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MODELLING THE RHEOLOGICAL BEHAVIOUR OF ELASTOMERS AND ELASTOMER COMPOUNDS

by

MOHINDER SINGH, BSc (Hons), MSc

A Doctoral thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the Loughborough University of Technology

February 1990

Supervisor: Philip K. Freakley, PhD, FPRI

Institute of Polymer Technology and Materials Engineering

© by Mohinder Singh, 1990
Dedicated to my mother and to the memory of my beloved father

* * * * *
ACKNOWLEDGEMENTS

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- Members of the technical staff at IPTME for their cooperation during the course of this study.
- Dr Jane Butler and Dr David Southwart for proof reading this thesis,
- Mrs Janet Smith for offering her secretarial skills in preparing the thesis.
ABSTRACT

The purpose of this research project is to model the rheological behaviour of elastomers and elastomer compounds. Two elastomers (natural rubber, SMR 20 and chlorosulphonated polyethylene, Hypalon 40) and three different grades of carbon black at three different levels of loading were chosen for this study. Mixing was carried out with a Farrel Bridge BR Banbury mixer, followed by subsequent milling on a two-roll mill. Rheological measurements were made with parallel plate, cone and plate and Negretti biconical rotor TMS rheometers. The effect of temperature on viscosity was investigated by determining the activation energy of viscous flow in terms of concentration and surface area of carbon black.

Computer programs were developed to evaluate various parameters in the models by non-linear optimisation technique. The steady state flow behaviour of gum elastomers was fitted by the Bird-Carreau model and a thixotropic model. The thixotropic model was modified to non-Newtonian flow but proved to be intractable for fitting the rheological properties of mixed rubber compounds. Two new models for the viscosity and stress relaxation of filled compounds were then developed, which give very promising results.
NOTATION

A - Arbitrary constant in the Arrhenius equation
A - Area
$A_1, A_2, A_{11}, A_{22}, A_{12}$ - Parameters in the stress relaxation model
$B_1, B_2, B_{12}$ - Parameters in the stress relaxation model
b - Compressive stress relaxation rate
$C_{ij}$ - Finger deformation tensor
$C_p$ - Specific heat at constant pressure
C - Concentration
d_p - Average particle diameter
E - Activation energy of viscous flow
$\dot{e}_{ij}$ - Rate of deformation tensor
G - Shear modulus
$G_0$ - Parameter in the Doi and Edward model
$g^{ij}, g_{ij}$ - Components of the metric tensor
K - Parameter in the kinetic model
$K_{qv}$ - An average deformation rate in the Bogue model
$k$ - Parameter in the power law viscosity model
$M(t-t')$ - Mooney function
m - Parameter in the kinetic model
n - Parameter in the kinetic model
n - Power-law index
n' - Power law index for gum elastomers
Pa - Pascal
p - Parameter in the kinetic model
$Q_{ij}$ - Function in the Doi and Edward model
R  - Radius of cone or rotor
R  - Gas constant in Arrhenius equation
r  - Shear stress relaxation rate
S  - Compressive stress
T  - Temperature
T  - Torque
T_c - Torque at the rotor's surface
T_e - Torque at the rotor's edge
t  - Time
t'  - Past time
tr  - Trace of a matrix or tensor
U  - Strain energy function in the BKZ model
V_i,V_j - Velocity component in the i and j direction
X_1,X_2,X_3 - Cartesian coordinates
X  - Mean
Y  - Depth of the rotor edge
y  - Separation between parallel plates
Z(α) - Riemann-Zeta function

Special Operators
F  - Spriggs operator
\partial/\partial t - Convective derivative due to Oldroyd
\partial/\partial t - Jaumann derivative
Σ  - Summation symbol
I,II  - Invariants of rate of deformation tensor
Greek Symbols

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

Rheology is the science of deformation and flow of matter. A body is said to be deformed when application of an appropriate force system alters its shape or size. A body is said to flow when the degree of deformation changes with time. The flow properties and deformation of polymers are considerably important in plastic and rubber technology, since measurement of rheological properties gives some guidance in controlling processing behaviour and choosing appropriate processing conditions.

Elastomers are never used on their own in the rubber industry. Fillers are frequently added to elastomers to confer certain properties and to cheapen the product. Carbon black is probably the most important and most widely used filler in the rubber industry. Therefore, the flow behaviour of carbon black filled compounds is of obvious technological importance.

The purpose of this research project is to model the rheological behaviour of elastomers and elastomer compounds in order to enable us to characterise the detailed response of these materials to the wide range of conditions encountered in practical processing. The study is confined to the behaviour of these materials in steady shearing flow and to their transient response when shear is removed (i.e. shear stress relaxation).
Clearly this does not indicate how the material is going to behave in other states of flow, such as elongational flow. However steady shear flow can be achieved easily in the laboratory and approximates closely to such practical processes as extrusion. An investigation of the rheological properties of elastomer compounds in this state of flow is therefore relevant.
CHAPTER 2
FUNDAMENTALS OF RHEOLOGY

2.1 INTRODUCTION

As mentioned in Chapter 1, rheology is the science of deformation and flow of matter. Fundamentals of rheology are discussed in detail in various textbooks [1-8] and only the points relevant to the present study will be outlined here.

2.2 KINEMATICS AND STRESSES

2.2.1 Kinematics

A fluid responds to stress by flowing. Flow is a process in which material deforms at a finite rate. The basic kinematic measure of the response of a fluid is the rate of deformation tensor, $\dot{e}_{ij}$. Assuming a rectangular Cartesian coordinate system $x_1$, $x_2$, $x_3$, then the components of $\dot{e}_{ij}$ are [9-11]:

$$
\dot{e}_{ij} = \frac{1}{2} \left( \frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i} \right) \quad i, j = 1, 2, 3
$$

(2.1)

where $V_1$, $V_2$, $V_3$ etc are the velocity components in the $x_1$, $x_2$ and $x_3$ direction.
2.2.2 Stresses

The dynamic variable which causes or arises from deformation is the stress tensor $\tau_{ij}$. The components of $\tau_{ij}$ in rectangular Cartesians are:

\[
\tau_{ij} = \begin{pmatrix}
\tau_{11} & \tau_{12} & \tau_{13} \\
\tau_{21} & \tau_{22} & \tau_{23} \\
\tau_{31} & \tau_{32} & \tau_{33}
\end{pmatrix}
\] (2.2)

For $i,j = 1, 2, 3$ the component $\tau_{ij}$ is the force acting in the $x_j$ direction on unit area of a surface perpendicular to the $x_i$ direction. For example, $\tau_{21}$ is the stress acting in the $x_1$ direction on the surface element perpendicular to the $x_2$ direction and so on. The components of the stress tensor are illustrated graphically in Figure 2.1.

The components $\tau_{11}$, $\tau_{22}$ and $\tau_{33}$ are called normal stresses since they act normally to surfaces and the mixed components $\tau_{12}$, $\tau_{13}$ and so forth, are called shearing stresses. Since there will be no resultant couple acting on the element then it follows that the stress tensor is symmetric [10] i.e.

\[
\tau_{ij} = \tau_{ji}
\] (2.3)

Thus there are only 6 independent components of the stress tensor.
2.3 STEADY SIMPLE SHEAR FLOW

One can define [12] shear flow as a flow in which:

1. there is a one parameter family of material surfaces, the shearing surfaces, which move isometrically, that is the distance between any two neighbouring particles in the surface is constant; and
2. the volume of every fluid element is constant.

Now if we consider the flow of a fluid contained between two parallel plates, separated by distance y, the upper one of which moves with a constant velocity \( V_1 \) as shown in Figure 2.2:
upper plate moves with constant velocity $v_1$.

The velocity profile in the gap is given by:

$$v_1 = \dot{\gamma} x_2, \quad v_2 = 0, \quad v_3 = 0 \quad (2.4)$$

and

$$e_{ij} = \frac{1}{2} \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.5)$$

where the velocity gradient $\dot{\gamma}$ is constant and is called the shear rate. This class of flow is known as the steady simple shear flow. The class also includes steady axial flow in a tube, torsional flow between rotating discs and flow in rotational viscometers such as cone and plate.

Now if we assume that the material is isotropic, that is, it has no preferred direction other than one introduced by the flow itself, and if we assume that the stress depends only on the kinematics (i.e. motion of the fluid) then the stress field must have the same symmetry
as the flow field. Thus in simple shear flow we have \[9.12\]

\[
\tau_{13} = \tau_{31} = \tau_{23} = \tau_{32} = 0
\]  \hspace{1cm} (2.6)

Thus the stress tensor, equation 2.2 reduces to

\[
\tau_{ij} = \begin{pmatrix}
\tau_{11} & \tau_{12} & 0 \\
\tau_{21} & \tau_{22} & 0 \\
0 & 0 & \tau_{33}
\end{pmatrix}
\]  \hspace{1cm} (2.7)

In an incompressible material, the state of stress is determined by the strain or strain history. The absolute value of any one normal component of stress is of no rheological significance [4,9]. However, the values of the differences between normal stress components are not altered by the hydrostatic pressure and presumably only depend on the rheological properties of the material. It follows, therefore, that in steady shear flow there are only three independent stress quantities of rheological significance which are:

- Shear stress: \(\tau_{21}\)
- Primary Normal Stress difference: \(\tau_{11} - \tau_{22}\)
- Secondary Normal Stress difference: \(\tau_{22} - \tau_{33}\)

From now on the subscripts on the shear stress \(\tau_{21}\) will be dropped and it will be represented by \(\tau\) only.

7
2.4 STEADY SHEAR FLOW MATERIAL FUNCTIONS

Coleman, Markovitz and Holl [13] have shown that in steady simple shear flow all transient stresses have died out and the steady state stresses depend only on the shear rate \( \dot{\gamma} \). The components of stress tensor may then be expressed in terms of three independent functions:

\[
\begin{align*}
\tau &= \eta(\dot{\gamma}) \dot{\gamma} \\
(\tau_{11} - \tau_{22}) &= \psi_1 (\dot{\gamma}) \dot{\gamma}^2 \\
(\tau_{22} - \tau_{33}) &= \psi_2 (\dot{\gamma}) \dot{\gamma}^2
\end{align*}
\]  

(2.8) \quad (2.9) \quad (2.10)

where \( \psi_1 \) and \( \psi_2 \) are known, respectively, as the primary and secondary normal stress functions. Like the viscosity function \( \eta(\dot{\gamma}) \) (also called the non-Newtonian viscosity or shear rate dependent viscosity), \( \psi_1 (\dot{\gamma}) \) and \( \psi_2 (\dot{\gamma}) \) are said to be material functions which depend only on the particular fluid and not on particular flow. In other words \( (\tau_{11} - \tau_{22}) \), for example, will have a unique value at a specified shear rate (at a given temperature) irrespective of whether the flow is through a slit, capillary or annular die.

Since \( \eta(\dot{\gamma}) \), \( \psi_1 (\dot{\gamma}) \) and \( \psi_2 (\dot{\gamma}) \) completely determine the state of stress in any rheologically steady shear flow, they are sometimes called viscometric functions. The viscosity function \( \eta(\dot{\gamma}) \) is the best known, experimentally, of the viscometric functions. Some typical plots of \( \eta(\dot{\gamma}) \) are shown in Figure 2.3 for a polymer melt. At low shear rates, the shear stress is proportional to \( \dot{\gamma} \), and the viscosity approaches a constant value \( \mu \), the zero-shear-rate viscosity. At higher shear rates the viscosity decreases with increasing shear rate.
For many engineering applications, this is the most important characteristic of polymeric fluids; almost all polymeric materials show this shear thinning or pseudoplastic behaviour. When plotted as log $n$ vs log $\dot{\gamma}$, the viscosity vs shear rate curve exhibits a pronounced linear region at high shear rates - often called the "power-law" region.

Finally at very high rates of shear the viscosity may again become independent of shear rate and approach $n_\infty$, the infinite-shear-rate viscosity. For melts, $n_\infty$, is not usually measurable since polymer degradation becomes a serious problem before sufficiently high shear rates can be obtained. However, in the case of polymer melts, $n_\infty$ is
generally very small compared with $\mu$ and is not an important material constant [14].

Since it is not possible to measure normal stresses in our laboratory, $\psi_1$ and $\psi_2$ will not be discussed any further in the present study.

2.5 TRANSIENT BEHAVIOUR IN SIMPLE SHEAR FLOW

So far we have only considered the steady state flow behaviour in which stresses are time-independent. Now we will consider an experiment in which stress is dependent on time as well as on the shear rate.

2.5.1 Stress Relaxation After Cessation of Steady Shear Flow

In this experiment (Figure 2.4) the fluid is first made to undergo steady shear flow with shear rate $\dot{\gamma}_o$ for $t < 0$. The constant shear rate has to be started sufficiently long before $t = 0$ so that the steady state stress has been achieved. Then at $t = 0$, the flow is stopped instantaneously so that $\dot{\gamma} = 0$ for $t > 0$. One can then observe the manner in which stress, $\tau(t)$ decays.

![Stress Relaxation Diagram](image)

**FIGURE 2.4: STRESS RELAXATION AFTER CESSATION OF STEADY SHEAR FLOW**
The time profile of a stress relaxation experiment is shown in Figure 2.5.

FIGURE 2.5: TIME PROFILE OF A SIMPLE SHEAR STRESS RELAXATION EXPERIMENT FOLLOWING CESSATION OF STEADY STATE

2.6 CONSTITUTIVE EQUATIONS

The relationships between stress strain (or strain rate) and time, when expressed mathematically, are known as constitutive equations or rheological equations of state.
3.1 CLASSIFICATION OF FLOW BEHAVIOUR [6-8]

3.1.1 The Ideal (Elastic) Solid

The ideal elastic solid obeys Hooke's law, i.e. stress in it is proportional to the strain. Thus for shear, one can write:

\[ \tau = G \gamma \]  

(3.1)

where \( \tau \) = shear stress  
\( G \) = shear modulus  
\( \gamma \) = shear strain

The behaviour of an ideal elastic solid is described by Figure 3.1. In Figure 3.1a a stress is applied at time \( t_1 \), a strain occurs instantaneously and remains constant until the stress is removed at time \( t_2 \). At this moment the strain also drops to zero. Figure 3.1b shows equation 3.1 graphically, the slope being equal to the modulus.

FIGURE 3.1: (a) STRESS-TIME AND STRAIN-TIME RELATIONSHIPS FOR AN IDEAL SOLID  
(b) STRESS-STRAIN RELATIONSHIPS FOR AN IDEAL SOLID

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3.1.2 Viscous Flow

Viscous flow can be sub-divided into Newtonian and non-Newtonian flow.

3.1.2.1 Newtonian flow

Whereas an ideal elastic solid produces an elastic displacement when a shear stress is applied, a fluid produces viscous flow. Newtonian flow implies that the shear stress is directly proportional to shear rate.

\[ \tau = \mu \gamma \]  (3.2)

where \( \mu \) = Newtonian viscosity (independent of shear rate).

Figure 3.2a shows the stress-time and strain-time relationships for a Newtonian fluid. Figure 3.2b shows the effect of plotting shear stress against shear rate for such a fluid, the slope in this case being the Newtonian viscosity.

FIGURE 3.2: (a) STRESS-TIME AND STRAIN-TIME RELATIONSHIPS FOR NEWTONIAN FLUID
(b) SHEAR STRESS vs SHEAR RATE RELATIONSHIP FOR NEWTONIAN FLUID
3.1.2.2 Non-Newtonian flow

The viscosity of Newtonian fluids is constant irrespective of the shear rate, and is independent of time. Many real materials, particularly polymer melts and elastomers do not, however, exhibit the simple characteristics of a Newtonian fluid. The deviation from Newtonian behaviour is usually taken as the criterion of classification. Thus time independent fluids are classified as pseudoplastic (when the shear viscosity decreases with increasing shear rate), dilatant (shear viscosity increasing with shear rate) or Bingham (if a yield stress is present below which the material does not flow) - see Figure 3.3.

\[ \tau = \eta(\dot{\gamma}) \dot{\gamma} \]  

(3.3)

Almost all polymer melts show pseudoplastic behaviour and there are no common polymers that show the dilatant behaviour [15].

Viscosity varies with shear rate, unlike the Newtonian viscosity and therefore cannot be described by a single constant viscosity. In this case one defines apparent viscosity, \( \eta \), at a given shear rate as:

\[ \tau = \eta(\dot{\gamma}) \dot{\gamma} \]

(3.3)
Another concept of classification is based on the time dependence of the material showing thixotropy (Figure 3.4). Thixotropy is defined as the recoverable change in flow behaviour which occurs with time or magnitude of flow. Thixotropic materials have an inherent structure which breaks down with applied shear leading to a decrease in viscosity with time. Rheopectic fluids show the reverse behaviour. In the past it was often assumed that polymer melts were time-independent but now there is enough evidence to suggest that disentanglement of molecules during shear causes time-dependent effects [8].

Polymeric materials can also show irreversible time dependent behaviour which occurs when some of the structure is permanently destroyed, for example during mastication and mixing.

![Diagram showing viscosity-time relationship for materials with time dependent structure](image)

**FIGURE 3.4: VISCOSITY-TIME RELATIONSHIP FOR MATERIALS WITH TIME DEPENDENT STRUCTURE**
3.1.3 Viscoelastic Behaviour

Elastomers are termed "Viscoelastic" fluids because they are neither purely elastic nor purely viscous but exhibit both viscous and elastic properties. In a purely elastic solid the stress corresponds to a given strain and is independent of time, whereas for viscoelastic substances the stress will gradually dissipate. In contrast to purely viscous liquids on the other hand, viscoelastic fluids flow when subjected to stress but part of their deformation is gradually recovered upon removal of stress.

The theory of viscoelasticity is covered in great detail in various textbooks [7,16,17].

3.2 DEPENDENCE OF VISCOSITY ON TEMPERATURE

3.2.1 Temperature Dependence of Newtonian (Zero-Shear) Viscosity

The flow behaviour of a Newtonian fluid depends on viscosity, which is a function of temperature only. The dependence of viscosity on temperature can be described by the well known Arrhenius equation [2]:

$$\mu = A \cdot e^{E/RT}$$  \hspace{1cm} (3.4)

where $A$ = arbitrary constant depending on the nature of the fluid
$E$ = activation energy of viscous flow
$R$ = gas constant (8.314 J/K.mol)
$T$ = absolute temperature.
Newtonian viscosity $\mu$ is independent of shear rate. Thus if a plot of $\log \mu$ vs $1/T$, when $\mu$ is obtained at different shear rates, is a straight line then that would indicate that we are in the Newtonian region. This fact should help us later in identifying zero-shear viscosity.

3.2.2 Temperature Dependence of non-Newtonian Viscosity

Unlike $\mu$, the non-Newtonian viscosity $\eta$ is a function of shear rate as well as a function of temperature. This is expressed by the functional equation:

$$\eta = \eta(\gamma, T)$$  \hfill (3.5)

Assuming that the temperature dependence of $\eta$ can be expressed through an equation of the form of the Arrhenius equation (equation 3.4), we have:

$$\eta = A \cdot e^{E_\gamma/RT}$$  \hfill (3.6)

where $E_\gamma$ = activation energy of viscous flow at a constant shear rate

Philippoff and Gaskins [18] determined the values of $E_\gamma$ at various shear rates for a polyethylene in the range of 108°C to 230°C. They found that the value of $E_\gamma$ decreased with increasing shear rate.
3.3 MODELS DESCRIBING THE RHEOLOGICAL BEHAVIOUR OF ELASTOMERS

3.3.1 Viscous Models

Various viscous models are cited in the literature [2,5], however only the few more useful ones will be discussed below.

a) Power Law

One of the simplest and most widely used models, portraying pseudoplasticity, is the so called "Power Law" model proposed by Ostwald de Waele [see Ref. 19]. In this model the viscosity, \( \eta \) is given by:

\[
\eta = k \sqrt{\dot{\gamma}^{n-1}} \tag{3.7}
\]

where \( k (\text{Pa.s}^n) \) and dimensionless \( n \) are taken to be constants characteristics of each polymer, commonly called the consistency constant and power law index respectively. Since \( n \) is less than unity for pseudoplastic materials, the power law predicts an infinite viscosity in the limit of vanishing shear rate. This, of course, is not observed in real fluids and is a drawback to the usefulness of the power law.

b) The Bingham Fluid [19]

This model describes the rheological response of lattices such as polymer emulsion systems used in "no drip" paints, and of pastes and slurries that are common rheological materials in the food processing industry.
The Bingham fluid is a deforming solid below a characteristic yield stress $\tau_y$ and a flowing fluid above it,

$$\eta = \infty \quad \tau \leq \tau_y \quad (3.8)$$

$$\eta = \eta_0 + \frac{\tau}{\dot{\gamma}} \quad \tau > \tau_y \quad (3.9)$$

The model thus has two parameters: $\tau_y$ with dimensions of stress (Pa) and $\eta_0$ with dimensions of viscosity (Pa·s).

c) Ellis Model [see Ref 20]

This model expresses viscosity in terms of the shear stress

$$\frac{\eta_0}{\eta} = 1 + \left( \frac{\tau}{\tau_{1/2}} \right)^{\alpha-1} \quad (3.10)$$

where $\eta_0$ is the zero-shear viscosity

$\tau_{1/2}$ is the value of the shear stress at which $\eta = \eta_0/2$

and $\alpha - 1$ is the slope of the curve $\log\left(\frac{\eta_0}{\eta}\right)$ vs $\log \left(\tau/\tau_{1/2}\right)$

The $\alpha$ in this model is equivalent to the $1/n$ in equation 3.7. This model is more difficult to use than the power law but is superior to it, since it predicts a Newtonian plateau at very low shear rates.

3.3.2 Thixotropic Models

Various thixotropic models have been reported in the literature in the past [21-23] but only the model proposed by Broaddock and co-workers [24-27] will be discussed in this work because of its simplicity.
Brodkey and co-workers developed a kinetic model for thixotropic materials which is descriptive of the viscosity change that occurs in polymer solutions. The kinetic theory has as its basis the assumption that the non-linear characteristics can be associated with some structural change of the material whether it involves particle associations and dissociations, link formations and ruptures or molecular entanglements and disentanglements.

The model is different from previous rate models in that molecular phenomena such as links, particle spheres, dipole moments, or hydrogen bonding are not used directly as the basis of the model. Instead it used a lumped parameter, FT, which can describe any or all or these phenomena. The subscript T denotes the thixotropic property. They defined the property FT as:

\[ F_T = \frac{\eta_T - \eta^a}{\mu - \eta^a} \]  \hspace{1cm} (3.11)

FT is the fraction of the internal fluid structure unchanged and \((1-F_T)\) is the fraction of the internal fluid structure changed. The viscosity terms, \(\mu\) and \(\eta_\infty\), are the lower and upper Newtonian viscosity limits respectively. They emphasised that \(\eta_T\) is a hypothetical viscosity associated with the changing structure. The term \(F_T\) is a convenient measure of this structure. They referred to the letter \(a\) in equation 3.11 as a structure parameter and for polymer solutions they took its value as \(1/3.5\).
The simplest differential rate equation to describe the transient change in $F_T$ is:

$$\frac{d(CF_T)}{dt} = k_1 \tau^P_1 (F_T C)^m - k_2 \tau^P_2 ((1 - F_T) C)^n \quad (3.12)$$

where $m$ and $n$ are forward and reverse orders of the reaction while $C$ is the concentration. The $k$'s and $P$'s are specific rate and susceptibility to stress constants, respectively.

At steady state the net rate of change of structure equals to 0 i.e. rate of structural breakdown equals the rate of structural formation and then equation 3.12 becomes:

$$k_1 \tau^P_1 (F_T C)^m = k_2 \tau^P_2 ((1 - F_T) C)^n \quad (3.13)$$

rearranging equation 3.13 gives:

$$\tau^P_1 - \frac{P_2}{k_1} = \frac{k_2}{k_1} \frac{((1 - F_T) C)^n}{(F_T C)^m} \quad (3.14)$$

Equation 3.14 is for steady state flow behaviour and can be used to describe the shear thinning (pseudoplastic behaviour).
3.3.3 Comments on Viscous and Thixotropic Models

The models discussed so far in Sections 3.3.1 and 3.3.2 are capable of describing steady state flow only. One cannot construct a "time-constant" from these models; this is a serious drawback if one wishes to tie together steady state flow phenomena with transient viscoelastic phenomena, for the description of which a characteristic time constant is necessary. Therefore it is apparent that if we want to describe transient behaviour, for example 'stress relaxation', then we need to look at models of a different class; i.e. viscoelastic models.

3.3.4 Viscoelastic Models

For viscoelastic fluids, two types of rheological equations of state have been developed, namely the differential type and the integral type. The former involves an explicit time derivative of stress and the latter an integral of the deformation history.

Reviews of several viscoelastic models are given by Spriggs, Hupler and Bird [28], Bogue and Doughty [29], Hupler et al [30], Tanner [31], Chen and Bogue [32], Han [9], Bird et al [12,33] and Tadmor and Gogos [19], however they will be reviewed again briefly in the present study.

3.3.4.1 Differential models

As discussed earlier in this Chapter, one can divide materials into elastic solids, where stress depends upon strain, or viscous fluids, where the stress depends solely on the rate of strain. Elastomers, however, respond to stress as if they were fluids with memory. The
material deforms continuously under the application of shear stress but exhibits elastic recoil upon release of stress; and exhibits stress relaxation if the flow is halted. Such viscoelastic materials, for which stress and strain have a linear relationship, are termed "linear viscoelastic". The idea of materials with incomplete memory was first discussed by Maxwell in 1866 [see Ref 10].

The Maxwell model consists of a spring with constant $G$, called the elastic modulus and a dashpot containing a viscous liquid with viscosity (i.e. as a Newtonian fluid) in series as shown in Figure 3.5.

![Diagram of Maxwell model](image)

**FIGURE 3.5: SPRING-DASHPOT MAXWELL MODEL**
The total strain, $\gamma$, in this model is the sum of strain in the spring and the strain in the dashpot:

$$\gamma = \frac{\tau}{G} + \int \frac{\tau}{\mu} \, dt$$  \hspace{1cm} (3.15)

Differentiating the above equation gives:

$$\frac{d\gamma}{dt} = \frac{1}{G} \frac{d\tau}{dt} + \frac{\tau}{\mu}$$ \hspace{1cm} (3.16)

Noting that $\frac{d\gamma}{dt} = \dot{\gamma}$, and rearranging the equation (3.16):

$$\tau + \frac{\mu}{G} \frac{d\tau}{dt} = \mu \dot{\gamma}$$ \hspace{1cm} (3.17)

Here $\mu/G$ has the dimension of time and is known as relaxation time $\lambda_1$.

$$\tau + \lambda_1 \frac{d\tau}{dt} = \mu \dot{\gamma}$$ \hspace{1cm} (3.18)

Equation 3.18 can be generalised to a three-dimensional form to give:

$$\tau_{ij} + \lambda \frac{\partial \tau_{ij}}{\partial t} = 2 \mu \mathbf{e}^{\dot{ij}}$$ \hspace{1cm} (3.19)
where \( \tau_{ij} \) is the stress tensor defined by equation 2.2 and \( \varepsilon_{ij} \) is the rate of deformation tensor defined by equation 2.1.

Equation 3.19 is called the classical Maxwell mechanical model and it is capable of qualitatively explaining viscoelastic phenomena, such as stress relaxation. However, use of equation 3.19 is limited to infinitesimally small deformations and also it is incapable of predicting either non-Newtonian viscosity or normal stress effects. Therefore, in order to describe non-linear viscoelastic phenomena (i.e. non-Newtonian viscosity, normal stress effects), equation 3.19 must be modified.

To modify equation 3.19 attempts were made to introduce different types of derivative of a stress (or a strain) with respect to time in place of partial derivatives \( \partial / \partial t \). They are the convected derivative due to Oldroyd [34] and the Jaumann derivative [35,36]. These are "time" derivatives that transform a tensor from convected or rotational to fixed coordinates.

For any second-order tensor (say \( \tau_{ij} \) for example), the convected derivative, \( \partial / \partial t \), is defined as [5,9]:

\[
\frac{\partial \tau_{ij}}{\partial t} = (\frac{\partial \tau_{ij}}{\partial t}) \ast \partial_{k} \partial_{l} \varepsilon_{kl} + \varepsilon_{ij} \frac{\partial \varepsilon_{kl}}{\partial x_{k}} + \varepsilon_{ik} \frac{\partial \varepsilon_{lj}}{\partial x_{l}} + \varepsilon_{ik} \frac{\partial \varepsilon_{lj}}{\partial x_{j}} \tag{3.20}
\]

for a covariant component of the tensor, and
for a contravariant component of the tensor.

For a second-order tensor the Jaumann derivative, $\partial/\partial t$, is defined as [5,9]:

$$\frac{\partial T_{ij}}{\partial t} = \left( \frac{\partial T_{ij}}{\partial t} \right) + v_k \left( \frac{\partial T_{ij}}{\partial x_k} \right) - \tau_{ik} \left( \frac{\partial V_i}{\partial x_k} \right) - \tau_{ik} \left( \frac{\partial V_k}{\partial x_i} \right)$$

(3.21)

Using the Jaumann derivative, Dewitt [35] generalised the equation 3.19 to give:

$$\tau_{ij} + \lambda_1 \left( \frac{\partial T_{ij}}{\partial t} \right) = 2\mu \varepsilon_{ij}$$

(3.24)

Equation 3.24 is capable of predicting shear-dependent viscosity as well as normal stress effects.

Also using the Jaumann derivative and by including second-order cross terms, Oldroyd [36] suggested the following form of rheological model:
\[
\tau_{ij} + \lambda_1 \left( \frac{\partial \tau_{ij}^T}{\partial t} \right) - \nu_1 \left( \tau_{ij} \delta_{ij} + \epsilon_{ij} \tau_{ij} \right) + \mu_0 \left( \text{tr} \tau_{ij} \right) \dot{\epsilon}_{ij} + \nu_1 \left( \text{tr} \tau_{ij} \right) \epsilon_{ij} \delta_{ij}
\]

\[
= 2 \mu \left( \epsilon_{ij} + \lambda_2 \frac{\partial \epsilon_{ij}}{\partial t} \right) - 2 \mu_2 \epsilon_{ij}^2 + \nu_2 \left( \text{tr} \epsilon_{ij} \right) \delta_{ij} \right) \tag{3.25}
\]

where \( \lambda_1, \mu_1, \mu_0, \nu_1, \mu, \lambda_2, \mu_2 \) and \( \nu_2 \) are constants.

\( \delta_{ij} \) is a unit tensor

\( \text{tr} \) is the trace of a matrix or tensor.

This model is also capable of predicting non-Newtonian viscosity and normal stress effects. However, it has the disadvantage of having eight material constants whose values cannot be determined uniquely from simple experiments.

White and Metzner [37] suggested the generalisation of the classical Maxwell model (equation 3.19), using convected derivatives (defined by equations 3.20 and 3.21), of the following form:

\[
\tau_{ij} + \lambda_1 \frac{\partial \tau_{ij}^T}{\partial t} = 2 \mu \left( \epsilon_{ij} + \lambda_2 \frac{\partial \epsilon_{ij}}{\partial t} \right) \tag{3.26}
\]

This model predicts a non-zero first normal stress function, however it is incapable of predicting non-Newtonian viscosity.

In 1962, Williams and Bird [38] modified the eight constant Oldroyd model (equation 3.25) by imposing the following conditions:
i) \[ \lambda_1 = \mu_1 \]

ii) \[ \nu_2 = \frac{2}{3} \lambda_1 \]

iii) \[ \lambda_2 = \mu_2 \]

iv) \[ \nu_2 = \frac{2}{3} \lambda_2 \]

v) \[ \nu_0 = 0 \]

and they obtained the following form of Oldroyd three-constant model:

\[
\tau_{ij} + \lambda_1 \left( \frac{\partial \tau_{ij}}{\partial t} - \tau_{ij} \ddot{e}_{ij} - \dot{e}_{ij} \tau_{ij} + \frac{2}{3} [\text{tr} \tau_{ij} \dot{\varepsilon}_{ij}] \varepsilon_{ij} \right)
\]

\[
= 2\mu \left( \ddot{e}_{ij} + \lambda_2 \left( \frac{\partial \dot{e}_{ij}}{\partial t} - 2 \dot{e}_{ij} \ddot{e}_{ij} + \frac{2}{3} [\text{tr} \dot{e}_{ij}^2] \varepsilon_{ij} \right) \right) \quad (3.27)
\]

Equation 3.27 predicts non-Newtonian viscosity and the first normal stress function but it gives the second normal stress function as zero.

The classical Maxwell model (equation 3.19) was derived by using a single "spring and dashpot" (Figure 3.5). However polymeric materials cannot be described by such a simple representation because of the complexity of the molecular structure [9]. One way of generalising the Maxwell model from the point of view of molecular structure is motivated by the idea that the total stress, \( \tau_{ij} \) in the material can be considered as the superposition of individual stresses, \( \tau_{ij}^P \), each arising from different modes of motion or from the motion of molecular segments of various sizes. Thus equation 3.19 may be generalised as:
\[ \tau_{ij}^p + \lambda_p \sum_{j=1}^{\infty} \tau_{ij}^p = \eta_p \epsilon_{ij} \]  

(3.28)

where
\[ \tau_{ij} = \sum_{p=1}^{\infty} \tau_{ij}^p \]  

(3.29)

here \( \tau_{ij}^p \) is the stress of the \( p \)th mode and \( \lambda_p \) and \( \eta_p \) are material constants of the corresponding mode. Equation 3.18, however, still fails to exhibit non-linear viscoelastic phenomena.

In 1965, Spriggs [39] proposed a non-linear extension of the equation 3.18 of the form:

\[ \tau_{ij}^p + \lambda_p \mathcal{F} \tau_{ij}^p = 2 \eta_p \epsilon_{ij} \]  

(3.30)

where
\[ \lambda_p = \frac{\lambda}{p^\alpha} \]  

(3.31)

\[ \eta_p = \mu \frac{\lambda_p}{p^\alpha} = \frac{\mu}{p^\alpha Z(\alpha)} \]  

(3.32)

\[ Z(\alpha) = \sum_{p=1}^{\infty} p^{-\alpha} \]  

(3.33)

here \( Z(\alpha) \) is called the Riemann Zeta function and Spriggs defined the operator \( \mathcal{F} \) as:
Spriggs model has four arbitrary constants: \( n_0, \lambda, \alpha \) and \( \tau \) and it predicts non-Newtonian viscosity, \( \eta(Y) \) and both the first \( (\psi_1) \) and second \( (\psi_2) \) normal stress functions.

In response to the use of differential models, Tanner and Simmons [40] have reported that differential models give rise to instabilities when computer solutions are attempted.

### 3.3.4.2 Integral models

The generalised Maxwell model (equation 3.28) in integral form can be written as follows [9,12]:

\[
\mathbf{T}_{ij}^P = \mathbf{D}_{ij}^P - (1 + \varepsilon)(\dot{e}_{ij}^P \mathbf{P}_{ij} + \mathbf{P}_{ij} \dot{e}_{ij}^P - \frac{2}{3} [\text{tr} (\mathbf{P}_{ij} \dot{e}_{ij}^P) \delta_{ij}]) \tag{3.34}
\]

Here \( \mathbf{D}_{ij}^P \) and \( \mathbf{P}_{ij} \) are constants with dimensions of time and viscosity respectively; \( t \) is the current time; \( t' \) denotes past time and \( e_{ij} \) is deformation tensor. Equation 3.35 can be obtained by integrating equation 3.28 which is a first order differential equation and equation 3.36 is obtained next by performing an integration by parts. The function in brackets in equation 3.35 is called the "relaxation
function" and that in equation 3.36 is termed the "memory function", $M$. Thus equation 3.36 can be written:

$$
\tau_{ij} = 2 \int_{-\infty}^{t} M(t-t') \epsilon_{ij}(t') \, dt'
$$

(3.37)

Equation 3.37 is also called the "general linear viscoelastic model". Independent of the development of rheological models from the point of view of mechanical response, Lodge [41,42] proposed an integral model, based on molecular theories involving the concept of entanglement networks, of the following form:

$$
\tau_{ij} = \int_{-\infty}^{t} M(t-t') \bar{F}_{ij}^{\infty}(t,t') \, dt'
$$

(3.38)

Here $M(t-t')$ is the memory function of the following form:

$$
M(t-t') = \sum_{p=1}^{N} \frac{G_p}{\lambda_p} e^{-\frac{(t-t')}{\lambda_p}}
$$

(3.39)

where $G_p$ and $\lambda_p$ are material constants.

$\bar{F}_{ij}$ in equation 3.38 is called the finite strain tensor and it is defined as [9]
where \( \delta_{ij} \) is the metric tensor; \( x \) and \( X \) are the coordinates of points at present time \( t \) and past time \( t' \) respectively.

The Lodge network model predicts that the viscosity and first normal stress function, in steady shear flow, are independent of shear rate. These predictions are due to the fact that during formulation of his theory Lodge assumed that the rates of creation and loss of network junctions are independent of the flow history.

Non-linear theory, that capable of predicting non-Newtonian viscosity and normal stress functions, involves somehow making the memory functions depend on the strain history. Bogue [43] suggested an integral model of the form:

\[
\tau_{ij} = \int_{-\infty}^{t} M(t-t', II(t')) \tau_{ij} \, dt' \ + \text{double integral term} \quad (3.41)
\]

where

\[
M(t-t', II(t')) = \sum_{p=1}^{\infty} \frac{G_p}{\lambda_p^{\text{eff}} e^{p(t-t')}}
\quad (3.42)
\]

\( \lambda_p^{\text{eff}} \), an effective time constant, is assumed to be a function of the second invariant of the rate of deformation tensor, \( II (= \varepsilon_{ij} \varepsilon_{ij}) \)
\[ \lambda_{\text{eff}} = \frac{\lambda_p}{1 + aK_{av}\lambda_p} \]  
(3.43)

\[ K_{av} = \frac{\int_{t-t'}^{0} |\mathbf{I}(t'')|^{1/2} \, dt''}{\int_{t-t'}^{0} \, dt''} \]  
(3.44)

An average deformation rate

Here \( t'' \) is a backward running time index and \( a \) is a constant. The double integral term in equation 3.41 is used to give a non-zero second normal stress function.

Having realised that double integral is much more difficult to perform than single integral, Bogue and White [see Ref 32] proposed an integral model of the form

\[ \mathbf{T}_{ij} = \int_{-\infty}^{t} \left[ M_1 (t-t', \mathbf{II}(t')) C_{ij} - M_2 (t-t', \mathbf{II}(t')) C_{ij} \right] dt' \]  
(3.45)

\[ M_1 (t-t', \mathbf{II}(t')) = (1 + \frac{\varepsilon}{2}) \sum_{p=1}^{\infty} \frac{G_p}{\lambda_p^{\text{eff}}} e^{-\frac{(t-t')}{\lambda_p^{\text{eff}}}} \]  
(3.46)

\[ M_2 (t-t', \mathbf{II}(t')) = \frac{\varepsilon}{2} M_1 (t-t', \mathbf{II}(t')) \]  
(3.47)

Here \( \varepsilon \) is a constant and \( \lambda_p^{\text{eff}} \) is defined by equation 3.43. The \( C_{ij}^{-1} \) and \( C_{ij} \) are respectively, the Finger and Cauchy deformation tensors defined by:
\[ C_{ij} = g_{ab} \frac{\partial X_i}{\partial x_a} \frac{\partial X_j}{\partial x_b} \]  

(3.48)

\[ C_{ij} = g_{ab} \frac{\partial X_a}{\partial x_i} \frac{\partial X_b}{\partial x_j} \]  

(3.49)

Bernstein, Kearsley and Zapas (BKZ) [44] proposed a non-linear integral model also of the same form as Bogue and White (equation 3.45). However the memory functions \( M_1 \) and \( M_2 \) in the BKZ model are unspecified scalar functions of \( t-t' \), and possibly of the first and second invariants \( I_{c^-}^-1 \) and \( II_{c^-}^-1 \) of the Finger deformation tensor \( C_{ij}^-1 \).

The invariants \( I_{c^-}^-1 \) and \( II_{c^-}^-1 \) are defined as:

\[ I_{c^-}^-1 = C_i \quad II_{c^-}^-1 = \frac{1}{2} (C_i \ C^-j) - \frac{1}{2} (C^-i \ C_j) \]  

(3.50)

In the BKZ theory \( M_1 \) and \( M_2 \) are not independent, but are related to strain energy \( U \) by

\[ M_1 = 2 \left( \frac{\partial U}{\partial I_{c^-}^-1} \right), \quad M_2 = 2 \left( \frac{\partial U}{\partial II_{c^-}^-1} \right) \]  

(3.51)

Strain energy \( U \) depends upon the invariants \( I_{c^-}^-1 \) and \( II_{c^-}^-1 \) as well as \( (t-t') \) which means

\[ U = E \left( I_{c^-}^-1, II_{c^-}^-1, t-t' \right) \]  

(3.52)
Han [9] has reported that the experimental determination of the strain energy \( U \) as a function of invariants \( I_c^{-1} \) and \( II_c^{-1} \) is very difficult.

Several attempts have been made in the past to modify the Lodge network theory (equation 3.38). Meister [45] proposed a molecular network theory by making the memory function depend on the second invariant of the rate of deformation tensor, \( II \), as well as \( t-t' \). He suggested a model of the following form:

\[
\tau_{ij} = \int_{-\infty}^{t} M(t-t', II(t')) \tilde{\tau}_{ij}^{-}(t,t')dt' \tag{3.53}
\]

where

\[
M = \sum_{p=1}^{\infty} \frac{G_p}{\lambda_p} e^{-\frac{C(t-t')}{\lambda_p}} \frac{1}{\lambda_p} \tag{3.54}
\]

Here \( C \) is an adjustable parameter. The set of constants \( G_p \) and \( \lambda_p \) are not adjustable and they are to be evaluated either from low shear rate stress relaxation data or low amplitude oscillatory data.

The Meister model is capable of predicting the non-Newtonian viscosity \( \eta(\dot{\gamma}) \) and first normal stress function \( \Psi_1(\dot{\gamma}) \), but it gives the second normal stress function \( \Psi_2(\dot{\gamma}) \) as zero.

By using concepts from the molecular theory of Rouse [46] and by allowing the junction-creation rate and the probability of loss of junctions to depend on the second invariant of the rate of deformation tensor, Bird and Carreau [47,48] proposed a model of the form:
\[ T_{ij} = \int_{-\infty}^{t} M(t-t', \Pi(t')) \left[ (1 + \frac{\varepsilon}{2}) \bar{\Gamma}_{ij} (t') - \frac{\varepsilon}{2} \bar{\Gamma}_{ij} (x) g_{ij} (x) \right] \Pi(t') \, dt' \]  

(3.55)

where finite strain tensors \( \bar{F}_{ij} \) and \( \Gamma_{ij} \) are defined by

\[ \bar{F}_{ij} (t') = -g_{ij} (x) + \frac{\partial x_i}{\partial x_a} \frac{\partial x_j}{\partial x_b} g_{ab} (x) \]  

(3.56)

\[ \Gamma_{ij} (t') = g_{ij} (x) + \frac{\partial x_i}{\partial x_a} \frac{\partial x_j}{\partial x_b} g_{ab} (x) \]  

(3.57)

and the memory function \( M(t-t', \Pi(t')) \) is of the form

\[ M(t-t', \Pi(t')) = \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda_{1p}} \frac{(-1)^{p+1}}{\lambda_{1p}^{(p+1)}} \left[ \frac{(t-t')}{\lambda_{1p}} \right] \]  

(3.58)

\[ \eta_p = \frac{\mu \lambda_{1p}}{\sum_{p=1}^{\infty} \lambda_{1p}} \]  

(3.59)

\[ \lambda_{1p} = \lambda_1 \left( \frac{2}{p+1} \right)^{\alpha_1} \]  

(3.60)

\[ \lambda_{2p} = \lambda_2 \left( \frac{2}{p+1} \right)^{\alpha_2} \]  

(3.61)
As the Bird-Carreau model was chosen to fit the experimental data in the present study, because of its simplicity and having fewer constants, it will be discussed in more detail here.

The constant $\varepsilon$ in equation 3.55 is introduced to give non-zero second normal stress difference. By assuming $\varepsilon$ as a zero (i.e. $W(Y) = 0$) the Bird-Carreau model contains five adjustable material constants, $\eta_0$, $\alpha_1$, $\alpha_2$, $\lambda_1$ and $\lambda_2$. These material parameters are empirical but have the following macroscopic rheological significance. The parameter $\eta_0$ is the Newtonian (i.e. zero shear) viscosity. The parameters $\alpha_1$ and $\alpha_2$ are related respectively to the slope of the plots of viscosity and first normal stress difference against shear rate in the power law region. The parameters $\lambda_1$ and $\lambda_2$ are macroscopic time constants characteristic of the relaxation processes which govern the viscous and elastic responses of the material and appear to be related to the reciprocal shear rate where the viscosity or normal stress difference is in transition from Newtonian or linear viscoelastic response to non-Newtonian or non-linear viscoelastic response.

For steady shear flow, the Bird-Carreau model yields the following expressions for viscosity at low and high shear rates respectively [48].

Low shear rate:

$$\frac{n}{\mu} = 1 - \frac{(2\alpha_1 \lambda_1)^2}{Z(a_1) - 1} \sum_{p=2}^{\infty} \frac{p - \alpha_1}{p^2 \alpha_1 + (2\alpha_1 \lambda_1)^2} \quad \text{(3.62)}$$
High shear rate:

\[
\eta = \frac{1}{Z(\infty_{\eta} - 1)} \left( \frac{1}{2 \alpha_1 \sin((\frac{1}{2 \alpha_1}) \pi)} \right)^{1-\alpha_1} \frac{1}{2\alpha_1} \frac{1 + \frac{1}{6} \alpha_1}{(\alpha_1 + 1)(2 \alpha_1 \lambda_{1\eta})^2} \frac{1}{2[1+(2 \alpha_1 \lambda_{1\eta})^2]}
\]

where \(Z(\alpha_1)\) is the Riemann Zeta function defined by equation 3.33.

In 1972 Carreau [49] modified the Bird-Carreau model and obtained a 7-constant model. However, for the evaluation of constants in this model, one also needs oscillatory data as well as steady shear data.

In 1978, Doi and Edwards [50-53] also proposed a molecular model, so called "the primitive chain model", of the form:

\[
\tau_{ij} = G_0 \int_{-\infty}^{t} M(t-t') Q_{ij} \left[ E(t,t') \right] dt'
\]

(3.64)

where

\[
M(t-t') = \sum_{p \text{ odd}} \frac{8}{p^2 \pi^2 \lambda_p} e^{-\frac{t}{\lambda_p}}
\]

(3.65)

\[
\lambda_p = \frac{\lambda_d}{p^2}
\]

(3.66)

\[
Q_{ij} = \left\langle \frac{(E.U)_i(E.U)_j}{|E.U|^2} - \frac{1}{3} \delta_{ij} \right\rangle
\]

(3.67)

here \(G_0\) is a constant, \(\lambda_d\) the longest relaxation time constant, \(E\) the deformation tensor, \(U\) the unit vector and symbol \(\langle ... \rangle\) signifies 'the average'.
However, the drawback with this model is that it gives material functions which have to be evaluated numerically.

3.4 FLOW BEHAVIOUR OF ELASTOMER COMPOUNDS

Rheological properties of elastomeric compounds are greatly affected by the amount and type of filler i.e. level of loading and particle size (or surface area). The major filler used with elastomers is carbon black.

Extensive experimental studies are available in the literature [54-66] for carbon black filled rubber compounds. Generally filler reinforced elastomers exhibit an increase in viscosity. Also the viscosity is strongly dependent upon particle size of the filler. The smaller the size of the particle (i.e. larger surface area) the larger the viscosity at any given volume loading. Carbon black reinforced polymers show "yield stress" values and thixotropic behaviour [60,61]. The sensitivity of viscosity to filler concentration [60,62,63,64,66] and surface area [59,65] diminishes progressively with increasing shear rate.

3.5 DEPENDENCE OF VISCOSITY OF FILLED COMPOUNDS ON TEMPERATURE

As already discussed in Section 3.2.2, the dependence of non-Newtonian viscosity at any given shear rate can be described by the Arrhenius equation (equation 3.6). The activation energy of viscous flow, $E_Y$, is a good measure of the temperature dependence of viscosity.
Zakharenko et al [54] have reported that for polyisobutylene rubber compounds the activation energy is independent of the nature and amount of filler. The same findings have also been reported [67-69] for various other elastomer compounds and filler reinforced thermoplastic melts.

### 3.6 MODELS FOR THE VISCOSITY OF FILLED COMPOUNDS

As mentioned in Section 3.4, there are numerous studies available in the literature on the rheological behaviour of elastomer compounds. Unfortunately, most of these studies are qualitative in nature and there have been relatively few attempts in the past to model the rheological behaviour of filled compounds quantitatively.

One of the simplest equations which describes the viscosity of filled systems is the Einstein equation [70]:

\[ \eta_f = \eta_g (1 + 2.5C) \]  

(3.68)

where \( \eta_f \) and \( \eta_g \) are the viscosity of the filled and unfilled medium respectively and \( C \) is the volume fraction of the filler.

To account for larger particle concentrations and thus significant interactions among particles equation 3.68 was modified by Guth, Simha and Gold [71,72] to

\[ \eta_f = \eta_g (1 + 2.5C + 14.1C^2) \]  

(3.69)
However, equation 3.69 does not predict the shear rate dependency of the viscosity. In 1974, Derringer [73] proposed an empirical model for variable shear rate viscosity of the following form:

$$\ln \eta_f = \ln \eta_g (\dot{\gamma}) + \lambda (\dot{\gamma}) F - \phi (\dot{\gamma}) P \quad (3.70)$$

where $F$ is filler level in parts per hundred (phr) by weight of rubber; $P$ is the plasticiser level in phr by weight of rubber and $\lambda$ and $\phi$ are constants which are shear rate dependent.

Also in 1974, White and Crowder [59] suggested the following form of dimensionless relationship for the viscosity of concentrated suspensions:

$$\frac{\eta_f - \eta_g}{\eta_g} = F (C, d_p, k, \dot{\gamma}) \quad (3.71)$$

in which $C$ is the volume fraction of the particles in the suspension, $d_p$ is the average particle diameter and $k$ is a constant i.e. measure of the black structure. They suggested the following form, for the function $F$:

$$\frac{\eta_f - \eta_g}{\eta_g} = A(\dot{\gamma}) \left( \frac{Ck}{d_p} \right) + B(\dot{\gamma}) \left( \frac{Ck}{d_p} \right)^2 \quad (3.72)$$

here $A(\dot{\gamma})$ and $B(\dot{\gamma})$ are functions which depend on shear rate. However, White and Crowder do not show any comparison between model prediction and experimental data and also they do not seem to give any indication how functions $A(\dot{\gamma})$ and $B(\dot{\gamma})$ can be evaluated.
In 1979, White [74] also proposed a 3-dimensional model, in terms of filler concentration, for polymer melts reinforced with small particles. However this model is far too complex, and moreover it requires the experimental determination of yield values and normal stresses which are not so easy to obtain.

It is apparent from the literature that there is no simple model available that can describe the viscosity of filled compounds in terms of filler loading and surface area of the filler.

3.7 MODELS FOR THE STRESS RELAXATION OF ELASTOMERS AND ELASTOMER COMPOUNDS

When elastomeric materials are deformed the stresses set up gradually decrease with time. This is the phenomenon of stress relaxation; it plays a very important role in processes like calendering, extrusion and during mould filling in injection moulding.

Cotton and Boonstra [75] showed that for longitudinal strain the compressive stress relaxation of gum and filled elastomers (both uncured and cured) obeyed the empirical equation of the form:

\[ S(t) = S_1 t^{-b} \]  

(3.73)

where \( S(t) \) is the compressive stress at any time \( t \), \( S_1 \) is a constant having units of Pa.s\(^b\) and some numerical value as stress at time 1 and \( b \) is a constant defined as relaxation rate of the material. From equation 3.73 they derived \( b \) as:
\[ b = \frac{1}{S} \frac{dS}{d(\log t)} = -\frac{d(\log S)}{d(\log t)} \]  

(3.74)

Therefore \( b \) is derived from the linear plot of \( \log S \) vs \( \log t \) as the fractional decrease in stress per unit logarithmic cycle of time.

In 1971 Voet, Cook and Sircar [75] found that the above relationship is also obeyed under shear deformation mode. Hence equation 3.73 can be written for shear deformation as:

\[ \tau(t) = \tau_1 t^{-r} \]  

(3.75)

where \( \tau(t) \) is the shear stress at any time \( t \), \( \tau_1 \) is a constant having units of \( \text{Pa.s}^{-r} \) and some numerical value as stress at time 1 and \( r \) is the relaxation rate of material in shear, also defined by equation 3.74 by just replacing \( S \) by \( \tau \).

The effect of carbon black on the relaxation times in uncured rubber is not well documented. Cotten and Boonstra [77] have shown that the rate of stress relaxation decreases, and thus relaxation time increases with increasing loading and decreasing particle size of carbon black.

3.8 RHEOLOGICAL MEASUREMENT TECHNIQUES [78,79]

Many methods have been devised to determine the rheological properties of polymers, but some of them only provide arbitrary variables for comparative measurements (e.g. melt flow index, plasticity). For elastomers and their compounds the following types of instrument are of particular interest:
i) Sandwich type rheometer
ii) Extrusion rheometer
iii) Rotational rheometer.

3.8.1 Sandwich Type Rheometers
The parallel plate rheometer is perhaps the simplest type of rheometer which can be constructed by sandwiching two sheets of material to be tested between the plates as shown in Figure 3.6. For normal liquids this is not practical.

![Diagram of Parallel Plate Rheometer](image)

**FIGURE 3.6: PARALLEL PLATE RHEOMETER**

However for elastomers and compounds it is very much so. Apparatus of this type have been designed and used by Zakharenk et al [54], Middleman [80], Goldstein [81], Fruta et al [82] and Tuki and White [63].
Viscosity with this apparatus is determined by using a method termed as "creep experiment" [5,54].

![Figure 3.7: Hypothetical Shear Strain Response to a Step Change in Shear Stress for a Viscoelastic Fluid](image)

Shear strain at a given time is obtained by dividing the displacement of the moving plate at time t by the average thickness of the rubber sample. Then from the linear portion of the plot of strain vs time, the shear rate, \( \dot{\gamma} \), can be obtained readily and hence, knowing the load, the viscosity is determined as follows:

\[
\text{Shear rate } \dot{\gamma} (s^{-1}) = \text{slope of strain vs time plot}
\]

Load applied, kg = \( m \)

Force, N = \( mg \), where \( g = 9.81 \text{ ms}^{-2} \)

Area, A, m\(^2\) = length \times width of the rubber sample

The total effective area is equal to 2xA because there are two elements of rubber in the test piece. Hence

\[
\text{Shear stress}, \tau = \frac{F}{2A}
\]

45
Finally viscosity is calculated by dividing shear stress by shear rate.

As shear rates obtained in creep experiments are very low, these viscosities are "zero-shear", viscosities, \( \eta_0 \) [5] - the elastomer is essentially Newtonian in its flow behaviour under these conditions.

3.8.2 Extrusion Rheometers

These are very popular devices because of the wide range of shear rates over which materials can be evaluated, i.e. 1-1000 S\(^{-1}\). The usual type of extrusion rheometer for polymer melts and elastomers consists of a heated barrel at the bottom of which is fitted a small die containing a capillary or slit die geometry. There are two basic variations of this design:

i) Imposed rate rheometers, in which a plunger is forced down into the barrel (filled with polymer which has been heated to bring it to the desired temperature) at a constant rate: the pressure required to do this is measured by a pressure transducer.

ii) Imposed pressure rheometers, in which a load is applied to the top of the polymer and the output rate for this load is measured.

Various assumptions and correction methods employed in the derivation of theory to determine viscosity from extrusion rheometer data are discussed in detail elsewhere [8,77,78].
3.8.3 Rotational Rheometers

These are the instruments in which one surface is rotated and the response of the material is measured by its action on a stationary surface. These instruments have two fundamental advantages over capillary viscometers [78]. Firstly, a particular sample can be sheared as long as is desired so that changes, temporary or permanent, in behaviour with time can be followed; secondly, with appropriate design, an approximately uniform shear rate can exist throughout the sample in contrast to the variation of the shear rate in a tube from zero at the axis to a maximum at the wall. The main problem with rotational rheometers is the excessive temperature rise in the sample at high shear rates. There are several types of rotational rheometers, but only those of particular relevance to the study of elastomers and their compounds will be discussed here.

3.8.3.1 Mooney viscometer

This is, perhaps, the most widely used rotational instrument. It consists of a cylindrical rotor which rotates in a heated cavity. The torque generated on the rotor is recorded with respect to time. The Mooney viscosity is obtained by a method which is normally expressed as the Mooney ML(1+4) test. This test involves 1 minute preheat time and 4 minutes running time prior to a measurement being made. The major drawback with this instrument is that it only gives a single torque value which is difficult to convert to viscosity, due to the rotor shape. However, it is still a very useful qualitative test for comparison purposes. The reason is the simplicity, speed and reproducibility of results.
3.8.3.2 Cone and plate rheometer

This instrument consists essentially of a flat, horizontal plate and an inverted cone, the apex of which is in near contact with the plate. The test sample is located in the gap between the cone and plate. There are two variations of this instrument - constant stress type or constant rate type. The constant-stress rheometer utilises a weight suspended from a string to apply the torque to rotate the cone. The angular displacement is commonly detected by reflection of a light beam. The constant-rate type rheometer uses some form of drive system to rotate one of the platens at a constant angular velocity. The rheological measurements from a cone and plate rheometer can be obtained as follows.

If we consider Figure 3.8, in which the cone is rotating at an angular speed of \(\omega\) (rads/s), the velocity at radius \(r\) will be given by \(rw\). The gap height at \(r\) is \(r \tan \theta\). The shear rate \((\dot{\gamma})\) at \(r\) is then given by:

\[
\dot{\gamma} = \frac{rw}{r \tan \theta} = \frac{\omega}{\tan \theta}
\]

(3.76)
If $\theta \leq 6^\circ$ then $\tan \theta \approx \theta$ (in radians)

$$\gamma = \frac{\psi}{\theta}$$  \hspace{1cm} (3.77)

Batchelor [83] has shown that inertial effects in cone and plate rheometers below shear rate of $1 \text{ s}^{-1}$ are insignificant. Thus if inertia forces are neglected then the torque at any element within the cone is given by:

$$dT = \tau A r$$  \hspace{1cm} (3.78)

where $A = \text{area of annulus at radius } r = 2 \pi r dr$, and torque $T$ is equal to $mgR$

$m = \text{load applied}$

$g = \text{gravitational constant (9.81 m/s}^2)$

By substituting the value of $A$ in equation 3.78 and then integrating between limits of $r = 0$ and $r = R$

$$T = 2 \pi \int_0^R r^2 dr = \frac{2}{3} \pi R^3 \tau$$  \hspace{1cm} (3.79)

Rearrangement of equation 3.79 gives:

$$\tau = \frac{3}{2} \frac{T}{\pi R^3}$$  \hspace{1cm} (3.80)

and then finally viscosity is obtained by dividing shear stress by shear rate.
One of the major drawbacks of the cone and plate instrument was reported by Hutton [84] in 1963. He found that the test sample fractured and exuded from the space between the cone and plate when the total elastic energy contained in the sheared sample exceeded a critical value. According to Hutton the upper limit of operable shear stress of this instrument is about $10^4$ N/m². Han [85] has also reported that this critical shear stress, at which the fracture takes place, can be applied uniformly, regardless of the type of test fluid (i.e. regardless of fluid viscosity).

3.8.3.3 Negretti TMS biconical rotor rheometer

The TMS (Turner, Moore, Smith) rheometer is a modification of the Mooney viscometer. It differs from the Mooney viscometer in the following ways:

i) The test cavity is filled from a preheat cavity by the transfer moulding method (see Figure 3.9).

ii) The rotors used in TMS are biconical to give an approximately uniform shear rate throughout the test sample.

iii) The TMS uses a stepper motor drive giving a programmable speed control between 0.1 and 100 rev/min.

iv) It is capable of measuring stress relaxation.
Figure 3.9a: Dimensions for T M S rheometer rotor

Figure 3.9b: Diagram for T M S biconical rotor rheometer
The transfer cavity filling method gives a high level of test to test repeatability. The test cavity is shut prior to filling, giving "flashless moulding" and accurate setting of the rotor to cavity distances; in comparison with the "open flash" compression moulding method used with the Mooney viscometer. Transfer filling also enables the cavity pressure to be controlled accurately by adjustment of the plunger pressure; and the test result is not dependent on sample size, provided sufficient material to fill the test cavity is used.

The total torque $T$ measured by the TMS is the sum due to the double surface of the cone $T_c$ and the couette flow at the edges $T_e$ [85]:

$$ T = 2 T_c + T_e $$ (3.81)

$$ T = 2 \left( \frac{4}{3} \pi R^3 \tau \right) + 2 \pi R^2 Y \tau. $$ (3.82)

$$ T = \frac{4}{3} \pi \tau R^2 (2R + \frac{3}{2} Y) $$ (3.83)

where $R$ is the rotor radius and $Y$ is the depth of the rotor edge.

Shear stress $\tau$ is obtained by the rearrangement of equation 3.83:

$$ \tau = \frac{3T}{4 \pi R^2 (2R + \frac{3}{2} Y)} $$ (3.84)

shear rate, $\dot{\gamma}$, using the biconical rotor is given by:

$$ \dot{\gamma} = \frac{\omega}{\theta} $$ (3.85)
where $\omega$ is the angular velocity in radians/sec and $\theta$ is the cone angle of the rotor.

Finally, viscosity can be obtained by dividing shear stress by shear rate: $\frac{\tau}{\dot{\gamma}}$.

It is only with microprocessor control of testing procedure and collection of results that the advantages of the TMS rheometer can be realised fully. A Negretti MPC 84 process controller provides all the control needed for the TMS. It controls the temperature in the dies and preheat cavity, the speed and the torque applied by the rotor. It is possible to design a test sequence which involves measurements over a wide range of speeds or a range of torques. It is also possible to collect and to analyse the results with the microprocessor system, but due to the relatively high volume of results and for sake of higher flexibility in the processing of these results, it is preferable to transfer the results to a second level IBM-XT computer and to store all the results there on a floppy disc.

The major drawback of the TMS rheometer is that the higher the shear rate, the greater is the heat generation in the test sample. However, currently methods are being developed at Loughborough University to correct for the excessive temperature rise in the sample at higher shear rates.
Stress Relaxation and Stress Growth Measurements Using the TMS Rheometer

The TMS rheometer can also be used to measure stress relaxation and stress growth. The former involves stopping the motor after a conditioning run at a specified shear rate and measuring the decay in stress with respect to time. The latter involves the measurement of stress with respect to time at the onset of a shear rate.
CHAPTER 4

EXPERIMENTAL

4.1 MATERIALS

The elastomers studied were natural rubber (SMR20) and chlorosulphonated polyethylene, CSM (Hypalon 40, Du Pont). The filler used was carbon black of three different grades. The characteristics of carbon black are given in Table 4.1:

<table>
<thead>
<tr>
<th>Filler</th>
<th>Supplier</th>
<th>Grade</th>
<th>Surface Area, m²/g (ASTM D3765, CTAB*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>Cabot Carbon</td>
<td>SRF (N762)</td>
<td>33</td>
</tr>
<tr>
<td>Black</td>
<td>Ellesmere Port (UK)</td>
<td>HAF (N330)</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAF (N110)</td>
<td>128</td>
</tr>
</tbody>
</table>

* CTAB - Cetyl trimethyl ammonium bromide

TABLE 4.1: CHARACTERISTICS OF CARBON BLACK

Other materials used were Nonox ZA (4-isopropylamino-diphenylamine, Supplier: ICI) as an antioxidant for natural rubber and Multisperse K-LD-90 (Supplier: Croxton and Garry Ltd, Surrey) as an acid acceptor for CSM. Multisperse K-LD-90 is a dispersion of litharge (90%) in a chlorinated polyethylene binder system (10%).

Formulations for both SMR20 and Hypalon 40 compounds are shown in Tables 4.2 and 4.3.
<table>
<thead>
<tr>
<th>Ingredients</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR20, phr</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Nonox ZA, phr</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SRF (N762), phr</td>
<td>-</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HAF (N330), phr</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>SAF (N110), phr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

**TABLE 4.2: SMR20 COMPOUNDS**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>Hypalon 40, phr</td>
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<tr>
<td>N762</td>
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<td>-</td>
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<td>30</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>N330</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>30</td>
<td>45</td>
</tr>
</tbody>
</table>

**TABLE 4.3: HYPALON 40 COMPOUNDS**
4.2 MIXING

4.2.1 Equipment
Mixing was carried out on a Farrel Bridge BR Banbury internal mixer having two wing rotors and mixing chamber volume of 1.57 litres, followed by subsequent milling on a Bridge two roll mill (both by Farrel Bridge, Rochdale, UK).

4.2.2 Procedure
SMR20 and Nonox ZA (1 part per hundred, phr by weight of rubber) were mixed with N762 at loading levels of 20, 40 and 60 phr by weight of rubber (equivalent to 0.092, 0.1685 and 0.2332 by volume fraction of filler). The same procedure was repeated for N330 and N110 - thus giving a total of nine mixes of SMR20 containing carbon black.

A small particle size filler like N110 is generally not added to CSM. Even N330 is only used at moderate loading levels and furthermore CSM is never used without an acid acceptor because of degradation problems [87]. CSM and 20 phr of litharge were mixed with N762 and N330 at loading levels of 15, 30 and 45 phr (equivalent to 0.085, 0.157 and 0.219 by volume fraction of carbon black). A mix of CSM containing 20 phr of litharge only was also prepared, which was treated as a base mix, in order to investigate the effect of carbon black on CSM.

The mixing procedure was as follows: first the rubber was mixed on the Banbury for half a minute. Then half the carbon black was added and mixed for two minutes. Finally, the rest of the carbon black and other ingredients were added and mixed for another three and a half
minutes - thus giving a total mixing time of six minutes. The following operating conditions were used on the Banbury mixer:

Rotor speed: 40 rpm
Circulating water temperature: 25°C
Ram pressure: 30 psi
Fill factor: 0.60

After mixing through the Banbury, each mix was passed through the two roll mill for 5 minutes.

To give the same mixing history to each batch, each unfilled rubber was also passed through the Banbury mixer and two roll mill for the same amount of time as the filled rubbers.

4.3 MEASUREMENT OF ZERO-SHEAR VISCOSITY

4.3.1 Equipment
Zero-shear viscosity was determined by using a parallel plate rheometer, a schematic diagram of which has previously been shown in Section 3.8.1 (Figure 3.6). It was constructed in the IPTME workshop at Loughborough University and it consists basically of three plates of mild steel of 4 mm thickness. The two outer plates were 100 mm long and 35 mm wide, and the inner plates 90 mm long and 17 mm wide. The outer plates contain some holes at the edges in order to keep the plates and samples in place by inserting bolts through them.
4.3.2 Procedure

For each rubber, sheets of uniform thickness of about 3 mm were prepared by compression moulding at 100°C. From these sheets, two samples of dimension 60 x 17 mm were prepared and inserted between the plates. The rheometer was then placed in an air oven for a preheat time of twenty minutes. The oven used had a transparent window and a temperature range of 50-200°C.

When the load was applied (see Figure 3.6), the displacement of the moving plate with respect to time was measured with a travelling microscope to the nearest 0.005 cm. The weights used ranged from 50 to 300 grams. By using the method outlined in Section 3.8.1 viscosities were then determined for SMR20 and Hypalon 40 rubbers at 80, 100 and 120°C.

4.4 VISCOSITY MEASUREMENTS ON CONE AND PLATE RHEOMETER

4.4.1 Description of Apparatus

The apparatus used was designed by Dr J Batchelor, former Director of IPTME at Loughborough University, and it was manufactured in the IPTME workshop. It was based on a design previously used by Dr Batchelor [83] to study the viscosity and recovery properties of some polymer melts. A constant shear stress is applied to the cone by weights on a cord wound round a pulley and attached to the rotating shaft. The resultant rotation is measured by some suitable device. The apparatus is described in great detail in Dr Batchelor's PhD thesis [83] - with the major difference being that in the original design the sample temperature was controlled by circulating water through the plate,
but in the present design the temperature is controlled by a band heater on the plate via a PI controller. However, several modifications were made to this rheometer and a schematic diagram of the modified cone and plate rheometer is shown in Figure 4.1. The cone, the pulley and the plate all have diameters of 50 mm.

4.4.2 Modifications made to the Cone and Plate Rheometer

i) The original rheometer had a mirror and light system for rotational measurements of the cone. For the sake of accuracy and ease of measurement, the mirror and light system was replaced by an angular displacement transducer mounted at the top of the pulley (see Figure 4.1). The transducer was connected to a chart recorder and calibrated for angular measurements.

ii) The original design contained only one external (or support) pulley. It was realised that if heavier loads were to be used then it would distort the rotating shaft to some extent. Therefore in order to distribute the load evenly on the shaft and thus prevent distortion, one more external pulley was installed.

iii) A Tufnol block was inserted between the cone and the shaft to reduce heat losses from the test sample.

iv) It was discovered that, after the test, the sample tended to stick to the surfaces of the cone and the plate. In order to facilitate the removal of the sample after the test, a release lever (see Figure 4.1) was installed.
FIGURE 4.1: SCHEMATIC DIAGRAM OF THE MODIFIED CONE AND PLATE RHEOMETER
4.4.3 Procedure

The viscosity measurements were made with two cones, whose dimensions are given in Table 4.4:

<table>
<thead>
<tr>
<th>Cone angle, °</th>
<th>Diameter, mm</th>
<th>Gap setting, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>50</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**TABLE 4.4: DIMENSIONS OF CONES USED**

Since the cones are truncated to eliminate friction during rotation, the plate must be adjusted so that the projected cone apex touches the plate. This is achieved by adjusting the micrometer until the cone and plate touch, which is indicated by electrical contact. The micrometer setting is taken and subsequently the plate can be adjusted to give the required gap separation when a sample is placed between the platens.

A test sample of about 40 mm diameter and 3 mm thick was cut from compression moulded sheet. It was then inserted between the cone and the plate and allowed to heat for 15 minutes to bring it to test temperature. The plate was then adjusted to give the required gap separation and the excess material was removed with a scalpel. When the adjustment was complete the plate assembly was clamped using the locking lever. Stresses introduced into the test sample during the adjustment of the gap settings were allowed to relax for 15 minutes before the experiments commenced.
The stresses were applied manually in a series of steps by hanging weights on the ends of two cords wound round the pulley assembly and then over two external pulleys. The shear rate in steady state was then determined by dividing the slope of the linear region of the angular displacement vs time graph, displayed on the recorder, by the cone angle.

The viscosities over a range of shear rates were determined for SMR20 and Hypalon 40 at 80, 100 and 120°C.

To investigate the friction in the air bearings, the torque which must be applied to rotate the cone, when no sample is present, was determined. The effect of shear heating on temperature rise in the test sample was also investigated.

4.5 VISCOSITY MEASUREMENTS ON FILLED COMPOUNDS WITH A SPECIALLY DESIGNED SHEAR TEST SPECIMEN

4.5.1 Introduction

When attempting to measure the steady state flow properties of filled compounds with the cone and plate rheometer, it was found that it is not possible to do so, because of fracture mechanics and the tendency of the material to come out of the gap. Therefore it was decided to try parallel plate samples in a tensile testing machine in an attempt to overcome this problem. Unlike the cone and plate, which operates under constant stress mode, the tensile testing machine runs under constant shear rate mode.
4.5.2 Design of a Transfer Mould to Produce Shear Test Specimens

A transfer mould was designed to produce shear test specimens. It is made of mild steel and was manufactured in the IPTME workshop of Loughborough University. A schematic diagram of the mould, together with dimensions of the test specimen, are shown in Figure 4.2. The test specimens produced by this method are basically parallel plate rheometers of the type which have been used previously for the measurement of zero shear viscosities (Section 4.3). However this design has the following advantages:

i) the thickness of the test samples between the plates is controlled precisely by the injection of rubber into the mould cavity.

ii) rubber to metal bonding is used to prevent slippage between the rubber and metal surfaces during the test.

4.5.3 Procedure

Preparation of shear test specimens: Before the preparation of test specimens, all plates were grit blasted to remove any grease or dirt from the surfaces. Two bonding agents (both from Durham Chemicals Ltd, Durham) were used - normally known as a primer (Chemlok 205) and a top coat (Chemlok 220).

A thin layer of primer followed by a thin layer of top coat was applied to the inner surfaces of the outer plates and both surfaces of the inner plate. The mould was closed and put in the press at 100°C for 10 minutes of preheating time. To ensure complete filling of the mould cavity, sufficient rubber was then placed in the transfer pot.
Rubber Sandwich Assembly
Plug Inserts (x4 OFF)
90 X20 x 4mm M.S. Plates (6 OFF)
Transformer Plunger
Transfer Pot
Pin-point gates (24 in total)
Guide Pillar (4 OFF)
Cavity
Guide Bush (x4 OFF)

SECTION X X

SECTION Y Y

Fig. 4.2: Schematic diagram of the transfer mould for producing Shear test specimens.
The mould was then put back in the press and the pressure increased until it became constant, indicating that the cavity was full.

After 10 minutes the mould was taken out of the press and allowed to cool. The test specimens were then removed from the mould. For the release of frozen in stresses they were left to rest overnight before starting the test.

**Viscosity measurements:** The test specimen was placed in the temperature controlled chamber of an Instron tensile tester. The machine was run at a constant speed and the stress required was recorded as a function of time. The tests were run at various speeds, ranging from 0.1 to 10 mm/min - corresponding to a shear rate range of $10^{-4}$ to $10^{-2}$ s$^{-1}$. Viscosity can be obtained by dividing the steady state stress by the corresponding shear rate.

### 4.6 VISCOSITY AND STRESS RELAXATION MEASUREMENT BY NEGRETTI TMS BICONICAL ROTOR RHEOMETER

#### 4.6.1 TMS Rheometer

The viscosity and shear relaxation as a function of shear rate and time respectively were measured using the TMS biconical rotor rheometer, manufactured by Negretti Automation Ltd.

The TMS is a die and rotor configuration rheometer for the measurement of the rheological characteristics of elastomers and other polymeric materials (schematic diagram of the TMS is shown in Figure 3.9). The instrument is very flexible, with the facility to measure torque under fixed or variable conditions of temperature or rotor speed - or rotor speed under fixed or variable conditions of temperature and torque.
The rheometer has a preheating transfer chamber for conditioning of the sample prior to its injection into the die cavity.

Control, data acquisition and programme sequence are effected through a MPC84 Process Controller governing the speed, torque and temperature function of the instrument. The data obtained from the TMS is transferred to a second level IBM-XT personal computer and analysed there. A photograph of the TMS is shown on the following page.

Machine Specifications:
Overall dimensions: 1.58m x 0.65m x 0.49m excluding MPC 84, VDU, keyboard and IBM-XT
Power supply: 240V
Air supply: 100 lbf/in² (689.4 kPa)

Operating Specification:
Rotor speed range: 0.1 to 100 rpm in steps of 0.1 rpm. 1 rpm equals 1 reciprocal second shear rate
Torque limits: 0 to 16.26 newton metres
Maximum sample rate: 100 per second
Temperature range: 50°C to 200°C

Rotor Speed:
The rotor is biconical for uniform shear rates over the rotor surface. The angle of the rotor is 6° and the diameter is 46 mm, ensuring that the revolutions per minute of the rotor are equal to reciprocal seconds shear rate.
Rotor speed is from 0.1 to 100 rpm in steps of 0.1 rpm. The speed is controlled by a stepper motor.
TMS RHEOMETER
(1) The IBM terminal
(2) VDU terminal for the MPC 84
(3) Rotor
(4) Upper Die
(5) Ram
(5) The Negretti MPC 84
Torque:
Torque is PID controlled from within the MPC84 controller.

Temperature:
Die temperature is 50°C to 200°C with steady state stability better than 0.3°C. Temperature changes are achieved very rapidly with minimal overshoot. Temperature control is by a PID system, from within the MPC 84.

Transfer Chamber:
The instrument has a preheated transfer chamber to enable the sample to be heated for a set period of time prior to injecting it into the die cavity.

4.6.2 Testing Procedure on TMS Rheometer
The basic procedure for measuring the viscous flow behaviour on the TMS rheometer is to increase the rotor speed in a series of steps. The results obtained indicate that when a step increase in shear rate was made the stress first overshoots (transient phenomenon) to a peak value and then drops to a steady value. The time required to achieve steady state reduces progressively with increasing shear rate. In order to make sure that steady state has been achieved, sufficient time was given at each step to reach a plateau.
The program originated by Negretti for creating the test sequence is named 'TM'. A typical example of a test sequence created by invoking this program is shown in Figure 4.3. The sample is cut and placed in the preheat cavity and the computer program is then activated. The sequence shown in Figure 4.3 is then performed automatically and the results relating shear stress to shear rate and time stored in a floppy disc for further analysis. The apparent viscosity at different shear rates is determined by dividing shear stress by shear rate.

Viscosity vs shear rate relationships in the shear rate range of 0.1-100 s\(^{-1}\) were obtained for unfilled and filled SMR 20 and Hypalon 40 at 80, 100 and 120\(^{\circ}\)C using a grooved rotor.

For stress relaxation measurements, the test samples were conditioned at a constant shear rate to obtain a steady state stress (for example see steps 3 and 4 in Figure 4.3), the flow was then stopped suddenly and the decay of this stress with time was recorded. Shear stress relaxation results for gum and filled SMR 20 and Hypalon 40 were obtained at 100 and 120\(^{\circ}\)C for different shear rates.

For all tests on TMS, standard times of 240 seconds for preheating and 120 seconds for filling were used.

4.6.3 Run to Run Repeatability Study on TMS

To test the reliability of the data from TMS three different sample lots of butyl rubber from Polysar were used.
Test Name: BUTYL.TST

Temperatures:
- Upper die: 100 deg C
- Lower die: 100 deg C
- Ram: 100 deg C

Pre-heat time: 240 sec
Filling time: 120 sec
Test mode: Varying shear stress
Sampling rate: 20 readings/s
Number of steps: 4

11:24:31
07-31-1989

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Step Duration (sec)</th>
<th>Rotor Speed (rpm)</th>
<th>Sampling Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>.1</td>
<td>Continuous</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1</td>
<td>Continuous</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>10</td>
<td>Continuous</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>0</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

F6 - cont  F7 - retry  F10 - main menu

FIGURE 4.3: A TYPICAL TEST SEQUENCE OF TMS
Steady state stress:

Ten tests were carried out on sample lot 1 each day over a five day period under the following conditions:

Temperature: 100°C
Preheat time: 1 minute
Test time: 8 minutes
Shear rate: 1 second⁻¹

Shear stress values were taken for each test after 4 minutes and statistical analysis was performed to calculate mean, standard deviation and coefficient of variation.

Using standard conditions (see Section 4.6.2), six runs each at temperatures of 100 and 120°C were carried out on sample lots 2 and 3. The mean, standard deviation and coefficient of variation of steady state stress were determined at shear rates of 0.1, 1.0, 10.0 and 30.0 s⁻¹.

Stress Relaxation

In order to investigate the repeatability of stress relaxation data, the mean and standard deviation of time to relax to 1/e of initial stress in steps from 1 s⁻¹ to 0 were determined for sample lots 2 and 3 at 100°C.
5.1 VISCOSITY MODELS

In the present study, a kinetic model proposed by Brodkey and co-workers [24-27] for polymer solutions was modified to model the flow behaviour of elastomers. A new model called a 'Hybrid Model' was developed for carbon black filled compounds. The Bird-Carreau model, discussed in Section 3.3.4.2, was also used to model the steady state flow of gum elastomers by developing computer software for non-linear optimisation.

5.1.1 Kinetic (or Thixotropic) Model

5.1.1.1 Introduction

As already discussed before in Section 3.3.4, Brodkey and co-workers developed a kinetic theory for thixotropic materials. It has its basis in the assumption that the non-linear characteristics can be associated with some structural change of material. The change in viscosity can be attributed to some internal mechanism such as entanglements, association, or unwinding of long chain molecules. For steady state flow behaviour the following equation was proposed:

\[
P_1 - P_2 = \frac{k_2}{k_1} \frac{[(1 - F_T)C]^n}{(F_T C)^m}
\]  

(5.1)
Here $P_1$, $P_2$, $k_1$, $k_2$, $m$ and $n$ are constants which are defined in Section 3.3.4; $C$ is the concentration, and parameter $F_T$ is defined as:

$$F_T = \frac{\eta_a - \eta_{\infty}}{\mu_a - \eta_{\infty}}$$

(5.2)

The viscosity terms $\mu$ and $\eta_{\infty}$ are the lower and upper Newtonian viscosity limits respectively, and $\eta$ is the viscosity associated with changing structure. The letter $a$ in equation 5.2 is a structure parameter - for polymer solutions Brodkey et al took its value as $1/3.5$.

5.1.1.2 Modification of the kinetic model

For elastomers $\eta_{\infty}$ is not usually measurable since polymer degradation becomes a serious problem before sufficiently high shear rates can be obtained. However in the case of elastomers, $\eta_{\infty}$ is generally very small and can be neglected [14]. Thus equation 5.2 reduces to:

$$F_T = \frac{\eta_a}{\mu_a}$$

(5.3)

Equation 5.1 takes account of the concentration, $C$, of the polymer in the solution. For elastomers, the concentration $C$ can be taken as equal to 1 since the materials used in the present study contained no solvent. Hence equation 5.1 can be written as:

$$\tau^{P_1-P_2} = \frac{k_2}{k_1} \frac{(1-F_T)^n}{(F_T)^m}$$

(5.4)
Since \( P_1, P_2, k_1 \) and \( k_2 \) are all constants, equation 5.4 can be reduced further by taking \((P_1 - P_2) = P\) and \((k_2/k_1) = K\).

\[
\tau P = K \frac{(1 - F_T)^n}{F_T^m} \tag{5.5}
\]

by inserting equation 5.3 into equation 5.5, one gets

\[
\tau P = K \frac{[1 - (\frac{n}{m})^a]^n}{[(\frac{n}{m})^a]^m} \tag{5.6}
\]

When equation 5.6 was used to model the steady state flow behaviour of elastomers it was found that better fit to the experimental data was obtained by taking the value of \( a \) as 1 rather than 1/3.5, or any other value. Equation 5.6 can finally be written as:

\[
\tau = \left[ \frac{K (1 - \frac{n}{m})^n}{(\frac{n}{m})^m} \right]^{1/P} \tag{5.7}
\]

Equation 5.7 was termed as the Modified Kinetic Model and it was used to fit the steady state experimental data for SMR 20 and Hypalon 40.

5.1.2 Hybrid Model

5.1.2.1 Definition of a hybrid model

A model which combines fundamental and empirical elements or, if totally empirical, contains adjustable parameters which are explicable by reference to the fundamental characteristics of the system being
modelled. For example, the models developed in the present study are based on power law equations for steady state viscous flow and stress relaxation of raw elastomers. The values of the constants of the basic power law equations for the raw elastomers can be related to the molecular weight characteristics of the elastomers. The effect of the carbon black loading and specific surface area on the constants of the basic equations is then described by empirical polynomial functions.

5.1.2.2 Development of the model

Predicting the dependence of the flow behaviour of rubber compounds on the loading levels and type of carbon black is of considerable technological importance to the performance of processing operations. Both the Bird-Carreau and the modified kinetic model proved to be unsuccessful in modelling the flow behaviour of carbon black filled compounds as the parameters obtained from both models could not be related to the level of loading and surface area of the filler. In view of this result and also because of the lack of a viscosity model in the literature for filled compounds, expressed in terms of loading levels and surface area of the filler, a new model was developed.

As already mentioned in Chapter 3, one of the simplest equations which describes the viscosity of filled elastomer systems is the Einstein equation [70]:

\[ \eta_f = \eta_g (1 + 2.5C) \]  

(5.8)

where \( \eta_f \) = viscosity of the filled medium
\( \eta_g \) = viscosity of the unfilled medium
\( C \) = the volume fraction of filler
Equation 5.8 was found to be inadequate for heavily filled systems. Therefore to account for larger particle concentrations and thus significant interactions among particles, equation 5.8 was modified by Guth, Simha and Gold [71,72].

\[ \eta_f = \eta_g (1 + 2.5C + 14.1C^2) \] (5.9)

Equation 5.9 does not take the filler particle size (or surface area) into account. Analysis of our experimental data showed that the viscosity of a compound at a given shear rate was a function of the volume fraction \( C \) and the specific surface area per unit volume of filler \( \psi \) and could be described adequately by an extension of equation 5.9 to allow for \( \psi \) by the addition of extra terms:

\[ (\eta_f)_{\text{ref}} = \eta_{g1} (1 + a_1C + a_2\psi + a_{11}C^2 + a_{22}\psi^2 + a_{12}C\psi) \] (5.10)

where \((\eta_f)_{\text{ref}} = \) viscosity of the filled compound at a reference shear rate (taken here as 1 s\(^{-1}\))

\( \eta_{g1} = \) viscosity of the gum elastomer at a reference shear rate of 1 s\(^{-1}\)

\( a_1, a_2, a_{11}, a_{22} \) and \( a_{12} \) are constants. The final term in equation 5.10 is an interaction term.

The rate of change of \( \eta_f \) with shear rate which we define here as \( (d(\log\eta_f)/d\log\dot{\gamma}) \), was also found to be a function of \( C \) and \( \psi \) and can be described adequately by a first order polynomial of the following form:
\[
\frac{d(\log n_f)}{d(\log \dot{\gamma})} = n' + \beta_1 c + \beta_2 \psi + \beta_{12} \psi
\]  \hspace{1cm} (5.11)

where \( n' \) = slope of the plot of \( \log n_f \) versus \( \log \dot{\gamma} \) for the gum elastomer

\( \beta_1, \beta_2 \) and \( \beta_{12} \) are constants.

It is apparent from equation 5.10 that it is incapable of predicting the shear rate dependency of the viscosity. It is well known that the viscosity of most polymers and their compounds can be represented by the so called 'power law' model in the pseudoplastic region. Therefore, in order to predict the shear rate dependence of viscosity the following 'power law' relationship was assumed:

\[
\eta_f = K \dot{\gamma}^{(n-1)}
\]  \hspace{1cm} (5.12)

where \( n \) is a constant, called the power law index and \( K \) is the viscosity at a reference shear rate.

Now by taking logs on both sides of equation 5.12 one finds that \((n-1)\) is the slope of the plot of \( \log \eta_f \) versus \( \log \dot{\gamma} \), which means

\[
(n-1) = \frac{d(\log \eta_f)}{d(\log \dot{\gamma})}
\]  \hspace{1cm} (5.13)

By substituting equation 5.11 into equation 5.13 one gets
By definition, $K$ is given by

$$K = (n_f)_{\text{ref}}$$  \hspace{1cm} (5.15)

Substitution of equation 5.10 into equation 5.15 gives

$$K = n_{g1} (1 + \alpha_1 C + \alpha_2 \Psi + \alpha_{11} C^2 + \alpha_{22} \Psi^2 + \alpha_{12} C \Psi)$$  \hspace{1cm} (5.16)

Finally, by substituting equations 5.14 and 5.16 into equation 5.12 one gets an equation which gives the variable shear-rate viscosity for filled compounds in terms of $C$ and $\Psi$:

$$\eta_f = n_{g1} (1 + \alpha_1 C + \alpha_2 \Psi + \alpha_{11} C^2 + \alpha_{22} \Psi^2 + \alpha_{12} C \Psi) \left( n^{'} + \beta_1 C + \beta_2 \Psi + \beta_{12} C \Psi \right)$$  \hspace{1cm} (5.17)

5.2 STRESS RELAXATION MODEL

5.2.1 Introduction

When elastomeric materials are deformed the stresses set up gradually decrease with time. This is the phenomenon of stress relaxation; it plays a very important role in processes like mixing, calendering, extrusion and during mould filling in injection moulding.

As already mentioned in Section 3.7, the shear stress relaxation of gum and filled elastomers (both uncured and cured) can be described by an empirical equation of the following form:
where \( \tau \) is the shear stress at any time \( t \)

\( \tau_1 \) is a constant having units of Pa.s\(^r\) and same numerical value as stress at time 1

\( r \) is the relaxation rate of material in shear, defined by equation 5.19

\[
\therefore r = -\frac{d(\log \tau)}{d(\log t)}
\] (5.19)

In the literature, the effect of filler addition on the stress relaxation of elastomers has only been investigated qualitatively. No attempt has been made in the past to model the stress relaxation behaviour of filled compounds quantitatively in terms of loading levels and surface area of the filler. To fill this gap in the literature, a model is proposed below, by adopting a similar approach to that used in the derivation of a hybrid model for viscosity.

5.2.2 Development of Model
The viscosity of filled compounds can be described by the Einstein equation [70], modified by Guth et al [71,72]:

\[
\eta_f = \eta_g (1 + 2.5c + 14.1c^2)
\] (5.20)

It has also been shown [88,89] that an equivalence exists in the concentration dependence of viscosity and shear modulus, \( G_f \) for filled compounds. The equation of Guth et al, equation 5.20 may thus be transformed into
\[ G_f = G_g (1 + 2.5C + 14.1C^2) \]  \hspace{1cm} (5.21)

where \( G_g \) is the shear modulus of the gum elastomer.

In the present study, analysis of the shear stress relaxation data for all the SMR 20 and Hypalon 40 compounds showed that \( \tau_1 \) in equation 5.18 at a given shear rate was dependent on filler loading and specific surface area, \( \psi \) of the filler; and can be adequately described by an equation similar in form to equation 5.21, by adding a few extra terms to account for \( \psi \).

\[ \tau_1 = \tau_{g1} (1 + A_1 C + A_2 \psi + A_{11} C^2 + A_{22} \psi^2 + A_{12} C \psi) \]  \hspace{1cm} (5.22)

where \( \tau_{g1} \) is the stress in the gum elastomer at time 1, and
\( A_1, A_2, A_{11}, A_{22} \) and \( A_{12} \) are constants and the final term in equation 5.22 is an interaction term.

The rate of relaxation \( r \) in equation 5.18, calculated from the slope of \( \log(\tau(t)) vs \log(t) \) plot for all the compounds, was also found to be function of \( C \) and \( \psi \); and can be described by an equation of the following form:

\[ r = r' + B_1 C + B_2 \psi + B_{12} C \psi \]  \hspace{1cm} (5.23)

where \( r' \) is the slope of the plot of \( \log \tau \) vs \( \log t \) for the gum elastomer and \( B_1, B_2 \) and \( B_{12} \) are constants.
Now, by substituting equations 5.22 and 5.23 into equation 5.18, an equation which describes shear stress relaxation of filled compounds, \( \tau_f(t) \), in terms of \( C \) and \( \psi \) is obtained

\[
\tau_f(t) = \tau_g(1 + A_1 C + A_2 \psi + A_{11} C^2 + A_{22} \psi^2 + A_{12} C \psi) t
\]

\[ (5.24) \]

5.3 COMPUTER PROGRAMMING

All the computing in this project was carried out on the Multics mainframe system at Loughborough University.

5.3.1 Bird-Carreau Model

The Bird-Carreau model is a non-linear mathematical model. The parameters in such models have to be determined by non-linear optimisation techniques. Bird and Carreau obtained the model parameters by using a computer program incorporating a subroutine (C0017-00/S0017-00) which was available at the University of Wisconsin Computer Centre (USA), but unfortunately this subroutine was not available at Loughborough University.

Therefore in order to determine the parameters in the Bird-Carreau model a computer program for multi-variable optimisation was developed in Fortran language by using the so called 'Pattern Search' method. The program is based on an algorithm, by Adby and Dempster [90].
The pattern search method involves taking incremental steps after suitable directions have been found by local exploration. If the search progresses well in terms of decrementing the objective function, the step size is increased; if it is not progressing because the minimum is near, the step size is reduced. When the step size is reduced below a set figure the search is ended.

If a multivariable search (i.e. the parameters $x_1, x_2 \ldots x_n$) is considered, the following is needed:

i) The experimental values - for example shear rate vs viscosity values.

ii) A function given by $E = f(x_1, x_2 \ldots x_n)$ which is to be minimised.

iii) A first approximation $x_{1,0}, x_{2,0} \ldots x_{n,0}$

iv) Initial parameter increments $\delta x_1, \delta x_2, \ldots \delta x_n$

v) Parameter increment below which the search is terminated.

The second suffix to the parameters $x_1, x_2 \ldots x_n$ is used to signify the iteration number. At each iteration the value of $x_1, x_2 \ldots$ and $x_n$ is used as a base for local exploration. When a direction has been found a pattern move is made to a new base.

The method and the algorithm are described in full detail by Adby and Dempster in their textbook [90]. For better understanding, a flow chart representation of the method is shown in Figures 5.1 and 5.2. The listing of the program is shown in Appendix A.
Figure 5.1: Flow chart for non-linear optimisation program
Figure 5.2: Flow chart for an exploration
To obtain the parameters in the Bird-Carreau model, the function to be minimised in the program was taken as the sum of the square of errors between the viscosity calculated by the model and the experimentally determined viscosity over the whole shear rate range. As mentioned before, the program requires initial guesses for the parameters. The value of zero shear viscosity $\eta_0$ obtained from creep experiments was fixed to the model whilst other parameters varied until minimum error was found. The error is defined as follows:

$$\text{Error} = \sum \left( \frac{\eta_{\text{calculated}} - \eta_{\text{experimental}}}{\eta_{\text{experimental}}} \right)^2$$

(5.25)

5.3.2 The Modified Kinetic Model

To obtain the parameters in the kinetic model, the same method as outlined in Section 5.3.1 was used. However a listing of the program for the kinetic model is also shown in Appendix B for the following reasons:

i) to show how the program can be used for two totally different models

ii) to show how the program can be changed from optimising two parameters to optimising four parameters

5.3.3 The Evaluation of Constants for the Hybrid Models

5.3.3.1 Viscosity model

All the constants in the model were determined by using a computer package called GLIM (Generalised Linear Interactive Modelling) [91] which is available on the Multics mainframe system at Loughborough University. The procedure was as follows:
i) For all the compounds, the ratios of viscosity of filled compound to that of gum elastomer were determined at a reference shear rate of 1 s⁻¹.

ii) The ratio of viscosities was then designated as a dependent variable and the loading level and the surface area of the filler as independent variables. For all the compounds, the ratios of viscosities in terms of loading levels (C) and the surface area of the filler (ψ) were then fed into the GLIM for a second order polynomial fit. GLIM then determined the constants α₁, α₂, α₁₁, α₂₂ and α₁₂ in equation 5.17 by minimising the error between calculated and experimental values.

iii) For the determination of constants β₁, β₂ and β₁₂ in equation 5.17, the slopes of the plots of log(viscosity) vs log(shear rate) for all the compounds in terms of C and ψ were calculated and fed into GLIM for a first order polynomial fit.

iv) Once all the constants had been determined, the viscosity at different shear rates was then calculated in terms of C and ψ. The sum of squares error (equation 5.25) was determined over the whole shear rate range.
5.3.3.2 Stress relaxation model

The constants in equation 5.24 were calculated as follows:

i) The ratios of stress of filled compounds to that of gum elastomer at a reference time of 1 second were calculated from experimental data in terms of $C$ and $\psi$ and fed into the GLIM. The constants $A_1$, $A_2$, $A_{11}$, $A_{22}$ and $A_{12}$ in equation 5.24 were then determined by fitting the data to a second order polynomial.

ii) The rates of relaxation for all the compounds, in terms of $C$ and $\psi$, were determined from the slopes of log(stress) vs log(time) plots. The data was then fed into the GLIM for a first order polynomial fit and the constants $B_1$, $B_2$ and $B_{12}$ in equation 5.24 obtained.

iii) The sum of square errors between the calculated and experimental stresses was determined over the time range studied. For stress relaxation, the error is defined as:

$$\text{Error} = \sum \left( \frac{\tau_f(t)_{\text{calculated}} - \tau_f(t)_{\text{experimental}}}{\tau_f(t)_{\text{experimental}}} \right)^2$$  

(5.26)
CHAPTER 6
RESULTS AND DISCUSSION

6.1 ZERO SHEAR VISCOSITY

6.1.1 Results
Zero shear viscosities, \( \mu \), for gum elastomers were obtained by parallel plate rheometry. The results for natural rubber (SMR 20) and chlorosulphonated polyethylene, CSM (Du Pont, Hypalon 40) at temperatures of 353, 373 and 393K are shown in Table 6.1.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( \dot{\gamma} ) (s(^{-1}))</th>
<th>( \mu ) (Pa.s)</th>
<th>( \dot{\gamma} ) (s(^{-1}))</th>
<th>( \mu ) (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>8.395x10(^{-5})</td>
<td>8.620x10(^6)</td>
<td>3.162x10(^{-4})</td>
<td>7.070x10(^5)</td>
</tr>
<tr>
<td>373</td>
<td>1.879x10(^{-4})</td>
<td>3.850x10(^6)</td>
<td>8.632x10(^{-4})</td>
<td>2.780x10(^5)</td>
</tr>
<tr>
<td>393</td>
<td>2.185x10(^{-4})</td>
<td>1.925x10(^6)</td>
<td>3.162x10(^{-3})</td>
<td>1.206x10(^5)</td>
</tr>
</tbody>
</table>

TABLE 6.1: ZERO SHEAR VISCOSSITIES FOR SMR 20 AND HYPALON 40

Plots of log (viscosity) vs (1/temperature) for SMR 20 and Hypalon 40 are shown in Figures 6.1 and 6.2 respectively. The values of activation energy, \( E \), of viscous flow are given in Table 6.2.

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Activation Energy E, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR 20</td>
<td>43.02</td>
</tr>
<tr>
<td>Hypalon 40</td>
<td>51.04</td>
</tr>
</tbody>
</table>

TABLE 6.2: ACTIVATION ENERGY OF VISCOUS FLOW
Fig. 6.1. Arrhenious plot. Ln Zero Shear Viscosity vs. 1/Temperature for gum SMR 20.

Fig. 6.2. Arrhenious plot. Ln Zero Shear Viscosity vs. 1/Temperature for gum Hypalon 40.
The sample metal contact area used for the determination of zero shear viscosity was $2.04 \times 10^{-3}$ m$^2$. In order to assess the edge effects it was changed to $1.7 \times 10^{-3}$ m$^2$. The results for SMR 20 are shown in Table 6.3.

To investigate the effect of slippage between the rubber sample and plates, a rheometer with grooves of 0.3 mm deep was also used.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>$1.554 \times 10^{-4}$</td>
<td>$8.560 \times 10^6$</td>
</tr>
<tr>
<td>373</td>
<td>$3.133 \times 10^{-4}$</td>
<td>$3.850 \times 10^6$</td>
</tr>
<tr>
<td>393</td>
<td>$3.823 \times 10^{-4}$</td>
<td>$1.893 \times 10^6$</td>
</tr>
</tbody>
</table>

**TABLE 6.3: VISCOSITY OF SMR 20 AT DIFFERENT TEMPERATURES AND SHEAR RATES**

6.1.2 Discussion

Using the parallel plate rheometer the zero shear viscosities were determined for SMR 20 and Hypalon 40 at different temperatures (see Tables 6.1 and 6.2). To test whether we are in the Newtonian region, the Arrhenius equation was applied to the results in Table 6.1. Since the viscosities shown in Table 6.1 are all at different shear rates, a straight line plot of $\ln(\eta)$ vs $1/T$ would indicate both that the Arrhenius equation is obeyed and the viscosities are in the Newtonian region. Plots of $\ln(\mu)$ vs $1/T$ for SMR 20 and Hypalon 40 are shown in Figures 6.1 and 6.2 respectively. It can be seen that fairly good straight line relationships are obtained in both figures, which
indicates that the viscosity is independent of shear rate and it only depends on temperature. The zero shear viscosities found are in the range of $10^5 - 10^6$ Pa.s. Similar results have been reported in the literature [54,62,63] for other elastomers.

Comparison of results in Tables 6.1 and 6.3 shows that increasing the shear rate, at a given temperature, has no effect on the viscosity of SMR 20. This observation shows again that at very low shear rates the viscosity is independent of shear rate.

By noting that similar values of viscosity are obtained using different sample lengths, one can conclude that the edge effects were small. Varying sample thickness between 2.5 and 3.0 mm caused no significant differences in the results. The effect of slippage between rubber sample and plates was investigated by using grooved plates. The results obtained by using grooved plates were in good agreement with those obtained from ungrooved plates. Thus it was concluded that there was no significant slip in the rheometer.

At very large deformations, non-linearity was observed in the deformation vs time plot. This was probably due to the fact that under these conditions the material tended to pull away from the metal surface, thus reducing the effective sample to metal contact area. When this happens, the stress ceases to be constant and hence the observed change in deformation rate.
Since it is practically impossible to measure viscosities of elastomers at very low shear rates by conventional techniques, such as capillary flow or cone and plate rheometer, the creep experiment provides a very important and simple method to measure zero shear viscosity.

Temperature dependence of the zero shear viscosity can be easily evaluated in terms of activation energy of viscous flow. The higher the activation energy, the higher the sensitivity to temperature. In the Newtonian region, activation energies of 43.02 and 51.04 kJ/mol were obtained for SMR 20 and Hypalon 40 respectively. From these results it follows that Hypalon 40 is more sensitive to temperature than SMR 20.

6.2 VISCOSITY MEASUREMENTS WITH CONE AND PLATE RHEOMETER

6.2.1 Results
The viscosity as a function of shear rate was determined for both gum elastomers from the cone and plate rheometer data by a method outlined in Section 3.8.3.2. Two cones (4° and 6°) were used and it was found that there were no significant differences between the results obtained from both cones. The weights used ranged from 0.15 to 3.0 kg.

When viscosity, obtained from the parallel plate, cone and plate and TMS rheometer were plotted against shear rate it was found that the flow curve was not continuous. A typical example for SMR 20 at 100°C is shown in Figure 6.3. It can be seen from the figure that the viscosity curve from cone and plate falls below that of parallel plate
Fig. 6.3. A typical example of Cone & Plate data for SMR 20 at 100°C before correction. Legend: • Parallel Plate data; △ Cone & Plate data; ■ TMS data.

Fig. 6.4. A typical example of Cone & Plate data for SMR 20 at 100°C after correction. Legend: • Parallel Plate data; △ Cone & Plate data; ■ TMS data.
and TMS data. The shift in curves is attributed to the sample temperature in the cone and plate rheometer being higher than the set temperature. Partially it could also be due to the fact that the data over a range of shear rates was obtained from entirely different instruments.

However, in all experiments it was found that the viscosity curve from the cone and plate was parallel to those obtained from the TMS and parallel plate rheometers. This meant the viscosity at each shear rate was displaced by an equal amount. Therefore in order to correct the cone and plate data a shift factor was used at each temperature.

With two parallel curves, the only distance which is constant between the two lines is the perpendicular distance from a tangent at any point on the curve. In order to find this distance the cone and plate curve was extrapolated downward. A tangent was drawn at any point on this curve and the perpendicular distance to the TMS curve was determined at a given temperature. Once this perpendicular distance had been obtained, the whole cone and plate curve at that temperature was then shifted upward by the same amount. To avoid repetition the corrected cone and plate results will be shown later on in Section 6.7.

The effect of viscous heating on temperature rise in the sample was investigated. Viscous flow is a dissipative process and energy will be converted into heat. To calculate the approximate temperature rise due to shear heating it was assumed that there is no heat loss from the sample. Clearly this will overestimate shear heating effects since
there will be some heat loss. However it will indicate if shear heating is likely to be significant.

The temperature rise, \( \Delta T \), per second of shearing is given by:

\[
\Delta T = \frac{J_t}{\rho C_p} \quad (6.1)
\]

where \( \rho \) is the density of the elastomer

\( C_p \) is the specific heat capacity of the elastomer

Typical results for SMR 20 are given in Table 6.4 for the highest shear rate encountered at each temperature. The specific heat capacities of SMR 20 natural rubber at 80, 100 and 120°C are 2370, 2450 and 2490 J/kg°C and the density is 930 kg/m³.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Maximum Temperature Rise in the Sample, °C/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>( 2.94 \times 10^{-4} )</td>
</tr>
<tr>
<td>100</td>
<td>( 2.36 \times 10^{-4} )</td>
</tr>
<tr>
<td>120</td>
<td>( 1.67 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

**TABLE 6.4: VISCOSOUS HEATING EFFECTS IN SMR 20 NATURAL RUBBER**

The friction in the bearing was estimated by determining the torque which must be applied to rotate the cone when no sample was present. The torque was calculated to be \( 1.225 \times 10^{-3} \) Nm.
It was not possible to determine the viscosity of filled compounds with the cone and plate rheometer as the sample tended to come out of the gap when stresses were applied. Even with gum elastomers it was noticed that the sample was beginning to exude slowly from the gap when shear stress was in the region of $1.5 \times 10^4 \text{ N/m}^2$.

6.2.2 Discussion

A typical example of uncorrected data from the cone and plate is shown in Figure 6.3 and the corrected version is shown in Figure 6.4. All the results obtained from cone and plate were corrected by using a shift factor at each temperature and will be shown later on in Section 6.7. Since the entire curve was shifted by an equal amount at a given temperature, it should not invalidate the results in any way when it comes to modelling the rheological behaviour.

Batchelor [83] has shown that inertial effects in a cone and plate rheometer below a shear rate of $1 \text{ s}^{-1}$ are insignificant. The inertial effects, therefore, were assumed to be negligible in the present study. This is a valid assumption since the maximum shear rate obtained for either elastomer was less than $0.05 \text{ s}^{-1}$.

The effect of friction in the bearing was investigated by determining the torque required to rotate the cone when no sample was present. The torque was found to be $1.225 \times 10^{-3} \text{ Nm}$. Since the lowest torque applied in the present experiments was $3.675 \times 10^{-2} \text{ Nm}$, friction in the bearings is unlikely to affect the results.
The effect of viscous heating on temperature rise in SMR 20 samples is shown in Table 6.3. The maximum temperature rise \((2.94 \times 10^{-4} \, ^\circ C/s)\) is observed at 80°C. Even at this temperature, continuous shearing for 30 minutes will only produce a temperature rise of 0.5°C. Since Hypalon 40 has lower viscosity than SMR 20, the temperature rise in Hypalon 40 samples will be even lower than SMR 20. In practice the temperature rise, because of heat losses, will be much smaller than shown in Table 6.3 but the results do show that viscous heating effects are small and can be neglected.

Lower than expected values of viscosity were obtained for both elastomers. This was largely due to the incorrect temperature control by the band heater on the plate. The temperature was controlled by a PI controller by inserting a thermocouple to the centre of the plate. The band heater provides heat to the surface of the plate and then the transfer of heat towards the centre takes place by conduction. When the temperature at the centre of the plate went below the set temperature the heater was automatically switched on. It then took some time for the temperature to reach the set point again, as the conduction of heat through metals is not an instantaneous process. During this time the heater remained switched on and the temperature near the edge of the plate went up several degrees above the set temperature. Thus a temperature distribution across the plate would be obtained, with temperature being highest at the edge and lowest at the centre. Since most of the shearing in a cone and plate geometry takes place towards the edge, any rise in temperature there would reduce the viscosity considerably as has been observed in our experiments.
It was attempted to determine the temperature distribution across the plate, but due to poor contact between the thermocouple and the plate very inconsistent results were obtained.

From the results one can conclude that the temperature cannot be controlled precisely by using a band heater on the plate. One way of eliminating this problem would be to control the sample temperature by circulating silicone oil through the plate from an external thermostatic tank. It would give a constant temperature profile across the plate.

The shift in viscosity, to some extent, could also be due to the fact that different instruments were used to obtain the data over the shear rate range studied. Malik and Carreau [66] have reported a similar shift in viscosity curve with data obtained from two different instruments. Before it could be verified how much of this shift is due to using different instruments further work will be required, after the problem with temperature control has been solved.

For filled compounds it was not possible to make any measurements as the sample tended to exude from the gap when load was applied. Similar findings have been reported by Hutton [84]. He found that the test sample fractures and exudes from the space between cone and plate when total elastic energy contained in the sample exceeds a critical value. According to Hutton [84] and Han [85] the upper limit of operable shear stress of this instrument is about $10^4$ N/m$^2$ and it is independent of the type of test fluid (i.e. regardless of fluid viscosity). In the present study however the upper limit of this stress was found to be about $1.5 \times 10^4$ N/m$^2$. 
Lobe and White [60] and Tanaka and White [61] have shown that carbon black reinforced polymers show "yield stress" values. Due to the presence of high yield stresses the operable shear stress was being exceeded in all the compounds and hence the fracture of the sample. With some compounds (for example 40 and 60 phr of N330 and N110) the upper limit of the operable stress was exceeded, even before the flow could begin.

6.3 VISCOSITY MEASUREMENTS WITH NEWLY DESIGNED SHEAR TEST SPECIMEN

6.3.1 Results
In order to determine the viscosity of filled compounds shear test specimens were prepared with the newly designed transfer mould. When these specimens were tested on an Instron tensile tester in the shear rate range of $10^{-4}$ to $10^{-2}$ s$^{-1}$, it was discovered that steady state stress could not be achieved, even after 100% strain. A typical stress-time relationship, obtained from the Instron, is shown in Figure 6.5.

![Stress vs Time Plot](image)

**FIGURE 6.5:** A TYPICAL STRESS VS TIME PLOT FROM THE INSTRON TENSILE TEST MACHINE
6.3.2 Discussion

The use of the transfer mould to produce good shear test specimens proved to be a success. The usefulness of using the rubber to metal bonding technique was also demonstrated when no slip was observed between the rubber sample and the metal plates during the test on the Instron.

Unfortunately, the analysis of the experimental data showed that steady state flow could not be achieved in the time scale of 100\% strain. These results agree with those obtained by Middleman [80] for polyisobutylene. Therefore it was concluded that it is not possible to measure viscosity of filled compounds at low shear rates by using this technique.

The failure, in the achievement of steady state flow in our experiments, could be explained by the fact that approach to equilibrium condition under constant shear rate mode is very slow, whereas under constant stress mode steady flow is attained rapidly. It can be demonstrated clearly by considering a Maxwell model (equation 3.16).

\[
\frac{d\gamma}{dt} = \frac{1}{G} \frac{d\tau}{dt} + \frac{\tau}{\mu} \quad (6.2)
\]

Integrating equation 6.2 at constant stress gives

\[
\gamma = \frac{\tau}{\mu} t \quad (6.3)
\]
Equation 6.3 describes the relationship between strain and time under constant stress mode.

By taking $\frac{d\dot{Y}}{dt} = \dot{Y}$, and $\frac{\gamma}{G} = \lambda$ (a relaxation time) and then rearranging equation 6.2 one gets

$$\frac{d\tau}{(\tau - \mu Y)} = -\frac{dt}{\lambda_1} \quad (6.4)$$

Integrating equation 6.4 at constant shear rate one obtains

$$\tau = \mu \dot{Y} \left(1 - e^{-t/\lambda}\right) \quad (6.5)$$

Equations 6.3 and 6.5 can be represented in a graphical form as shown in Figure 6.6.

**FIGURE 6.6: DEFORMATION OF MAXWELL MODEL**
From Figure 6.6 it can be clearly seen that under constant shear rate
the approach to equilibrium condition is very slow, whereas under
constant stress steady flow is attained rapidly. In order to obtain
viscosities at low shear rates therefore, one has to use instruments
which operate under constant stress rather than constant shear rate.

6.4 REPEATABILITY STUDY ON NEGRETTI TMS BICONICAL ROTOR RHEOMETER

6.4.1 Results

Steady State Stress:
To test the reliability of the data from the TMS three different
sample lots of butyl rubber were used.

Ten tests were carried out on sample lot 1 each day over a five day
period at 100°C. For each run, mean stress (\(\bar{\tau}\)) (at a shear rate of
1 s\(^{-1}\)) and standard deviation (\(\sigma\)) are shown in Table 6.5.

For day to day variation over five days, the coefficient of variation
(COV)\(^*\) of the means was found to be 0.096\%. For the whole 50 tests,
COV was calculated to be 0.47\%.

<table>
<thead>
<tr>
<th>Run</th>
<th>Mean ((\bar{\tau})) (for 10 tests)</th>
<th>Standard Deviation ((\sigma))</th>
<th>COV, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>125.32</td>
<td>0.40</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>125.54</td>
<td>0.95</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>125.33</td>
<td>0.64</td>
<td>0.51</td>
</tr>
<tr>
<td>4</td>
<td>125.41</td>
<td>0.43</td>
<td>0.34</td>
</tr>
<tr>
<td>5</td>
<td>125.22</td>
<td>0.43</td>
<td>0.34</td>
</tr>
</tbody>
</table>

* Coefficient of Variation (COV) = \(\left(\frac{\text{Standard deviation, } \sigma}{\text{mean, } \bar{\tau}}\right) \times 100\%\)
To study the reliability of data at different shear rates and temperatures, six runs at each temperature and shear rate were carried out on sample lots 2 and 3. The mean, standard deviation and coefficient of variation for sample lots 2 and 3 are shown in Tables 6.5 and 6.7 respectively.

<table>
<thead>
<tr>
<th>( \gamma (s^{-1}) )</th>
<th>( \bar{x} ) (kPa)</th>
<th>( \sigma )</th>
<th>COV(%)</th>
<th>( \bar{x} ) (kPa)</th>
<th>( \sigma )</th>
<th>COV(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>52.14</td>
<td>0.77</td>
<td>1.47</td>
<td>24.25</td>
<td>0.38</td>
<td>1.57</td>
</tr>
<tr>
<td>1.0</td>
<td>106.45</td>
<td>4.25</td>
<td>3.99</td>
<td>67.10</td>
<td>0.49</td>
<td>0.73</td>
</tr>
<tr>
<td>10.0</td>
<td>176.12</td>
<td>1.64</td>
<td>0.93</td>
<td>141.87</td>
<td>1.30</td>
<td>0.92</td>
</tr>
<tr>
<td>30.0</td>
<td>184.52</td>
<td>0.57</td>
<td>0.31</td>
<td>172.71</td>
<td>0.47</td>
<td>0.27</td>
</tr>
</tbody>
</table>

**TABLE 6.6: STATISTICAL ANALYSIS ON SAMPLE LOT 2**

<table>
<thead>
<tr>
<th>( \gamma (s^{-1}) )</th>
<th>( \bar{x} ) (kPa)</th>
<th>( \sigma )</th>
<th>COV(%)</th>
<th>( \bar{x} ) (kPa)</th>
<th>( \sigma )</th>
<th>COV(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>56.35</td>
<td>0.80</td>
<td>1.42</td>
<td>27.15</td>
<td>0.44</td>
<td>1.62</td>
</tr>
<tr>
<td>1.0</td>
<td>106.60</td>
<td>0.96</td>
<td>0.90</td>
<td>71.51</td>
<td>1.65</td>
<td>2.32</td>
</tr>
<tr>
<td>10.0</td>
<td>174.38</td>
<td>1.88</td>
<td>1.08</td>
<td>154.20</td>
<td>1.28</td>
<td>0.83</td>
</tr>
<tr>
<td>30.0</td>
<td>181.51</td>
<td>0.59</td>
<td>0.32</td>
<td>175.36</td>
<td>0.45</td>
<td>0.26</td>
</tr>
</tbody>
</table>

**TABLE 6.7: STATISTICAL ANALYSIS ON SAMPLE LOT 3**

**Stress Relaxation**

In order to investigate the repeatability of stress relaxation data the mean (of six test runs) and standard deviation of time to relax to 1/\( e \) of initial stress in step from 1 \( s^{-1} \) to 0 were determined for sample lots 2 and 3 at 100°C. The results are shown in Table 6.8.
### TABLE 6.8: STATISTICAL ANALYSIS ON STRESS RELAXATION DATA

<table>
<thead>
<tr>
<th>Material</th>
<th>$\bar{X}$ (seconds)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample lot 2</td>
<td>3.63</td>
<td>0.24</td>
</tr>
<tr>
<td>Sample lot 3</td>
<td>4.29</td>
<td>0.54</td>
</tr>
</tbody>
</table>

#### 6.4.2 Discussion

The results in Tables 6.5, 6.6 and 6.7 show that for steady state flow behaviour the run to run repeatability of TMS is quite good. For sample lot 1 the test to test variation (for 50 tests) was calculated to be 0.47% and day to day variation as 0.096%.

In order to investigate the repeatability at different temperatures and shear rates, tests were carried out on sample lots 2 and 3 at two different temperatures and four different shear rates. The results are shown in Tables 6.6 and 6.7. It can be seen from the results that the change in the coefficient of variation is not very significant. From these results one can conclude that the repeatability of TMS is independent of temperature, shear rate and the type of material used.

From Table 6.8, it is seen that the repeatability of stress relaxation data is also fairly good. For sample lots 2 and 3, the standard deviations of 0.24 and 0.54 are obtained respectively.

By carrying out this study on the TMS rheometer we have obtained a repeatability base-line against which the significance of inter-sample comparisons can be assessed in future.
6.5 VISCOSITY AND STRESS RELAXATION MEASUREMENTS WITH TMS RHEOMETER

6.5.1 Results
Viscosity in the shear rate range of 0.1-100 s⁻¹ was measured with the TMS rheometer at temperatures of 80, 100 and 120°C.

However it was discovered that for some of the compounds it was not possible to measure their viscosities at the following temperatures:

80°C: SMR 20 containing 40 and 60 phr of N330 and N110
     : Hypalon 40 containing 45 phr of N762 and N330
100°C: SMR 20 containing 60 phr of N330 and N110
120°C: SMR 20 containing 60 phr of N330 and N110.

The viscosity data from the TMS at 100 and 120°C is used to model the steady shear flow of elastomers and their compounds and is shown in Section 6.7. The data at 80°C is given in Appendix C.

The shear stress relaxation behaviour of elastomers and their compounds, at temperatures of 100 and 120°C was also measured with the TMS rheometer and is shown in Section 6.8.

6.5.2 Discussion
Because of the failure in obtaining results from the parallel plate and the cone and plate rheometers, only the TMS rheometer data is used to model the rheological behaviour of filled compounds. The results obtained from the TMS rheometer are shown in Sections 6.7 and 6.8.
During measurements with the TMS rheometer, it was discovered that for some of the compounds it was not possible to measure their viscosities because of incomplete, or no injection at all, of the material into the test cavity. This occurred because the yield stresses of these compounds were far too high for the flow to take place from the transfer pot to the test cavity.

Analysis of the steady state data showed that in many cases the values of shear stresses were higher at a shear rate of 40 s\(^{-1}\) than at 60 s\(^{-1}\). This was tentatively attributed to the temperature rise in the sample due to shear heating but further work is needed for confirmation. Because of this temperature rise problem it was decided not to use TMS data above a shear rate of 40 s\(^{-1}\). However methods are currently being developed at Loughborough University to correct for the temperature rise in the sample at higher shear rates. Therefore, hopefully, in the near future it will be possible to use the TMS data over its full range of shear rate.

6.6 TEMPERATURE DEPENDENCE OF VISCOSITY OF FILLED COMPOUNDS

6.6.1 Results
Temperature dependence of viscosity of filled compounds was evaluated in terms of activation energy, \(E_\gamma\), at constant shear rate by using the Arrhenius equation

\[ \eta = A e^{E_\gamma/RT} \]  \hspace{1cm} (6.6)
It can be seen from equation 6.6 that a plot of ln(\(\eta\)) vs (1/T) would give the slope as \(E_\gamma/R\). Plots of ln (viscosity) vs (1/Temperature) are shown in Figures 6.6 and 6.7 for SMR 20 compounds and in Figures 6.8 and 6.9 for Hypalon 40 compounds at a shear rate of 1 s\(^{-1}\). Figures 6.10 and 6.11 show results for SMR 20 compounds at a shear rate of 5 s\(^{-1}\).

The activation energy (\(E_\gamma\)) of the viscous flow was evaluated from the slopes of ln (viscosity) vs (1/Temperature) plots and are shown in Tables 6.9 and 6.10.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Activation Energy, (E_\gamma), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\dot{\gamma} = 1) s(^{-1})</td>
</tr>
<tr>
<td>SMR 20</td>
<td>13.77</td>
</tr>
<tr>
<td>SMR 20 + 20 phr N762</td>
<td>12.62</td>
</tr>
<tr>
<td>SMR 20 + 40 phr N762</td>
<td>10.83</td>
</tr>
<tr>
<td>SMR 20 + 20 phr N330</td>
<td>14.55</td>
</tr>
<tr>
<td>SMR 20 + 40 phr N330</td>
<td>11.64</td>
</tr>
<tr>
<td>SMR 20 + 20 phr N110</td>
<td>12.61</td>
</tr>
</tbody>
</table>

TABLE 6.9: VALUES OF ACTIVATION ENERGY OF VISCOS FLOW FOR SMR 20 COMPOUNDS AT SHEAR RATES OF 1 AND 5 s\(^{-1}\)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Activation Energy, (E_\gamma), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypalon*</td>
<td>33.21</td>
</tr>
<tr>
<td>Hypalon + 15 phr N762</td>
<td>31.70</td>
</tr>
<tr>
<td>Hypalon + 30 phr N762</td>
<td>28.53</td>
</tr>
<tr>
<td>Hypalon + 15 phr N330</td>
<td>29.12</td>
</tr>
<tr>
<td>Hypalon + 30 phr N330</td>
<td>27.23</td>
</tr>
</tbody>
</table>

* Hypalon = Hypalon 40 + 20 phr litharge

TABLE 6.10: VALUES OF ACTIVATION ENERGY OF VISCOS FLOW FOR HYPALON 40 COMPOUNDS AT A SHEAR RATE OF 1 s\(^{-1}\)
Fig. 6.7. Arrhenious plot. Log Viscosity vs. $1/T$ for SMR 20 compounds at a shear rate of 1 per second. Legend:
- SMR 20;
- 20phr N762;
- 40 phr N762.

Fig. 6.8. Arrhenious plot. Log Viscosity vs. $1/T$ for SMR 20 compounds at a shear rate of 1 per second. Legend:
- 20 phr N330;
- 20 phr N110;
- 40 phr N330.
Fig. 6.9. Arrhenius plot. Log Viscosity vs. $1/T$ for Hypalon 40 compounds at a shear rate of 1 per second. Legend: • Hypalon 40; △ 15 phr N762; ■ 30 phr N762.

Fig. 6.10. Arrhenius plot. Log Viscosity vs. $1/T$ for Hypalon 40 compounds at a shear rate of 1 per second. Legend: • 15 phr N330; △ 30 phr N330.
Fig. 6.11. Arrhenious plot. Log Viscosity vs. $1/T$ for SMR 20 compounds at a shear rate of 5 per seconds. Legend:
- • SMR 20;
- △ 20phr N762;
- ■ 40 phr N762.

Fig. 6.12. Arrhenious plot. Log Viscosity vs. $1/T$ for SMR 20 compounds at a shear rate of 5 per seconds. Legend:
- • 20 phr N330;
- △ 20 phr N110;
- ■ 40 phr N330.
6.6.2 Discussion

Numerical determination of the thermal dependence of flow is easily evaluated in terms of activation energy at constant shear rate. Activation energy is a useful constant for characterisation of non-Newtonian polymer flow. The values of activation energy ($E$) of viscous flow for compounds are shown in Tables 6.9 and 6.10. For brevity, the values of $E$ were evaluated at two different shear rates only. Figures 6.6-6.11 show that viscosity at a given shear rate is decreased by increase in temperature.

It can be seen from Tables 6.9 and 6.10 that the change in activation energy for the viscous flow of filled compounds at a given shear rate is not significant. This indicates that the activation energy of the viscous flow of filled compounds is almost independent of the level of loadings and particle size (or specific surface area) of the filler. This result is in agreement with that of other authors [54,67-69] who have reported similar findings for various other elastomer compounds and filler reinforced thermoplastic melts. From these results, it can now be realised that the flow in elastomer compounds takes place predominantly in the elastomer phase [67]. That is, the relative flow of filler takes place together with the adsorbed elastomeric layer. Thus, the molecular flow mechanism for compounds is the same as that of pure elastomers.

From Table 6.9 it is seen that the activation energy decreases with increasing shear rate. This result is in agreement with that of Phillipoff and Gaskins [18]. They carried out extensive studies on polyethylene to determine the dependence of activation energy on shear.
rate and found that the values of $E$ decreased with increasing shear rate. The reduction in activation energy with increasing shear rate is possibly due to the fact that the resistance to viscous flow is shear rate dependent. With increase in shear, the rate of disentanglements and entanglements will increase. This will result in lower resistance to viscous flow and hence the reduction in activation energy with increase in shear rate.

Comparison of Tables 6.9 and 6.10 shows that at a given shear rate lower values of activation energy are obtained for SMR 20 compounds than for Hypalon 40 compounds. This result indicates that the viscosity of Hypalon 40 compounds is more temperature sensitive than SMR 20 compounds.

6.7 MODELLING THE STEADY STATE SHEAR FLOW OF ELASTOMERS AND THEIR COMPOUNDS

6.7.1 Bird-Carreau Model

6.7.1.1 Results

The non-linear rheological model of Bird-Carreau [47,48] was used to model the steady state flow behaviour of gum SMR 20 and Hypalon 40. As discussed earlier in Chapter 3 the following expressions for viscosity at low and high shear rates respectively were used.

Low shear rate:

$$n = 1 - \frac{(2^a_1 \lambda_1 \gamma)^2}{2(a_1) - 1} \sum_{p=2}^{\infty} \frac{p^{-a_1}}{p^2a_1 + (2^a_1 \lambda_1 \gamma)^2}$$ (6.7)
High shear rate: 
\[
\mu = \frac{1}{2(\alpha_1)^{-1}} \left\{ \frac{\alpha_1}{\lambda_1 \gamma} \left( \frac{1-\alpha_1}{\alpha_1} \right) \pi \right\} - \frac{1}{2 \sin(\frac{1+\alpha_1}{2} \pi)} - \frac{1}{(a_1+1)(2^{a_1} \lambda_1)^2} \frac{1}{2[1+(2^{a_1} \lambda_1)^2]} \right\}
\]

For both elastomers, the zero shear viscosity \( \mu \), was determined directly from the parallel plate rheometer. A non-linear optimisation programme (see Appendix A) was then used to obtain the values of \( \alpha_1 \) and \( \lambda_1 \), which minimised the square error between calculated and experimental viscosity data over the whole shear rate range (i.e., data from parallel plate, cone and plate TMS rheometers). The Bird-Carreau model parameters and the error estimates for SMR 20 and Hypalon 40 are listed in Tables 6.11 and 6.12 respectively.

The model fit and the experimental data at temperatures of 80, 100 and 120°C are shown in Figures 6.13 and 6.14 for SMR 20 and Hypalon 40 respectively.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \mu ) (Pa.s)</th>
<th>( \alpha_1 )</th>
<th>( \lambda_1 ) (sec)</th>
<th>Error = ( \frac{\eta_{calc} - \eta_{exp}}{\eta_{exp}} )²</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>8.620x10⁶</td>
<td>4.78</td>
<td>148.0</td>
<td>0.111</td>
</tr>
<tr>
<td>100</td>
<td>3.850x10⁶</td>
<td>3.73</td>
<td>126.0</td>
<td>0.096</td>
</tr>
<tr>
<td>120</td>
<td>1.925x10⁶</td>
<td>3.26</td>
<td>100.2</td>
<td>0.123</td>
</tr>
</tbody>
</table>

**TABLE 6.11: THE BIRD-CARREAU MODEL PARAMETERS FOR SMR 20**
Fig. 6.13. Shear flow of SMR 20 natural rubber.
Exptl pts.: ● 80°C; △ 100°C; ■ 120°C.
Bird–Carreau model fit: —— 80°C; ---- 100°C; ------ 120°C.
Fig. 6.14. Shear flow of Hypalon 40 rubber. Exptl pts. : • 80°C; △ 100°C; ■ 120°C. Bird–Carreau model fit :— 80°C ;—-100°C ;——— 120°C.
| Temperature (°C) | μ (Pa.s) | α₁ | λ₁ (sec) | Σ (|μₕₑₐₓ| - μₑₓ)² |
|-----------------|---------|----|----------|------------------|
| 80              | 7.079x10⁵ | 2.52 | 12.0     | 0.134 |
| 100             | 2.780x10⁵ | 2.01 | 11.2     | 0.086 |
| 120             | 1.206x10⁵ | 1.72 | 13.0     | 0.047 |

**TABLE 6.12: THE BIRD-CARREAU MODEL PARAMETERS FOR HYPALON 40**

### 6.7.1.2 Discussion

The Bird-Carreau model fits the steady state data very well for both elastomers (Figures 6.13 and 6.14). Over the shear rate range investigated, the sum of square of errors between experimental and calculated values are in the range of 4 to 13% (see Tables 6.11 and 6.12). These error estimates are similar to those reported by Blank et al [92]. They used the Bird-Carreau model to analyse the steady shearing flow of aqueous Sepran solutions.

The model parameters are shown in Tables 6.11 and 6.12. To obtain the parameters the low and high shear rate equations, equations 6.7 and 6.8, were used. The use of low and high shear rate limiting forms requires a criterion for shifting from one equation, equation 6.7, at low shear rates, to the other, equation 6.8, at high shear rates. In their original discussion of the model, Carreau [48] suggests a shift criterion based on the value of the group 2⁰₁λ₁. They suggest using the low shear rate form of the Bird-Carreau model, equation 6.7, when
$2^{a_1\lambda_1\dot{Y}}$ is less than 7. For values of $2^{a_1\lambda_1\dot{Y}}$ greater than 7 they suggest the use of the high shear rate equation, equation 6.8. However, Blank and co-workers [92] have reported this method of shifting from one equation to the other to be unsatisfactory. Therefore, in the present study the method suggested by Carreau was not used. Instead the non-linear optimisation programme was written in such a way so that equations 6.7 and 6.8 were used in a combination of low and high shear rates which gave the minimum error between the calculated and experimental values of viscosity over the whole range of shear rates.

It can be seen from Figures 6.13 and 6.14 that both elastomers show Newtonian behaviour (i.e. viscosity independent of shear rate) at very low shear rates and 'pseudoplastic' behaviour (i.e. the apparent viscosity decreases with increasing shear rate) at high shear rates. Pseudoplastic behaviour can be described by molecular explanations such as the network model [4] or the highly solvated molecular model [8]. The network model based on the concepts of rubber-like liquids suggested by Lodge [4] proposes that strong interactions between molecules, due to an entanglement network, behave as temporary cross-links formed between molecules which have some physical interactions. In this model the viscosity decreasing with increasing shear rate is explained by the increase in loss of junctions at high shear rates whilst the rate of creation of new junctions is unaffected. The highly solvated molecular model [8] proposes that with an increase in shear rate the solvated layers may be sheared away, resulting in decreased interaction of molecules due to their smaller effective size and, subsequently, a reduction in the apparent viscosity.
The parameter, \( a_1 \), in the Bird-Carreau model is related to the slope, in the power law region, of \( \log (\text{viscosity}) \) vs \( \log (\text{shear rate}) \) plot as \( (1-a_1)/a_1 \) [12]. This means the higher the value of \( a_1 \) the higher the slope of \( \log (\eta) \) vs \( \log (\dot{\gamma}) \) plot in the power law region. In other words higher values of \( a_1 \) means greater shear rate dependence of viscosity (i.e. higher pseudoplasticity). On this basis therefore it is observed from Tables 6.11 and 6.12 that the shear rate sensitivity of viscosity for both elastomers decreases with increasing temperature. It can also be seen from Tables 6.11 and 6.12 that at any given temperature higher values of \( a_1 \) are obtained for SMR 20 than for Hypalon 40. This means SMR 20 is more pseudoplastic than Hypalon 40. The possible explanation for this behaviour being that SMR 20 has a higher number of branches, or longer branches than Hypalon 40 which are more susceptible to shear and hence higher pseudoplasticity.

The parameter, \( \lambda_1 \), decreases with increasing temperature for SMR 20 whereas for Hypalon 40 it remains almost unchanged. According to Carreau [48] the parameter \( \lambda_1 \) appears to be related to the reciprocal shear rate where the viscosity is in transition from Newtonian to non-Newtonian response. Comparison of results in Tables 6.11 and 6.12 show that at any given temperature the value of \( \lambda_1 \) is higher for SMR 20 than for Hypalon 40. Thus, from these results it would be predicted that the transition from Newtonian to non-Newtonian response occurs at lower shear rates for SMR 20 than for Hypalon 40. The experimental results in Figures 6.13 and 6.14 confirm the validity of this prediction.
The Bird-Carreau model was also applied to filled compounds, but proved to be unsuccessful as the model parameters could not be related to loading levels and the surface area of the filler.

6.7.2 Modified Kinetic Model

6.7.2.1 Results

Gum Elastomers:
The steady shear flow behaviour of gum SMR 20 and Hypalon 40 was also modelled by the modified kinetic model (see Section 5.1.1). The Bird-Carreau model gives the viscosity in terms of shear rate, whereas the modified kinetic model is in terms of shear stress. The following modified version of the kinetic model was used

$$\tau = \left[ K \left( \frac{1 - n/\mu}{n/\mu} \right)^n \right]^{1/P} \left( \frac{n/\mu}{n/\mu} \right)^m$$  \hspace{1cm} (6.9)

The non-linear optimisation programme used for determining the parameters in the Bird-Carreau model was modified to obtain the parameters in the kinetic model (see Appendix B). The best values of $K$, $n$, $m$ and $P$, which minimised the sum of squares error between calculated and experimental data over the whole stress range, were obtained. The model parameters and the error estimates for SMR 20 and Hypalon 40 are listed in Tables 6.13 and 6.14 respectively.

The model fit and the experimental data at temperatures of 80, 100 and 120° are shown in Figures 6.15 and 6.16 for SMR 20 and Hypalon 40 respectively.
Fig. 6.15. Shear flow of SMR 20 natural rubber. Exptl pts.: • 80°C; △ 100°C; ■ 120°C. Kinetic model fit: —80°C; ——100°C; ——120°C.
Fig. 6.16. Shear flow of Hypalon 40 rubber. Exptl pts.: ● 80°C; △ 100°C; ■ 120°C. Kinetic model fit: —— 80°C; —— 100°C; ——— 120°C.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>log K</th>
<th>n</th>
<th>m</th>
<th>P</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>10.86</td>
<td>0.798</td>
<td>0.570</td>
<td>2.40</td>
<td>0.096</td>
</tr>
<tr>
<td>100</td>
<td>10.23</td>
<td>0.484</td>
<td>0.892</td>
<td>2.40</td>
<td>0.087</td>
</tr>
<tr>
<td>120</td>
<td>9.78</td>
<td>0.459</td>
<td>1.094</td>
<td>2.40</td>
<td>0.127</td>
</tr>
</tbody>
</table>

**TABLE 6.13: THE MODIFIED KINETIC MODEL PARAMETERS FOR SMR 20**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>log K</th>
<th>n</th>
<th>m</th>
<th>P</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>10.52</td>
<td>1.984</td>
<td>0.695</td>
<td>2.10</td>
<td>0.086</td>
</tr>
<tr>
<td>100</td>
<td>11.16</td>
<td>1.911</td>
<td>1.533</td>
<td>2.40</td>
<td>0.171</td>
</tr>
<tr>
<td>120</td>
<td>10.43</td>
<td>1.972</td>
<td>2.237</td>
<td>2.40</td>
<td>0.076</td>
</tr>
</tbody>
</table>

**TABLE 6.14: THE MODIFIED KINETIC MODEL PARAMETERS FOR HYPALON 40**

**Filled Compounds:**

An attempt was also made with the modified kinetic model to fit the steady shear flow of elastomer compounds. Unfortunately it proved to be unsuccessful since the model parameters could not be related to the levels of loading and the surface area of the filler.
6.7.2.2 Discussion

During modelling a drawback of the kinetic model, though not serious in terms of fitting the data, was realised. It was found that the model does not predict the Newtonian plateau behaviour. It can be seen from equation 6.9 that when $\eta = \gamma$ the model gives the stress as zero which is clearly not the case in practice. In order to avoid this problem the stress at which the viscosity is Newtonian was not used in the computer programme during the determination of model parameters. Instead the modelling was started from the first data point immediately after the Newtonian viscosity.

As can be seen from Figures 6.15 to 6.16 the modified kinetic model fits the steady state data very well. It does an equally good job as the Bird-Carreau model since the error estimates obtained in both models are very similar. Although the model fails to predict the Newtonian behaviour, however it does predict the transition region correctly for both elastomers.

The model parameters are shown in Tables 6.13 and 6.14. For SMR 20 the values of parameters $K$ and $n$ decrease with increasing temperature whereas in the case of Hypalon 40 no such trend is observed. The parameter $m$ increases with temperature for both elastomers. The parameter $P$ is found to have a constant value of 2.40 for both elastomers irrespective of temperature - the exception being at 80°C for Hypalon 40 which could possibly be due to a small error in experimental data. Since $P$ is independent of temperature and type of elastomer the kinetic model (equation 6.9) could be reduced further to
\[ \tau = \left( \frac{K(1-\eta/\mu)^n}{(\eta/\mu)^m} \right)^{1/2.4} \]  
(6.10)

However before jumping to any conclusion about the universal validity of equation 6.10, more experimental work is needed to confirm whether the value of \( P \) is also obtained as 2.40 for other elastomers and polymer melts at different temperatures.

The modified kinetic model was also tried for modelling the steady shear flow behaviour of filled compounds, but unfortunately it proved to be unsuccessful. The model parameters could not be related to the level of loadings and the surface area of the filler as no general trends in their values were observed.

6.7.3 A New Viscosity Model (Hybrid Model) for Filled Compounds

6.7.3.1 Results

The steady shear flow behaviour of filled compounds was modelled by the newly developed viscosity model - so called a Hybrid Model. The development of the model has been shown previously in Section 5.1.2.2 and also in reference number 93. The model can be described by the following equation:

\[ \eta_f = \eta_{g1} \left( 1 + a_1 c + a_2 \psi + a_{11} c^2 + a_3 \psi^2 + a_{12} c \psi \right)^{n'_1 + \beta'_1 c + \beta'_2 \psi + \beta'_3 c \psi} \]  
(6.11)

In equation 6.11 \( \eta_{g1} \) is the viscosity of gum elastomer at a reference shear rate of 1 s\(^{-1}\) and \( n' \) is the slope of the log (viscosity) vs log (shear rate) plot for gum elastomers. The remaining parameters in
equation 6.11 were obtained by a method described in Section 5.3.3.1. The model parameters for SMR 20 and Hypalon 40 compounds at temperatures of 100 and 120°C are listed in Table 6.15.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SMR Compounds</th>
<th>Hypalon 40 Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>120°C</td>
<td>100°C</td>
</tr>
<tr>
<td>( \eta_1 ), Pa.s</td>
<td>85300</td>
<td>65200</td>
</tr>
<tr>
<td>( n' )</td>
<td>-0.7034</td>
<td>-0.6804</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>-0.1024</td>
<td>2.755</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>0.3094x10^{-2}</td>
<td>-0.8023x10^{-2}</td>
</tr>
<tr>
<td>( a_{11} )</td>
<td>13.54</td>
<td>2.441</td>
</tr>
<tr>
<td>( a_{22} )</td>
<td>-0.3028x10^{-5}</td>
<td>0.5631x10^{-4}</td>
</tr>
<tr>
<td>( a_{12} )</td>
<td>0.161x10^{-1}</td>
<td>0.3363x10^{-1}</td>
</tr>
<tr>
<td>( \beta_1 )</td>
<td>-0.2405</td>
<td>-0.1104</td>
</tr>
<tr>
<td>( \beta_2 )</td>
<td>-0.1402x10^{-2}</td>
<td>0.5162x10^{-3}</td>
</tr>
<tr>
<td>( \beta_{12} )</td>
<td>-0.3408x10^{-2}</td>
<td>-0.7033x10^{-2}</td>
</tr>
</tbody>
</table>

**TABLE 6.15: MODEL PARAMETERS (EQUATION 6.11) FOR SMR 20 AND HYFALON 40 COMPOUNDS**

The rate of change of viscosity with shear rate (i.e. pseudoplasticity or shear sensitivity) was defined previously as \( (d(\log \eta F)/d(\log \gamma)) \) and it is given by the following equation:

\[
\frac{d (\log \eta F)}{d (\log \gamma)} = n' + \beta_1 C + \beta_2 \psi + \beta_{12} C \psi
\]  

(6.12)

The values of \( (d(\log \eta F)/d(\log \gamma)) \) for SMR 20 compounds are shown in Table 6.16. The sum of squares of error between the calculated and experimental values of viscosity was determined over the whole shear rate range and is also shown in Table 6.16. Table 6.17 shows the error estimates and \( (d(\log \eta F)/d(\log \gamma)) \) values for Hypalon 40 compounds.
### TABLE 6.16: ERROR ESTIMATES AND \( \frac{d(\log n_r)}{d(\log \gamma)} \) VALUES FOR SMR 20 COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \frac{d(\log n_r)}{d(\log \gamma)} )</th>
<th>Error = ( \Sigma \left( \frac{n_r - n_r^{\text{expt}}}{n_r^{\text{calc}}} \right)^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
<td>120°C</td>
</tr>
<tr>
<td>20 phr N762</td>
<td>-0.7405</td>
<td>-0.6948</td>
</tr>
<tr>
<td>40 phr N762</td>
<td>-0.7675</td>
<td>-0.7210</td>
</tr>
<tr>
<td>60 phr N762</td>
<td>-0.7903</td>
<td>-0.7432</td>
</tr>
<tr>
<td>20 phr N330</td>
<td>-0.7637</td>
<td>-0.7015</td>
</tr>
<tr>
<td>40 phr N330</td>
<td>-0.8039</td>
<td>-0.7552</td>
</tr>
<tr>
<td>20 phr N110</td>
<td>-0.7836</td>
<td>-0.7073</td>
</tr>
<tr>
<td>40 phr N110</td>
<td>-0.8354</td>
<td>-0.7846</td>
</tr>
</tbody>
</table>

* Hypalon = Hypalon 40 + 20 phr Litharge

### TABLE 6.17: ERROR ESTIMATES AND \( \frac{d(\log n_r)}{d(\log \gamma)} \) VALUES FOR HYPALON 40 COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \frac{d(\log n_r)}{d(\log \gamma)} )</th>
<th>Error = ( \Sigma \left( \frac{n_r - n_r^{\text{expt}}}{n_r^{\text{calc}}} \right)^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
<td>120°C</td>
</tr>
<tr>
<td>15 phr N762</td>
<td>-0.6314</td>
<td>-0.5594</td>
</tr>
<tr>
<td>30 phr N762</td>
<td>-0.6722</td>
<td>-0.5926</td>
</tr>
<tr>
<td>45 phr N762</td>
<td>-0.7073</td>
<td>-0.6211</td>
</tr>
<tr>
<td>15 phr N330</td>
<td>-0.6405</td>
<td>-0.5857</td>
</tr>
<tr>
<td>30 phr N330</td>
<td>-0.6910</td>
<td>-0.6469</td>
</tr>
<tr>
<td>45 phr N330</td>
<td>-0.7344</td>
<td>-0.6995</td>
</tr>
</tbody>
</table>

* Hypalon = Hypalon 40 + 20 phr Litharge
The comparisons between the experimental data and the model predictions for both SMR 20 and Hypalon 40 compounds at different temperatures are shown in Figures 6.17-6.30. The experimental values are denoted by symbols and the model predictions by lines. In all the figures "experimental points" are abbreviated to "Exptl. pts".

6.7.3.2 Discussion

Qualitatively, the experimental results shown in Figures 6.17-6.30 are in agreement with those reported by other investigators in the literature [54-66] for carbon black filled rubber compounds. Generally the viscosity increases with filler concentration. Also the viscosity is strongly dependent upon the surface area of the filler. The larger the surface area of filler, the larger the viscosity at any given loading. The reinforcement of elastomers by carbon black has been explained using concepts of bound-rubber, occluded rubber, and chemical interaction between elastomer and filler which immobilises the polymer; and are discussed in detail elsewhere [58,67,94,95].

The model predictions and the experimental data for both elastomer compounds are shown in Figures 6.17-6.30. It is seen from these figures that the new viscosity model fits the experimental data fairly well. The error estimates for SMR 20 and Hypalon 40 compounds are listed in Tables 6.16 and 6.17 respectively. In comparison to SMR 20 compounds, larger error estimates are obtained for Hypalon 40 compounds. A small deviation of theory from experiment, particularly in the case of Hypalon 40, is noted at low shear rates. This is due to the fact that the gum elastomers deviate from the power law model in the low shear rate range. Since our model is based on the power law
Fig. 6.17. Shear flow of SMR 20 compounds at 100°C. 
Exptl. pts.: • 20 phr N762; ■ 60 phr N762. 
Model fit: —— 20 phr N762; —— 60 phr N762.

Fig. 6.18. Shear flow of SMR 20 compounds at 100°C. 
Exptl. pts.: • 40 phr N762; ■ 40 phr N330. 
Model fit: —— 40 phr N762; ——— 40 phr N330.
Fig. 6.19. Shear flow of SMR 20 compounds at 100°C.
Experimental points: • 20 phr N330.
Model fit: —— 20 phr N330.

Fig. 6.20. Shear flow of SMR 20 compounds at 100°C.
Exp. pts.: • 20 phr N110; ■ 40 phr N110.
Model fit: —— 20 phr N110; ----- 40 phr N110.
Fig. 6.21. Shear flow of SMR 20 compounds at 120°C.
Exptl. pts.: • 20 phr N762; ■ 60 phr N762.
Model fit: —— 20 phr N762; ——— 60 phr N762.

Fig. 6.22. Shear flow of SMR 20 compounds at 120°C.
Exptl. pts.: • 40 phr N762; ■ 40 phr N330.
Model fit: —— 40 phr N762; ——— 40 phr N330.
Fig. 6.23. Shear flow of SMR 20 compounds at 120°C.
Experimental points: • 20 phr N330.
Model fit: — 20 phr N330.

Fig. 6.24. Shear flow of SMR 20 compounds at 120°C.
Exptl. pts.: • 20 phr N110; ■ 40 phr N110.
Model fit: —— 20 phr N110; ——— 40 phr N110.
Fig. 6.25. Shear flow of Hypalon 40 compounds at 100°C.
Exptl. pts.: • 15 phr N762; ■ 45 phr N762.
Model fit: —— 15 phr N762; ——— 45 phr N762.

Fig. 6.26. Shear flow of Hypalon 40 compounds at 100°C.
Exptl. pts.: • 15 phr N330; ■ 45 phr N330.
Model fit: —— 15 phr N330; ——— 45 phr N330.
Fig. 6.27. Shear flow of Hypalon 40 compounds at 100°C.  
Exptl. pts.: • 30 phr N762; ■ 30 phr N330.  

Fig. 6.28. Shear flow of Hypalon 40 compounds at 120°C.  
Exptl. pts.: • 15 phr N762; ■ 45 phr N762.  
Model fit: — 15 phr N762; — 45 phr N762.
Fig. 6.29. Shear flow of Hypalon 40 compounds at 120°C.
Exptl. pts.: • 15 phr N330; ■ 45 phr N330.

Fig. 6.30. Shear flow of Hypalon 40 compounds at 120°C.
Exptl. pts.: • 30 phr N762; ■ 30 phr N330.
Model fit: --- 30 phr N762; ---- 30 phr N330.
model, a deviation from it in any region will also cause an error in the model predictions in that region.

At higher shear rates a deviation of theory from experiment is observed again. This has been tentatively attributed to viscous heating effects in the test sample in the TMS rheometer but further work is needed for confirmation. It is seen from results that the deviation is more pronounced in Hypalon 40 compounds. Very recently it has been shown by Ghafouri and Freakley at Loughborough University that viscous heating can cause a substantial temperature rise in the test sample in the TMS rheometer at higher shear rates. We have shown earlier (Section 6.6) that the viscosity of Hypalon 40 compounds is more sensitive to temperature than SMR 20. Therefore any temperature rise in the test sample would give a comparatively higher reduction in the viscosity of Hypalon 40 compounds. This would cause the deviation to be higher and thus explain the existence of relatively higher values of error estimates for Hypalon compounds.

It is seen from Tables 6.16 and 6.17 that for both elastomer compounds the rate of change of viscosity with shear rate (or the shear rate sensitivity) increases with increasing concentration and surface area of the filler, i.e. the increase in viscosity caused by the filler is greatest at low shear rates. Filled systems containing carbon black with higher concentration and higher surface area have higher initial viscosities because of increased bonding between the polymer and carbon black. These bonds are however progressively disrupted by increasing shear rate and thus leading to an enhanced shear rate sensitivity. Comparison of \( \frac{d(\log \eta_p)}{d(\log \dot{\gamma})} \) values reveals that SMR
20 compounds are more shear sensitive than Hypalon 40 compounds. Similar behaviour has also been observed previously for gum elastomers (Section 6.7.1).

The results in Tables 6.16 and 6.17 also show that shear rate sensitivity of viscosity at a given concentration and surface area of filler decreases with increasing temperature. A possible explanation for this behaviour could be that at higher temperatures the carbon black can probably form more bonds with the elastomer. In other words the interaction between elastomer and carbon black is enhanced with increase in temperature - thus reducing the shear rate sensitivity of viscosity.

An examination of the results in Figures 6.17-6.30 shows that the sensitivity of viscosity to filler concentration and surface area diminishes progressively with increasing shear rate. This observed behaviour is in agreement with that of other authors [59, 60, 62-66]. The viscosity model correctly predicts this behaviour.

Analysis of the results has shown that development of the new viscosity model provides an excellent means of correlating experimental data for carbon black filled rubber compounds. Viscosity vs shear rate relationships (flow curves) are the basic means by which the processing characteristics of a material are defined, as the dependence of viscosity on both shear rate and temperature will determine the gross process-material interaction.
6.8 MODELLING THE SHEAR STRESS RELAXATION BEHAVIOUR OF ELASTOMERS AND THEIR COMPOUNDS

6.8.1 Results

The shear stress relaxation of filled compounds was modelled by the newly developed stress relaxation model. The development of the model has been shown previously in Section 5.2 and also in reference number 96. The model can be described by the following equation:

\[ \tau_t(t) = \tau_{g1}(1 + A_1C + A_2\psi + A_{11}C^2 + A_{22}\psi^2 + A_{12}\psi)t^{-(r' + B_C + B_\psi + B_{C\psi})} \]

(6.13)

For gum elastomers, equation 6.13 reduces to

\[ \tau(t) = \tau_{g1} t^{-r'} \]

(6.14)

where \( \tau_{g1} \) is the stress of the gum elastomer at time 1

\( r' \) is relaxation rate for gum elastomer \((d(\log(\tau(t)))/d(\log(t)))\)

The parameters in equation 6.13 were determined by a method described in Section 5.3.3.2. The model parameters for SMR 20 and Hypalon 40 compounds at different temperatures and a conditioning shear rate of 5 s\(^{-1}\) are listed in Table 6.19.
Once the parameters have been determined the relaxation rates, \( r \), for different compounds can be obtained from the following equation (see Section 5.2):

\[
r = r' + B_1 C + B_2 \psi + B_{12} C \psi
\]  

(6.15)

The rates of relaxation, \( r \), for SMR 20 compounds at a conditioning shear rate of 5 s\(^{-1}\) are listed in Table 6.20. The sum of squares of error between calculated (equation 6.13) and experimental values of stress as a function of time for SMR 20 compounds is also shown in Table 6.20.
### TABLE 6.20: RATES OF RELAXATION AND ERROR ESTIMATES FOR SMR 20 COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Rate of Relaxation, $r$</th>
<th>Error $= \Sigma((\tau_f(t)<em>{\text{calc}} - \tau_f(t)</em>{\text{expt}})/\tau_f(t)_{\text{expt}})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypalon +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>120°C</td>
<td>100°C 120°C</td>
</tr>
<tr>
<td>Ophr carbon</td>
<td>0.3022 0.3013</td>
<td>0.0076 0.0197</td>
</tr>
<tr>
<td>20phr N762</td>
<td>0.2748 0.2805</td>
<td>0.0209 0.0168</td>
</tr>
<tr>
<td>40phr N762</td>
<td>0.2482 0.2607</td>
<td>0.0112 0.0101</td>
</tr>
<tr>
<td>60phr N762</td>
<td>0.2256 0.2440</td>
<td>0.0017 0.0017</td>
</tr>
<tr>
<td>20phr N330</td>
<td>0.2595 0.2687</td>
<td>0.0034 0.0018</td>
</tr>
<tr>
<td>40phr N330</td>
<td>0.2142 0.2353</td>
<td>0.0004 0.0074</td>
</tr>
<tr>
<td>20phr N110</td>
<td>0.2463 0.2585</td>
<td>0.0002 0.0171</td>
</tr>
<tr>
<td>40phr N110</td>
<td>0.1849 0.2135</td>
<td>0.0015 0.0012</td>
</tr>
</tbody>
</table>

### TABLE 6.21: RELAXATION RATES AND ERROR ESTIMATES FOR HYPALON 40 COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Rate of Relaxation, $r$</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypalon +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>120°C</td>
<td></td>
</tr>
<tr>
<td>Ophr carbon</td>
<td>0.5310 0.5329</td>
<td>0.0025 0.0070</td>
</tr>
<tr>
<td>15phr N762</td>
<td>0.5074 0.4836</td>
<td>0.0208 0.0137</td>
</tr>
<tr>
<td>30phr N762</td>
<td>0.4776 0.4724</td>
<td>0.0386 0.0226</td>
</tr>
<tr>
<td>45phr N762</td>
<td>0.4520 0.4626</td>
<td>0.0103 0.0020</td>
</tr>
<tr>
<td>15phr N330</td>
<td>0.5145 0.4260</td>
<td>0.0220 0.0193</td>
</tr>
<tr>
<td>30phr N330</td>
<td>0.4756 0.4128</td>
<td>0.0115 0.0047</td>
</tr>
<tr>
<td>45phr N330</td>
<td>0.4422 0.4015</td>
<td>0.0067 0.0065</td>
</tr>
</tbody>
</table>
The shear rate dependence of relaxation rates after a time of 0.4 seconds was determined for some of the compounds. The results are shown in Table 6.22.

<table>
<thead>
<tr>
<th>( \dot{\gamma} (\text{s}^{-1}) )</th>
<th>Relaxation Rates, ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SMRO + 40 phr N330 ( T = 100^\circ \text{C} )</td>
</tr>
<tr>
<td>1</td>
<td>0.2117</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.2252</td>
</tr>
<tr>
<td>5</td>
<td>0.2142</td>
</tr>
<tr>
<td>10</td>
<td>0.2295</td>
</tr>
</tbody>
</table>

**TABLE 6.22: RELAXATION RATES AT DIFFERENT SHEAR RATES**

Comparison between the experimental data and the model predictions (equation 6.13) at different temperatures and a conditioning shear rate of 5 \( \text{s}^{-1} \) are shown in Figures 6.31-6.45.

6.8.2 Discussion

It is seen from Figures 6.31-6.45 that the shear stress relaxation model (equation 6.13) does an excellent job in fitting the experimental data for both SMR 20 and Hypalon 40 compounds. The error estimates between the experimental and calculated results are shown in Tables 6.20 and 6.21. This model does an even better job than the viscosity model in correlating the experimental data. Since the stress relaxation measurements were made at a lower shear rate of
Fig. 6.31. Stress relaxation of SMR20 compounds at 100°C.
Exptl. pts.: • gum SMR20; ■ 20 phr N762.
Model fit: — gum SMR20; —— 20 phr N762.

Fig. 6.32. Stress relaxation of SMR20 compounds at 100°C.
Exptl. pts.: • 40 phr N762; ■ 60 phr N762.
Model fit: — 40 phr N762; —— 60 phr N762.
Fig. 6.33. Stress relaxation of SMR20 compounds at 100°C.
Exppl. pts.: ● 20 phr N330; ■ 40 phr N330.
Model fit: —— 20 phr N330; —— 40 phr N330.

Fig. 6.34. Stress relaxation of SMR20 compounds at 100°C.
Exppl. pts.: ● 20 phr N110; ■ 40 phr N110.
Model fit: —— 20 phr N110; —— 40 phr N110.
Fig. 6.35. Stress relaxation of SMR20 compounds at 120°C.
Exptl. pts.: • gum SMR20; ■ 20 phr N762.
Model fit: — gum SMR20; —— 20 phr N762.

Fig. 6.36. Stress relaxation of SMR20 compounds at 120°C.
Exptl. pts.: • 40 phr N762; ■ 60 phr N762.
Model fit: — 40 phr N762; —— 60 phr N762.
Fig. 6.37. Stress relaxation of SMR20 compounds at 120°C.
Exptl. pts.: • 20 phr N330; □ 40 phr N330.
Model fit: -- 20 phr N330; ---- 40 phr N330.

Fig. 6.38. Stress relaxation of SMR20 compounds at 120°C.
Exptl. pts.: • 20 phr N110; □ 40 phr N110.
Model fit: -- 20 phr N110; ---- 40 phr N110.
Fig. 6.39. Stress relaxation of Hypalon 40 at 100 & 120 °C.
Exptl. pts.: ● 100 C; ■ 120 C.
Model fit: — 100 C; — 120 C.

Fig. 6.40. Stress relaxation of Hypalon 40 compounds at 100°C.
Exptl. pts.: ● 15 phr N762; ■ 30 phr N762.
Model fit: — 15 phr N762; — 30 phr N762.
Fig. 6.41. Stress relaxation of Hypalon 40 compounds at 100°C.
Exptl. pts.: • 15 phr N330; ■ 30 phr N330.

Fig. 6.42. Stress relaxation of Hypalon 40 compounds at 100°C.
Exptl. pts.: • 45 phr N762; ■ 45 phr N330.
Model fit: — 45 phr N762; — 45 phr N330.
Fig. 6.43. Stress relaxation of Hypalon 40 compounds at 120°C.
Exptl. pts.: • 15 phr N762; ■ 30 phr N762.
Model fit: -- 15 phr N762; ---- 30 phr N762.

Fig. 6.44. Stress relaxation of Hypalon 40 compounds at 120°C.
Exptl. pts.: • 15 phr N330; ■ 30 phr N330.
Model fit: -- 15 phr N330; ---- 30 phr N330.
Fig. 6.45. Stress relaxation of Hypalon 40 compounds at 120°C.

Exptl. pts.: • 45 phr N762; ■ 45 phr N330.

Model fit: —— 45 phr N762; ---- 45 phr N330.
5 s\(^{-1}\), the experimental errors associated with temperature rise of the sample at higher shear rates in the viscosity model, are avoided in the relaxation model.

The shear stress relaxation rates, \( r \), for SMR 20 and Hypalon 40 compounds are listed in Tables 6.20 and 6.21 respectively. For both elastomers, its value is decreased by increasing loading levels and specific surface area of the filler. These results are in agreement with those reported by Cotton and Boonstra [77] for uncured rubber compounds. In the pure gum the reversible stress relaxation phenomena are believed to be due to rearrangement of chains and chain segments following the deformation [89]. In filled compounds the carbon black may be acting as a barrier and thereby slowing down the rate of rearrangement of chains and chain segments, and thus decreasing the rate of shear stress relaxation with increasing filler concentration and specific surface area.

Table 6.22 shows the effect of shear rate on the relaxation rate, \( r \), of two elastomer compounds. For both compounds the change in \( r \) with shear rate is insignificant. Thus one may conclude that after a time of 0.4 seconds the rate of shear stress relaxation is independent of shear rate. Cotton and Boonstra [75] have also reported similar results for unvulcanised rubbers. They have shown that the compression stress relaxation rate is independent of the rate of compression of the sample. It is seen from Table 6.20 that \( r \) increases with increasing temperature for all the SMR 20 compounds. However, for Hypalon 40 compounds (Table 6.21) the variation in \( r \) with temperature is found to be random.
Stress relaxation measurements have a practical significance in the processing of rubber compounds. Low stress relaxation rate corresponds to higher elasticity, whereas high rate of stress relaxation means a more viscous nature. Stress relaxation behaviour can control the rate of incorporation of carbon black in the mixing process through the mode of flow of the elastomer. For rapid incorporation a predominantly viscous characteristic is needed to enable the elastomer to flow around and wet out the filler agglomerates quickly and effectively. Also pronounced elasticity can lead to stresses exceeding fracture values, causing crumbling of the batch. A high stress relaxation rate will enable stresses put into the material to be dissipated rapidly, thus maintaining a predominantly viscous behaviour. Stress relaxation behaviour also plays a large role in downstream processes, such as extrusion. For example, in an extrusion process a rubber compound with very low stress relaxation rate (i.e. high elasticity) would be very difficult to handle, whereas a compound with high stress relaxation rate (i.e. more viscous nature) would be much easier to handle.

It is seen from Tables 6.20 and 6.21 that the relaxation rates obtained for Hypalon 40 compounds are almost double that of SMR 20 compounds. This means SMR 20 is a substantially more elastic material than Hypalon 40, or in other words. Hypalon 40 is more viscous than SMR 20.
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The objective of this research programme was to model the rheological behaviour of elastomers and elastomer compounds. The investigation in this project concentrated mainly on modelling the steady shear flow and shear stress relaxation behaviour. A summary of conclusions resulting from this investigation can be stated as follows:

1. Zero-shear viscosities for gum elastomers can be determined from a parallel plate rheometer (creep experiment).

2. Both elastomers (natural rubber: SMR 20 and chlorosulphonated polyethylene: Hypalon 40) show Newtonian behaviour in the low shear rate region and pseudoplastic behaviour in the high shear rate region.

3. During measurements of viscosity with cone and plate rheometer, the sample temperature cannot be controlled by using a band heater as a temperature distribution is obtained across the plate.

4. The viscosities of filled compounds cannot be measured with the cone and plate rheometer because the sample exudes from the space between the cone and plate due to fracture.
The stress at which the fracture of the samples starts are found to be in the region of $1.5 \times 10^4 \text{ N/m}^2$.

5. In order to measure the viscosities of filled compounds at low shear rates a transfer mould was designed which produced good shear test specimens. However when these test specimens were put in the Instron Tensile Tester to measure viscosity it was discovered that steady state flow could not be achieved under constant shear rate mode due to fracture of the sample.

6. Repeatability studies on the Negretti TMS biconical rotor rheometer reveals that the TMS gives results which are quite consistent. However at high shear rates the reliability of results is in doubt, since substantial temperature rise in the test sample is obtained due to viscous heating effects.

7. Both the Bird-Carreau model and the modified kinetic model fit the steady shear flow of gum elastomers quite well. However both models proved to be intractable for fitting the rheological properties of mixed rubber compounds and also the kinetic model fails to predict the Newtonian plateau behaviour.

8. Temperature dependence of viscosity of filled compounds was determined from the Arrhenius relationship. At a given shear rate, the activation energies of viscous flow are independent of loading levels and surface area of the filler.
The viscosity of Hypalon 40 shows greater sensitivity to temperature than SMR 20. This is attributed to the difference in their molecular structures.

9. A new model (so called a Hybrid model) has been developed for predicting the viscosity, in the power law region, of elastomers containing carbon black. It predicts the steady state shear rate dependent viscosity in terms of the gum elastomer behaviour, the filler concentration and the surface area. The model fits the experimental data quite well.

10. Generally the viscosity of filled compounds is increased by increasing loading levels and increasing surface area of the filler. However the sensitivity of viscosity to filler concentration and surface area diminishes progressively with increasing shear rate.

SMR 20 compounds are found to be more sensitive to shear rate than Hypalon 40 compounds.

11. In addition to the viscosity model, one more new model has been developed in the present study for predicting the shear stress relaxation behaviour of carbon black filled elastomers in terms of filler concentration and the filler surface area. The agreement between the model prediction and experimental data is excellent.
12. For all the compounds the rate of shear stress relaxation is decreased by increasing loading levels and specific surface area of the filler.

After a time of 0.4 seconds the rate of shear stress relaxation is found to be independent of shear rate prior to the start of stress relaxation.

Generally the relaxation rates for Hypalon 40 compounds are found to be almost double those of SMR 20 compounds.

7.2 RECOMMENDATIONS

From the results obtained in this research programme some areas have shown potential for further investigation. Suggestions include the following:

1. In the cone and plate rheometer, one way of eliminating temperature control problems would be to try using circulating silicone oil through the plate from an external thermostatic tank.

2. To measure the viscosity of filled compounds at low shear rates, the instruments which operate under constant stress mode and have an enclosed test cavity should be tried. For example, one possibility would be the modification of the Mooney viscometer to operate under constant stress conditions.
3. Different elastomers and polymer melts, other than SMR 20 and Hypalon 40, should be tried to confirm the universal validity of the modified kinetic model.

4. The new models developed in the present study are termed Hybrid models. The conception and first successful application of these models opens up a very large and exciting field for future work. A number of areas are identified below. For each it is feasible to select well established mathematical models and then expand the adjustable parameters into polynomial equations containing material and treatment variables:

i) Additional carbon black characteristics, such as structure and surface activities;

ii) Introduce mixing treatment variables into models, in addition to carbon black characteristics;

iii) Modelling of properties other than steady-state viscosity and stress relaxation of uncured compounds (including vulcanisate properties such as strength, dynamic moduli, fatigue and abrasion resistance);

iv) Use models other than power-law;

v) Investigate elastomers other than SMR 20 and Hypalon 40;

vi) Investigate fillers other than carbon black, such as white fillers;

vii) Obtain models for the influence of carbon black loading and properties on extrudate swell and establish relationship with stress relaxation.
REFERENCES


87. A private communication, J. Williams, Du Pont, Hemel Hempstead, UK.


APPENDICES
APPENDIX A

NON-LINEAR OPTIMISATION PROGRAM FOR DETERMINING THE PARAMETERS IN THE BIRD-CARREAU MODEL

implicit double precision (a-h,o-z)
dimension n(2),gmad1(22), etaexp(22), etacal(22)
dimension alfa(2), x(2), deltx(2)
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Open files, one for reading the experimental data
c and the other one for storing the results
c from the program.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
open (9, file='data.sm80', form='formatted')
open (10, file='results.sm80', form='formatted')
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c ncomp defines the number of experimental data
c points.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
ncomp=22

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Read shear rate and viscosity values from an
c external file.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
do 22 j=1,22
read (9,*) gmad1(j), etaexp(j)
22 continue

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Print the value of Zero-Shear viscosity on to the
c screen.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
print *, "eta0=
read *, eta0

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Assign a large guess value for the error.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
erref=10e6

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c II defines the number of data points for which the
c first equation in the Bird-Carreau model is to be
used for the low shear rate range.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
ll=0
1000 ll=ll+1

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Assign initial guess values to the model
c parameters.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
x(1)=1.0
x(2)=200

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c k defines the number of times the step size is to
c halved before the termination of the program.
k = 4

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++

Assign the step size values for the parameters.

deltx(1) = 0.06
deltx(2) = 2.0

kk = 0
iter = 0

lflag1 = 0
lflag2 = 1

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++

Set array n to be zero for both model parameters.

n(1) = 0
n(2) = 0

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++

When kk = k, the search will terminate.

if (kk .eq. k) goto 100

10 alfa(1) = x(1)
alfa(2) = x(2)
call function (ncomp, eta0, alfa, gmad1, etaexp, error,
c etacal, ll)

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++

Search for minimum error. Check the error at the
c values of "(parameter + step size)" and
c "(parameter - step size)" and then change the
c parameters to the values which give the minimum
c error. Store the changes made to the array n for
c both parameters. n then defines the direction for
c pattern search.

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++

fmin = error
do 25 i = 1, 2
alfa(i) = x(i) + deltx(i)
call function (ncomp, eta0, alfa, gmad1, etaexp, error,
c etacal, ll)
fmin1 = error
if (fmin1 .lt. fmin) then
fmin = fmin1
endif
alfa(i) = x(i) - deltx(i)
call function (ncomp, eta0, alfa, gmad1, etaexp, error,
c etacal, ll)
fmin2 = error
if (fmin2 .lt. fmin) then
fmin = fmin2
endif
if (fmin .eq. fmin1) then
n(i) = n(i) + 1
x(i) = x(i) + deltx(i)
endif
if (fmin .eq. fmin2) then
n(i) = n(i) - 1
x(i) = x(i) - deltx(i)
endif
alfa(i) = x(i)
25 continue
do 30 ijk=1,2
if(n(ijk).lt.0.or.n(ijk).gt.0) then
  lflag1=1
endif
30 continue
if(lflag1.eq.0) goto 80
lflag1=0
if(lflag2.eq.0) then
  lflag2=0
else
  if((fmin.gt.fmin0) then
    x(1)=x1f
    x(2)=x2f
    goto 5
  endif
endif

c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Make a pattern move to the new base.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
50 x1f=x(1)
x2f=x(2)
fmin0=fmin
x(1)=x(1)+n(1)*deltx(1)
x(2)=x(2)+n(2)*deltx(2)
iter=iter+1
goto 20

50 continue

100 if(error.ge.fmin0) then
    error=fmin0
    goto 1000
else
  c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c When array n is equal to zero then the step
  c size is halved.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
80 deltx(1)=deltx(1)/2
deltx(2)=deltx(2)/2
kk=kk+1
goto 10

200 format(14hiteration no =,i5,10x,7herror =,f10.5)
write (10,300) alfa
300 format(7halfa1 =,f10.5,10x,7halfa2 =,f10.5)
write (10,400) (ll-1)
400 format(26hno. of pts eq 1 valid for =,i5)
write (10,500)
500 format(10x,12hshear rate ,10x,12hetacalculated,10x,
c 9hlogetacal)
do 700 jkl=1,22
write (10,600) gmad1(jkl),etacal(jkl),log10(etacal(jkl))
600 format(10x,f12.8,10x,f12.1,10x,f10.5)
700 continue
endif
stop
end
Subroutine for determining the calculated viscosity values and the error between the calculated and experimental values over the whole shear rate range.

Subroutine function (ncomp,eta0,alfa,gmad1,etaexp, 1 error,etacal,ll )
implicit double precision (a-h,o-z)
dimension gmad1(22) , etaexp(22),etacal(22),alfa(2)
pi=3.14
error=0.0
do 9000 m=1,22
gmad=gmad1(m)
eta=etaexp(m)
calculation of Riemann-Zeta function
ir=50
za=0.0
do 8000 j=1,ir
za=za+ (j**(-alfa(1)))
8000 continue
za1=1.0/(za-1.0)
zzm=(2.0**alfa(1))*alfa(2)*gmad
zb1=pi*(zzm**((1.0-alfa(1))/alfa(1)))
zb2=((1.0+alfa(1))*pi)/(2.0*alfa(1))
zb2=sin(zb2)
zb2=2.0*alfa(1)*zb2
zn1=zb1/zb2
zb3=1.0/(alfa(1)+1.0)*(zzm**2.0))
zn2=zn1-zb3
zb4=(1.0+(1.0/6.0)*alfa(1))/(2.0*(1.0+(zzm**2.0)))
zn=zn2-zb4
etacal(m)=eta0*za1*zn
errorn=((etacal(m)-eta)/eta)**2.0
error=error+errorn
9000 continue
if(ll.eq.1) goto 7000
do 9050 jk=1,(ll-1)
gmad=gmad1(jk)
eta=etaexp(jk)
zzm=(2.0**alfa(1))*alfa(2)*gmad
zc1=(zzm**2.0)/(za-1.0)
sjp=0.0
do 9100 jp=2,50
rjp=real(jp)
sp=jsp+(rjp**(-alfa(1)))/(rjp**2*(2*alfa(1))+zzm**2)
9100 continue
zc1=zcz1*sjp
zc2=1.0-zc1
etacal(jk)=eta0*zc2
errorn=((etacal(jk)-eta)/eta)**2
error=error+errorn
9050 continue
7000 return
end
APPENDIX B

NON-LINEAR OPTIMISATION PROGRAM FOR DETERMINING THE PARAMETERS IN THE MODIFIED KINETIC MODEL

implicit double precision (a-h,o-z)
dimension n(4),torexp(21),etaexp(21),torcal(21)
dimension alfa(4), x(4), deltx(4)

Open files, one for reading the experimental data and the other one for storing the results from the program.

open (9,file='tordatahypalon120',form='formatted')
open (30,file='kineticmodel',form='formatted')
ncomp defines the number of experimental data points.
ncomp=21
Print the value of Zero-Shear viscosity on to the screen.
print *, 'etaO=' read *, etaO
Read shear stress and viscosity values from an external file.
do 1 j=1,21
read (9,*),torexp(j),etaexp(j) 1 continue
Assign initial guess values to the model parameters.
x(1)=6.91213e9
x(2)=1.0
x(3)=1.0
x(4)=2.4
k defines the number of times the step size is to halved before the termination of the program.
k=8
Assign the step size values for the parameters.
deltx(1)=5.0e7
deltx(2)=0.2
deltx(3)=0.2
deltx(4)=0.2
kk=0
iter=0
iflag=0
iflag1=1

Set array n to be zero for all the parameters.

When kk=k, the search will terminate.

if( kk.eq.k ) goto 100

alfa(1)=x(1)
alfa(2)=x(2)
alfa(3)=x(3)
alfa(4)=x(4)
call function(ncomp,eta0,alfa,etaexp,torexp
1 ,error,torcal)

Search for minimum error. Check the error at the
values of "(parameter + step size)" and
"(parameter - step size)" and then change the
parameters to the values which give the minimum
error. Store the changes made to the array n for
call the parameters. n then defines the direction
c for pattern search.

fmin=error
do 25 i=1,4
alfa(i)=x(i)+deltx(i)
call function(ncomp,eta0,alfa,etaexp,torexp,
1 ,error,torcal)
fmin1=error
if(fmin1.lt.fmin) then
fmin=fmin1
endif
alfa(i)=x(i)-deltx(i)
call function(ncomp,eta0,alfa,etaexp,torexp,
1 ,error,torcal)
fmin2=error
if(fmin2.lt.fmin) then
fmin=fmin2
endif
if(fmin.eq.fmin1) then
n(i)=n(i)+1
x(i)=x(i)+deltx(i)
endif
if(fmin.eq.fmin2) then
n(i)=n(i)-1
x(i)=x(i)-deltx(i)
endif
alfa(i)=x(i)
do 30 ijk=1,4
if(n(ijk).lt.0.or.n(ijk).gt.0) then
  lflag=1
endif
30    continue
if(lflag.eq.0) goto 80
lflag=0
if(lflag1.eq.1) then
  lflag1=0
  goto 50
endif
if(fmin.gt.fmin0) then
  x(1)=x1f
  x(2)=x2f
  x(3)=x3f
  x(4)=x4f
  goto 5
endif
50    c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c Make a pattern move to a new base.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
xlf=x(1)
x2f=x(2)
x3f=x(3)
x4f=x(4)
fmin0=fmin
  x(1)=x(1)+n(1)*deltx(1)
x(2)=x(2)+n(2)*deltx(2)
x(3)=x(3)+n(3)*deltx(3)
x(4)=x(4)+n(4)*deltx(4)
itcr=itcr+1
  goto 20
57    c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c When array n is equal to zero then the step size is halved.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
  delt(1)=delt(1)/2
delt(2)=delt(2)/2
delt(3)=delt(3)/2
delt(4)=delt(4)/2
  kk=kk+1
  goto 10
80    c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
c When optimisation is complete store the results in an external file.
c ++++++++++++++++++++++++++++++++++++++++++++++++++++++
100   write (30,200) iter,fmin
200    format(i4,15x,f10.7)
      write(30,300) alfa(1),alfa(2)
300    format(7halfa1 =,f16.1,10x,7halfa2 =,f10.3)
      write (30,400) alfa(3),alfa(4)
400    format(7halfa3 =,f10.3,10x,7halfa4 =,f10.3)
      write (30,500)
500    format(12heta exp1 =,10x,18heta calculated =,10x,
            118heta experimental =)
      do 700 jkl=1,21
        write (30,600) etaexp(jkl),torcal(jkl),torexp(jkl)
700    format(f12.0,15x,f18.1,15x,f16.1)
Subroutine for determining the calculated stress values and the error between the calculated and the experimental values.

```fortran
subroutine function(ncomp,eta0,alfa,etaexp,torexp,
error,torcal)
implicit double precision (a-h,o-z)
dimension torexp(21),etaexp(21),torcal(21),alfa(4)
error=0.0
do 9000 m=1,21
eta=etaexp(m)
tor=torexp(m)
aa=(eta/eta0)
bb=(1.0-aa)**alfa(2)
cc=aa**alfa(3)
torcal(m)=(alfa(I)*bb/cc)**(1/alfa(4))
errom=((torcal(m)-tor)/tor)**2.0
error=error+errom
9000 continue
return
end
```
### APPENDIX C

**STEADY SHEAR FLOW DATA FOR ELASTOMER COMPOUNDS AT 80°C**

#### NATURAL RUBBER (SMR 20) COMPOUNDS

<table>
<thead>
<tr>
<th>$\dot{\gamma}$ (s(^{-1}))</th>
<th>20 phr N762</th>
<th>40 phr N762</th>
<th>60 phr N762</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau$ (Pa)</td>
<td>$\eta$ (Pa\cdot s)</td>
<td>$\tau$ (Pa)</td>
</tr>
<tr>
<td>0.1</td>
<td>59100</td>
<td>59100</td>
<td>85000</td>
</tr>
<tr>
<td>0.2</td>
<td>73900</td>
<td>369500</td>
<td>102800</td>
</tr>
<tr>
<td>0.5</td>
<td>95600</td>
<td>191200</td>
<td>126300</td>
</tr>
<tr>
<td>1.0</td>
<td>116000</td>
<td>116000</td>
<td>148100</td>
</tr>
<tr>
<td>2.0</td>
<td>132100</td>
<td>66050</td>
<td>166600</td>
</tr>
<tr>
<td>5.0</td>
<td>158600</td>
<td>31720</td>
<td>193000</td>
</tr>
<tr>
<td>10.0</td>
<td>175800</td>
<td>17580</td>
<td>208100</td>
</tr>
<tr>
<td>20.0</td>
<td>190700</td>
<td>9535</td>
<td>221500</td>
</tr>
<tr>
<td>40.0</td>
<td>214800</td>
<td>3580</td>
<td>234300</td>
</tr>
</tbody>
</table>

#### NATURAL RUBBER COMPOUNDS

<table>
<thead>
<tr>
<th>$\dot{\gamma}$ (s(^{-1}))</th>
<th>20 phr N330</th>
<th>40 phr N330</th>
<th>20 phr N110</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau$ (Pa)</td>
<td>$\eta$ (Pa\cdot s)</td>
<td>$\tau$ (Pa)</td>
</tr>
<tr>
<td>0.1</td>
<td>81100</td>
<td>81100</td>
<td>104100</td>
</tr>
<tr>
<td>0.2</td>
<td>98900</td>
<td>494500</td>
<td>121900</td>
</tr>
<tr>
<td>0.5</td>
<td>121500</td>
<td>243000</td>
<td>145000</td>
</tr>
<tr>
<td>1.0</td>
<td>143600</td>
<td>143600</td>
<td>165900</td>
</tr>
<tr>
<td>2.0</td>
<td>160300</td>
<td>80150</td>
<td>181400</td>
</tr>
<tr>
<td>5.0</td>
<td>186800</td>
<td>37360</td>
<td>207100</td>
</tr>
<tr>
<td>10.0</td>
<td>202900</td>
<td>20250</td>
<td>222500</td>
</tr>
<tr>
<td>20.0</td>
<td>215800</td>
<td>10790</td>
<td>235700</td>
</tr>
<tr>
<td>40.0</td>
<td>228000</td>
<td>5700</td>
<td>247400</td>
</tr>
</tbody>
</table>
## CHLOROSULPHONATED POLYETHYLENE (HYPALON 40) COMPOUNDS
(ALSO CONTAINING 20 phr LITHARGE)

<table>
<thead>
<tr>
<th>15 phr N762</th>
<th>30 phr N762</th>
<th>15 phr N330</th>
<th>30 phr N330</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \dot{\gamma}(s^{-1}) )</td>
<td>( \tau(Pa) )</td>
<td>( \eta(Pa.s) )</td>
<td>( \tau(Pa) )</td>
</tr>
<tr>
<td>0.1</td>
<td>84900</td>
<td>849000</td>
<td>110100</td>
</tr>
<tr>
<td>0.2</td>
<td>113700</td>
<td>568500</td>
<td>146400</td>
</tr>
<tr>
<td>0.5</td>
<td>161500</td>
<td>323000</td>
<td>201200</td>
</tr>
<tr>
<td>1.0</td>
<td>211000</td>
<td>211000</td>
<td>251700</td>
</tr>
<tr>
<td>2.0</td>
<td>255500</td>
<td>127750</td>
<td>293200</td>
</tr>
<tr>
<td>5.0</td>
<td>311600</td>
<td>62320</td>
<td>334800</td>
</tr>
<tr>
<td>10.0</td>
<td>340000</td>
<td>34000</td>
<td>361500</td>
</tr>
<tr>
<td>20.0</td>
<td>367000</td>
<td>18350</td>
<td>388900</td>
</tr>
<tr>
<td>40.0</td>
<td>381600</td>
<td>9540</td>
<td>408800</td>
</tr>
</tbody>
</table>

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APPENDIX D

PAPERS PUBLISHED FROM THE RESULTS OF THIS THESIS


A model for the viscosity of carbon black filled rubber compounds

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(Received 10 June 1989; revised version received and accepted 3 July 1989)

Abstract: A new model is developed for predicting the viscosity in the power law region of elastomers containing carbon black. It predicts the steady-state shear-rate dependent viscosity in terms of the gum elastomer, the filler concentration and the filler surface area. The agreement between the model prediction and the experimental data is very promising.

1 Introduction

Predicting the dependence of the flow behaviour of rubber compounds on the loading and type of carbon black is of considerable technological importance to the performance of processing operations. This paper presents a new predictive model.

One of the simplest equations which describes the viscosity of filled elastomer systems is the Einstein equation:

\[ \eta = \eta_0 (1 + 2.5C) \]  

(1)

where \( \eta \) and \( \eta_0 \) are the viscosity of the filled and unfilled medium respectively and \( C \) is the volume fraction of filler. To account for larger particle concentrations and thus significant interactions among particles, eqn (1) was modified by Guth, Simha and Gold:

\[ \eta = \eta_0 (1 + 2.5C + 14.1C^2) \]  

(2)

However, eqn (2) does not predict the shear-rate dependency of the viscosity. In 1974, Derringer proposed an empirical model for variable shear-rate viscosity of the following form:

\[ \ln \eta = \ln \eta_0 (\gamma) + \lambda (\gamma) F - \phi (\gamma) P \]  

(3)

where \( \eta_0 (\gamma) \) is the viscosity of gum elastomer, \( \gamma \) is the shear rate, \( F \) is the filler level in per cent weight of rubber, \( P \) is the plasticiser level in per cent weight of rubber and \( \lambda \) and \( \phi \) are constants which are shear-rate dependent.

The viscosity models discussed thus far do not take the filler particle size into account. The model proposed in this paper includes terms for particle size via specific surface area (surface area per unit volume of filler).

2 Development of the model

Analysis of experimental data showed that the viscosity of a compound at a given shear rate was a function of the volume fraction (\( C \)) and the specific surface area (\( \psi \)) of the filler and could be described adequately by an extension of Guth, Simha and Gold equation to allow for \( \psi \) by the addition of extra terms:

\[ \eta = \eta_0 (1 + \alpha_1 C + \alpha_2 \psi + \alpha_3 C^2 + \alpha_4 \psi^2 + \alpha_5 C \psi) \]  

(4)

where \( \eta_0 \) is the viscosity of gum elastomer at a reference shear rate of 1 s\(^{-1}\), \( \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5 \) and \( \alpha_6 \) are constants. The final term in eqn (4) is an interaction term.

The rate of change of viscosity with shear rate, which we define here as \( (d(\log \eta)/d(\log \gamma)) \), was also found to be a function of \( C \) and \( \psi \) and can be described by an equation of the following form:

\[ \frac{d(\log \eta)}{d(\log \gamma)} = n_1 + \beta_1 C + \beta_2 \psi + \beta_3 C \psi \]  

(5)

where \( n_1 \) is the slope of the plot of \( \log \eta \) versus \( \log \gamma \) for the gum elastomer and \( \beta_1, \beta_2 \) and \( \beta_3 \) are constants.

It is well known that the viscosity of most polymeric materials in the pseudo-plastic region can be represented by the power law:

\[ \eta = K \gamma^{n-1} \]  

(6)

where \( K \) is the viscosity at a reference shear rate and \( n \) is a constant, called the power law index.

By combining eqns (4), (5) and (6), one gets an equation which gives the variable shear-rate...
viscosity in terms of $C$ and $\psi$:
$$
\eta_r = \eta_0 \left[ 1 + \alpha_1 C + \alpha_2 C^2 + \alpha_3 C^3 \right]
+ \alpha_2 \psi + \alpha_3 (C^\psi) f_{\alpha_1}^{\alpha_2} f_{\alpha_3}^{\alpha_4} (\psi^{\alpha_5}) \quad (7)
$$

3 Experimental

3.1 Materials

The elastomers studied were natural rubber (SMR20) and chlorosulphonated polyethylene, CSM (Du Pont Hypalon 40). Three different grades of carbon black from Cabot Carbon were used, the characteristics of which are given in Table 1.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Grade</th>
<th>Surface area (m$^2$/g)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>SRF (N762)</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>HAF (N230)</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>SAF (N110)</td>
<td>128</td>
</tr>
</tbody>
</table>

* Cabot figures.

3.2 Mixing

All grades of carbon black were mixed with SMR20 and CSM rubber at loading levels of 20, 40 and 60 per cent weight of rubber (equivalent to 0.092, 0.1685 and 0.2332 by volume fraction of filler for SMR20).

Mixing was carried out on a BR Banbury Internal mixer, followed by milling on a two-roll mill (both by Farrel Bridge, Rochdale, UK).

3.3 Rheological measurement

Viscosity of the gum and filled elastomers was measured as a function of shear rate and temperature using a TMS biconical-rotor rheometer (Negretti Automation, Aylesbury, UK).

4 Results

For brevity, only the fitting of the new model (eqn (7)) to selected SMR20 compounds at 100°C is presented here. All the constants in eqn (7) were evaluated and are shown in Table 2. The comparison between eqn (7) and experimental data is shown in Figs 1 and 2.

5 Discussion

The experimental results shown in Figs 1 and 2 are similar to those reported in the literature for compounds of thermoplastic melts and elastomers with carbon black.$^4,5$ The viscosity is increased by increasing loading levels and specific surface area of the filler. The sensitivity of viscosity to filler concentration and surface area diminishes progressively with increasing shear rate. The new viscosity model correctly predicts this behaviour (see Figs 1 and 2). The agreement between the model prediction and the experimental data is good but a deviation of...
theory from experiment will be noted at high shear rates. This has been tentatively attributed to viscous heating, but further work is needed for confirmation.

6 Conclusion

A new viscosity model for filled compounds has been developed with very promising results. It has also been applied to different elastomeric compounds at various temperatures and the full set of results together with the method for evaluation of the constants in eqn (7) will be presented in due course. It is also anticipated that the model will be valid for other polymers and fillers.

References

2. GUTH, E., SIMHA, R. & GOLDS, O., Z. Physik 74 (1936) 266.
A model for the stress relaxation of carbon black filled rubber compounds

M. Singh, J. Batchelor & P. K. Frawley

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(Received 10 June 1989; revised version received and accepted 28 July 1989)

Abstract: A new model is developed for predicting the shear stress relaxation behaviour of carbon black filled elastomers in terms of the filler concentration and the filler surface area. The agreement between the model prediction and experimental data is very promising.

1 Introduction

When elastomeric materials are deformed, the stresses set up gradually decrease with time. This is the phenomenon of stress relaxation; it plays a very important role in processes like calendering, extrusion and during mould filling in injection moulding.

Cotton and Boonstra\(^1\) showed that for longitudinal strain the compressive stress relaxation of gum and filled elastomers (both uncured and cured) obeyed the empirical equation of the form

\[ S(t) = S(1 - b) \]

where \( S \) is the compressive stress at any time \( t \), \( S(1) \) is a constant having units of Pa \(^s\) \(^{-1}\) and same numerical value as stress at time 1 and \( b \) is a constant defined as relaxation rate of the material. From eqn (1) they derived \( b \) as

\[ b = \frac{1}{S \log(1 + \log S)} \frac{d \log S}{d \log t} \] \hspace{1cm} (2)

Therefore \( b \) is derived from the linear plot of \( \log S \) versus \( \log t \) as the fractional decrease in stress per unit logarithmic cycle of time.

In 1971 Voet et al.\(^2\) found that the above relationship is also obeyed under shear deformation mode. Hence eqn (1) can be written for shear deformation as

\[ \tau(t) = \tau_0 (1 - b') \] \hspace{1cm} (3)

where \( \tau \) is the shear stress at any time \( t \), \( \tau_0 \) is a constant having units of Pa \(^s\) \(^{-1}\) and same numerical value as stress at time 1 and \( b' \) is the relaxation rate of material in shear, also defined by eqn (2) by replacing \( S \) with \( \tau \).

2 Development of model

The viscosity of filled compounds can be described by the Einstein\(^3\) equation, modified by Guth et al.\(^4\)

\[ \eta_f = \eta_0 (1 + 2.5C + 14.1C^2) \] \hspace{1cm} (4)

where \( \eta_0 \) is the viscosity of gum elastomer and \( C \) is the volume fraction of filler. It has also been shown\(^5,6\) that eqn (2) can be extended to predict shear modulus \( G_f \) for filled compounds

\[ G_f = G_0 (1 + 2.5C + 141C^2) \] \hspace{1cm} (5)

where \( G_0 \) is the shear modulus of the gum elastomer.

In this work, analysis of the stress relaxation data showed that \( \tau_0 \) in eqn (3) at a given shear rate was dependent on filler loading and specific surface area, \( \psi \) of the filler; and can be adequately described by an equation similar in form to eqn (5), by adding a few extra terms to account for \( \psi \).

\[ \tau_0 = \tau_0 (1 + A_1 C + A_2 \psi + A_3 C \psi) \] \hspace{1cm} (6)

where \( \tau_0 \) is the stress in the gum elastomer at time 1 and \( A_1, A_2, A_3, A_4, A_5 \) are constants and the final term in eqn (6) is an interaction term.

The rate of relaxation \( r \) in eqn (3) was also found to be a function of \( C \) and \( \psi \); and can be described by an equation of the following form:

\[ r = r_0 + B_1 C + B_2 \psi + B_3 C \psi \] \hspace{1cm} (7)

where \( r_0 \) is the slope of the plot of log \( r \) versus log \( t \) for the gum elastomer and \( B_1, B_2, B_3 \) are constants.

By combining eqns (3), (6) and (7) an equation which describes shear stress relaxation of filled compounds, \( \tau(t) \), in terms of \( C \) and \( \psi \) is obtained.

\[ \tau(t) = \tau_0 (1 + A_1 C + A_2 \psi + A_3 C \psi) \] \hspace{1cm} (8)

3 Experimental

3.1 Materials

The elastomers studied were natural rubber (SMR20) and chloro-sulphonated polyethylene...
(CSM) [Hypalon 40, Du Pont, Hemel Hempstead, UK]. Three different grades of carbon black from Cabot Carbon (Ellesmere Port, UK) were used; the characteristics of which are given in Table 1.

Table 1. Characteristics of carbon black

<table>
<thead>
<tr>
<th>Filler</th>
<th>Grade</th>
<th>Surface area (m²/g)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>SRF (N762)</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>HAF (N330)</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>SAF (N110)</td>
<td>128</td>
</tr>
</tbody>
</table>

*Cabot figures.

Table 2. Constants in eqn (8) for SMR20 compounds at 100°C and a conditioning shear rate of 5 s⁻¹

<table>
<thead>
<tr>
<th>Compound</th>
<th>SMR20 +</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum 20 phr N762</td>
<td>45679</td>
</tr>
<tr>
<td>40 phr N762</td>
<td>6094</td>
</tr>
<tr>
<td>60 phr N762</td>
<td>0.8796 x 10⁻²</td>
</tr>
<tr>
<td>20 phr N110</td>
<td>2791</td>
</tr>
<tr>
<td>40 phr N110</td>
<td>-0.9056 x 10⁻⁴</td>
</tr>
<tr>
<td>20 phr N110</td>
<td>0.1316</td>
</tr>
<tr>
<td>40 phr N110</td>
<td>0.1901</td>
</tr>
<tr>
<td>20 phr N762</td>
<td>-0.1406 x 10⁻³</td>
</tr>
<tr>
<td>40 phr N762</td>
<td>0.4789 x 10⁻²</td>
</tr>
</tbody>
</table>

3.2 Mixing

All grades of carbon black were mixed with SMR20 and CSM rubber at loading levels of 20, 40 and 60 parts per hundred (phr) by weight of rubber (equivalent to 0.092, 0.1685 and 0.2332 by volume fraction of filler for SMR20).

Mixing was carried out on a Farrel Bridge BR Banbury internal mixer (Rochdale, UK) and then followed by subsequent milling on a Bridge two roll mill (Rochdale, UK).

3.3 Stress relaxation measurements

Shear stress relaxation of the gum and filled elastomers was measured using a TMS biconical rotor rheometer manufactured by Negretti Automation (Aylesbury, UK). The test samples were conditioned at a constant shear rate to obtain the steady state stress, the flow was then stopped suddenly and the decay of this stress with time was recorded.

4 Results

Only the fitting of the new model (eqn (8)) to selected SMR20 compounds at 100°C and a conditioning shear rate of 5 s⁻¹ is presented here for brevity. The constants in eqn (8) were determined and are shown in Table 2. The rates of relaxation for
these compounds, calculated from eqn (7), are shown in Table 3. Comparison between the prediction of eqn (8) and experimental data is shown in Figs 1 and 2.

5 Discussion

The experimental results reported in Figs 1 and 2 and Table 3 are similar to those found by Cotton and Boonstra\textsuperscript{1} for raw elastomer compounds. The rate of relaxation is decreased by increasing loading levels and specific surface area of the filler (see Table 3). The agreement between the model prediction and experimental data is fairly good.

6 Conclusions

A new model for describing shear stress relaxation behaviour of carbon black filled compounds has been developed which looks very promising. It has also been applied to different elastomeric compounds at various temperatures and the full set of results will be presented in due course.

References

4. GUTH, E., SIMHA, R. & GOLD, O., Koloid Z., 74 (1936) 266.
5. GUTH, E., Rubber Chem. & Tech., 23 (1945) 635.
had been stored at different humidities, plastisol viscosity appeared to fall with increasing moisture content. This is in stark contrast to a Russian paper in which Merinov et al** claim that viscosity at low shear rates rises with increasing moisture content. The rise in viscosity is attributed to a reduction in zeta potential caused by the higher moisture content. Such observations not only conflict with Underdal et al's work on moisture content but also Collins et al** who have demonstrated that a decrease in interparticle repulsion (measured by a fall in zeta potential) causes low shear viscosity to fall, not rise.

1.7. PARTICLE SIZE MEASUREMENTS.

When considering the task of particle size analysis of PVC resins it soon becomes apparent that no one currently available technique can be successfully used for all types of product, as no single technique can quantify a PS range of 0.01 to 1,000µ. Indeed, when faced with the problem of obtaining a full PSD on a single sample of paste forming polymer it is usually recognised that a combination of techniques, with its attendant difficulties, is required. An indication of the particle sizes involved is given in Table 1.4.

TABLE 1.4 - PVC PARTICLE SIZE MEASURABLE BY VARIOUS TECHNIQUES. FROM REF.(7).

<table>
<thead>
<tr>
<th>Product type</th>
<th>Technique</th>
<th>Suspension mass</th>
</tr>
</thead>
</table>
|                       | Particle size 
|                       | (µm)            |
|                       | 10^{-2} | 10^{-1} | 10   | 10^{1} | 10^{2} | 10^{3} |
| Product type          | Technique      | Suspension mass |
|                       | Particle size 
|                       | (µm)            |
|                       | 10^{-2} | 10^{-1} | 10   | 10^{1} | 10^{2} | 10^{3} |
| Unseeded emulsion latex| Microscopy     | Suspension mass |
|                       | Sieving        | Suspension mass |
|                       | Sedimentation (gravimetric) |                 |
|                       | Sedimentation (centrifugal) |               |
|                       | Coulter Principle |                  |
|                       | Laser diffraction |                 |
|                       | Light blockage  |                  |

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