STUDIES OF PURE HOMOGENEOUS DEFORMATIONS
IN UNFILLED NATURAL AND BUTYL RUBBERS

by

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in unfilled natural and butyl rubbers

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SUMMARY

Observed deviations from the kinetic theory of rubberlike elasticity have been reviewed, and particular attention focussed upon the Mooney parameter $C_2$.

Stress measurements have been made upon thin rubber sheets in a state of pure homogeneous biaxial strain, and the stress relaxation behaviours of a natural rubber and a butyl rubber are reported.

Analysis of the results allowed an examination of the stored energy function $W$ over a strain invariant range $3 < I_1 < 12$ and $3 < I_2 < 30$. Finite values of $\frac{\partial W}{\partial I_2}$ were found under conditions for which there was no observed stress relaxation. This is at variance with the kinetic theory, for which $\frac{\partial W}{\partial I_2}$ is zero.
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List of symbols

\( W \)  stored elastic energy per unit volume

\( C_1, C_2, A_{pq} \)  elastic material parameters

\( I_1, I_2, I_3 \)  strain invariants, defined by equations 2.2 and 2.3

\( \lambda_1, \lambda_2, \lambda_3 \)  principal extension ratios

\( \lambda, \alpha, \lambda' \)  extension ratios

\( \Omega \)  a function of \( J_1, J_2 \) and \( \tau \)

\( B_{pq} \)  viscoelastic materials parameters

\( J_1, J_2 \)  strain invariants, defined by equations 7.5

\( e_{ij} \)  elastic strain, tensor for infinitesimal displacements

\( u_i \)  infinitesimal displacement vector

\( S_{ij} \)  strain tensor for a viscoelastic body

\( E_{ijkl} \)  strain tensor defined by equation A.14

\( x_i \)  coordinates of a particle at the current time \( t \)

\( X_\alpha \)  coordinates of a particle in the undeformed material

\( x'_\alpha \)  coordinates of a particle at some past time \( t' \)

\( t \)  current time

\( t' \)  past time

\( \tau \)  \( t-t' \)

\( N(t-t') \)  lifetime distribution function for crosslinks

\( P_{ij} \)  stress tensor

\( t_1 \)  principal stresses

\( f \)  uniaxial tensile force per unit unstrained cross-sectional area

\( p, p' \)  isotropic pressures

\( \delta_{ij} \)  unit matrix
$Y_j$ defined by equation 7.11

$V \lambda_1 \lambda_2 \lambda_3$

$V_r$ volume fraction of rubber in the swollen sample

$r_i^2$ mean square network chain length in the unstrained rubber

$r_i^2$ mean square end to end length of an isolated single molecule

$N$ number of molecular network chains per unit volume

$k$ Boltzmann's constant

$T$ absolute temperature

$J$ mechanical equivalent of heat

$\rho$ density of rubber

$c$ specific heat of rubber
1 Introduction

With the development and increased use of elastomeric materials, with their ability to support reversible finite strains, considerable effort has been made in recent years to evolve an adequate theory for large elastic deformations of isotropic materials.

General relationships have been proposed between the state of strain of a deformed elastic material and the applied stress system (Rivlin 1948, 1949). However, to describe the stress-strain behaviour of a particular material it is necessary to substitute into the generalized equations some functions which represent the elastic properties of that material. This Note is largely an examination of the form of such functions.

The elastic properties of a material are completely determined if the energy which is stored in an isothermal deformation can be expressed as a function of the strain only. Two fundamentally different approaches have been made to this problem.

Statistical mechanical studies of the thermal motion of the molecular network of an idealized elastomer (the kinetic theory of rubberlike elasticity) have led to a stored energy function which is expressed in terms of the geometry of the deformation, and one material parameter. (reviews, Treloar 1958, Volkenstein 1963). A second approach considers only the continuous macroscopic nature of the material and its observed behaviour and suggests that the stored energy can be described in terms of the geometry of deformation, and any number of material parameters, (review, Rivlin 1956).

Experimental measurements of the stress-strain behaviour of elastomers for various simple deformations have shown apparent inadequacies in the form of the stored energy function suggested by the statistical theory. It has been suggested that this form is therefore only a first approximation of the more general function derived from the continuum approach. No function has yet been suggested which will give stress-strain relationships for an elastomer fitting all the experimentally determined results. It should also be possible to find the molecular mechanisms which are responsible for each material parameter. Suggestions have been made and accepted only for the one parameter which is common to both approaches.

The view has been expressed (Ciferri and Flory 1959) that the stored energy function obtained from the kinetic theory is essentially correct, and that it is the inadequacy and misinterpretation of experimental results which has led to the position outlined above. Rubbers are not perfectly elastic but are viscoelastic in nature. If measurements are made before the materials obtain their final equilibrium shape under the applied stress systems then the results should not be treated in terms of an elastic theory. According to Ciferri and Flory, observed deviations from the statistical theory are time dependent in origin and go to zero at true equilibrium.

This Note describes the current position over the dichotomy presented...
by the two different approaches to the derivation of a stored energy function. The observed deviations from the kinetic theory are reviewed. A description is then given of the measurements made upon the stress system needed to maintain sheet rubber in a state of pure homogeneous strain. Non-equilibrium effects are considered. If the theory developed from the statistical approach is correct then it should be possible to describe the stress system in terms of one material parameter only.

2. The stored energy function

The kinetic theory of rubberlike elasticity leads to a description of \( W \), the stored elastic energy per unit volume, in terms of a single time dependent material parameter \( C_1 \) and the geometry of deformation.

\[
W = C_1(I_1 - 3) \tag{2.1}
\]

where \( I_1 \) is the first strain invariant and is related to the principal extension ratios \( \lambda_1, \lambda_2, \) and \( \lambda_3 \), of a pure homogeneous deformation by

\[
I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \tag{2.2}
\]

An alternative approach to rubber elasticity is to consider only the continuum properties and behaviour of the material. A major advance in continuum mechanics is due to Rivlin (1948, 1949, 1956) who solved a number of problems involving finite deformations of isotropic materials using a completely general form for the stored energy function. Rivlin argued that when a material, which is isotropic in its undeformed state, is in a state of pure homogeneous strain defined by the principal extension ratios \( \lambda_1, \lambda_2, \) and \( \lambda_3 \), then the energy per unit undeformed volume stored elastically in the material must be a function of \( \lambda_1, \lambda_2, \) and \( \lambda_3 \). Furthermore this stored energy must be unaltered by rigid body rotation of the material, and therefore the analytical description of the stored energy does not depend upon the direction of the chosen reference system of cartesian coordinates, and must be a function of the strain invariants \( I_1, I_2, \) and \( I_3 \).

The second and third strain invariants, \( I_2 \) and \( I_3 \), are given by

\[
I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \tag{2.3}
\]

and

\[
I_3 = \lambda_1^2\lambda_2^2\lambda_3^2
\]

Since \( W = W(I_1, I_2, I_3) \) then it can be expressed without loss of generality as a power series in \( I_1, I_2, \) and \( I_3 \).

\[
W = \sum_{p, q, r=0}^{\infty} A_{pqr} (I_1 - 3)^p(I_2 - 3)^q(I_3 - 1)^r \tag{2.4}
\]
where \( A_{000} = 0 \), and \((I_1-3), (I_2-3),\) and \((I_3-1)\) are used in preference to \( I_1, I_2, \) and \( I_3 \) so that \( W \) will be zero for zero deformation. The constants \( A_{pq} \) may be considered material parameters which describe the elastic behaviour of the material. Particular forms for the stored energy function can obviously be generated by retaining only specific terms in the series expansion of \( W \). For example, Mooney (1940, 1964) derived a form for \( W \) based upon an observed linear relationship between stress and simple shear in unfilled rubber

\[
W = C_1(I_1-3) + C_2(I_2-3)
\]

(2.5)

This may be considered to be the first two terms of the series expansion (2.4) with \( A_{100} = C_1 \) and \( A_{010} = C_2 \).

It may be noted that \( I_3 = 1 \) for an incompressible material and then \( W \) can be written \( W(I_1, I_2) \). If corresponding values of \( W, I_1 \) and \( I_2 \) are plotted on an orthogonal three dimensional coordinates system with axes \( W, I_1, \) and \( I_2, \) then the complete description of \( W \) involves the characterisation of the surface \( W(I_1,I_2) \) over the complete range of values of \( I_1, \) and \( I_2 \) normally encountered.

3. Deviations from the kinetic theory

The stored energy functions derived from the continuum and kinetic theories are differentiated by the existence of material parameters other than the first in (2.4) the series expansion of \( W \). Studies of various simple deformations (Rivlin and Saunders 1951) have suggested that for an natural rubber gumstock

\[
W = C_1(I_1-3) = \Phi(I_2-3)
\]

(3.1)

where \( \Phi(I_2-3) \) is some decreasing function of \( (I_2-3) \) and hence represents the deviation of the experimental results from the kinetic theory. Most of the experimental studies of the form of \( \Phi(I_2-3) \) have been limited to simple elongations, when the behaviour for moderate extensions can be characterized by the Mooney stored energy function. This suggests the identification of \( 2C_1 \) with \( NkT \left( \frac{I_2}{I_0^2} \right) \), where \( N \) is the number of molecular chains per unit volume and \( k \) is Boltzmanns constant. The mean square end to end length of an isolated single chain at absolute temperature \( T \), is \( \frac{I_0^2}{I_1^2} \) and \( \frac{I_2}{I_0^2} \) is the mean square network chain length in the unstrained rubber.

This definition has been examined extensively and reviewed by, for example, Mullins and Thomas (1963), and will not be considered further.
The stored energy function for incompressible materials, \( W(I_1, I_2) \), is represented graphically by a surface when \( W, I_1 \) and \( I_2 \) are chosen as the three coordinate axes. The Mooney function then can be assumed to describe the surface contour line which follows the definition of simple elongation that is \( \lambda_1 = \lambda \) and \( \lambda_2 = \lambda_3 = \lambda^{-2} \). It has been suggested by Ciferri and Flory (1959) that \( C_2 \) is an artefact which has arisen from misinterpretation of simple extension data. This is a necessary but not a sufficient condition for the conclusion that the Gaussian function \( W = C_1(I_1-3) \) is adequate to represent the mechanical properties up to moderate extensions.

3.1 The Mooney parameter \( C_2 \)

A molecular mechanism is not yet available which explains completely the observed behaviour corresponding to \( C_2 \), which will now be outlined.

According to the kinetic theory the stress-strain relationship for a swollen incompressible rubber in simple extension is given by (James and Guth, Flory and Rehner, 1943).

\[
f = N k T v_0^{1/3} \left( \alpha - \frac{1}{\alpha^2} \right) \tag{3.2}
\]

where \( f \) is the tensile force per unit cross sectional area of the swollen unstrained rubber, \( v_0 \) is the volume fraction of rubber in the swollen sample, and the extension ratio \( \alpha \) refers to the unstrained swollen state.

Gee (1946) examined the function \( f v_0^{-2/3} (\alpha - \frac{1}{\alpha^2})^{-2} \) for natural rubber swollen in toluene and found it to decrease with increasing strain at variance with (3.2). This deviation from the kinetic theory was much reduced as the degree of swelling increased.

This work was extended by Gumbrell, Mullins and Rivlin (1953) to a number of rubber-liquid systems, and the results analysed in terms of the Mooney parameters for the swollen rubber, \( C_{1S} \) and \( C_{2S} \), defined such that

\[
\theta = \frac{f}{v_0^{-1/3} \left( \alpha - \frac{1}{\alpha^2} \right)} = C_{1S} + C_{2S} \lambda \tag{3.3}
\]

\( C_{2S} \) was determined from the gradient of the observed linear relationship between \( \theta \) and \( 1/\lambda \) and found to be independent of the nature of the diluent, but decreased progressively with decreasing \( v_0 \). This decrease may be associated with steric hindrances due to bulky side groups. A number of sulphur accelerated synthetic and natural rubber vulcanisates were considered. \( C_2 \) was independent of the styrene content in butadiene - styrene copolymers, and had the same value (about 1 kg.cm\(^{-2}\)) for butadiene - acrylonitrile, and natural rubber. It was therefore concluded that \( C_2 \) was not dependent upon
the presence of bulky side groups or polar groups. Smaller values (about 0.8 kg.cm\(^{-2}\)) were found for peroxide cured natural rubber.

Gumbrell et al. suggest that \( C_2 \) is associated with the volume filling properties of the chain. Then some dependence upon extension might be expected but is not apparent in their results over the strain invariant range \( 3 < I_1 < 6, 3 < I_2 < 5 \). However, a decrease in \( \frac{\partial W}{\partial I_2} \) with increasing \( I_2 \) is shown in the more general results of Rivlin and Saunders (1951) over the range \( 3 < I_1 < 12, 3 < I_2 < 30 \), and is confirmed by the variation of \( \frac{\partial W}{\partial I_1} \) with \( I_1 \) and \( I_2 \) shown in Figure 4. Swelling would naturally reduce finite volume effects.

The dependence of \( C_2 \) on \( \nu_r \) was confirmed by Mullins (1959) who found that simple extension data on swollen peroxide and sulphur cured natural rubber could be described by

\[
\theta = C_1 + \frac{C_2 \nu_r^{4/3}}{\lambda} \tag{3.4}
\]

where \( C_1 \) and \( C_2 \) are the Mooney parameters for the dry rubber.

An experimental examination of the forces necessary to maintain a rubber tube in a state of simultaneous extension, inflation, and torsion, led Gent and Rivlin (1952) to observe that the amount of hysteresis in a complete load-deformation cycle appeared to be associated with \( \frac{\partial W}{\partial I_2} \). Therefore, the mechanism which accounts for hysteresis may give rise to terms in \( W \) which are additional to the kinetic theory. An important contribution to hysteresis could be the failure to attain the equilibrium stress-strain state necessary for the thermodynamic analysis of the kinetic theory.

Priss (1957) considered a network of chains of random orientations. Deformation of the bulk rubber was considered to produce an instantaneous affine displacement of all chain segments followed by a co-operative movement of the chain links over a long period of time. The end to end distances of the chains are assumed to be constant during this movement.

The stored energy function derived by Priss for this network involves time dependent terms which are additive to the Gaussian term and contain incomplete elliptic integrals. No details of the derivation are given, and no details are given to substantiate the claim that this function describes experimental data in simple extension compression, biaxial deformation and shear.

The first detailed investigations into the time dependence of \( C_2 \) were performed by Ciferri and Flory (1959). A correlation between \( C_2 \) and hysteresis was observed from simple extension measurements on a number of elastomers. Changes in the experimental conditions to aid the approach
to equilibrium were found to decrease $C_2$. The effect of increasing the time interval between the imposed elongation and the measured stress was examined. Cross linked poly methyl methacrylate, which has a glass transition temperature ca.110°C, exhibits considerable stress relaxation at 145°C. At this temperature $C_2$ decreased from 2.4 Kg. cm$^{-2}$ to 1.8 cm$^{-2}$ as the time interval increased from 3 minutes to 30 minutes, but a small, decrease only (0.80 Kg.cm$^{-2}$ to 0.76 Kg.cm$^{-2}$) was observed for sulphur accelerated natural rubber at 34°C over the same period. $C_2$ was found to decrease with increasing temperature (below degradation temperatures). For example, as the temperature of P.M.M.A. increased from 145°C to 175°C, $C_2$ decreased from 2.40 Kg.cm$^{-2}$ to 1.30 Kg.cm$^{-2}$. $C_2$ was also found to decrease when increasing amounts of diluent was absorbed by the polymer networks. The minimum observed value of $C_2$ was 0.04 Kg.cm$^{-2}$ for a silicone rubber crosslinked in a highly swollen state but the minimum values for natural rubber were an order of magnitude larger. Ciferri and Flory suggested that under ideal equilibrium conditions $C_2$ will be zero.

Mason (1959) used wave propagation techniques to superimpose small dynamic strains upon strips of stretched natural rubber. If the dynamic modulus is defined by

$$ E = \lambda \frac{d\sigma}{d\lambda} $$

where $\sigma$ is the true stress given by $\sigma = f\lambda$ and $f$ is given by

$$ f = 2(\lambda - 1/\lambda^2) (C_1 + C_2/\lambda) $$

then

$$ F_1 E = C_1 + F_2 C_2 $$

where $F_1 = \frac{\lambda}{2(2\lambda^2+1)}$ and $F_2 = \frac{\lambda^3+2}{\lambda(2\lambda^2+1)}$. Mason considered the in-phase and out of phase components of the modulus and Mooney parameters, and found that (3.7) was obeyed up to about 150% extension over the temperature range -20°C to 50°C, at a constant frequency. Both components of $C_2$ decreased with increasing temperature, presumably because of increasing chain mobility and therefore a closer approach to equilibrium.

Halpin (1964, 1965) examined simple extension data obtained from creep, stress relaxation, and stress-strain measurements at constant strain rate. He factorised the appropriate modulus into a time dependent term, and a term which is a function of the strain only, and may be considered to represent the equilibrium behaviour. He concluded that for certain highly crosslinked polymers the equilibrium behaviour was adequately represented by the kinetic theory involving the inverse Langevin function.
However, he mentions unpublished data obtained on polymers of low crosslink density which exhibit deviations from the kinetic theory.

Mullins (1953), in contradiction to Ciferri and Flory, found that $C_2$ for natural rubber under near equilibrium conditions increased with an increase in temperature.

Roe and Krigbaum examined $C_2$ for a natural rubber (1962) and a fluoroelastomer (1963) and allowed at least 24 hours to approach equilibrium after successive elongations. No stress relaxation was observed after a few hours but the values of $C_2$ were still finite. For a natural rubber at $45^\circ C$, $C_2 = 0.438 \text{ kg cm}^{-2}$. The entropy component only of the retractive force was used in the Mooney equation for simple extension, (5.3 with $v_r = 1$), and the corresponding values of the Mooney parameters were determined. $C_2$ was reduced by about 50% for natural rubber, and became negligible for the fluoroelastomer, which suggests that considerable contributions are made by the internal energy.

The constant volume condition assumed by Mooney in his derivation of the stored energy function 2.5 has been disregarded by van der Hoff (1965). He assumed that the Mooney stored energy function would describe the elastic energy stored during swelling as well as in extending rubber, and was able to derive (3.4), the empirical equation of Mullins. Doubt is therefore cast upon the assumption of Ciferri and Flory (1959) that a reduction in the observed value of $C_2$ with swelling is a consequence of reduced hysteresis.

There are a number of modifications to the energy and entropy of a deformed rubber network which were not considered during the derivation of (2.1), the kinetic theory form of the stored energy function. The mechanisms responsible for these changes may contribute to a $C_2$ term. Very little is known, for example, upon the effect of intermolecular forces upon the elasticity of rubber. Gee (1946) suggested that local ordering within the network would affect the entropy. Volkenstein, Gotlib and Ptitsyn (1959) and Bartenev and Khazanovich (1960) considered the mutual orientation of segments of neighbouring molecules. Dobson and Gordon (1964) examined the contribution to the network entropy of short chains of one or two bonds which are capable of orientation but not extension, and Di Marzio (1962) considered the reduction in available configurations because of molecular packing. The possible magnitude of the contributions to $C_2$ has been discussed by the individual authors. It is of particular interest to note that Gee (1966) concluded that $C_2$ is not a consequence of the excluded volume effect.

It has been suggested that a time dependent $C_2$ term may arise because of the presence in the network of slipping entanglements (Kraus and Moczvgenba 1964) or unspecified labile crosslinks (Ciferri and Hermans 1964). The former authors found that for a polybutadiene rubber $C_2$ increased as the number of entanglements and total crosslink density increased. Bristow (1965) observed, for peroxide cured natural rubber and cis-1,4 - polyisoprene
that $C_2$ varied with $C_1$ and went through a maximum at $C_1 \approx 2.0 \text{ kg cm}^{-2}$. The dependence upon crosslink density is at variance with the results of Gumbrell, Mullins and Rivlin (1953).

A large proportion of the free energy of deformation of rubber is due to entropy changes, and therefore deformation is accompanied by a heat build up. It is shown in Appendix 3 that an adiabatic deformation can give rise to a $C_2$ type term. However the magnitude of this term is considerably less than the values determined from simple extension measurements. Furthermore this contribution will be time dependent and decay to zero at a rate dependent upon the rate of heat exchange between the sample and its surroundings.

In summary it may be said that no single mechanism has been accepted as the source of $C_2$. It is therefore unlikely that a single constant material parameter is adequate to describe the effect upon the mechanical properties of all the mechanisms described. A positive $C_2$ will explain the experimental curves in pure shear and simple elongation at moderate strains which fall below the Gaussian curves before showing the expected upturn at high strains.

A number of empirical or semi-empirical stored energy functions and stress-strain relationships have been proposed to fit the experimental data obtained for various deformations.

### 3.2 Empirical stress-strain and stored energy functions

The limitations of the kinetic theory and Mooney stored energy functions in predicting the mechanical behaviour of rubber has been discussed fully by Treloar (1958). A number of empirical or semi-empirical functions have been proposed.

Martin, Roth and Stichler (1956) found that isochronous stress-strain curves obtained from creep measurements in simple extension were represented up to $\lambda = 2$ by the empirical equation

$$f = E \left( \frac{1}{\lambda} - \frac{1}{\lambda^2} \right) \exp A \left( \frac{1}{\lambda} - \frac{1}{\lambda^2} \right)$$

where $E$ is Young's modulus at $\lambda = 1$, and $A$ is a constant. Wood (1958) applied (3.8) to the data of Rivlin and Saunders (1951) and found a reasonable fit for $0.5 < \lambda < 3$. Fritz and Johnson (1963) applied (3.8) to irradiated polyurethane elastomers and found $A$ to be a slowly varying function of dose while $E$ varied exponentially.

Bartenev and Khazonovich (1960) considered the orientation of segments of the molecules during deformation, and obtained a two parameter relationship for the principal stresses $t_1$ and $t_2$ in a pure homogeneous deformation.
where $A$ and $B$ are constants. This equation was found to fit the simple extension, pure shear, and pure shear plus extension results of Rivlin and Saunders. Bartenev and Vishnitskaya (1961) compared the simple extension form of (3.9) with the three parameter equation of Zagorski (1959), i.e.

$$ f \lambda = A(\lambda^4 - 1) + B(\lambda^2 - 1) + C(\lambda - 1) \quad (3.10) $$

where $A$, $B$, and $C$ are constants. They found that both equations described their results on natural and synthetic rubbers reasonably well up to $\lambda = 3$, but (3.9) gave a better fit for $\lambda > 3$.

Another three parameter function has been developed (Carmichael and Holdaway 1961) to express the principal stresses in terms of the induced principal extension ratios

$$ t_i - p = \frac{A}{2} \exp\left[B\left(\frac{1}{\lambda_i}\right)\right] - C\left(\frac{1}{\lambda_i^2} + \frac{1}{\lambda_i^2} - 2\right) \quad (3.11) $$

where $A$, $B$, and $C$ are interdependent material constants and $p$ is an arbitrary hydrostatic pressure. Carmichael and Holdaway have shown that (3.11) fits experimental results obtained by Treloar (1944b) in simple extension, simple shear, and equi-biaxial strain.

A number of stored energy functions have been proposed. Thomas (1955) modified the free energy of a single gaussian chain by an empirical additive term $A\sqrt{r^2}$. The network stored energy function for a general homogeneous strain then involves an incomplete elliptic integral. Gent and Thomas examined a substantially equivalent function (1958).

$$ W = W_1(I_1 - 3) + W_2 \ln\left(\frac{I_2}{3}\right) \quad (3.12) $$

where $W_1$ and $W_2$ are constants. This function is in qualitative agreement with the uniaxial stress-strain data, and the strain dependence of $\delta W / \delta I_1$ determined by Rivlin and Saunders. However, the Thomas function, at variance with (3.12) also predicted a small decrease in $\delta W / \delta I_1$ with increasing strain.

Priss (1957) has stated that

$$ W = C_1(I_1 - 3) + k\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3} - 3\right) \quad (3.13) $$

where $C_1$ is the Mooney parameter, and $k$ is a constant. This function qualitatively reproduces a number of stress-strain relationships.
The complex three parameter stored energy function of Carmichael and Holdaway (1961) has been discussed by Klingbeil and Shield (1964). They examined theoretically the inflation of a flat circular sheet and found that with the inclusion of this three parameter function their equations then described the experimental work of Treloar (1944c). Furthermore $\frac{\partial W}{\partial I_1}$ appeared to be independent of $I_2$ and $\frac{\partial W}{\partial I_2}$ decreased with $I_2$ up to $I_2$ ca.1000.

Empirical formulae have recently been proposed (Hart-Smith 1966) to fit all the data of Treloar (1944a) and Rivlin and Saunders.

$$\frac{\partial W}{\partial I_1} = G \exp \left[ k_1 (I_1 - 3)^2 \right], \frac{\partial W}{\partial I_2} = \frac{G k_2}{I_2}$$

(3.14)

$\frac{\partial W}{\partial I_1}$ then exhibits the upturn at high extensions that might be expected because of the finite extensibility of the network chains.

4. Stress-strain relationships for the pure homogeneous deformation of sheet rubber

The theory outlined below is based on that of Rivlin (1948a, 1948b) who derived relationships between the general pure homogeneous strain imposed on compressible and incompressible elastic isotropic materials, and the applied stress system.

Consider a unit cube of elastic isotropic incompressible material, with its edges parallel to the coordinate axes $x_i$ (where $i$ is equal to 1, 2 or 3). Let this cube be transformed into a rectangular parallelepiped by extension ratios $\lambda_i$ along the directions $x_i$. The direction $x_i$ are the principal strain axes which for this material are coincident with the principal stress axes, and hence the applied stress system can be represented by $\tau_{ij}$.

The virtual work done in producing a further incremental deformation $\delta \lambda_i$ is

$$\delta W = t_1 \delta \lambda_1 \delta \lambda_2 \delta \lambda_3 + t_2 \delta \lambda_1 \delta \lambda_3 \delta \lambda_2 + t_3 \delta \lambda_1 \delta \lambda_2 \delta \lambda_3$$

(4.1)

and since $W$, the elastically stored energy, is a function of $\lambda_1, \lambda_2, \text{ and } \lambda_3$

$$\delta W = \frac{\partial W}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial W}{\partial \lambda_2} \delta \lambda_2 + \frac{\partial W}{\partial \lambda_3} \delta \lambda_3$$

(4.2)

and for equilibrium under isothermal conditions

$$\delta W_1 - \delta W = 0$$

(4.3)
and hence
\[
(t_1 \lambda_2 \lambda_3 - \frac{\partial W}{\partial \lambda_1}) \delta \lambda_1 + (t_2 \lambda_1 \lambda_3 - \frac{\partial W}{\partial \lambda_2}) \delta \lambda_2 + (t_3 \lambda_1 \lambda_2 - \frac{\partial W}{\partial \lambda_3}) \delta \lambda_3 \quad (4.4)
\]
\[= 0\]

For an incompressible material, the volume \( V \) of the deformed element is given by
\[V = \lambda_1 \lambda_2 \lambda_3 = 1 \quad (4.5)\]
and any arbitrary function of the volume \( f(V) \) is equal to \( f(1) \).

Therefore
\[
\frac{\partial f(V)}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial f(V)}{\partial \lambda_2} \delta \lambda_2 + \frac{\partial f(V)}{\partial \lambda_3} \delta \lambda_3 = 0 \quad (4.6)
\]
or
\[
\frac{\partial f(V)}{\partial V} \left[ \frac{\partial V}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial V}{\partial \lambda_2} \delta \lambda_2 + \frac{\partial V}{\partial \lambda_3} \delta \lambda_3 \right] = 0 \quad (4.7)
\]

Hence by substituting (4.5) into (4.7) the most general condition for incompressibility is
\[P[I_2 \delta \lambda_2 + \lambda_1 \lambda_3 \delta \lambda_3 + \lambda_1 \lambda_2 \delta \lambda_1 = 0 \quad (4.8)\]
where \( p \) is the arbitrary constant \( \frac{\partial f(V)}{\partial V} \).

Now (4.4) is valid for values of \( \delta \lambda_1 \) which satisfy (4.8). Comparing coefficients of \( \delta \lambda_1 \)
\[\delta \lambda_1 = \lambda \frac{\partial V}{\partial \lambda_1} \quad (4.9)\]
where
\[
\frac{\partial W}{\partial \lambda_1} = \frac{\partial W}{\partial I_1} \frac{\partial I_1}{\partial \lambda_1} + \frac{\partial W}{\partial I_2} \frac{\partial I_2}{\partial \lambda_1} \quad (4.10)
\]

now, from (2.2) and (2.3),
\[I_1 = \sum_{i=1}^{3} \lambda_i^2 \quad \text{and} \quad I_2 = \sum_{i=1}^{3} \lambda_i^{-2} \quad \text{since} \]
\[\lambda_1 \lambda_2 \lambda_3 = 1 \quad (4.11)\]

and hence (4.9) becomes
For a pure homogeneous strain in which forces are applied only to the faces of the cube which are normal to the \( x_1 \) and \( x_2 \) axes, \( t_3 = 0 \).

Therefore

\[
t_1 = 2 \left( \lambda_1 \frac{\partial W}{\partial I_1} - \lambda_2 \frac{\partial W}{\partial I_2} \right)
\]

\[
t_2 = 2 \left( \lambda_2 \frac{\partial W}{\partial I_1} - \lambda_1 \frac{\partial W}{\partial I_2} \right)
\]

Now consider the unit cube to be an element of a thin plane square of side 1 and uniform thickness \( h \). Let the major surfaces of this thin square be normal to the \( x_3 \) axis, and its edges parallel to the \( x_1 \) and \( x_2 \) axes. If forces \( f_1 \) and \( f_2 \) are applied to the faces normal to the \( x_1 \) and \( x_2 \) axes then the corresponding stresses \( t_1 \) and \( t_2 \) can be calculated from

\[
t_1 = \frac{f_1 \lambda_1}{h^2}
\]

\[
t_2 = \frac{f_2 \lambda_2}{h^2}
\]

Equations (4.13) can be solved for \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) and give

\[
\frac{\partial W}{\partial I_1} = \frac{\lambda_1^2 \lambda_2^2 - \lambda_1 \lambda_2 \lambda_3^2}{2(\lambda_1^2 - \lambda_2^2)}
\]

and

\[
\frac{\partial W}{\partial I_2} = \frac{\lambda_1 \lambda_2^2 - \lambda_1^2 \lambda_2 \lambda_3^2}{2(\lambda_2^2 - \lambda_1^2)}
\]

Therefore measurement of the forces \( f_1 \) and \( f_2 \), for a pure homogeneous deformation characterised by \( \lambda_1 \) and \( \lambda_2 \) allows the value of \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) to be calculated.

The deformation can alternatively be characterised by the values of the strain invariants \( I_1 \) and \( I_2 \), and therefore the variation of \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) with \( I_1 \) and \( I_2 \) can be investigated.
Furthermore, if $\lambda_1 = \lambda_2 = \lambda$ then from (4.13)

$$t_1 = t_2 = t = 2 \left( \lambda^2 - \frac{1}{\lambda^4} \right) \left( \frac{\partial W}{\partial I_1} + \lambda^2 \frac{\partial W}{\partial I_2} \right)$$  \hspace{1cm} (4.16)

since $t_3 = 0$ as before.

5. Experimental Apparatus and Procedure

An attempt has been made to examine the stored energy function $W(I_1, I_2)$ by an experiment in which there is no causal relationship between $I_1$ and $I_2$. The method used was to measure the force system needed to produce a pure homogeneous deformation in two perpendicular directions in the plane of a rectangular sheet of rubber.

The experimental arrangement is essentially that of Treloar (1948) and Rivlin and Saunders (1951), but the method of applying and measuring the force system has been modified to facilitate stress relaxation studies.

The complete test piece was cut from a single moulded sheet of rubber as shown in Figure 1, and the surface marked in ink with a 3 cm. square grid of 1 cm. squares. The thick lags considerably reduced sample failure by tearing. Strings were attached to the lags by clamps, and a pure homogeneous biaxial deformation produced in the plane of the sample by applying tensions to those strings.

Details of the sample preparation and the recipes of the rubbers are given in Appendix 1.

Ideal conditions for stress relaxation studies involve a step function strain history. In order to deform the samples rapidly each set of five strings was attached to a rigid bar, and hence the problem of applying tensions separately to twenty strings resolved itself into moving four bars outwards from the sample to predetermined positions.

Details of the system used are given in Figure 2. Coarse adjustments to the deformation was provided at each side of the test piece by the threaded rods $A$, which traversed nuts mounted on the supporting table and controlled the position of the attachment points to the large drawbars $B$. Fine adjustment was provided by threaded rods on the ends of the central three strings attached to $B$.

Stress relaxation studies involve the determination of the time dependence of the stress system which maintains the deformation constant. Preliminary experiments using dummy samples determined the position of $B$ which would produce a particular pure homogeneous deformation characterised by the values of $\lambda_1$ and $\lambda_2$. The threaded rods were adjusted so that the marked grid on the sample fitted exactly a rectangular grid marked on perspex which represented the desired deformation. The actual test piece was then mounted and deformed by fixing the drawbars at these predetermined positions.
Fine adjustments were sometimes necessary to complete the deformation which took less than one minute to perform.

Rivlin and Saunders (1951) had shown that the stresses necessary to produce a homogeneous strain over the area of the test piece marked by the grid can be calculated, within a $4\%$ error, from the forces acting over the central three strings of each side. Preliminary experiments further established that the tension in any one of the three central strings deviated from the arithmetic mean of the three tensions by less than $5\%$.

The total tensile forces, acting over the central three strings on each of two adjacent sides, were determined by noting the deflection of a stiff phosphor bronze ring $R$. Four resistance strain gauges were fixed to each ring at the positions of greatest flexure, and incorporated in a bridge network which gave an out of balance current proportional to the load applied to the ring.

The bridge (Phillips PT1200) was temperature compensated, and the proof ring calibrations were unaltered over the range of ambient temperatures encountered, (18 ± 2°C). Over the time period of the measurements the bridge output current meter was subject to zero drift. A clamp was installed which allowed the sample to be maintained in its strained state as the load was removed from each proof ring and the zero corrected.

Stress measurements were made on a lightly crosslinked natural rubber, and a butyl rubber which were maintained at 25 ± 0.5°C in a suitable enclosure. The temperature gradients in the enclosure produced differences of less than 0.2°C between any two points on the test pieces.

Measurements were also made on the butyl rubber maintained at 0°C in a mixture of ice and water. The ice-water mixture completely covered the sample and was contained in a deep sided tray. The supporting strings passed through gelatine windows in the tray which kept water losses to a minimum without causing errors in the force measurement due to friction.

No stress relaxation was observed for the butyl rubber at 25°C and the variation of $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ with $I_1$ and $I_2$ was examined. Following the procedure of Rivlin and Saunders (1951) groups of deformation were chosen which represented particular constant values of $I_1$ and $I_2$. The relationships between $\lambda_1$ and $\lambda_2$ for constant values of $I_1$ and $I_2$ were derived by rearranging (4.11) and are shown graphically in Figure 3. The broken lines represent the relationships between $\lambda_1$ and $\lambda_2$ for simple extension in the $x_1$ and $x_2$ directions. Deformations represented by points to the left and below these lines would require at least one compressive force and are not relevant to this experiment.

A further series of measurements on butyl rubber at 25°C involved equibiaxial extensions when $\lambda_1 = \lambda_2$. These results were compared with simple extension measurements at the same temperature upon test pieces cut from the same rubber sheet.
6. Experimental Results

6.1 Butyl rubber at 25°C

No stress relaxation was observed. The forces necessary to maintain a series of deformations were measured, and the corresponding values of \( t_1 \) and \( t_2 \) and \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) were calculated from (4.14) and (4.15). The dependence of \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) on \( I_1 \) and \( I_2 \) is shown graphically in Figure 4. The results are tabulated in Table 1.

The results obtained under conditions of equi-biaxial strain \( (\lambda_1 = \lambda_2 = \lambda) \) are given in Table 2. The function

\[
\frac{\partial W}{\partial I_1} + \lambda^2 \frac{\partial W}{\partial I_2}
\]

was calculated from (4.16).

The same state of strain could have been obtained by a pure compressive stress \( t_3 \). Then \( t_1 = t_2 = 0 \) and from (4.12), \( t_3 \) is given by

\[
t_3 = 2 \left( \lambda^2 - \frac{1}{\lambda^2} \right) \left( \frac{\partial W}{\partial I_1} + \frac{1}{\lambda^2} \frac{\partial W}{\partial I_2} \right) \tag{6.1}
\]

where \( \lambda' = \lambda^{-2} \). It is interesting to compare these results with simple extension measurements on the same rubber. For an extension \( \lambda' \) in the \( x_3 \) direction \( \lambda_3 = \lambda' \) and \( \lambda_1 = \lambda_2 = (\lambda')^{-\frac{1}{2}} \) and therefore from (4.12) since \( t_1 = t_2 = 0 \),

\[
t_3 = 2 \left( \lambda' - \frac{1}{\lambda'} \right) \left( \frac{\partial W}{\partial I_1} + \frac{1}{\lambda^2} \frac{\partial W}{\partial I_2} \right) \tag{6.2}
\]

The simple extension results are given in Table 3. The values of the function \( \frac{\partial W}{\partial I_1} + \frac{1}{\lambda^2} \frac{\partial W}{\partial I_2} \) have been plotted against \( \frac{1}{\lambda^2} \) for the equibiaxial and simple extension experiments. (Figure 5).

6.2 Natural rubber at 25°C, and butyl rubber at 0°C

The principal stresses needed to maintain a number of constant deformations \( (\lambda_1 = \lambda_2) \) decreased over a period of time to equilibrium values (Figures 6 to 8). The parameters \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) were calculated from corresponding values of \( t_1 \) and \( t_2 \) using (4.15) and their variation with time is shown in Figures 9 to 12 and tables 4 and 5.

7. Analysis and discussion of the results

7.1 Butyl rubber at 25°C

There was no relaxation of the forces acting on the butyl rubber at 25°C. The strain dependence of \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) has been represented in Figure 4.
by straight line relationships. The positions of the continuous straight 
lines describing $\frac{\partial W}{\partial I_1}$ as a function of $I_1$ and $I_2$, and $\frac{\partial W}{\partial I_2}$ as a function of $I_2$ were determined by the least squares method.

The small positive gradient (0.00097) of the continuous line between $\frac{\partial W}{\partial I_1}$ and $I_1$ cannot have any significance because of the larger scatter of the experimental points, but $\frac{\partial W}{\partial I_1}$ appears to be an increasing function of $I_2$, for $3 < I_2 < 30$, such that

$$\frac{\partial W}{\partial I_1} = 1.45 + 0.00917 I_2$$

(7.1)

This is at variance with the observations upon sulphur cured natural rubber of Rivlin and Saunders (1951) who found $\frac{\partial W}{\partial I_1}$ to be independent of $I_1$ and $I_2$. If $\frac{\partial W}{\partial I_1}$ is independent of $I_1$ then the top diagram in Figure 4 should be represented by the series of horizontal lines shown. The height of each short line above the $I_1$ axis is the value of $\frac{\partial W}{\partial I_1}$ taken from the linear relationship between $\frac{\partial W}{\partial I_1}$ and $I_2$. The experimental points are reasonably compatible with this hypothesis with the exception of the points obtained when $I_2 = 20$.

$\frac{\partial W}{\partial I_2}$ is a decreasing function of $I_2$ such that

$$\frac{\partial W}{\partial I_2} = 0.138 - 0.00348 I_2$$

(7.2)

At any constant value of $I_2$ there is no trend in the variation of $\frac{\partial W}{\partial I_2}$ with $I_1$. The magnitude of $\frac{\partial W}{\partial I_2}$ represented by the short horizontal lines has been abstracted from the observed dependence of $\frac{\partial W}{\partial I_2}$ on $I_2$, and represents the experimental results reasonably well.

The equivalence, to within a hydrostatic stress, of the equi-biaxial deformation and a uniaxial (compression) deformation, has been discussed in section (6.1). The values of $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda' \frac{\partial W}{\partial I_2}}$ have been calculated from (6.1) and quoted in Table 2 for the range $1 < 1/\lambda' < 4$. The same function has been obtained from simple extension measurements on the same rubber, (6.2 and Table 3), over the range $0.2 < 1/\lambda' < 0.9$. The variation of $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda' \frac{\partial W}{\partial I_2}}$ over the range $0.2 < 1/\lambda' < 4$ is shown in Figure 5.
Simple extension measurements, before finite chain extensibility and crystallisation effects are significant, (at about $1/\lambda' = 0.4$ in Figure 5) are usually interpreted assuming that $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ are material constants. However, $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ is clearly not a single linear function of $\frac{1}{\lambda'}$ over the range $0.4 < \frac{1}{\lambda'} < 4$.

The experimental points in Figure 5 suggest a continuity of the function over the complete range of $1/\lambda'$ which can only be explained in terms of a strain dependence of $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$.

Corresponding values of $1/\lambda'$ and $I_2$, from Tables 5 and 6 have been substituted into 7.1 and 7.2 to find $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$. The predicted values of this function are given in Table 6 and compared with the experimental values in Figure 5. The butyl rubber used in the general biaxial deformation experiments was nominally the same as that used for the equibiaxial and simple extension measurements. It is however probable that the vertical shift between the experimental and predicted values of $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ is due to batch variation in the rubber. If the two sets of values are normalised at $1/\lambda' = 1$, then the rate of change of $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ with $I_2$ fits the observed dependence of $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ on $1/\lambda'$ for equibiaxial strains, but is completely inadequate to describe simple extension.

Equibiaxial experiments have been performed by Rivlin and Saunders (1951) who measured the deformation at the pole of a sulphur cured natural rubber sheet inflated by a known air pressure. They found that $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ decreases from about 1.9 kg.cm$^{-2}$ at $1/\lambda' = 1.5$ to a minimum of about 1.7 kg.cm$^{-2}$ at $1/\lambda' = 7$, and then increased to 1.85 kg.cm$^{-2}$ at $1/\lambda' = 12$, the maximum deformation observed. For continuity in their results in the transition from 'compression' to simple extension there must be a second turning point, a maximum, in the function of $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ in the region of $1/\lambda' = 1$.

It is however probably a coincidence that the experimental point at $1/\lambda' = 0.849$ lies below the linear portion of the simple extension curve, and therefore shows perfect continuity with the equibiaxial strain results.

It can be seen from 6.2 that significant errors in $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ are possible as $1/\lambda'$ approaches unity.
7.2 The stress relaxation of natural rubber at 25°C, and butyl rubber at 0°C

The principal stresses \( t_1 \) and \( t_2 \) which are necessary to maintain the deformation in the butyl rubber at 0°C, decrease to equilibrium values about 100 minutes after the application of the strain (Table 4 and Figure 8). However a number of the principal stresses applied to the natural rubber are still decreasing after 250 minutes. (Table 5, Figures 6 and 7). Corresponding values of \( t_1 \) and \( t_2 \) have been substituted into 4.15 to give the parameters \( \frac{\partial W}{\partial I_1} \) and \( \frac{\partial W}{\partial I_2} \) as a function of time. (Tables 4 and 5, Figures 9 to 12). For the butyl rubber these parameters must, of course, reach equilibrium values in 100 minutes. Indeed, within the scatter of the points in Figure 11, \( \frac{\partial W}{\partial I_2} \) may be invariant with time. It is interesting to observe that \( \frac{\partial W}{\partial I_2} \) also appear to become constant for the natural rubber after about 100 minutes although \( \frac{\partial W}{\partial I_2} \) for most deformations is continuously decreasing.

A number of workers have attempted to explain the large strain viscoelastic behaviour of elastomers in terms of an elastic liquid theory. We shall consider A.3, the constitutive equation of state for a viscoelastic incompressible liquid postulated by Kaye (1962)* and in another form by Bernstein, Kearsley, and Zapas (1963). Kaye defines the deformation in terms of the relative positions of a particle at the current time \( t \) and some past time \( t^1 \), and replaces the constants \( A_{pqr} \) in 2.4, the series expansion of the stored energy function, by functions of the elapsed time \( t - t^1 \).

If an instantaneous deformation characterised by extension ratios \( \lambda_i \) in the directions \( x_i \) is applied to the sample at time \( t = 0 \), and maintained constant, then according to Kaye (1963), the principal stresses \( t_1 \) and \( t_2 \) at time \( t > 0 \), are given by:

\[
t_1 - t_3 = 2(\lambda_1^2 - \lambda_3^2) \int_{-\infty}^{0} \frac{\partial W}{\partial J_1} dt' - 2(\lambda_1^2 - \lambda_3^2) \int_{-\infty}^{0} \frac{\partial W}{\partial J_2} dt'
\]

* Kaye's equation of state is an extension of the equation of state for a viscoelastic liquid developed by Lodge (1956). It is a logical generalisation of the stress-strain relationships derived by Rivlin (1948, 1949) to describe large elastic deformations in incompressible materials, and is discussed further in Appendix 2. It is also shown in Appendix 2 that Lodge's equation fulfills the necessary condition that for small strains it describes a linear viscoelastic material.
where \( j \) is 1 or 2, and \( \Omega \) is the equivalent to 2.4, the elastic stored energy function, but describes an incompressible viscoelastic liquid.

Then \( \Omega = \sum_{p,q=0}^{\infty} B_{pq} (J_1-3)^p(J_2-3)^q \) with \( B_{00} = 0 \) \hspace{1cm} (7.4)

where \( J_1 \) and \( J_2 \) are the first and second invariants of the deformation tensor \( S_{ij} = \varepsilon_{ij} \sum_{\alpha} \frac{\partial \alpha}{\partial x^i} \frac{\partial \alpha}{\partial x^j} \), (see Appendix 2(i))

using the usual dummy suffix summation, so that

\[ J_1 = S_{\alpha\alpha} \] \hspace{1cm} (7.5)

and \[ J_2 = \frac{1}{2}(S_{\alpha\alpha}^2 - S_{\alpha\beta}S_{\beta\alpha}) \]

The parameters \( B_{pq} \) are functions of \( t - t' \) which tend to zero as \( t - t' \) tends to infinity. By comparing (7.3) with (4.13), the equivalent equations for an elastic solid it can be seen that

\[ \frac{\partial W}{\partial t_1} = \int_{t-t'}^{\infty} \frac{\partial \Omega}{\partial J_1} d(t-t') \] \hspace{1cm} (7.6)

and \[ \frac{\partial W}{\partial t_2} = \int_{t-t'}^{\infty} \frac{\partial \Omega}{\partial J_2} d(t-t') \]

If (7.4) is to represent a viscoelastic solid then at least one of the parameters \( B_{pq} \) must be finite as \( t \) approaches infinity. It is reasonable to consider \( \Omega \) such that

\[ \Omega = B_{10}(J_1-3) + B_{01}(J_2-3) \] \hspace{1cm} (7.7)

where \( B_{10} \) and \( B_{01} \) are decreasing functions of \( t - t' \), but are finite as \( t - t' \) approaches infinity. For example, assume:

\[ B_{10} = A e^{\alpha t'} + B e^{-k_1(t-t')} \] \hspace{1cm} (7.8)

and \[ B_{01} = C e^{\beta t'} + D e^{-k_2(t-t')} \]

If the major surfaces of the sheet rubber sample are force free, then (7.3) becomes

\[ t_j = 2(\lambda_j^2 - \lambda_3^2)\left( \frac{\alpha}{\lambda_j} + \frac{B}{k_1} e^{-k_1 t} \right) - 2(\lambda_j^{-2} - \lambda_3^{-2})\left( \frac{C}{\beta} + \frac{D}{k_2} e^{-k_2 t} \right) \] \hspace{1cm} (7.9)
The time dependence of $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ for this particular form of $\Omega$ is found by substituting (7.9) into (4.15), or by comparing (7.9) with (4.12)

then $\frac{\partial W}{\partial I_1} = \frac{A}{\alpha} + \frac{B}{k_1} e^{-k_1 t}$

and $\frac{\partial W}{\partial I_2} = \frac{C}{\beta} + \frac{D}{k_2} e^{-k_2 t}$

Consider the applicability of (7.9) and (7.10) to the results obtained on the butyl rubber at 0°C. Assuming that $\frac{\partial W}{\partial I_2}$ is invariant with time then, from (7.10), $D/K_2$ must be zero, and (7.9) becomes

$$Y_j = t_j - 2(\lambda_1^2 - \lambda_2^2)A + 2(\lambda_1^2 - \lambda_2^2)C = 2(\lambda_1^2 - \lambda_2^2)B e^{-k_1 t}$$

$C/\beta$ has been determined from Table 4 as the mean value of $\frac{\partial W}{\partial I_2}$ for each deformation. For each $C/\beta$ two values of $A/\alpha$ have been found from (7.11) by considering the equilibrium values of $t_1$ and $t_2$ (Table 7). The two values for each deformation are essentially the same, as indeed they must be if the experimental results are correct. This further suggests that the small amount of inhomogeneity in each sample does not affect the stress measurement. Each deformation was carried out using a different test piece. Although each test piece was cut from sheets made under identical conditions from the same uncured rubber mixture it is probable that variations in $A/\alpha$ and $C/\beta$ are due to sample variations. There is no correlation of $A/\alpha$ or $C/\beta$ with $I_1$ or $I_2$.

$Y_j$ has been plotted on a logarithmic scale as a function of the relaxation time in Figure 13. For some of the deformations there are deviations from the linear relationships suggested by (7.11), at times greater than about 50 minutes. The logarithmic scale magnifies the effect of any errors in small values of $Y_j$, but the consistency in the direction of curvature suggest that, if (7.6) is valid, some of the chosen equilibrium stress levels were too high.

The relaxation constant $K_1$ has been taken as the gradient of the best straight line through the experimental points at time less than 50 minutes. $B/K_1$ has been determined from the intercept of these straight lines with the $t = 0$ axis (Table 7).
Table 7 The material parameters of (8.24). The first and second values of \( A/\alpha \), \( K_1 \), and \( B/K_1 \), for each deformation correspond to \( Y_1 \) and \( Y_2 \) respectively.

The material parameters all vary in an apparently random manner with deformation. The variation of \( C/\beta \) and \( A/\alpha \) corresponds to the scatter of experimental points in Figure 4 in which 

\[
\frac{\partial W}{\partial I_1} \text{ and } \frac{\partial W}{\partial I_2}
\]

are shown as a function of the strain invariants for butyl rubber under equilibrium conditions. If these variations can be ascribed completely to sample variations, then (7.11) represents the stress relaxation behaviour of butyl rubber at 0°C, at least up to relaxation times of 50 minutes.

There can be no advantage in repeating this analysis for the natural rubber at 25°C. Similar sample variations can be expected, and the analysis is complicated by the existence of two exponential functions, because \( d/K_2 \) is not zero for this rubber.

Berstein, Kearsley and Zapas (1963), and Zapas and Craft (1965) have found that \( A.3 \) describes the stress relaxation behaviour of a number of elastomers in simple extension when \( \Omega \) contains three strain dependent terms such that

\[
\Omega = P(J_1-3) + Q(J_2-5) + R(J_1-3)^2
\]  

(7.12)
where P, Q, and R are interdependent functions of the elapsed time \((t-t')\) (Appendix 2 ii).

Zapas (1966) has reproduced (7.3), the equation of state derived by Kaye (1963) to describe stress relaxation for a homogeneous biaxial deformation.

Using a rather complicated potential function containing three material parameters he is then able to describe the pure shear data of Rivlin and Saunders (1951) on natural rubber, and a long term stress-strain isochrone for butyl rubber in biaxial extension at an unstated temperature. He also examined the biaxial creep behaviour of butyl rubber at small initial deformations \((I_1 \approx I_2 \approx 1.1)\) over a time period up to 164 hours, and found \(\frac{\partial W}{\partial I_2}\) to increase continuously from a negative value of about \(-100 \text{ g.cm}^{-2}\) at 3 hours to about \(+200 \text{ g.cm}^{-2}\). Negative value of \(\frac{\partial W}{\partial I_2}\) at small strains have also been reported by Miguel and Landel (1966) from the biaxial extension data of a castor oil extended polyurethane elastomer, for the strain invariant range \(3 < I_1, I_2 < 5.1\).

It is obviously possible to define P, Q, and R, or the material parameters of Zapas, as particular functions of the elapsed time, in a further attempt to describe the observed stress relaxation behaviour of the natural and butyl rubbers. However there was no observed correlation between the material constants in (7.9) and the strain, which suggests that the 'Mooney type' potential function is adequate to describe the limited number of deformations studied. A modification of (7.9) would probably be necessary to describe the range of deformations covered by the biaxial extensions on the butyl rubber at \(25^\circ\text{C}\).

8. Summary

The principal observations which have been made about the behaviour of rubber in a state of pure homogeneous finite strain can be summarised.

1. Homogeneous biaxial strains have been imposed upon a butyl rubber in order to examine the variation of \(\frac{\partial W}{\partial I_1}\) and \(\frac{\partial W}{\partial I_2}\) with strain under equilibrium conditions. \(\frac{\partial W}{\partial I_2}\) exhibits the strain dependence reported by Rivlin and Saunders for natural rubber, but \(\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}\) is a continuously increasing function of \(\frac{1}{\lambda'}\) over the range \(0.4 < \frac{1}{\lambda'} < 4\). \(\lambda'\) is the uniaxial extension (or 'compression') ratio.

2. The stress system needed to maintain butyl rubber (at \(0^\circ\text{C}\)) in a state of biaxial strain, reduces to an equilibrium value in about 100 minutes, but \(\frac{\partial W}{\partial I_2}\) appears to be constant over the complete time range. Within the limitations imposed by sample to sample variations the results can be
described by a viscoelastic 'Mooney type' stored energy function. Equilibrium values of \( \frac{\partial W}{\partial I_2} \) are also observed for a highly crosslinked natural rubber which exhibits continuous stress relaxation over the time period of the measurements.

3. It has been shown theoretically that the heat build up during an adiabatic deformation gives rise to a term in the stress-strain relationship which corresponds to \( C_2 \). However the calculated magnitude of \( C_2 \) is too small.

It is extremely difficult to decide upon a practical criterion for the equilibrium state of a deformed rubber. However the results described in this Note suggest that \( \frac{\partial W}{\partial I_2} \) is a finite positive constant when all observable stress relaxation has ceased. Furthermore a constant value of \( \frac{\partial W}{\partial I_2} \) has been observed under stress-strain conditions which are obviously not at equilibrium. There is therefore strong evidence that \( \frac{\partial W}{\partial I_2} \) is finite under equilibrium conditions and the kinetic theory is not adequate to describe the gum rubber in biaxial extension. The kinetic theory is therefore inadequate to describe completely the elastic mechanical behaviour of unfilled rubber.

References

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50. Van der Hoff. Polymer. 1965, 6 (7), 397.

Acknowledgements

The author is indebted to Professor D.W. Saunders for his continual interest and encouragement, and to Mr. J.M. Stuart who prepared most of the samples.
Appendix 1. Sample preparation

The samples were prepared under controlled conditions. The detailed recipes are given in Table 8, in which the numbers denote parts by weight.

<table>
<thead>
<tr>
<th>Component</th>
<th>Natural rubber samples</th>
<th>Butyl rubber samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Butyl rubber (Esso</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>grade 218)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Accelerator</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Dicumyl peroxide</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

The biaxial and tensile samples were cut from sheets 25 cms. square and about 0.25 cms. thick, which had been moulded and cured for fifteen minutes at 150°C. Each moulded sheet contained four 5 cm. square indentations which were used for biaxial measurements. This allowed the lugs on the biaxial samples to be cut from the thicker sheet.

The flow of excess rubber through the escape holes in a mould will always result in an article which is mechanically anisotropic and inhomogenous. The anisotropy in the samples was reduced to a minimum by using moulds with a large number of symmetrically disposed flow holes, and by using the minimum amount of rubber necessary to fill a mould.

A (secant) modulus variation of about 5% was found for microtensile samples cut in different orientations and positions from the plane of a 25 cm. square sheet.

Further work showed that swelling measurements are a comparatively insensitive method of estimating the degree of anisotropy and inhomogeneity. Tensile samples which had shown a 1.5% modulus variation, (cut from a rejected sheet), were immersed in benzene, and the equilibrium lengths of the swollen samples measured. The increase in length for all the tensile samples varied by only 0.6%. The expected inverse relationship between the order of stiffness, and the order of degree of swelling, was observed. The degree of anisotropy, measured as a modulus variation, was not reduced after swelling and deswelling the samples. There was no correlation between modulus variations and accurate density measurements.
Appendix 2

Equations of state for viscoelastic materials

(i) The equations of Lodge and Kaye

Lodge (1956) has extended the kinetic theory of rubberlike elasticity by assuming that the crosslinks in the network have a finite lifetime, and derives an equation of state:

\[ P_{ij} - \delta_{ij} = \int_{-\infty}^{t} kT N(t-t') \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} \, dt' \]  \hspace{1cm} (A.1)

which describes an incompressible viscoelastic liquid. \( P_{ij} \) is the stress tensor and \( x_i \) and \( x'_i \) are the rectangular cartesian coordinates of a particle at the current time \( t \), and a past time \( t' \) respectively. The repeated suffix denotes summation. \( N(t-t') \) is the distribution function for the lifetimes of the effective network crosslinks. \( p \) is an arbitrary isotropic pressure, and \( \delta_{ij} \) is the unit matrix.

The stress-strain relationships derived by Rivlin (1948, 1949) to describe large elastic deformations in incompressible materials, can be written.

\[ \frac{\partial W}{\partial I_1} \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} = 2 \left( \frac{\partial W}{\partial I_2} \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} - \frac{\partial W}{\partial I_1} \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} \right) \]  \hspace{1cm} (A.2)

where \( x_i \) and \( X_i \) are the rectangular cartesian coordinates of a particle in the deformed and undeformed states respectively.

Kaye (1962) points out that (A.1) can be considered a mathematical generalisation of (A.2) if the elastic material obeys the kinetic theory, that is if \( \frac{\partial W}{\partial I_2} = 0 \). He then examined a class of viscoelastic liquids for which

\[ P_{ij} - \delta_{ij} = 2 \int_{-\infty}^{t} \left[ \frac{\partial \Omega}{\partial J_1} \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} - \frac{\partial \Omega}{\partial J_2} \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} \right] \]  \hspace{1cm} (A.3)

where \( \Omega = \Omega[J_1(t,t'), J_2(t,t')] \) and \( J_1 \) and \( J_2 \) are invariants of the deformation tensor \( S_{ij} = \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\alpha} \), using the usual summation convention, and are given by (7.5).

Zapas (1966) reports that an equation of state developed by Bernstein, Kearsley and Zapas (1963, 1964) for an incompressible viscoelastic liquid can be manipulated into a form which is equivalent to (A.3).
If (A.1) and therefore (A.2) are to be useful for describing non-linear viscoelastic behaviour, then in the limiting case of infinitesimal strain (A.1) must reduce to a description of linear viscoelasticity.

The equation of state for a linear viscoelastic incompressible material can be written, (Lockett 1965),

\[
P_{ij} - \rho \delta_{ij} = \int_{-\infty}^{t} \phi(t-t') \rho_y \, dt'
\]

where \( \phi(t-t') \) is a function of the elapsed time \( t-t' \), \( \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \), the strain tensor for infinitesimal displacements \( u_i \), and \( \rho_{ij} \) represents the differentiation of \( \rho_{ij} \) with respect to the elapsed time.

Now \( x_i = X_i + u_i \), and \( x_i' = X_i + u_i' \), and therefore \( x_i - x_i' = u_i - u_i' \) or

\[
\frac{dx_i}{d\tau} = \frac{du_i}{d(t-t')} \, d(t-t') = \dot{u}_i \, d\tau
\]

where \( \tau = t-t' \).

Hence \( x_i = x'_i + u_i \, d\tau \) (A.6)

We wish to examine the strain function of (A.1), \( S_{ij} = \frac{\partial x_i}{\partial x^\alpha} \frac{\partial x_j}{\partial x^\beta} \).

If (A.6) is differentiated with respect to \( x^\alpha \), then

\[
\frac{\partial x_i}{\partial x^\alpha} = \delta_{ij} \frac{\partial \dot{u}_i}{\partial \tau} \quad \text{(A.7)}
\]

and therefore for infinitesimal strains \( S_{ij} \) is given by

\[
S_{ij} = \left( \delta_{ij} + \frac{\partial \dot{u}_i}{\partial x^\alpha} \, d\tau \right) \left( \delta_{ij} + \frac{\partial \dot{t}_j}{\partial x^\alpha} \, d\tau \right)
\]

If the second order term involving \( \frac{\partial u_i}{\partial x_j} \) are discarded then

\[
S_{ij} = \delta_{ij} + \frac{\partial \dot{u}_i}{\partial x^\alpha} \, d\tau + \frac{\partial \dot{t}_j}{\partial x^\alpha} \, d\tau
\]

or

\[
S_{ij} = \delta_{ij} + 2 \dot{\varepsilon}_{ij} \, d\tau
\]

\( \dot{\varepsilon}_{ij} \)
If \( T \) has a range of values from 0 to \( \infty \), then substitution of (A.10) into (A.1) gives

\[
P_{ij} - p' \delta_{ij} = \int_{-\infty}^{t} 2kT.N(t-t')e_{ij}dT'
\]  

when \( p' = p + kT.N(t-t') \). This is of the form of (A.4), the equation of state of a linear viscoelastic material.

(ii) The potential function of Bernstein, Kearsley and Zapas

In attempting to describe the stress relaxation of certain elastomers in simple extension, Bernstein et. al. (1965) have used an equation of state equivalent to (A.3) in which \( \Omega \) is given by

\[
\Omega = mK_1 + \frac{a}{2} K_1^2 + bK_2 \tag{A.12}
\]

where \( m \), \( a \), and \( b \) are functions of \( t-t' \), and \( K_1 \) and \( K_2 \) are invariants of the strain tensor \( E_{kl} \), such that

\[
K_1 = \text{tr}E_{kl} \tag{A.13}
\]

\[
K_2 = \text{tr}(E^2)_{kl} \tag{A.14}
\]

and

\[
E_{kl} = \frac{1}{2} \left[ \delta_{ij} \frac{\partial x^i_k}{\partial x^j_l} + \frac{\partial x^i_k}{\partial x^j_l} - \delta_{kl} \right] \tag{A.15}
\]

Now consider the deformation

\[
x_1 = \lambda_1 x_1^1
\]

\[
x_2 = \lambda_2 x_2^1
\]

\[
x_3 = \lambda_3 x_3^1
\]

Then from (A.13), (A.14) and (A.15)

\[
K_1 = \frac{1}{2}[\lambda_1^2 + \lambda_2^2 + \lambda_3^2] = \frac{1}{2}[J_1 - 3] \tag{A.16}
\]

and

\[
K_2 = \frac{1}{4}[(\lambda_1^2-1)^2 + (\lambda_2^2-1)^2 + (\lambda_3^2-1)^2] = \frac{1}{4}[J_1 - 2J_2 - 2J_1 + 3]
\]

since

\[
J_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad \text{and} \quad J_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}
\]
Hence (A.12) may be rewritten

\[ \Omega = \frac{m}{2}(J_1 - 3) + \frac{a}{3}(J_1 - 3)^2 + \frac{b}{4}(J_1^2 - 2J_2 - 2J_1^2) \]  
\[ = P(J_1 - 3) + Q(J_2 - 3) + R(J_1 - 3)^2 \]

where \( P = \frac{m}{2} + b, Q = -\frac{b}{2}, \) and \( R = \frac{a}{8} + \frac{b}{4}. \) Therefore the viscoelastic potential function of Bernstein et. al. is an extension of the 'Mooney type' viscoelastic function (7.7).

Appendix 3

The evolution of heat in simple extension

The virtual work done in producing incremental deformations \( \delta \lambda_1, \delta \lambda_2, \) and \( \delta \lambda_3 \) in an isotropic material which is in a state of pure homogeneous strain defined by the principal extension ratios \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) is given by

\[ \delta W = t_1 \lambda_2 \lambda_3 \delta \lambda_1 + t_2 \lambda_1 \lambda_3 \delta \lambda_2 + t_3 \lambda_1 \lambda_2 \delta \lambda_3 \]  
(A.19)

where \( t_1, t_2, \) and \( t_3 \) are the principal stresses.

If the deformation is isoenergetic and adiabatic

\[ \delta W = J \delta Q = J \rho \lambda_1 \lambda_2 \lambda_3 c \delta T \]  
(A.20)

where \( \delta Q \) is the heat evolved

\( \rho \) density of material of specific heat \( c. \)

\( \delta T \) increase in temperature

\( J \) mechanical equivalent of heat

\[ \therefore J \rho c \delta T = t_1 \frac{\delta \lambda_1}{\lambda_1} + t_2 \frac{\delta \lambda_2}{\lambda_2} + t_3 \frac{\delta \lambda_3}{\lambda_3} \]  
(A.21)

For simple extension \( t_2 = t_3 = 0, \) and from (4.12)

\[ t_1 = 2(\lambda_1^2 - \frac{1}{\lambda_1}) \frac{\partial W}{\partial I_1} + \frac{1}{\lambda_1} \frac{\partial W}{\partial I_2} \]  
(A.22)

and therefore the increase in temperature \( \delta T \) for a finite increase \( \Delta \lambda_1 \) in \( \lambda_1 \) is given by (dropping the suffix for convenience).
In order to estimate the magnitude of $\delta T$ it is sufficient to assume the kinetic theory of elasticity. Then $\frac{\partial W}{\partial I_1} = C_1$ and $\frac{\partial W}{\partial I_2} = 0$, and

$$J_{pc}\delta T = C_1[2\lambda\Delta\lambda + \Delta\lambda^2 + 2(\lambda+\Delta\lambda)^{-1}-2\lambda^{-1}]$$  \hspace{1cm} (A.24)

Adiabatic stress-strain relationships must take the temperature increase into account.

The tensile stress $t$ is a function of $T$ and $\lambda$ and therefore an increment in stress $\delta t$ is given by

$$\delta t = \frac{\partial t}{\partial T} \delta T + \frac{\partial t}{\partial \lambda} \delta \lambda$$  \hspace{1cm} (A.25)

If $t$ is given by the kinetic theory (isothermal) relationship

$$t = NkT(\lambda^2 - \frac{1}{\lambda})$$  \hspace{1cm} (A.26)

and since from (A.21) \( \frac{\partial t}{\partial \lambda} = J_{pc} \delta T \) \hspace{1cm} (A.27)

then by substituting (A.26) and (A.27) into (A.25) the adiabatic stress $t_a$ is given by

$$t_a = \int_0^1 t_a \, \text{d}T = \int_0^1 \frac{N^2k^2T}{J_{pc}\lambda}(\lambda^2 - \frac{1}{\lambda}) \, \text{d}\lambda + t$$  \hspace{1cm} (A.28)

$$= (\lambda^2 - \frac{1}{\lambda})\left[ NkT + \frac{N^2k^2T}{J_{pc}} \frac{(\lambda^5/4 - 2\lambda^3 + 2\lambda^2/4 - 1/2\lambda)}{(\lambda^3-1)} \right]$$  \hspace{1cm} (A.29)

If the temperature increase give rise to a Mooney parameter $C_2$ then (A.29) must be compared with

$$t_a = 2(\lambda^2 - \frac{1}{\lambda})(C_1 + C_2)$$  \hspace{1cm} (A.30)

where $C_1 = \frac{1}{2}NkT$

Then

$$\frac{C_2}{C_1} = \frac{Nk}{J_{pc}} \frac{(\lambda^6/4 - 2\lambda^3 + 2\lambda^2/4 - 1/2\lambda)}{(\lambda^3-1)}$$  \hspace{1cm} (A.31)
Typically $N_k = 3.10^4$ dynes.cm$^{-2}$ deg.$^{-1}$C

$\rho = 0.95$ cm.$^{-3}$

$c = 0.47$ cal. g$^{-1}$ deg.$^{-1}$C

Then if $\lambda = 4$

$$\frac{C_2}{C_1} \approx \frac{1}{50} \quad (A.32)$$

This is considerably less than the value of $C_2$ which would be expected if experimental simple extension data for this hypothetical sample was analysed in terms of the Mooney form of the stored energy function. For example Rivlin and Saunders (1951) found from simple extension data that $C_2 \approx 0.81 C_1$. 
<table>
<thead>
<tr>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
<th>$t_1$ (g.cm$^{-2}$)</th>
<th>$t_2$ (g.cm$^{-2}$)</th>
<th>$\frac{\partial W}{\partial I_1}$ (g.cm$^{-2}$)</th>
<th>$\frac{\partial W}{\partial I_2}$ (g.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
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<td>5</td>
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<td>0.95</td>
<td>11,950</td>
<td>2,560</td>
<td>1465</td>
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</tbody>
</table>

Table 1. Biaxial strain results for butyl rubber at 25°C
Table 1. (Continued) Biaxial strain results for butyl rubber at 25°C
\[
\begin{array}{cccccc}
\lambda_1 = \lambda_2 = \lambda & \frac{1}{\lambda} (= \lambda') & t_1 = t_2 & \frac{\partial \mu}{\partial I_1} \frac{1}{\lambda} & \frac{\partial \mu}{\partial I_2} & I_1 \quad \text{cm}^2 \\
& & & (2/\lambda' + \lambda'^2) & (2\lambda' + 1/\lambda'^2) \\
1.083 & 1.17 & 337\pm36 & 1840 & 3.07 & 3.08 \\
1.167 & 1.36 & 608\pm8 & 1920 & 3.26 & 3.32 \\
1.25 & 1.56 & 788\pm17 & 1900 & 3.53 & 3.71 \\
1.33 & 1.77 & 921\pm4 & 1870 & 3.86 & 4.26 \\
1.417 & 2.01 & 1086\pm7 & 1945 & 4.52 & 5.05 \\
1.50 & 2.25 & 1223\pm20 & 1990 & 4.74 & 5.97 \\
1.58 & 2.49 & 1342\pm57 & 2020 & 5.14 & 7.00 \\
1.67 & 2.79 & 1411\pm60 & 1972 & 5.71 & 8.52 \\
1.75 & 3.06 & 1497\pm62 & 1972 & 6.23 & 10.01 \\
1.833 & 3.36 & 1625\pm45 & 2028 & 6.90 & 11.90 \\
1.916 & 3.67 & 1734\pm74 & 2050 & 7.42 & 14.04 \\
2.00 & 4.00 & 1836\pm88 & 2065 & 8.06 & 16.50 \\
\end{array}
\]

Table 2. Equibiaxial strain results for butyl rubber at 25°C. The values of \(t\) are the mean values of \(t_1\) and \(t_2\).
<table>
<thead>
<tr>
<th>$t_3$ (g.cm(^{-2}))</th>
<th>$\lambda'$</th>
<th>$\frac{1}{\lambda'}$</th>
<th>$\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ (g.cm(^{-2}))</th>
<th>$I_1$ (2/(\lambda' + \lambda'^2))</th>
<th>$I_2$ (2(\lambda' + 1/\lambda'^2))</th>
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Table 3. Simple extension results for butyl rubber at 25°C.
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<th>$\frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$</th>
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<th>$I_2$</th>
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Table 2. Equibiaxial strain results for butyl rubber at 25°C. The values of $t$ are the mean values of $t_1$ and $t_2$. 
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<th>( \lambda' )</th>
<th>( \frac{1}{\lambda'} )</th>
<th>( \frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2} ) (g.cm(^{-2}))</th>
<th>( I_1 ) (2/(\lambda'+\lambda'^2))</th>
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**Table 3.** Simple extension results for butyl rubber at 25°C.
<table>
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<th>I₁ = 6.448</th>
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Table 4. Relaxation of the principal stresses τ₁ and τ₂ for various biaxial deformations of butyl rubber at 0°C. \( \frac{dW}{dτ₁} \) and \( \frac{dW}{dτ₂} \) were calculated from Eq. 15. All quoted values are in g cm⁻².
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Table 4 (continued)
### Table 5. Relaxation of the principal stress $t_1$ and $t_2$ for various biaxial deformation of natural rubber at $25^\circ\text{C}$. $\frac{\partial \tau}{\partial \sigma_1}$ and $\frac{\partial \tau}{\partial \sigma_2}$ were calculated from 3.15. All quoted values are in g.cm$^{-2}$.

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Table 6. $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'} \frac{\partial W}{\partial I_2}$ calculated from 7.1 and 7.2.
FIGURE 2. ONE SIDE OF THE BIAXIAL STRETCHING RIG
FIGURE 1. THE TEST PIECE

FIGURE 3. THE VARIATION OF $\lambda_1$ WITH $\lambda_2$ FOR VARIOUS CONSTANT VALUES OF $I_1$ and $I_2$
**Figure 4.** The variation of $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ with $I_1$ and $I_2$ for butyl rubber at 25°C.

**Figure 5.** The variation of $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda} \frac{\partial W}{\partial I_2}$ with $\frac{1}{\lambda^2}$ for butyl rubber at 25°C in simple extension and equibiaxial strain. Note the change in scale at $\lambda^2 = 1$. 

- Experimental points
- Calculated from 8-19 and 8-20
FIGURE 6. RELAXATION OF THE PRINCIPAL STRESSES $t_1$ and $t_2$ FOR NATURAL RUBBER AT 25°C.

FIGURE 7. RELAXATION OF THE PRINCIPAL STRESSES $t_1$ AND $t_2$ FOR NATURAL RUBBER AT 25°C.
FIGURE 8 RELAXATION OF THE PRINCIPAL STRESSES $t_1$ and $t_2$ FOR BUTYL RUBBER AT 0°C
Figure 9. $\frac{\partial W}{\partial t}$ as a function of the relaxation time, for natural rubber at 25°C.
Figure 10. $\frac{\Delta W}{\Delta t}$ as a function of the relaxation time, for natural rubber at 25°C.
FIGURE 11. \( \frac{\partial W}{\partial t} \) AS A FUNCTION OF THE RELAXATION TIME, FOR BUTYL RUBBER AT 0°C

FIGURE 12. \( \frac{\partial W}{\partial t} \) AS A FUNCTION OF THE RELAXATION TIME, FOR BUTYL RUBBER AT 0°C
FIGURE 13: AN EXAMINATION OF 7.11 FOR BUTYL RUBBER AT 0°C

KEY AS FOR FIGURE 42

$Y_1 (g/cm^2)$

$t$, TIME IN MINUTES