T_g$ glass transition temperature
$T_0$ reference temperature
$U$ internal energy
$U$ right stretch tensor
$V$ particle velocity
$V$ volume
$W$ strain energy density function
$X$ reference coordinate

$a$ sample radius
$a_T$ time-temperature superposition shift factor
$a_c$ shift factor of Schapery constitutive equation
$c$ phase lag
$d$ rate of strain tensor
$g$ body force
$h$ sample height
$H$ parameter of Huet model
$h_0(\varepsilon)$  material function of Schapery constitutive equation
$h_1(\varepsilon)$  material function of Schapery constitutive equation
$h_2(\varepsilon)$  material function of Schapery constitutive equation
$k$  thermal conductivity
$k$  parameter of Huet model
$\ell$  extended sample length
$\ell_0$  undeformed sample length
$m$  negative gradient of log-log plot of relaxation spectrum against relaxation time
$m$  material parameter associated with 'n' strain measure
$n$  material parameter associated with 'n' strain measure
$p$  mechanical pressure
$q$  heat flux
t  time
$t_0$  reference time
$u$  displacement
$v$  field velocity
$x$  spatial coordinate

$\Gamma(.)$  gamma function
$\Delta E(t)$  transient component of tensile relaxation modulus
$\Delta G(t)$  transient component of shear relaxation modulus
$\Delta \varepsilon(t)$  time dependent component of applied strain

$\gamma$  shear strain
$\gamma_0$  shear strain amplitude
$\delta$  loss angle
$\delta_{ij}$  Kronecker delta
$\delta(t)$  Dirac delta function
$\delta F$  amplitude of oscillatory force
$\varepsilon$  infinitesimal strain tensor
$\varepsilon_i$  component of infinitesimal strain tensor
$\varepsilon(t)$  strain component relative to undeformed sample dimensions
$\varepsilon_s$  steady component of applied strain
$\varepsilon_0$  strain amplitude relative to extended sample length
$\eta$  viscosity
$\eta_0$  zero shear viscosity
\( \eta^* \) complex viscosity
\( \theta \) displacement of upper platen
\( \theta_1 \) displacement amplitude of upper platen
\( \theta_2 \) displacement amplitude of lower platen
\( \lambda \) extension ratio
\( \lambda_\alpha \) principal extension ratio
\( \rho \) density
\( \rho' \) reduced time of Schapery constitutive equation
\( \sigma \) component of Cauchy stress tensor
\( \sigma = \) Cauchy stress tensor
\( \sigma_e \) equilibrium (or quasi-equilibrium) stress component
\( \sigma_n \) component of nominal stress tensor
\( \sigma_{\text{eq}} \) nominal stress tensor
\( \sigma_\alpha \) Cauchy principal stress
\( \sigma_0 \) stress amplitude
\( \sigma' = \) deviatoric part of Cauchy stress tensor
\( \tau \) relaxation time
\( \tau \) parameter of Huet model
\( \varphi \) volume fraction of filler
\( \chi \) amplitude ratio
\( \omega \) frequency
\( \omega_0 \) natural frequency
Appendix I

Theory of Elliptical Plots for the Determination of Incremental Dynamic Moduli

The oscillatory component of the force defined in [6.59] can be expressed as

\[ F'(t) = \delta F \cos(\omega t + c) , \tag{A1.1} \]

where \( \delta F \) is the amplitude of the oscillatory component of the force, and \( c \) is the phase shift between the oscillatory components of force and displacement. The oscillatory component of the displacement is given by

\[ \epsilon(t) = \ell \epsilon_0 \cos \omega t , \tag{A1.2} \]

where \( \epsilon_0 \) is the strain amplitude relative to the deformed configuration, and \( \ell \) is the length of the extended sample.

Plotting the oscillatory displacement on the x-axis, and the oscillatory force on the y-axis, we may write

\[ x = \ell \epsilon_0 \cos \omega t \tag{A1.3} \]
\[ y = \delta F \cos(\omega t + c) . \]

Eliminating \( t \) from \( A1.3 \) yields

\[ (\ell \epsilon_0)^2 y^2 + (\delta F)^2 x^2 - 2\ell_0 \delta F \cos \epsilon_0 xy - (\ell_0 \delta F \sin \epsilon_0)^2 = 0 . \tag{A1.4} \]

Equation \( A1.4 \) is the general equation for an ellipse.

For the general conic section

\[ ax^2 + 2hxy + by^2 + c = 0 \tag{A1.5} \]

the lengths of the semi-axes \( r_1 \) and \( r_2 \) (see Figure A1.1) are given by
the roots of the equation

\[ \frac{C^2}{r^4} + (a+b) \frac{C}{r^3} + ab - h^2 = 0 . \]  \[\text{[A1.6]}\]

Thus for the case of the ellipse given by [A1.4] it can be shown that

\[ r_1 r_2 = \varepsilon_0 \delta \text{F sinc} . \]  \[\text{[A1.7]}\]

Now the area of the ellipse in Figure A1.1 is \( \pi r_1 r_2 \), while that of the rectangle which encloses it is \( 4\varepsilon_0 \delta \text{F} \). Thus from [A1.7]

\[ \frac{\text{area of ellipse}}{\text{area of rectangle}} = \frac{\pi \varepsilon_0 \delta \text{F sinc}}{4\varepsilon_0 \delta \text{F}} \]  \[\text{[A1.8]}\]

and hence

\[ \text{sinc} = \frac{4}{\pi} \frac{\text{area of ellipse}}{\text{area of rectangle}} . \]  \[\text{[A1.9]}\]
### TABLE 2.1

**COMPOUNDING DATA FOR THE FILLED AND UNFILLED MATERIALS**

#### Unfilled Material

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>LOADING (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Krynac 806</td>
<td>100</td>
</tr>
<tr>
<td>MC Sulphur</td>
<td>15</td>
</tr>
<tr>
<td>ZnO</td>
<td>50</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>10</td>
</tr>
<tr>
<td>Octamine</td>
<td>10</td>
</tr>
<tr>
<td>SRF N774</td>
<td>0</td>
</tr>
<tr>
<td>TMTD</td>
<td>2.5</td>
</tr>
<tr>
<td>CBS</td>
<td>10</td>
</tr>
</tbody>
</table>

#### Filled Material

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>LOADING (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Krynac 806</td>
<td>100</td>
</tr>
<tr>
<td>MC Sulphur</td>
<td>15</td>
</tr>
<tr>
<td>ZnO</td>
<td>50</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>10</td>
</tr>
<tr>
<td>Octamine</td>
<td>10</td>
</tr>
<tr>
<td>SRF N774</td>
<td>50</td>
</tr>
<tr>
<td>TMTD</td>
<td>2.5</td>
</tr>
<tr>
<td>CBS</td>
<td>10</td>
</tr>
</tbody>
</table>

Standard mixing and milling.

Cure 150°C according to rheometer trace.

Post cure 24 hrs at 150°C.
<table>
<thead>
<tr>
<th>MATERIAL (loadings in pts per hundred by wt.)</th>
<th>MODE OF DEFORMATION</th>
<th>PLOT</th>
<th>SUPERPOSABLE</th>
<th>REDUCTION FACTOR</th>
<th>TEMP. °C</th>
<th>HORIZONTAL SHIFT</th>
<th>VERTICAL SHIFT</th>
<th>TEMP. RANGE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARTIN &amp; MALGUARNERA</td>
<td>TYRE STOCK</td>
<td>OScILLATORY SHEAR</td>
<td>$G', G''$</td>
<td>$T/T_0$</td>
<td>21</td>
<td>/</td>
<td>/</td>
<td>-63~21</td>
</tr>
<tr>
<td>J. Elastomers &amp; Plastics 13 139 1981</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FERRY &amp; FITZGERALD</td>
<td>BUTYL 325 RUBBER STOCK containing 40% MPC black POLYISOBUTYLENE containing 33.3% SRF black</td>
<td>OSCILLATORY SHEAR</td>
<td>$J, J'$</td>
<td>$T_p/(T_0p_0)$</td>
<td>25</td>
<td>/</td>
<td>/</td>
<td>0~100</td>
</tr>
<tr>
<td>Rubb. Chem. Tech. 55 1403 1982</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>FITZGERALD</td>
<td>CIS-POLYBUTADIENE-STYRENE-BUTADIENE containing 58% N229 black</td>
<td>OSCILLATORY SHEAR</td>
<td>$G', G''$</td>
<td>PARTIALLY</td>
<td>-</td>
<td>/</td>
<td>/</td>
<td>-5.8~69</td>
</tr>
<tr>
<td>Polym. Bull. 8 331 1982</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FITZGERALD &amp; FERRY</td>
<td>CIS-POLYBUTADIENE-STYRENE-BUTADIENE 58% N229 CIS-POLYBUTADIENE-STYRENE BUTADIENE 80% N234 black</td>
<td>OSCILLATORY SHEAR</td>
<td>$J, J'$</td>
<td>PARTIALLY*</td>
<td>22.3</td>
<td>-</td>
<td>/</td>
<td>2.6~76.9*</td>
</tr>
<tr>
<td>ISONO &amp; FERRY</td>
<td>STYRENE-BUTADIENE 1502 containing 50% N299 black</td>
<td>OSCILLATORY SHEAR</td>
<td>$G', G''$</td>
<td>25</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>-22.5~63</td>
</tr>
<tr>
<td>Rubb. Chem. Tech. 57 925 1984</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PAYNE 'The Rheology of Elastomers' Pergamon Press 1958</td>
<td>NATURAL RUBBER LOADED WITH CARBON BLACK</td>
<td>OSCILLATORY SHEAR</td>
<td>$G'$</td>
<td>$T_p/(T_0p_0)$</td>
<td>0</td>
<td>/</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* Not at 2.6°C and 11.5°C

**TABLE 3.1**

TIME TEMPERATURE SUPERPOSITION FOR CARBON BLACK FILLED ELASTOMERS UNDER SMALL STRAINS
**TABLE 4.1**

COMPARISON OF NUMERICAL AND ANALYTIC DYNAMIC MODULI VALUES

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$G'$ analytic $\times 10^7$ dyne/cm$^2$</th>
<th>$G'$ numerical $\times 10^7$ dyne/cm$^2$</th>
<th>$G''$ analytic $\times 10^7$ dyne/cm$^2$</th>
<th>$G''$ numerical $\times 10^7$ dyne/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.80</td>
<td>3.79</td>
<td>2.07</td>
<td>2.07</td>
</tr>
<tr>
<td>10</td>
<td>4.77</td>
<td>4.73</td>
<td>3.02</td>
<td>3.00</td>
</tr>
<tr>
<td>15</td>
<td>4.55</td>
<td>4.64</td>
<td>3.34</td>
<td>3.43</td>
</tr>
<tr>
<td>20</td>
<td>5.47</td>
<td>5.45</td>
<td>4.12</td>
<td>4.15</td>
</tr>
<tr>
<td>25</td>
<td>6.10</td>
<td>6.04</td>
<td>4.68</td>
<td>4.71</td>
</tr>
<tr>
<td>30</td>
<td>6.57</td>
<td>6.47</td>
<td>5.29</td>
<td>5.32</td>
</tr>
<tr>
<td>35</td>
<td>6.80</td>
<td>6.64</td>
<td>5.89</td>
<td>5.92</td>
</tr>
<tr>
<td>40</td>
<td>7.47</td>
<td>7.26</td>
<td>6.10</td>
<td>6.13</td>
</tr>
<tr>
<td>45</td>
<td>6.90</td>
<td>6.61</td>
<td>6.82</td>
<td>6.86</td>
</tr>
<tr>
<td>50</td>
<td>7.82</td>
<td>7.46</td>
<td>7.36</td>
<td>7.40</td>
</tr>
<tr>
<td>55</td>
<td>9.00</td>
<td>8.56</td>
<td>7.90</td>
<td>7.95</td>
</tr>
<tr>
<td>60</td>
<td>8.78</td>
<td>8.25</td>
<td>8.49</td>
<td>8.55</td>
</tr>
</tbody>
</table>

Results are for data obtained on the unfilled sample at 20°C at an oscillatory amplitude of 0.01 rad with torsion bar of restoring constant $K = 8650000$ dyne cm/rad.
### Table 4.2

**RAW DATA FOR PLOTS IN FIGURE 4.6**

20°C

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>x</th>
<th>c (deg)</th>
<th>(x^2 - 2xc\cos c + 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.22</td>
<td>21.4</td>
<td>0.63</td>
</tr>
<tr>
<td>10</td>
<td>0.44</td>
<td>18.2</td>
<td>0.36</td>
</tr>
<tr>
<td>15</td>
<td>1.51</td>
<td>-28.2</td>
<td>0.62</td>
</tr>
<tr>
<td>20</td>
<td>0.55</td>
<td>-120.2</td>
<td>1.85</td>
</tr>
<tr>
<td>25</td>
<td>0.26</td>
<td>-129.5</td>
<td>1.39</td>
</tr>
<tr>
<td>30</td>
<td>0.17</td>
<td>-131.8</td>
<td>1.25</td>
</tr>
<tr>
<td>35</td>
<td>0.12</td>
<td>-131.4</td>
<td>1.17</td>
</tr>
<tr>
<td>40</td>
<td>0.09</td>
<td>-135.2</td>
<td>1.14</td>
</tr>
<tr>
<td>45</td>
<td>0.07</td>
<td>-131.1</td>
<td>1.10</td>
</tr>
<tr>
<td>50</td>
<td>0.06</td>
<td>-133.4</td>
<td>1.09</td>
</tr>
<tr>
<td>55</td>
<td>0.05</td>
<td>-131.3</td>
<td>1.07</td>
</tr>
<tr>
<td>60</td>
<td>0.05</td>
<td>-133.1</td>
<td>1.06</td>
</tr>
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</table>

0°C

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>x</th>
<th>c (deg)</th>
<th>(x^2 - 2xc\cos c + 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.96</td>
<td>1.3</td>
<td>0.0024</td>
</tr>
<tr>
<td>10</td>
<td>0.98</td>
<td>0.5</td>
<td>0.0004</td>
</tr>
<tr>
<td>15</td>
<td>1.01</td>
<td>-0.2</td>
<td>0.0002</td>
</tr>
<tr>
<td>20</td>
<td>1.06</td>
<td>-0.9</td>
<td>0.0039</td>
</tr>
<tr>
<td>25</td>
<td>1.12</td>
<td>-1.7</td>
<td>0.0159</td>
</tr>
<tr>
<td>30</td>
<td>1.20</td>
<td>-2.7</td>
<td>0.0414</td>
</tr>
<tr>
<td>35</td>
<td>1.31</td>
<td>-4.4</td>
<td>0.1012</td>
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<tr>
<td>40</td>
<td>1.45</td>
<td>-6.3</td>
<td>0.2217</td>
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<tr>
<td>45</td>
<td>1.65</td>
<td>-8.9</td>
<td>0.4560</td>
</tr>
<tr>
<td>50</td>
<td>1.92</td>
<td>-12.8</td>
<td>0.9393</td>
</tr>
</tbody>
</table>
### Table 4.3 (a,b,c)

**RAW DATA FOR PLOTS IN FIGURE 4.5**

(a)

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$\chi$</th>
<th>$c$ (deg)</th>
<th>$\chi^2 - 2\chi \cos c + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.83</td>
<td>10.7</td>
<td>0.058</td>
</tr>
<tr>
<td>10</td>
<td>0.94</td>
<td>4.1</td>
<td>0.004</td>
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<tr>
<td>15</td>
<td>1.02</td>
<td>-1.9</td>
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<td>20</td>
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<tr>
<td>25</td>
<td>1.29</td>
<td>-17.2</td>
<td>0.199</td>
</tr>
<tr>
<td>30</td>
<td>1.45</td>
<td>-29.1</td>
<td>0.569</td>
</tr>
<tr>
<td>35</td>
<td>1.52</td>
<td>-42.6</td>
<td>1.073</td>
</tr>
<tr>
<td>40</td>
<td>1.55</td>
<td>-58.9</td>
<td>1.801</td>
</tr>
<tr>
<td>45</td>
<td>1.41</td>
<td>-77.2</td>
<td>2.363</td>
</tr>
<tr>
<td>50</td>
<td>1.23</td>
<td>-89.6</td>
<td>2.496</td>
</tr>
<tr>
<td>55</td>
<td>0.97</td>
<td>-103.9</td>
<td>2.407</td>
</tr>
<tr>
<td>60</td>
<td>0.81</td>
<td>-110.2</td>
<td>2.215</td>
</tr>
</tbody>
</table>

$K = 8650000$ dyne cm/rad

$\omega_0 = 13.8\text{Hz}$

(b)

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$\chi$</th>
<th>$c$ (deg)</th>
<th>$\chi^2 - 2\chi \cos c + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.37</td>
<td>34.5</td>
<td>0.527</td>
</tr>
<tr>
<td>10</td>
<td>0.51</td>
<td>26.7</td>
<td>0.349</td>
</tr>
<tr>
<td>15</td>
<td>0.61</td>
<td>20.6</td>
<td>0.230</td>
</tr>
<tr>
<td>20</td>
<td>0.70</td>
<td>15.6</td>
<td>0.142</td>
</tr>
<tr>
<td>25</td>
<td>0.81</td>
<td>10.3</td>
<td>0.062</td>
</tr>
<tr>
<td>30</td>
<td>0.93</td>
<td>3.9</td>
<td>0.009</td>
</tr>
<tr>
<td>35</td>
<td>1.09</td>
<td>-4.4</td>
<td>0.015</td>
</tr>
<tr>
<td>40</td>
<td>1.29</td>
<td>-14.8</td>
<td>0.170</td>
</tr>
<tr>
<td>45</td>
<td>1.51</td>
<td>-29.6</td>
<td>0.654</td>
</tr>
<tr>
<td>50</td>
<td>1.63</td>
<td>-50.4</td>
<td>1.579</td>
</tr>
<tr>
<td>55</td>
<td>1.57</td>
<td>-71.3</td>
<td>2.458</td>
</tr>
<tr>
<td>60</td>
<td>1.29</td>
<td>-89.5</td>
<td>2.642</td>
</tr>
</tbody>
</table>

$K = 50050000$ dyne cm/rad

$\omega_0 = 33.3\text{Hz}$
(c)

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>χ</th>
<th>c (deg)</th>
<th>χ²-2χcos(c+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.21</td>
<td>41.3</td>
<td>0.729</td>
</tr>
<tr>
<td>10</td>
<td>0.31</td>
<td>35.0</td>
<td>0.588</td>
</tr>
<tr>
<td>15</td>
<td>0.38</td>
<td>30.1</td>
<td>0.487</td>
</tr>
<tr>
<td>20</td>
<td>0.45</td>
<td>26.1</td>
<td>0.394</td>
</tr>
<tr>
<td>25</td>
<td>0.53</td>
<td>21.1</td>
<td>0.292</td>
</tr>
<tr>
<td>30</td>
<td>0.61</td>
<td>18.0</td>
<td>0.212</td>
</tr>
<tr>
<td>35</td>
<td>0.70</td>
<td>13.1</td>
<td>0.126</td>
</tr>
<tr>
<td>40</td>
<td>0.81</td>
<td>7.6</td>
<td>0.050</td>
</tr>
<tr>
<td>45</td>
<td>0.96</td>
<td>1.0</td>
<td>0.002</td>
</tr>
<tr>
<td>50</td>
<td>1.21</td>
<td>-10.7</td>
<td>0.086</td>
</tr>
<tr>
<td>55</td>
<td>1.44</td>
<td>-26.6</td>
<td>0.498</td>
</tr>
<tr>
<td>60</td>
<td>1.59</td>
<td>-48.6</td>
<td>1.425</td>
</tr>
</tbody>
</table>

\[ K = 96100000 \text{ dyne cm/rad} \quad (\omega_0 = 46.8\text{Hz}) \]
### TABLE 5.1

**VARIATION OF PHASE LAG WITH INPUT AMPLITUDE**

<table>
<thead>
<tr>
<th>Input Amplitude (rad)</th>
<th>Phase lag at 20°C (deg)</th>
<th>Phase lag at -5°C (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>25.1</td>
<td>6.1</td>
</tr>
<tr>
<td>0.008</td>
<td>25.3</td>
<td>6.5</td>
</tr>
<tr>
<td>0.010</td>
<td>25.9</td>
<td>6.5</td>
</tr>
<tr>
<td>0.012</td>
<td>26.0</td>
<td>6.8</td>
</tr>
<tr>
<td>0.014</td>
<td>26.4</td>
<td>7.0</td>
</tr>
<tr>
<td>0.016</td>
<td>26.4</td>
<td>7.2</td>
</tr>
<tr>
<td>0.018</td>
<td>26.7</td>
<td>7.4</td>
</tr>
<tr>
<td>0.020</td>
<td>26.5</td>
<td>7.5</td>
</tr>
<tr>
<td>0.022</td>
<td>26.7</td>
<td>7.6</td>
</tr>
<tr>
<td>0.024</td>
<td>27.0</td>
<td>7.7</td>
</tr>
<tr>
<td>0.026</td>
<td>27.0</td>
<td>7.8</td>
</tr>
<tr>
<td>0.028</td>
<td>27.2</td>
<td>8.1</td>
</tr>
<tr>
<td>0.030</td>
<td>27.0</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Data refer to the unfilled sample at 5Hz.
### TABLE 5.2

**DEPENDENCE OF AMPLITUDE RATIO AND PHASE LAG UPON TORSION BAR CONSTANT**

<table>
<thead>
<tr>
<th>Torsion Bar Constant (dyne cm/rad)</th>
<th>Amplitude Ratio</th>
<th>Phase Lag (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 650 000</td>
<td>0.797</td>
<td>5.5</td>
</tr>
<tr>
<td>50 050 000</td>
<td>0.369</td>
<td>34.5</td>
</tr>
<tr>
<td>96 100 000</td>
<td>0.207</td>
<td>41.3</td>
</tr>
<tr>
<td>2 202 000 000</td>
<td>0.003</td>
<td>49.7</td>
</tr>
</tbody>
</table>

Data refer to the unfilled sample at 5Hz and 0.006 rad input amplitude at 5°C.
### TABLE 5.3

**VARIATION IN AMPLITUDE RATIO AND PHASE LAG WITH FREQUENCY**

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Amplitude Ratio</th>
<th>Phase Lag (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.06</td>
<td>24.6</td>
</tr>
<tr>
<td>0.5</td>
<td>0.08</td>
<td>15.0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.09</td>
<td>11.7</td>
</tr>
<tr>
<td>5.0</td>
<td>0.10</td>
<td>7.0</td>
</tr>
<tr>
<td>10.0</td>
<td>0.11</td>
<td>5.8</td>
</tr>
<tr>
<td>50.0</td>
<td>0.13</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Data refer to the unfilled sample at -5°C and input amplitude 0.01 rad.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Relaxation Modulus</th>
<th>Relaxation Spectrum†</th>
<th>Observations on Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.J. Nutting J. Franklin Inst. 191 679 1921</td>
<td>$G_e \left[ 1+\left(\frac{t}{t_0}\right)^{-n} \right]$</td>
<td>$C_e \frac{\Gamma(n)}{\Gamma(n)} \left(\frac{\tau}{t_0}\right)^{-n}$</td>
<td>monotonic decreasing function of $\tau$</td>
</tr>
<tr>
<td>T.L. Smith J. Polym. Sci. Part C 35 39 1971</td>
<td>$G_e + \frac{G-G_e}{(1+t/t_0)^n}$</td>
<td>$C_e \frac{\Gamma(n)}{\Gamma(n)} \left(\frac{\tau}{t_0}\right)^{-n} e^{-t_0/\tau}$</td>
<td>precipitous positive gradient for small relaxation times</td>
</tr>
<tr>
<td>R.B. Bird, R.C. Armstrong O.Hassager 'Dynamics of Polymeric Liquids' Vol I. John Wiley &amp; Sons New York 1977</td>
<td>$\frac{2m}{\pi} \cos\left[\frac{\pi \tau}{2}\right] \Gamma(n) t^{-n}$</td>
<td>$(G-G_e) \sin(n\pi/2) \pi \left[ \cosh(n\ln(t/t_0)) + \cos(n\pi/2) \right]$</td>
<td>symmetrical function of log $\tau$</td>
</tr>
</tbody>
</table>

† Here $\Gamma(\ )$ is the gamma function and $H(\ )$ the Heavyside function.

**TABLE 5.4**

**ANALYTIC FORMS FOR RELAXATION SPECTRUM DERIVED FROM RELAXATION MODULUS**
# TABLE 5.5

HUET MODEL PARAMETERS

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G - G_e$ (dyne/cm²)</th>
<th>$\delta$</th>
<th>$\tau$ (sec)</th>
<th>h</th>
<th>k</th>
<th>$G_e$ (dyne/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled</td>
<td>1.05x10^10</td>
<td>1.01</td>
<td>0.0016</td>
<td>0.11</td>
<td>0.58</td>
<td>0.25x10^8</td>
</tr>
<tr>
<td>Filled</td>
<td>1.28x10^10</td>
<td>0.71</td>
<td>0.0430</td>
<td>0.26</td>
<td>0.59</td>
<td>1.50x10^8</td>
</tr>
<tr>
<td>CONSTITUTIVE EQUATION</td>
<td>$E'(\omega, \lambda)$</td>
<td>$E''(\omega, \lambda)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------------------</td>
<td>----------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chang, Bloch &amp; Tschoegl [5.09]</td>
<td>$\frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] E'(\omega)$</td>
<td>$\frac{2}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] E''(\omega)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sullivan [5.11]</td>
<td>$\frac{2E_e}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] + E'(\omega) - E_e$</td>
<td>$E''(\omega)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equation [5.19]</td>
<td>$\frac{2E_e}{3} \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] + \frac{2}{3} \left[ \lambda^m + \frac{\lambda^{-m/2}}{2} \right] [E'(\omega) - E_e]$</td>
<td>$\frac{2}{3} \left[ \lambda^m + \frac{\lambda^{-m/2}}{2} \right] E''(\omega)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schapery [5.25]</td>
<td>$\lambda \frac{d\sigma_e}{d\lambda} + \lambda^2 h_1(\lambda-1) \frac{d}{d\lambda} \left{ h_2(\lambda-1) \left( \lambda-1 \right) \right} [E'(\omega_e) - E_e]$</td>
<td>$\lambda^2 h_1(\lambda-1) \frac{d}{d\lambda} \left{ h_2(\lambda-1) \left( \lambda-1 \right) \right} E''(\omega_e)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 6.1**

INCREMENTAL DYNAMIC MODULI PREDICTIONS IN SIMPLE TENSION OF NON-LINEAR CONSTITUTIVE EQUATIONS
### RELAXATION SPECTRUM FUNCTION

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_1(\tau, \lambda) = A(m) \frac{dE'(\omega, \lambda)}{d \ln \omega} )</td>
<td></td>
</tr>
</tbody>
</table>
where \( A(m) = \frac{\sin(m\pi/2)}{m\pi/2} \) |

### WILLIAMS & FERRY RELAXATION SPECTRUM FORMULA

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H(\tau) = A(m) \frac{dG'(\omega)}{d \ln \omega} )</td>
<td></td>
</tr>
</tbody>
</table>
where \( A(m) = \frac{\sin(m\pi/2)}{m\pi/2} \) |

### RELAXATION SPECTRUM FUNCTION

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_2(\tau, \lambda) = B(m) \left[ E^n(\omega, \lambda) - \left( \frac{dE^n(\omega, \lambda)}{d \ln \omega} \right) \right] )</td>
<td></td>
</tr>
</tbody>
</table>
where \( B(m) = \frac{\sin[\pi(1+i\lambda)/2]}{\pi(1+i\lambda)/2} \) |

### WILLIAMS & FERRY RELAXATION SPECTRUM FORMULA

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H(\tau) = B(m) \left[ G^n(\omega) - \frac{dG^n(\omega)}{d \ln \omega} \right] )</td>
<td></td>
</tr>
</tbody>
</table>
where \( B(m) = \frac{\sin[\pi(1+i\lambda)/2]}{\pi(1+i\lambda)/2} \) |

### RELAXATION SPECTRUM FUNCTION

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{sr}(\tau, \lambda) = -M(m) \frac{d\sigma(t, \lambda)}{d \ln t} )</td>
<td></td>
</tr>
</tbody>
</table>
where \( M(m) = \frac{1}{\Gamma(m+1)} \) |

### WILLIAMS & FERRY RELAXATION SPECTRUM FORMULA

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H(\tau) = -M(m) \frac{dG(t)}{d \ln t} )</td>
<td></td>
</tr>
</tbody>
</table>
where \( M(m) = \frac{1}{\Gamma(m+1)} \) |

The above moduli and stress are measured in dyne/cm², time \( t \) and relaxation time \( \tau \) in seconds, and frequency \( \omega \) in rad/sec. \( m = -d\ln H/d\ln \tau \).

### TABLE 6.2

RELAXATION SPECTRUM FUNCTIONS AND THE CORRESPONDING WILLIAMS & FERRY RELAXATION SPECTRUM FORMULAE
<table>
<thead>
<tr>
<th>CONSTITUTIVE EQUATION</th>
<th>$F_1(\tau, \lambda)$</th>
<th>$F_2(\tau, \lambda)$</th>
<th>$F_{SR}(\tau, \lambda)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chang, Bloch &amp; Tschoegl [5.09]</td>
<td>$2 \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] H(\tau)$</td>
<td>$2 \left[ \lambda^n + \frac{\lambda^{-n/2}}{2} \right] H(\tau)$</td>
<td>$\frac{2}{n} \left[ \lambda^n - \lambda^{-n/2} \right] H(\tau)$</td>
</tr>
<tr>
<td>Sullivan [5.11]</td>
<td>$3H(\tau)$</td>
<td>$3H(\tau)$</td>
<td>$\frac{2}{n} \left[ \lambda^{m-n} - \lambda^{-m/2} \right] H(\tau)$</td>
</tr>
<tr>
<td>Equation [5.19]</td>
<td>$2 \left[ \lambda^m + \frac{\lambda^{-m/2}}{2} \right] H(\tau)$</td>
<td>$2 \left[ \lambda^m + \frac{\lambda^{-m/2}}{2} \right] H(\tau)$</td>
<td>$\frac{2}{m} \left[ \lambda^m - \lambda^{-m/2} \right] H(\tau)$</td>
</tr>
<tr>
<td>Schapery [5.25]</td>
<td>$3\lambda^2h_1(\lambda-1) \frac{d}{d\lambda} {h_2(\lambda-1)[\lambda-1]} H(\tau/a_x)$</td>
<td>$3\lambda^2h_1(\lambda-1) \frac{d}{d\lambda} {h_2(\lambda-1)[\lambda-1]} H(\tau/a_x)$</td>
<td>$3\lambda(\lambda-1)h_1(\lambda-1)h_2(\lambda-1)H(\tau/a_x)$</td>
</tr>
</tbody>
</table>

**TABLE 6.3**

SPECTRUM FUNCTION PREDICTIONS OF NON-LINEAR CONSTITUTIVE EQUATIONS
<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>Mode of Deformation</th>
<th>Stretch Ratio</th>
<th>Temp °C</th>
<th>Separability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagley &amp; Dixon</td>
<td>STYRENE-BUTADIENE 1502 with various types of carbon black fillers up to 50 phr loading</td>
<td>STRESS RELAXATION FOLLOWING UNIAXIAL EXTENSION</td>
<td>up to 2</td>
<td>22.7</td>
<td>/</td>
</tr>
<tr>
<td>Cotten &amp; Boonstra</td>
<td>BUTADIENE RUBBER STYRENE-BUTADIENE 1500 both containing up to 80phr of various blacks</td>
<td>STRESS RELAXATION FOLLOWING UNIAXIAL EXTENSION</td>
<td>up to 3.5</td>
<td>24</td>
<td>/</td>
</tr>
<tr>
<td>Djiau &amp; Gent</td>
<td>BUTADIENE-STYRENE 60:40 Ameripol 1513 POLYISOPRENE, both containing 50phr ISAF N220 carbon black</td>
<td>STRESS RELAXATION FOLLOWING UNIAXIAL EXTENSION</td>
<td>up to 2</td>
<td>23</td>
<td>/</td>
</tr>
<tr>
<td>Isono &amp; Ferry</td>
<td>STYRENE-BUTADIENE STYRENE BUTADIENE with 50phr N299 carbon black</td>
<td>STRESS RELAXATION FOLLOWING SHEAR</td>
<td>up to 1.077</td>
<td>25</td>
<td>/</td>
</tr>
<tr>
<td>Kawabata &amp; Kawai</td>
<td>JSR STYRENE BUTADIENE 1500 JSR STYRENE BUTADIENE 1500 with 40phr carbon black</td>
<td>STRESS RELAXATION FOLLOWING BIAXIAL EXTENSION</td>
<td>up to approx 1.7</td>
<td>23</td>
<td>/</td>
</tr>
<tr>
<td>McKenna &amp; Zapas</td>
<td>NBS 388j BUTYL RUBBER with 50phr NBS 378b HAF carbon black</td>
<td>STRESS RELAXATION FOLLOWING UNIAXIAL EXT. CREEP IN UNIAXIAL EXTENSION AND CYCLIC LOADING</td>
<td>up to 4</td>
<td>26</td>
<td>/</td>
</tr>
<tr>
<td>Sulllivan &amp; Demery</td>
<td>NATURAL RUBBER with 34.5phr N351 carbon black</td>
<td>STRESS RELAXATION FOLLOWING SIMPLE TENSION AND PURE SHEAR</td>
<td>up to 1.8</td>
<td>55</td>
<td>/</td>
</tr>
<tr>
<td>Sullivan</td>
<td>NATURAL RUBBER with approximately 46phr carbon black</td>
<td>STRESS RELAXATION FOLLOWING BIAXIAL EXTENSION</td>
<td>up to 2.5</td>
<td>55.7</td>
<td>/</td>
</tr>
<tr>
<td>Gent</td>
<td>NATURAL RUBBER with 54phr HAF carbon black BUTADIENE-STYRENE COPOLYMER 54phr HAF</td>
<td>STRESS RELAXATION IN UNIAXIAL EXTENSION * FOLLOWING 25% MOMENTARY EXTENSION CREEP IN UNIAXIAL EXTENSION</td>
<td>approx 3</td>
<td>Room</td>
<td>/</td>
</tr>
</tbody>
</table>

* SULLIVAN 1986 states that this loading should have been 46phr

1 One dimension held constant

**Table 6.4**

**TIME-STRAIN SEPARABILITY**
<table>
<thead>
<tr>
<th>REFERENCE</th>
<th>MATERIAL (loadings in pts per hundred by wt.)</th>
<th>MODE OF DEFORMATION</th>
<th>PLOT</th>
<th>SUPERPOSABLE</th>
<th>REDUCTION FACTOR</th>
<th>REF. TEMP. °C</th>
<th>HORIZONTAL SHIFT</th>
<th>VERTICAL SHIFT</th>
<th>TEMP. RANGE °C</th>
<th>STRETCH RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>COTTEN &amp; BOONSTRA J. Appl. Polym. Sci. 2 3395 1965</td>
<td>BUTADIENE RUBBER STYRENE-BUTADIENE 1500 both with up to 80% various blacks</td>
<td>STRESS RELAXATION IN UNIAXIAL EXTENSION</td>
<td>Force v. t</td>
<td></td>
<td></td>
<td>24</td>
<td></td>
<td></td>
<td>-9~80</td>
<td></td>
</tr>
<tr>
<td>MARTIN &amp; MALGUARNERA J. Elastomers &amp; Plastics 13 139 1981</td>
<td>TYRE STOCK</td>
<td>OSCILLATORY SHEAR</td>
<td>G',G'' v. \omega \tau</td>
<td>X</td>
<td>T/T₀</td>
<td>-</td>
<td>-</td>
<td>-63~21</td>
<td>up to 1.14</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 6.5**

TIME-TEMPERATURE SUPERPOSITION FOR FILLED ELASTOMERS UNDER NON-INFINITESIMAL STRAIN
### Experimental Apparatus

<table>
<thead>
<tr>
<th></th>
<th>Comments</th>
<th>$G''$ (dyne/cm²)</th>
<th>$G'$ (dyne/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheogoniometer</td>
<td>Sample scragged at experimental strain amplitude (ie. $&lt;0.003$, see §5.1)</td>
<td>$6.1 \times 10^6$</td>
<td>$2.2 \times 10^7$</td>
</tr>
<tr>
<td>Rheogoniometer</td>
<td>Sample scragged by imposing 100% extension, and mounted in rheo. after relaxing for approximately 30 min</td>
<td>$5.4 \times 10^6$</td>
<td>$1.9 \times 10^7$</td>
</tr>
<tr>
<td>Servohydraulic Testing Machine</td>
<td>Values estimated from tensile incremental dynamic moduli (see §7.2.3)</td>
<td>$5.0 \times 10^6$</td>
<td>$1.3 \times 10^7$</td>
</tr>
</tbody>
</table>

The above data relate to the unfilled material at a frequency of 1Hz and at room temperature.

**TABLE 7.1**

**COMPARISON OF DYNAMIC MODULI DERIVED FROM MEASUREMENTS ON A RHEOGONIOMETER AND SERVOHYDRAULIC TESTING MACHINE WITH SAMPLES SUBJECTED TO VARIOUS PRECONDITIONING PROGRAMMES**
<table>
<thead>
<tr>
<th></th>
<th>log H(τ) at 23°C (dyne/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>logτ (sec)</td>
</tr>
<tr>
<td>Linear Relaxation Spectrum (Shifted)</td>
<td>-0.65</td>
</tr>
<tr>
<td>Relaxation Spectrum Function Prediction (using [7.25])</td>
<td>-0.58</td>
</tr>
</tbody>
</table>

**TABLE 7.2**

**Comparison of Relaxation Spectrum Values Calculated from Linear and Non-Linear Data**
TABLE 7.3

COMPARISON OF DYNAMIC MODULI DERIVED FROM MEASUREMENTS ON A RHEOGONIOMETER AND SERVOHYDRAULIC TESTING MACHINE WITH SAMPLES SUBJECTED TO VARIOUS PRECONDITIONING PROGRAMMES
<table>
<thead>
<tr>
<th>log ( \tau ) (sec)</th>
<th>( \lambda )</th>
<th>(incremental) storage modulus data</th>
<th>(incremental) loss modulus data</th>
<th>Huet model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Relaxation Spectrum (Shifted)</td>
<td>-1.15</td>
<td>6.77</td>
<td>7.18</td>
<td>7.80</td>
</tr>
<tr>
<td>Relaxation Spectrum Function Prediction (using [7.25])</td>
<td>-0.80</td>
<td>5.13</td>
<td>7.31</td>
<td>7.60</td>
</tr>
</tbody>
</table>

**TABLE 7.4**

Comparison of relaxation spectrum values calculated from linear and non-linear data
Fig 2.1 Temperature Dependence of a Typical Polymer

- Glassy state
- Secondary transitions
- Glass transition region
- Rubbery plateau
- Rubbery flow
- Liquid flow
Fig 3.1 Time-temperature Superposition Schematic
Fig 4.1 ARRANGEMENT OF THE WEISSENBERG RHEOGONIOMETER
Fig 4.2 Mounting of Samples
Fig 4.3 Computer Control of Weissenberg Rheogoniometer
Fig 4.4 Temperature Chamber & Temperature Control System
Fig 4.5  Resonance Effects with different Torsion Bars

(a)  \( K = 8650000 \text{ dyne cm} / \text{rad} \)

(b)  \( K = 50050000 \text{ dyne cm} / \text{rad} \)

(c)  \( K = 96100000 \text{ dyne cm} / \text{rad} \)
Fig 4.5 Resonance Effects with different Torsion Bars

data refer to the unfilled sample at 5°C

(a) $G' \times 10^8 \text{ dyne/cm}^2$

Legend
- $G'$ EXPERIMENTAL
  - $K = 8650000 \text{ dyne cm/rod}$
  - $\omega_0 = 13.8 \text{ Hz}$

(b) $G' \times 10^8 \text{ dyne/cm}^2$

Legend
- $G'$ EXPERIMENTAL
  - $K = 50050000 \text{ dyne cm/rod}$
  - $\omega_0 = 33.3 \text{ Hz}$
Fig 4.5  Resonance Effects with different Torsion Bars

Data refer to the unfilled sample at 5°C

Legend

\( G' \) EXPERIMENTAL

\[
K = 96100000 \text{ dyne cm} / \text{ rad}
\]

\( \omega_0 = 46.8 \text{ Hz} \)
Fig 4.6 Resonance Effects at Different Temperatures

data refer to the unfilled sample at 0.01 rad. input amplitude.
Fig 5.1 Dynamic Moduli against Input Amplitude

data refer to the unfilled sample at 5 Hz.
Fig 5.2 Dynamic Moduli against Input Amplitude

data refer to the filled sample at 5 Hz.
Fig 5.3 Comparison of data at Fixed Amplitude & Fixed Frequency

data refer to the unfilled sample at 15°C and input amplitude 0.01 rad.
Fig 5.4 Composite Curves for the Unfilled Material Reduced to 2.5 °C
Fig 5.5 Composite Curves for Filled Material Reduced to 2.5°C

\[ \log G' \text{ dyne/cm}^2 \]

\[ \log \omega \text{ (Hz.)} \]

\[ \log G'' \text{ dyne/cm}^2 \]

\[ \log \omega \text{ (Hz.)} \]
Fig 5.6 WLF fit to manually determined shift factors for the Unfilled Material

Legend
× log \( a_T \) MANUAL
WLF Equation
Fig 5.7  WLF fit to manually determined shift factors for the Filled Material

Legend

\( \times \) \( \log a, \) MANUAL

WLF Equation
Fig 5.8 Modified Spriggs Model fit to data for the Unfilled Material

(a)  temp.= 20°C
(b)  temp.= 15°C
(c)  temp.= 10°C
Fig 5.8 Modified Spriggs Model fit to data for the Unfilled Material

(a)

\[ G'' \times 10^3 \text{dyn/cm}^2 \]

\[ \text{frequency Hz.} \]

temp. = 20°C; \( \alpha = 1.55 \); \( m = 1.86 \times 10^6 \ \text{dyne sec}^{-\alpha} \ \text{cm}^{-2} \)

\[ G = 2.99 \times 10^7 \ \text{dyne cm}^{-2} \]

Legend

- THEORY
- \( G' \) EXPERIMENTAL
- \( G'' \) EXPERIMENTAL

(b)

\[ G'' \times 10^3 \text{dyn/cm}^2 \]

\[ \text{frequency Hz.} \]

temp. = 15°C; \( \alpha = 1.53 \); \( m = 4.57 \times 10^6 \ \text{dyne sec}^{-\alpha} \ \text{cm}^{-2} \)

\[ G = 4.37 \times 10^7 \ \text{dyne cm}^{-2} \]
Fig 5.8 Modified Spriggs Model fit to data for the Unfilled Material

Legend

= THEORY  
O G' EXPERIMENTAL  
X G'' EXPERIMENTAL

temp. = 10°C; \( \alpha = 1.61 \); \( m = 1.29 \times 10^7 \) dyne sec\(^{-\alpha}\) cm\(^{-2}\)  
\( G = 4.13 \times 10^7 \) dyne cm\(^{-1}\)
Fig 5.9 Modified Spriggs Model fit to data for the Filled Material

Legend

- THEORY
- \( G' \) EXPERIMENTAL
- \( G'' \) EXPERIMENTAL

\[ G'' = 2 \times 10^8 \text{ dyne/cm}^2 \]

\[ G = 1.34 \times 10^8 \text{ dyne/cm}^2 \]

Temperature: \( 20^\circ \text{C} \);
\( \alpha = 2.01; m = 2.49 \times 10^7 \text{ dyne sec}^{-\alpha} \text{ cm}^{-2} \)

\[ G = 1.34 \times 10^8 \text{ dyne/cm}^2 \]

Temperature: \( 15^\circ \text{C} \);
\( \alpha = 2.12; m = 5.84 \times 10^7 \text{ dyne sec}^{-\alpha} \text{ cm}^{-2} \)

\[ G = 0.97 \times 10^8 \text{ dyne/cm}^2 \]
Fig 5.10 Chebyshev Polynomial fit to Composite Curve Data for the Unfilled Material

Legend

- Chebyshev Polynomial
Fig 5.11 Chebyshev Polynomial fit to Composite Curve Data for the Filled Material
Fig 5.12 Relaxation Spectrum for Unfilled Material at 2.5°C
Fig 5.13 Relaxation Spectrum for Filled Material at 2.5°C
Fig 5.14 Mechanical Representation of the Huet Model
Fig 5.15  Huet Model fit to Composite Curve Data for the Unfilled Material

Legend

- THEORY
Fig 5.16 Huet Model fit to Composite Curve Data for the Filled Material
Fig 5.17 Comparison with results of Jones & Davies

Data refer to the unfilled sample at 15°C
Fig 6.1 Cyclic Deformation History Schematic
Fig 7.1 Servohydraulic Testing Machine Schematic
Fig 7.2 Data Acquisition for Non-linear Experiments
Fig 7.3 Non-linear Experiments Schematic
Fig 7.4 Self-tightening Grips used in Non-linear Experiments
Fig 7.5 Quasi-equilibrium Stress against Extension Ratio for the Unfilled Material at 23°C
Fig 7.6 Sine of the Phase Angle against Frequency for the Unfilled Material at various extension ratios

Legend

- $\lambda = 1.08$
- $\lambda = 1.15$
- $\lambda = 1.33$
- $\lambda = 1.44$
- $\lambda = 1.72$
- $\lambda = 1.73$
- $\lambda = 1.83$
- $\lambda = 1.97$
Fig 7.7 Incremental Loss Modulus against Frequency for the Unfilled Material at various extension ratios

Legend

- $\lambda = 1.08$
- + $\lambda = 1.15$
- $\times \lambda = 1.33$
- @ $\lambda = 1.44$
- $\triangle \lambda = 1.72$
- $\times \lambda = 1.73$
- $\square \lambda = 1.83$
- $\bigcirc \lambda = 1.97$
Fig 7.8 Incremental Storage Modulus against Frequency for the Unfilled Material at various extension ratios
Fig 7.9 Incremental Dynamic Moduli against Extension Ratio for the Unfilled Material at 1 Hz.
Fig 7.10 Comparison of dependencies of $E''(\omega,\lambda)$ and $E'(\omega,\lambda)-\lambda d\sigma_e/d\lambda$ upon Extension Ratio for the Unfilled sample at 1 Hz.
Fig 7.11 Incremental Dynamic Moduli against Extension Ratio for the Unfilled Material at 0.1 Hz.

Legend

- $E'(\omega, \lambda)$
- $E''(\omega, \lambda)$
- THEORY

![Graph showing incremental dynamic moduli against extension ratio for the unfilled material at 0.1 Hz.](image)
Fig 7.12 Relaxation Spectrum Function $F_1(\tau, \lambda)$
for Unfilled Material at $23^\circ C$
Fig 7.13 Relaxation Spectrum Function $F_2(\tau, \lambda)$ for Unfilled Material at $23^\circ C$

Legend

- $\lambda = 1.08$
- $\lambda = 1.15$
- $\lambda = 1.33$
- $\lambda = 1.44$
- $\lambda = 1.72$
- $\lambda = 1.73$
- $\lambda = 1.83$
- $\lambda = 1.97$
Fig 7.14 Relaxation Spectrum Function $F_{sr}(\tau,\lambda)$ for Unfilled Material at $23^\circ$C

Legend

+ $\lambda = 1.15$
$\times \lambda = 1.33$
$\triangledown \lambda = 1.72$
$\star \lambda = 1.73$
$\square \lambda = 1.83$
Fig 7.15. Relaxation Spectrum Function $F_{s}\left(\tau,\lambda\right)$ against Extension Ratio at $\log\sigma=2.1$ sec. for Unfilled Material.
Fig 7.16 Quasi-equilibrium Stress against Extension Ratio for the Filled Material at 23°C
Fig 7.17  Sine of Phase Angle against Frequency for the Filled Material at various extension ratios

Legend

\( \triangle \lambda = 1.07 \)

\( + \lambda = 1.24 \)

\( \times \lambda = 1.45 \)

\( \circ \lambda = 1.61 \)

\( \triangledown \lambda = 1.73 \)

\( \times \lambda = 1.86 \)

\( \square \lambda = 2.13 \)
Fig 7.18 Incremental Loss Modulus against Frequency for the Filled Material at various extension ratios

Legend
- $\lambda = 1.07$
- $\lambda = 1.24$
- $\lambda = 1.45$
- $\lambda = 1.61$
- $\lambda = 1.73$
- $\lambda = 1.86$
- $\lambda = 2.13$
Fig 7.19 Incremental Storage Modulus against Frequency for the Filled Material at various extension ratios

Legend

△ λ = 1.07
+ λ = 1.24
× λ = 1.45
◊ λ = 1.61
▼ λ = 1.73
☆ λ = 1.86
□ λ = 2.13
Fig 7.20 Incremental Dynamic Moduli against Extension Ratio for Filled Material at 0.3 Hz.
Fig 7.21 Comparison of dependencies of $E''(\omega,\lambda)$ and $E'(\omega,\lambda)-\lambda d\sigma_\theta/d\lambda$ upon Extension Ratio for the Filled sample at 0.3 Hz.

Legend
- $E'(\omega,\lambda)-\lambda d\sigma_\theta/d\lambda$ RAPRA
- $E'(\omega,\lambda)-\lambda d\sigma_\theta/d\lambda$ Plymouth
- $E''(\omega,\lambda)$ RAPRA
- $E''(\omega,\lambda)$ Plymouth
Fig 7.22 Relaxation Spectrum Function $F_1(\tau, \lambda)$
for Filled Material at 23°C

Legend
- $\lambda = 1.07$
- $\lambda = 1.24$
- $\lambda = 1.45$
- $\lambda = 1.61$
- $\lambda = 1.73$
- $\lambda = 1.86$
- $\lambda = 2.13$
Fig 7.23 Relaxation Spectrum Function $F_2(\tau, \lambda)$ for Filled Material at 23°C

Legend
△ $\lambda = 1.07$
+ $\lambda = 1.24$
× $\lambda = 1.45$
○ $\lambda = 1.61$
▽ $\lambda = 1.73$
☆ $\lambda = 1.86$
□ $\lambda = 2.13$
Fig 7.24 Relaxation Spectrum Function $F_{sr}(\tau, \lambda)$ for Filled Material at 23°C

Legend

$\lambda = 1.07$

$\lambda = 1.24$

$\lambda = 1.45$

$\lambda = 1.61$

$\lambda = 1.73$

$\lambda = 1.86$

$\lambda = 2.13$
Fig 8.1 Comparison of dependencies of $E''(\omega, \lambda)$ and $E'(\omega, \lambda) - \lambda \sigma_0 / d\lambda$ upon Extension Ratio calculated from data of Meinecke & Maksin on a styrene–butadiene copolymer containing 50 phr. HAF
Fig 8.2 Comparison of dependencies of $E''(\omega, \lambda)$ and $E'(\omega, \lambda) - \lambda d\sigma_\theta/d\lambda$ upon Extension Ratio calculated from data of Meinecke & Maksin on an unfilled styrene–butadiene copolymer.
Fig 8.3 Comparison of dependencies of $E'(\omega, \lambda)$ and $E''(\omega, \lambda)$ upon Extension Ratio calculated from data of Sullivan & Demery on a natural rubber containing N351 carbon black in simple tension at 55°C.
Fig 8.4 Comparison of dependencies of $E''(\omega, \lambda)$ and $E'(\omega, \lambda) - \lambda d\sigma_e/d\lambda$
upon Extension Ratio calculated from data of Sullivan & Demery
on a natural rubber containing N351 carbon black in simple tension at 30°C
Fig 8.5 Model fits to Sullivan & Demery data on filled natural rubber in simple tension at 55°C
Fig 8.6 Model fit to Sullivan & Demery data on filled natural rubber in simple tension at 30°C.

Legend
- $E'(\omega, \lambda)$
- $E''(\omega, \lambda)$
- THEORY

Graph showing $E'(\omega, \lambda) \times 10^3$ dyne/cm$^2$ vs. $\lambda$. The graph includes data points and a theoretical line for comparison.
Fig 8.7 Model fit to Sullivan & Demery data on filled natural rubber in pure shear at 55°C
Fig A1.1 Elliptical Plots for the Determination of Incremental Dynamic Moduli
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