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STUDIES OF PURE HOMOGENEOUS DEFORMATIONS IN UNFILLED NATURAL AND BUTYL RUBBERS

by

M. M. HALL

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Studies of pure homogeneous deformations in unfilled natural and butyl rubbers

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M.M. Hall, B.Sc., Ph.D., A.Inst.P.

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 $3 < I_2 \leqslant 30$. 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_{pqr}	elastic material parameters
I_1, I_2, I_3	strain invariants, defined by equations 2.2 and 2.3
λ_1, λ_2, λ_3	principal extension ratios
λ, α, λ'	extension ratios
Ω	a function of J_1, J_2 and τ
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
$E_{k\ell}$	strain tensor defined by equation A.14
x_i	coordinates of a particle at the current time t
X_α	coordinates of a particle in the undeformed material
x'_α	coordinates of a particle at some past time t'
t	current time
t'	past time
τ	$t-t'$
$N(t-t')$	lifetime distribution function for crosslinks
P_{ij}	stress tensor
t_i	principal stresses
f	uniaxial tensile force per unit unstrained cross-sectional area
p, p'	isotropic pressures
δ_{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
$\overline{r_i^2}$	mean square network chain length in the unstrained rubber
$\overline{r_o^2}$	mean square end to end length of an isolated single molecule
N	number of molecular network chains per unit volume
k	Boltzmanns constant
T	absolute temperature
J	mechanical equivalent of heat
ρ	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.

i.e. $$W = C_1(I_1-3) \qquad (2.1)$$

where I_1 is the first strain invariant and is related to the principal extension ratios λ_1, λ_2, and λ_3, of a pure homogeneous deformation by

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \qquad (2.2)$$

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 λ_1, λ_2, and λ_3, then the energy per unit undeformed volume stored elastically in the material must be a function of λ_1, λ_2, and λ_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

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \qquad (2.3)$$

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.

$$W = \sum_{p,q,r=o}^{\infty} A_{pqr}(I_1-3)^p(I_2-3)^q(I_3-1)^r \qquad (2.4)$$

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_{pqr} 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

$$\text{i.e.} \qquad W = C_1(I_1-3) + C_2(I_2-3) \tag{2.5}$$

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

$$W = C_1(I_1-3) = \phi(I_2-3) \tag{3.1}$$

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 $NkT\left(\frac{\bar{r}_i^2}{\bar{r}_o^2}\right)$, 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 $\bar{r}_o^2$, and $\bar{r}_i^2$ 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 $\lambda_2 = \lambda_3 = \lambda^{-\frac{1}{2}}$. 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).

$$f = NkTv_r^{1/3}\left(\alpha - \frac{1}{\alpha^2}\right) \qquad (3.2)$$

where f is the tensile force per unit cross sectional area of the swollen unstrained rubber, v_r is the volume fraction of rubber in the swollen sample, and the extension ratio α refers to the unstrained swollen state.

Gee (1946) examined the function $f\, v_r^{-1/3}\left(\alpha - \frac{1}{\alpha^2}\right)^{-1}$ 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

$$\theta = \frac{f}{v_r^{1/3}\left(\alpha - \frac{1}{\alpha^2}\right)} = C_{1S} + C_{2S}/\lambda \qquad (3.3)$$

C_{2S} was determined from the gradient of the observed linear relationship between θ and $1/\lambda$ and found to be independent of the nature of the diluent, but decreased progressively with decreasing v_r. 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 dependance 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 $\frac{\partial W}{\partial I_1}$, and $\frac{\partial W}{\partial I_2}$ with I_1 and I_2 shown in Figure 4. Swelling would naturally reduce finite volume effects.

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

$$\theta = C_1 + \frac{C_2 v_r^{4/3}}{\lambda} \qquad (3.4)$$

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 smal, 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

$$E = \lambda \frac{d\sigma}{d\lambda} \qquad (3.5)$$

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

$$f = 2(\lambda - 1/\lambda^2)\ (C_1 + C_2/\lambda) \qquad (3.6)$$

then $$F_1E = C_1 + F_2C_2 \qquad (3.7)$$

where $F_1 = \frac{\lambda}{2(2\lambda^3+1)}$ and $F_2 = \frac{\lambda^3+2}{\lambda(2\lambda^3+1)}$ 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 (1958), 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°C, $C_2 = 0.438$ kg.cm ^{2}. The entropy component only of the retractive force was used in the Mooney equation for simple extension, (3.3 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 ca.2.0 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 Stiehler (1956) found that isochronous stress-strain curves obtained from creep measurements in simple extension were represented up to $\lambda = 2$ by the empirical equation

$$f = E\left(\frac{1}{\lambda} - \frac{1}{\lambda^2}\right) \exp A\left(\lambda - \frac{1}{\lambda^2}\right) \qquad (3.8)$$

where E is Youngs 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 homgeneous deformation.

$$t_i = A(\lambda_i-\lambda_3)[1+BI_1+2B(\lambda_i+\lambda_3)(\lambda_1+\lambda_2+\lambda+_3-3)] \quad (i=1,2) \tag{3.9}$$

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.

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

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

$$t_i - p = \frac{A}{2}\exp[B(\lambda_i-\frac{1}{\lambda_i})] - C(\lambda_i^2 + \frac{1}{\lambda_i^2} - 2) \quad (i = 1,2,3) \tag{3.11}$$

where A, B and C are interdependent material constants and p is an arbitary 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/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).

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

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 $\frac{\partial W}{\partial I_1}$ determined by Rivlin and Saunders. However, the Thomas function, at variance with (3.12) also predicted a small decrease in $\frac{\partial W}{\partial I_1}$ with increasing strain.

Priss (1957) has stated that

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

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.

$$\frac{\partial W}{\partial I_1} = G \exp.\left[k_1(I_1-3)^2\right], \frac{\partial W}{\partial I_2} = G\frac{k_2}{I_2} \qquad (3.14)$$

$\frac{\partial W}{\partial I_1}$ 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 parallelopiped by extension ratios λ_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 t_i.

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

$$\delta W_1 = t_1\lambda_2\lambda_3\delta\lambda_1 + t_2\lambda_1\lambda_3\delta\lambda_2 + t_3\lambda_1\lambda_2\delta\lambda_3 \qquad (4.1)$$

and since W, the elastically stored energy, is a function of λ_1, λ_2, and λ_3

$$\delta W = \frac{\partial W}{\partial \lambda_1}\delta\lambda_1 + \frac{\partial W}{\partial \lambda_2}\delta\lambda_2 + \frac{\partial W}{\partial \lambda_3}\delta\lambda_3 \qquad (4.2)$$

and for equilibrium under isothermal conditions

$$\delta W_1 - \delta W = 0 \qquad (4.3)$$

and hence

$$(t_1\lambda_2\lambda_3 - \frac{\partial W}{\partial\lambda_1})\delta\lambda_1 + (t_2\lambda_1\lambda_3 - \frac{\partial W}{\partial\lambda} + (t_3\lambda_1\lambda_2 - \frac{\partial W}{\partial\lambda_3})\delta\lambda_3 = 0 \quad (4.4)$$

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

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

Hence by substituting (4.5) into (4.7) the most general condition for incompressibility is

$$P[\lambda_2\lambda_3\delta\lambda_1 + \lambda_1\lambda_3\delta\lambda_2 + \lambda_1\lambda_2\delta\lambda_3 = 0 \quad (4.8)$$

where p is the arbitrary constant $\frac{\partial f(V)}{\partial V}$

Now (4.4) is valid for values of $\delta\lambda_i$ which satisfy (4.8). Comparing coefficients of $\delta\lambda_i$

$$t_i - p = \lambda_i\frac{W}{\partial\lambda_i} \quad (4.9)$$

where

$$\frac{\partial W}{\partial\lambda_i} = \frac{\partial W}{\partial I_1}\,\frac{\partial}{\partial\lambda_i} + \frac{\partial W}{\partial I_2}\,\frac{\partial I_2}{\partial\lambda_i} \quad (4.10)$$

now, from (2.2) and (2.3),

$$I_1 = \sum_{i=1}^{3}\lambda_i^2 \text{ and } I_2 = \sum_{i=1}^{3}\lambda_i^{-2} \text{ since}$$

$$\lambda_1\lambda_2\lambda_3 = 1 \quad (4.11)$$

and hence (4.9) becomes

$$t_i - p = 2\left(\lambda_i^2 \frac{\partial W}{\partial I_1} - \lambda_i^{-2} \frac{\partial W}{\partial I_2}\right) \qquad (4.12)$$

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

$$t_1 = 2\left(\lambda_1^2 - \frac{1}{\lambda_1^2\lambda_2^2}\right)\left(\frac{\partial W}{\partial I_1} + \lambda_2^2 \frac{\partial W}{\partial I_2}\right)$$

$$t_2 = 2\left(\lambda_2^2 - \frac{1}{\lambda_1^2\lambda_2^2}\right)\left(\frac{\partial W}{\partial I_1} + \lambda_1^2 \frac{\partial W}{\partial I_2}\right) \qquad (4.13)$$

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

$$t_1 = \frac{f_1\lambda_1}{h\ell} \qquad t_2 = \frac{f_2\lambda_2}{h\ell} \qquad (4.14)$$

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

$$\frac{\partial W}{\partial I_1} = \frac{\dfrac{\lambda_1^2 t_1}{\lambda_1^2 - \lambda_1^{-2}\lambda_2^{-2}} - \dfrac{\lambda_2^2 t_2}{\lambda_2^2 - \lambda_1^{-2}\lambda_2^{-2}}}{2(\lambda_1^2 - \lambda_2^2)}$$

and

$$\frac{\partial W}{\partial I_2} = \frac{\dfrac{t_1}{\lambda_1^2 - \lambda_1^{-2}\lambda_2^{-2}} - \dfrac{t_2}{\lambda_2^2 - \lambda_1^{-2}\lambda_2^{-2}}}{2(\lambda_2^2 - \lambda_1^2)} \qquad (4.15)$$

Therefore measurement of the forces f_1 and f_2, for a pure homogeneous deformation characterised by λ_1 and λ_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)

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

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 lugs 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 λ_1 and λ_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 phospher 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 o°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 λ_1 and λ_2 for constant values of I_1 and I_2 were derived by re-arranging (4.11) and are shown graphically in Figure 3. The broken lines represent the relationships between λ_1 and λ_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

$$t_3 = 2\left(\frac{1}{\lambda^4} - \lambda^2\right)\left(\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'}\frac{\partial W}{\partial I_2}\right) \tag{6.1}$$

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

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

The simple extension results are given in Table 3. The values of the function $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'}\frac{\partial W}{\partial I_2}$ have been plotted against $\frac{1}{\lambda'}$ 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

$$\frac{\partial W}{\partial I_1} = 1.45 + 0.00917\, I_2 \qquad (7.1)$$

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

$$\frac{\partial W}{\partial I_2} = 0.138 - 0.00348\, I_2 \qquad (7.2)$$

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 $1 < 1/\lambda' \leqslant 4$. 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 $0.4 < 1/\lambda' < 4$.

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 w and 3 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 $1/ \quad = 7$, 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 $1/\lambda' = 1$.

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*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 λ_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:-

$$t_j - t_3 = 2(\lambda_j^2 - \lambda_3^2)\int_{-\infty}^{0} \frac{\partial\Omega}{\partial J_1} dt' - 2(\lambda_j^{-2} - \lambda_3^{-2})\int_{-\infty}^{0} \frac{\partial\Omega}{\partial J_2}\, dt' \qquad 7.3$$

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[*] Kayes' 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 Lodges' equation fulfills the necessary condition that for small strains it describes a linear viscoelastic material.

where j is 1 or 2, and Ω is the equivalent to 2.4, the elastic stored energy function, but describes an incompressible viscoelastic liquid.

Then $$\Omega = \sum_{p,q=o}^{\infty} B_{pq}(J_1-3)^p(J_2-3)^q \text{ with } B_{oo} = 0 \qquad (7.4)$$

where J_1 and J_2 are the first and second invariants of the deformation tensor $S_{ij} = \frac{\partial x_i}{\partial x'_\alpha}\frac{\partial x_j}{\partial x'_\alpha}$, (see Appendix 2(i)) using the usual dummy suffix summation, so that

$$J_1 = S_{\alpha\alpha} \qquad (7.5)$$

and $$J_2 = \tfrac{1}{2}(S^2_{\alpha\alpha} - S_{\alpha\beta}S_{\beta\alpha})$$

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

$$\frac{\partial W}{\partial I_1} = \int_t^{\infty} \frac{\partial\Omega}{\partial J_1}\, d(t-t') \qquad (7.6)$$

and $$\frac{\partial W}{\partial I_2} = \int_t^{\infty} \frac{\partial\Omega}{\partial J_2}\, d(t-t')$$

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 Ω such that

$$\Omega = B_{10}(J_1-3) + B_{01}(J_2-3) \qquad (7.7)$$

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

$$B_{10} = Ae^{\alpha t'} + Be^{-k_1(t-t')} \qquad (7.8)$$

and $$B_{01} = Ce^{\beta t'} + De^{-k_2(t-t')}$$

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

$$t_j = 2(\lambda_j^2-\lambda_3^2)\left(\frac{A}{\alpha} + \frac{B}{k_1}e^{-k_1 t}\right) - 2(\lambda_j^{-2}-\lambda_3^{-2})\left(\frac{C}{\beta} + \frac{D}{k_2}e^{-k_2 t}\right) \qquad (7.9)$$

The time dependence of $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ for this particular form of Ω is found by substituting (7.9) into (4.15), or by comparing (7.9) with (4.12)

then $$\frac{\partial W}{\partial I_1} = \frac{A}{\alpha} + \frac{B}{k_1}e^{-k_1 t} \qquad (7.10)$$

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

$$Y_j = t_j - 2(\lambda_j^2 - \lambda_3^2)\frac{A}{\alpha} + 2(\lambda_j^{-2} - \lambda_3^{-2})\frac{C}{\beta} = 2(\lambda_j^{-2} - \lambda_3^{-2})\frac{B}{K_1}e^{-K_1 t} \qquad (7.11)$$

$^C/_\beta$ 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/α and C/β are due to sample variations. There is no correlation of A/α or C/β 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 though 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).

I_1	I_2	C/β g.cm^{-2}	A/α g.cm^{-2}	$K_1 \times 10^2$ (mins)$^{-1}$	B/K_1 g.cm^{-2}
5.179	5	95	1490 1490	5.79 6.37	108 97
4.27	5	180	1440 1465	1.19 2.83	95 87
6.648	10	140	1160 1155	4.15 4.03	96 114
6.448	10	132	1310 1305	5.36 3.14	62 78
5	5.283	127	1385 1370	2.52 2.09	85 94
5	6.011	137	1455 1440	2.23 3.58	104 117
7	10.725	67	1515 1535	3.35 2.02	148 165

Table 7 The material parameters of (8.24). The first and second values of $A/$, 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/β and A/α 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 Ω contains three strain dependent terms such that

$$\Omega = P(J_1-3) + Q(J_2-3) + R(J_1-3)^2 \qquad (7.12)$$

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 $(I_1 \simeq I_2 \simeq 3.1)$ 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 g.cm^{-2} at 3 hours to about $+200$ 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 $3 < I_1, I_2 < 3.1$.

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°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 $0.4 < \frac{1}{\lambda'} < 4$. λ' is the uniaxial extension (or 'compression') ratio.

2. The stress system needed to maintain butyl rubber (at 0°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 lughly 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.

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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.

Component	Natural rubber samples	Butyl rubber samples
Natural rubber	100	-
Butyl rubber (Esso grade 218)	-	100
Sulphur	-	2
Zinc oxide	-	5
Stearic acid	-	3
Accelerator	-	1.5
Dicumyl peroxide	0.5	-

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 variationoof 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 14% 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:-

$$P_{ij} - p\delta_{ij} = \int_{-\infty}^{t} kT.N(t-t')\frac{\partial x_i}{\partial x'_\alpha}\;\frac{\partial x_j}{\partial x'_\alpha}\,dt' \tag{A.1}$$

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 δ_{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.

$$P_{ij} - p\delta_{ij} = 2\left(\frac{\partial W}{\partial I_1}\;\frac{\partial x_i}{\partial X_\alpha}\frac{\partial x_j}{\partial X_\alpha} - \frac{\partial W}{\partial I_2}\frac{\partial X_\alpha}{\partial x_i}\frac{\partial X_\alpha}{\partial x_j}\right) \tag{A.2}$$

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

$$P_{ij} - p\delta_{ij} = 2\int_{-\infty}^{t}\left[\frac{\partial \Omega}{\partial J_1}\;\frac{\partial x_i}{\partial x'_\alpha}\frac{\partial x_j}{\partial x'_\alpha} - \frac{\partial \Omega}{\partial J_2}\frac{\partial x'_\alpha}{\partial x_i}\frac{\partial x'_\alpha}{\partial x_j}\right] \tag{A.3}$$

where $\Omega = \Omega[J_1(t,t'), J_2(t,t'), t-t']$ 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),

$$P_{ij} - p\delta_{ij} = \int_{-\infty}^{t} \phi(t-t')\dot{\rho}_{y}dt' \tag{A.4}$$

where $\phi(t-t')$ is a function of the elapsed time $t-t'$, $e_{ij} = \frac{1}{2}(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i})$, the strain tensor for infinitesimal displacements u_i, and $\dot{\rho}_{ij}$ represents the differentiation of ρ_{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

$$dx_i = du_i = \frac{du_i}{d(t-t')}\, d(t-t') = \dot{u}_i d\tau \tag{A.5}$$

where $\tau = t-t'$.

$$\text{Hence } x_i = x'_i + u_i d\tau \tag{A.6}$$

We wish to examine the strain function of (A.1), $S_{ij} = \frac{\partial x_i}{\partial x'_\alpha}\frac{\partial x_j}{\partial x'_\alpha}$.
If (A.6) is differentiated with respect to x'_α, then

$$\frac{\partial x_i}{\partial x'_\alpha} = \delta_{i\alpha} + \frac{\partial \dot{u}_i}{\partial x'_\alpha} d\tau \tag{A.7}$$

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

$$S_{ij} = \left(\delta_{i\alpha} + \frac{\partial \dot{u}_i}{\partial x'_\alpha} d\tau\right)\left(\delta_{j\alpha} + \frac{\partial \dot{u}_j}{\partial x'_\alpha} d\tau\right) \tag{A.8}$$

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

$$S_{ij} = \delta_{ij} + \frac{\partial \dot{u}_i}{\partial x'_j} d\tau + \frac{\partial \dot{u}_j}{\partial x'_i} d\tau \tag{A.9}$$

or

$$S_{ij} = \delta_{ij} + 2\dot{e}_{ij} d\tau \tag{A.10}$$

since $$\frac{\partial \dot{u}_i}{\partial x'_j} = \frac{\partial \dot{u}_i}{\partial X_j}$$

If τ has a range of values from 0 to ∞, then substitution of (A.10) into (A.1) gives

$$P_{ij} - p'\delta_{ij} = \int_{-\infty}^{t} 2kT.N(t-t\ )\dot{e}_{ij}dt' \qquad (A.11)$$

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) <u>The potential function of Bernstein, Kearsley and Zapas</u>

In attempting to describe the stress relaxation of certain elastomers in simple extension, Bernstein et. al. (1963) have used an equation of state equivalent to (A.3) in which Ω is given by

$$\Omega = mK_1 + \frac{a}{2}K_1^2 + bK_2 \qquad (A.12)$$

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

$$K_1 = tr.E_{k\ell} \qquad (A.13)$$

$$K_2 = tr.(E^2)_{k\ell}$$

and $$E_{k\ell} = \tfrac{1}{2}\left[\delta_{ij}\frac{\partial x_i}{\partial x'_k}\frac{\partial x_j}{\partial x'_\ell} - \delta_{k\ell}\right] \qquad (A.14)$$

Now consider the deformation

$$x_1 = \lambda_1 x_1^1$$
$$x_2 = \lambda_2 x_2^1 \qquad (A.15)$$
$$x_3 = \lambda_3 x_3^1$$

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

$$K_1 = \tfrac{1}{2}[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3] = \tfrac{1}{2}[J_1-3] \qquad (A.16)$$

and $$K_2 = {}^1/_4[(\lambda_1^2-1)^2 + (\lambda_2^2-1)^2 + (\lambda_3^2-1)^2] = {}^1/_4[J_1-2J_2-2J_1+3]$$

since $J_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and $J_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$

Hence (A.12) may be rewritten

$$\Omega = \frac{m}{2}(J_1-3) + \frac{a}{8}(J_1-3)^2 + \frac{b}{4}(J_1^2 - 2J_2 - 2J_1+3) \qquad (A.17)$$

$$= P(J_1-3) + Q(J_2-3) + R(J_1-3)^2 \qquad (A.18)$$

where $P = m/2 + b$, $Q = -b/2$, and $R = a/8 + b/4$. 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 λ_1 λ_2 and λ_3 is given by

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

where t_1, t_2 and t_3 are the principal stresses.

If the deformation is isoenergetic and adiabatic

$$\delta W = J.\delta Q = J\rho\lambda_1\lambda_2\lambda_3 C.\delta T \qquad (A.20)$$

where δQ is the heat evolved

ρ density of material of specific heat c.

δT increase in temperature

J mechanical equivalent of heat

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

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

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

and therefore the increase in temperature δT for a finite increase $\Delta\lambda_1$ in λ_1 is given by (dropping the suffix for convenience).

$$J\rho c.\delta T = \int_{\lambda}^{\lambda+\Delta\lambda} 2(\lambda - \frac{1}{\lambda^2})(\frac{\partial W}{\partial I_1} + \frac{1}{\lambda}\frac{\partial W}{\partial I_2}) \qquad (A.23)$$

In order to estimate the magnitude of δT 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 $$J\rho c.\delta T = C_1[2\lambda.\Delta\lambda + \Delta\lambda^2 + 2(\lambda+\Delta\lambda)^{-1} - 2\lambda^{-1}] \qquad (A.24)$$

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

The tensile stress t is a function of T and λ and therefore an increment in stress δt is given by

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

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

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

and since from (A.21) $$\frac{t.\delta\lambda}{\lambda} = J\rho c.\delta T \qquad (A.27)$$

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

$$t_a = \int_{0}^{t_a} dt = \int_{1}^{\lambda} \frac{N^2k^2T}{J\rho c\lambda}(\lambda^2 - \frac{1}{\lambda})d\lambda + t \qquad (A.28)$$

$$= (\lambda^2 - \frac{1}{\lambda})\left[NkT + \frac{N^2k^2T}{J\rho c}\ \frac{(\lambda^5/4 - 2\lambda^2 + 9\lambda/4 - 1/2\lambda)}{(\lambda^3 - 1)}\right] \qquad (A.29)$$

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

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

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

Then
$$\frac{C_2}{C_1} = \frac{Nk}{J\rho c}\ \frac{(\lambda^6/4 - 2\lambda^3 + 9\lambda^2/4 - 1/2)}{(\lambda^3 - 1)} \qquad (A.31)$$

Typically $Nk = 3.10^4$ dynes.cm^{-2} deg.$^{-1}$C

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

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

Then if $\lambda = 4$

$$\frac{C_2}{C_1} \simeq \frac{1}{50} \tag{A.32}$$

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 $C_2 \simeq 0.81\ C_1$.

I_1	I_2	λ_1	λ_2	t_1 $g.cm^{-2}$	t_2 $g.cm^{-2}$	$\frac{\partial W}{\partial I_1}$ $g.cm^{-2}$	$\frac{\partial W}{\partial I_2}$ $g.cm^{-2}$
5.179	5	2.0	0.95	11,950	2,560	1465	157
5.848	5	2.2	0.85	13,810	1,620	1620	83
4.993	5	1.93	1.00	10,850	2,630	1740	83
4.493	5	1.7	1.16	8,040	3,870	1320	130
4.270	5	1.5	1.33	7,340	5,880	1450	114
8.215	10	2.6	1.16	23,900	5,330	1705	66
7.823	10	2.5	1.21	21,000	5,750	1580	85
7.480	10	2.4	1.27	18,950	5,560	1615	41
7.141	10	2.3	1.32	17,200	6,030	1570	52
6.853	10	2.2	1.38	16,050	6,560	1605	46
6.648	10	2.1	1.46	14,400	7,610	1475	114
6.448	10	2.0	1.53	13,450	8,150	1595	60
9.701	20	2.6	1.70	22,900	11,750	1550	68
9.434	20	2.5	1.77	20,450	11,960	1360	92
9.233	20	2.4	1.85	19,600	12,140	1610	36
9.028	20	2.3	1.92	17,450	12,350	1585	25
8.892	20	2.2	2.00	16,000	13,800	1310	94
11.404	30	2.7	2.02	28,500	16,500	1700	23
11.203	30	2.6	2.10	26,200	18,100	1680	55

Table 1. Biaxial strain results for butyl rubber at 25°C

I_1	I_2	λ_1	λ_2	t_1 g.cm^{-2}	t_2 g.cm^{-2}	$\frac{\partial W}{\partial I_1}$ g.cm^{-2}	$\frac{\partial W}{\partial I_2}$ g.cm^{-2}
5	5.283	1.9	1.07	12,210	3,780	1550	183
5	6.011	1.8	1.25	9,980	4,900	1495	89
5	6.521	1.7	1.40	9,250	6,330	1575	75
5	6.567	1.65	1.45	8,540	6,700	1460	100
7	7.431	2.4	1.05	17,900	4,350	1430	153
7	9.095	2.3	1.25	17,550	5,850	1560	87
7	10.725	2.2	1.44	16,050	7,760	1490	100
7	12.156	2.0	1.70	12,620	9,270	1500	41
9	15.218	2.6	1.47	24,100	8,800	1660	66
9	17.342	2.5	1.64	22,300	11,650	1485	115
9	18.941	2.4	1.79	21,400	12,900	1665	68
9	19.961	2.3	1.92	19,250	13,950	1645	50
9	20.394	2.2	2.03	17,950	15,550	1665	55
11	27.282	2.7	1.92	27,200	15,250	1660	60
11	28.795	2,6	2.05	25,900	16,750	1790	27
11	29.328	2.55	2.11	24,000	17,450	1585	58
11	30.073	2.5	2.18	24,700	19,350	1785	47
11	30.048	2.4	2.27	21,000	18,900	1730	17

Table 1. (Continued) Biaxial strain results for butyl rubber at 25°C

$\lambda_1 = \lambda_2 = \lambda$	$\frac{1}{\lambda'}(=\lambda^2)$	$t_1 = t_2 = t$ g.cm^{-2}	$\frac{\partial W}{\partial I_1}+\frac{1}{\lambda'}\frac{\partial W}{\partial I_2}$ g.cm^{-2}	I_1 $(2/\lambda'+\lambda'^2)$	I_2 $(2\lambda'+1/\lambda'^2)$
1.083	1.17	337±36	1840	3.07	3.08
1.167	1.36	608±8	1920	3.26	3.32
1.25	1.56	788±17	1900	3.53	3.71
1.33	1.77	921±4	1870	3.86	4.26
1.417	2.01	1086±7	1945	4.52	5.05
1.50	2.25	1223±20	1990	4.74	5.97
1.58	2.49	1342±57	2020	5.14	7.00
1.67	2.79	1411±60	1972	5.71	8.52
1.75	3.06	1497±62	1972	6.23	10.01
1.833	3.36	1625±45	2028	6.90	11.90
1.916	3.67	1734±74	2050	7.42	14.04
2.00	4.00	1836±88	2065	8.06	16.50

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.

t_3 g.cm^{-2}	λ'	$\frac{1}{\lambda'}$	$\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'}\frac{\partial W}{\partial I_2}$ (g.cm^{-2})	I_1 $(2/\lambda'+\lambda'^2)$	I_2 $(2\lambda'+1/\lambda'^2)$
1915	1.18	0.849	1740	3.08	3.08
2870	1.275	0.785	1710	3.20	3.17
3760	1.365	0.733	1670	3.33	3.27
4600	1.455	0.688	1625	3.50	3.38
5540	1.545	0.648	1595	3.68	3.51
6400	1.635	0.611	1565	3.89	3.74
7350	1.73	0.578	1530	4.15	3.79
8350	1.82	0.550	1510	4.41	3.94
9390	1.91	0.524	1505	4.70	4.09
10320	2.00	0.500	1475	5.00	4.25
11520	2.095	0.478	1475	5.35	4.43
12450	2.18	0.459	1450	5.67	4.57
13450	2.275	0.440	1415	6.06	4.74
14690	2.365	0.423	1415	6.44	4.91
16950	2.545	0.393	1390	7.27	5.24
18250	2.64	0.379	1385	7.74	5.42
19550	2.73	0.366	1385	8.17	5.59
20900	2.82	0.355	1380	8.66	5.77
22400	2.91	0.344	1380	9.15	5.94
25200	3.09	0.324	1370	10.23	6.28
26800	3.18	0.315	1365	10.75	6.45
30300	3.37	0.297	1375	11.95	6.83
34100	3.55	0.282	1385	13.16	7.18

Table 3. Simple extension results for butyl rubber at 25°C.

time	$I_1 = 5.179$ $I_2 = 5$				$I_1 = 4.270$ $I_2 = 5$				$I_1 = 6.648$ $I_2 = 10$				$I_1 = 6.448$ $I_2 = 10$			
(mins.)	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$
1	12330	2390	1577	88	9150	4470	1460	167	13280	7600	1233	148	13000	8500	1350	140
10	12030	2360	1534	94	9030	4450	1433	180	13050	7470	1207	147	12780	8350	1320	137
20	11800	2330	1501	96	8950	4430	1408	183	12870	7370	1193	145	12670	8280	1313	137
30	11680	2310	1490	95	8880	4420	1397	183	12730	7280	1183	143	12620	8220	1313	132
40	11620	2300	1480	95	8830	4400	1377	187	12670	7220	1180	140	12580	8200	1313	129
50	11580	2290	1473	94	8770	4380	1360	190	12630	7210	1177	140	12570	8170	1313	130
60	11560	2290	1473	95	8730	4350	1367	187	12620	7200	1167	138	12570	8150	1320	127
70					8700	4320	1370	180	12600	7180	1170	139				
80	11550	2290	1468	96	8670	4300	1363	177	12580	7170	1173	138	12570	8150	1320	127
90					8670	4280	1370	173	12530	7150	1168	137				
100	11550	2290	1468	96					12520	7150	1165	138	12570	8150	1320	127
110									12500	7150	1162	138				
120					8670	4280	1370	173	12500	7150	1162	138				
140									12500	7150	1162	138				

Table 4. Relaxation of the principal stresses t_1 and t_2 for various biaxial deformations of butyl rubber at 0°C. $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ were calculated from 8.15. All quoted values are in g.cm^{-2}.

time	$I_1 = 5$	$I_2 = 5.283$			$I_1 = 5$	$I_2 = 6.011$			$I_1 = 7$	$I_2 = 10.725$		
(mins.)	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$
1	10850	3480	1463	130	10730	5430	1557	133	17130	7970	1313	77
10	10700	3450	1440	128	10570	5380	1522	140	16800	7750	1297	67
20	10620	3420	1432	127	10430	5320	1503	140	16580	7620	1277	67
30	10570	3400	1420	127	10350	5280	1487	143	16420	7520	1267	63
40	10520	3370	1413	127	10280	5250	1477	137	16300	7470	1260	62
50	10470	3370	1403	127	10230	5230	1463	143	16180	7430	1243	63
60	10420	3370	1400	128	10180	5200	1457	138	16080	7400	1227	63
70	10380	3350	1393	128	10130	5180	1450	140	16020	7370	1223	63
80	10350	3330	1392	127	10120	5160	1453	137	15920	7350	1203	67
90	10320	3320	1390	125					15850	7330	1197	65
100	10280	3320	1380	127	10120	5120	1470	128	15780	7320	1183	68
110									15750	7300	1187	68
120	10270	3320	1373	128	10120	5120	1470	128	15720	7300	1173	70
130									15700	7300	1170	70
140	10270	3320	1373	128					15670	7300	1167	72
160									15670	7300	1167	72
180									15670	7300	1167	72

Table 4 (continued)

time	$I_1 = 5.179$ $I_2 = 5$				$I_1 = 4.270$ $I_2 = 5$				$I_1 = 6.648$ $I_2 = 10$				$I_1 = 6.448$ $I_2 = 10$			
(mins.)	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$
1	5600	1270	674	87	3930	1800	680	51	5600	3200	520	66	5570	3500	618	42
10	5420	1240	650	88	3670	1730	613	62	5280	3050	482	62	5280	3330	585	41
20	5300	1220	635	87	3550	1660	598	58	5730	2970	470	60	5130	3210	575	37
30	5250	1200	629	85	3500	1630	595	54	5050	2920	463	59	5050	3200	557	42
40	5200	1180	627	83	3480	1600	600	48	4950	2870	450	59	4950	3170	533	45
50	5180	1170	624	80	3470	1580	600	45	4900	2830	448	58	4900	3140	523	44
60	5170	1160	625	73	3450	1570	598	43	4870	2820	445	58	4870	3120	523	44
70	5160	1140	628	73	3440	1570	598	44	4830	2800	442	58	4830	3090	520	43
80	5150	1130	628	72	3430	1570	597	43	4810	2770	442	56	4810	3070	523	43
90									4780	2750	440	55	4770	3060	513	44
100	5130	1130	625	73	3400	1550	590	43	4770	2720	445	52	4770	3030	518	40
110									4730	2700	440	52	4730	3030	508	43
120	5130	1130	624	73	3350	1530	580	45	4730	2760	440	52	4730	3030	508	43
130													4730	3030	508	43
140	5120	1130	622	73	3330	1500	587	37	4730	2700	440	52	4730	3030	508	43
160	5100	1130	621	74	3320	1500	580	38	4730	2700	440	52	4730	3030	508	43
180	5100	1130	618	74	3310	1500	577	40	4730	2700	440	52	4730	3030	508	43
200	5090	1130	618	75	3300	1500	573	40	4730	2700	440	52	4730	3030	508	43
220	5030	1130	617	75	3280	1500	570	43								
240	5070	1130	615	75	3280	1500	567	43								
260					3270	1500	563	44								
280					3270	1500	563	44								
300					3250	1500	563	46								

Table 5. Relaxation of the principal stress t_1 and t_2 for various biaxial deformation of natural rubber at 25°C. $\frac{\partial W}{\partial I_1}$ and $\frac{\partial W}{\partial I_2}$ were calculated from 8.15. All quoted values are in $g.cm^{-2}$.

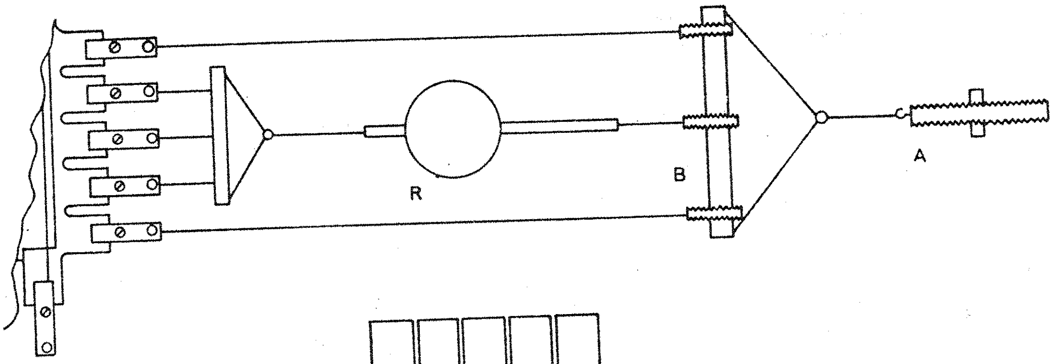
time	$I_1 = 5$ $I_2 = 5.283$				$I_2 = 6.011$ $I_1 = 5$				$I_1 = 7$ $I_2 = 10.725$				$I_1 = 9.434$ $I_2 = 20$			
(mins.)	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$	t_1	t_2	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$
1	5920	1720	844	29	4700	2320	701	47	6970	3380	642	44	8230	4800	521	37
10	5820	1680	830	28	4450	2250	647	57	6530	3100	616	35	7570	4530	487	41
20	5730	1670	814	30	4320	2200	621	59	6250	2960	590	33	7320	4410	456	41
30	5650	1650	802	31	4250	2170	613	58	6090	2900	571	34	7180	4340	453	40
40	5610	1630	799	29	4200	2170	596	62	6050	2870	572	32	7130	4270	450	39
50	5600	1630	795	30	4180	2150	594	62	6033	2840	573	31	7030	4230	447	39
60	5570	1630	792	31	4170	2140	592	61	6020	2820	573	29	7000	4200	445	38
70	5540	1630	785	32	4140	2130	587	61	5980	2800	572	28	6950	4170	443	37
80	5520	1620	782	32	4130	2130	588	61	5960	2800	570	29	6930	4140	443	37
90	5490	1620	777	32	4130	2120	591	62	5940	2780	568	28	6900	4110	443	36
100	5470	1610	773	31	4130	2100	596	58	5930	2770	567	28	6880	4100	443	36
120	5440	1600	768	32	4120	2090	593	58	5900	2760	562	28	6850	4080	440	36
140	5430	1600	776	33	4100	2090	593	54	5860	2750	558	28	6830	4070	440	35
160	5430	1600	766	32	4100	2080	593	54	5830	2730	557	29	6820	4050	439	36
180	5410	1600	765	33	4090	2070	595	53	5790	2727	552	28	6810	4040	442	35
200	5400	1600	761	34	4080	2070	591	53	5760	2710	549	28	6800	4020	445	34
220	5390	1600	760	35	4070	2070	586	55	5730	2700	543	29	6800	4000	448	33
240	5380	1600	758	35	4060	2070	583	55	5690	2683	540	29	6800	3980	447	32
260	5370	1600	755	36	4050	2070	582	56					6780	3970	448	31
280					4040	2070	577	57					6770	3940	452	30
300													6770	3920	455	29

Table 5 (continued)

$\frac{1}{\lambda'}$	I_2 $(2\lambda'+1/\lambda'^2)$	$\frac{\partial W}{\partial I_1}+\frac{1}{\lambda'}\frac{\partial W}{\partial I_2}$ (g.cm^{-2})
0.282	7.18	1.54
0.324	6.28	1.55
0.344	5.94	1.54
0.355	5.77	1.55
0.366	5.59	1.55
0.379	5.42	1.55
0.393	5.24	1.54
0.423	4.91	1.54
0.440	4.74	1.55
0.459	4.57	1.55
0.478	4.43	1.55
0.500	4.25	1.55
0.524	4.09	1.56
0.550	3.94	1.56
0.578	3.79	1.55
0.611	3.74	1.56
0.643	3.51	1.56
0.688	3.38	1.57
0.733	3.27	1.57
0.785	3.20	1.58
0.849	3.08	1.59
1.17	3.08	1.63
1.36	3.32	1.65
1.56	3.71	1.68
1.77	4.26	1.71
2.01	5.05	1.74
2.25	5.97	1.76
2.49	7.0	1.79
2.79	8.52	1.83
3.06	10.01	1.86
3.36	11.90	1.89
3.67	14.04	1.91
4.0	16.50	1.92

Table 6. $\frac{\partial W}{\partial I_1}+\frac{1}{\lambda'}\frac{\partial W}{\partial I_2}$ calculated from 7.1 and 7.2.

2.



1.

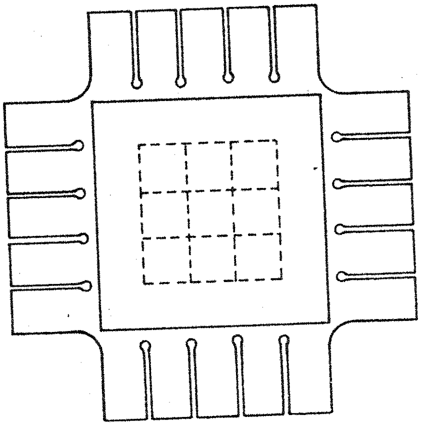


FIGURE 2. ONE SIDE OF THE BIAXIAL STRETCHING RIG

FIGURE 1. THE TEST PIECE

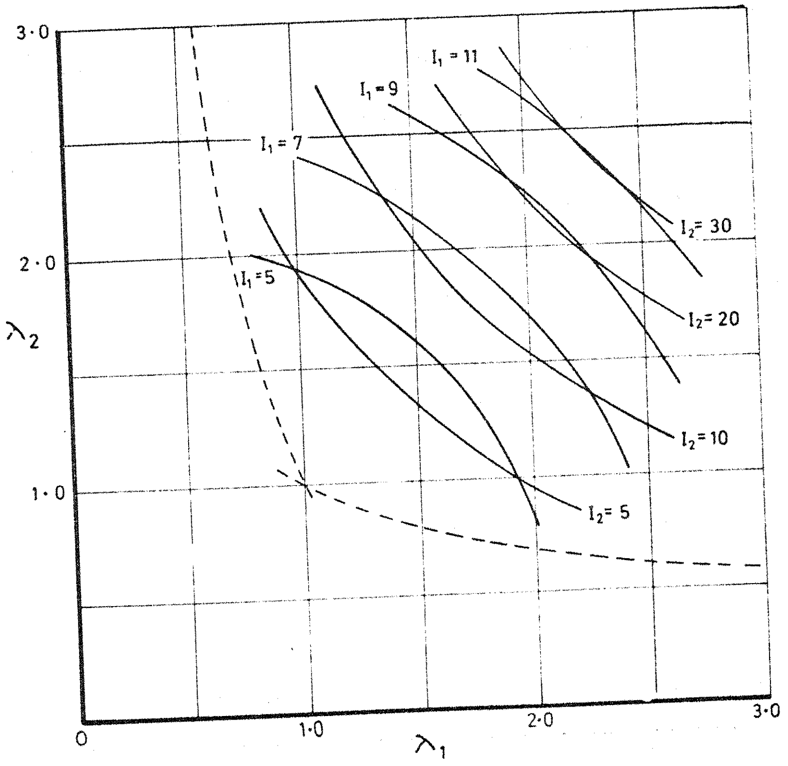


FIGURE 3 THE VARIATION OF λ_1 WITH λ_2 FOR VARIOUS CONSTANT VALUES OF I_1 and I_2

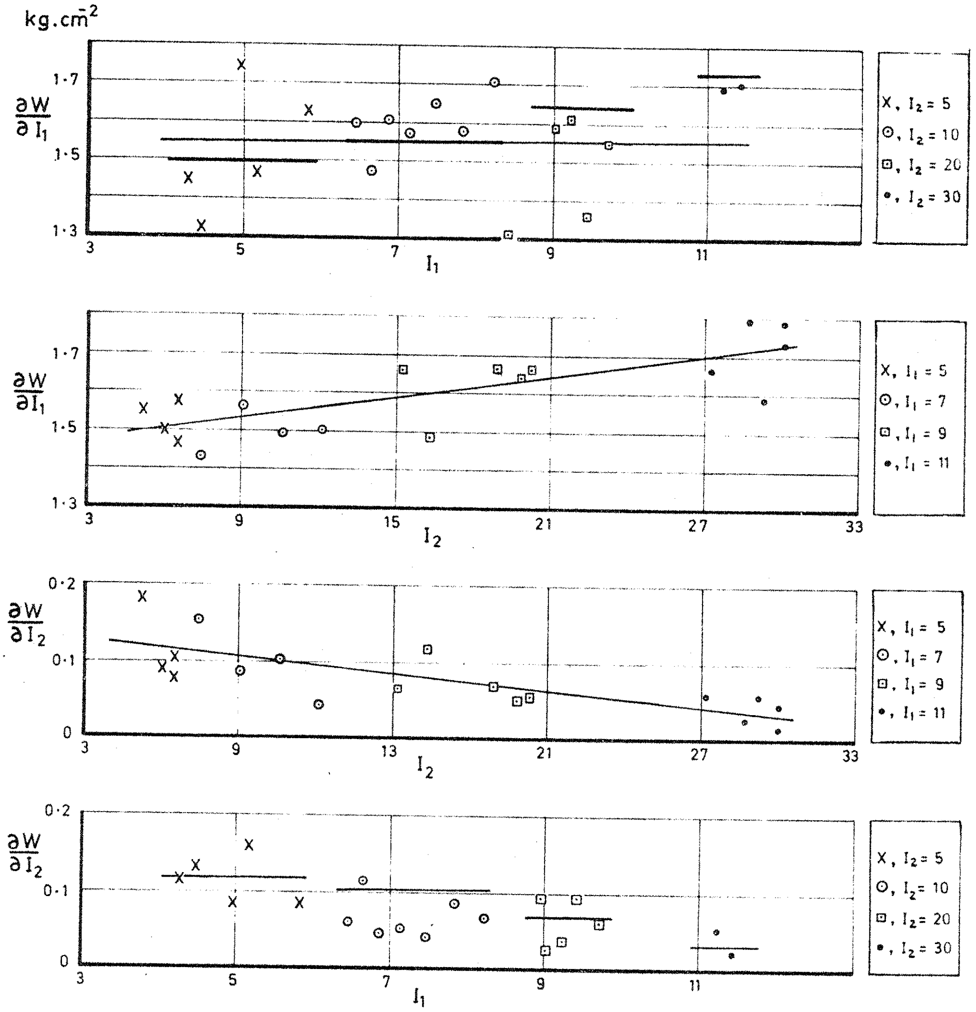


FIGURE 4. THE VARIATION OF $\frac{\partial W}{\partial I_1}$ AND $\frac{\partial W}{\partial I_2}$ WITH I_1 AND I_2 FOR BUTYL RUBBER AT 25°C.

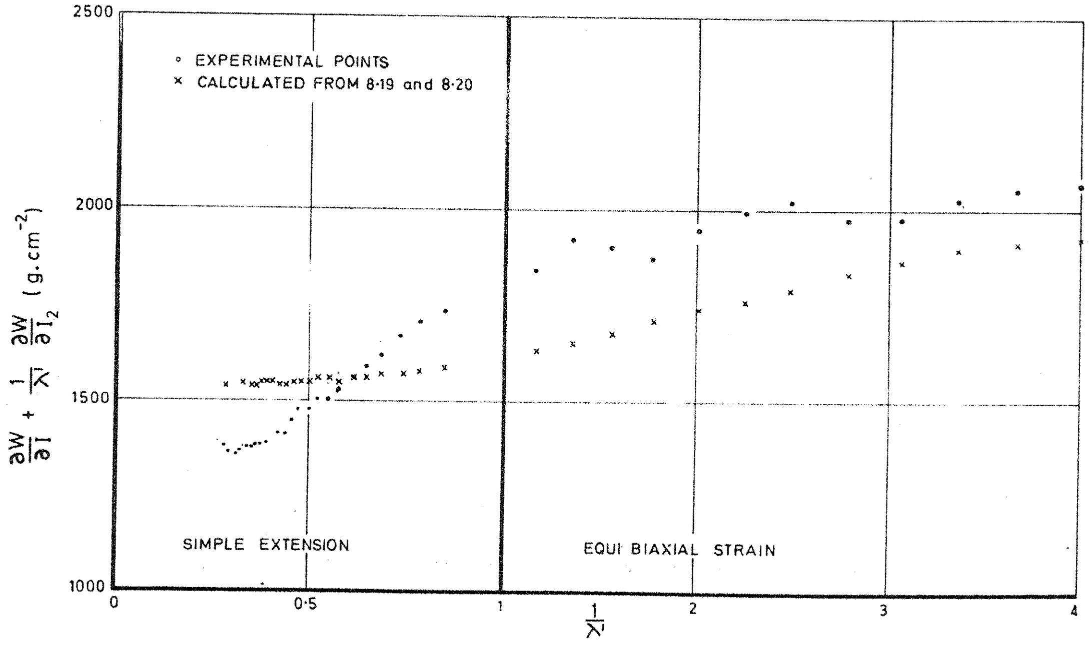


FIGURE 5. THE VARIATION OF $\frac{\partial W}{\partial I_1} + \frac{1}{\lambda'}\frac{\partial W}{\partial I_2}$ WITH $\frac{1}{\lambda'}$ FOR BUTYL RUBBER AT 25°C IN SIMPLE EXTENSION AND EQUIBIAXIAL STRAIN. NOTE THE CHANGE IN SCALE AT $\lambda' = 1$

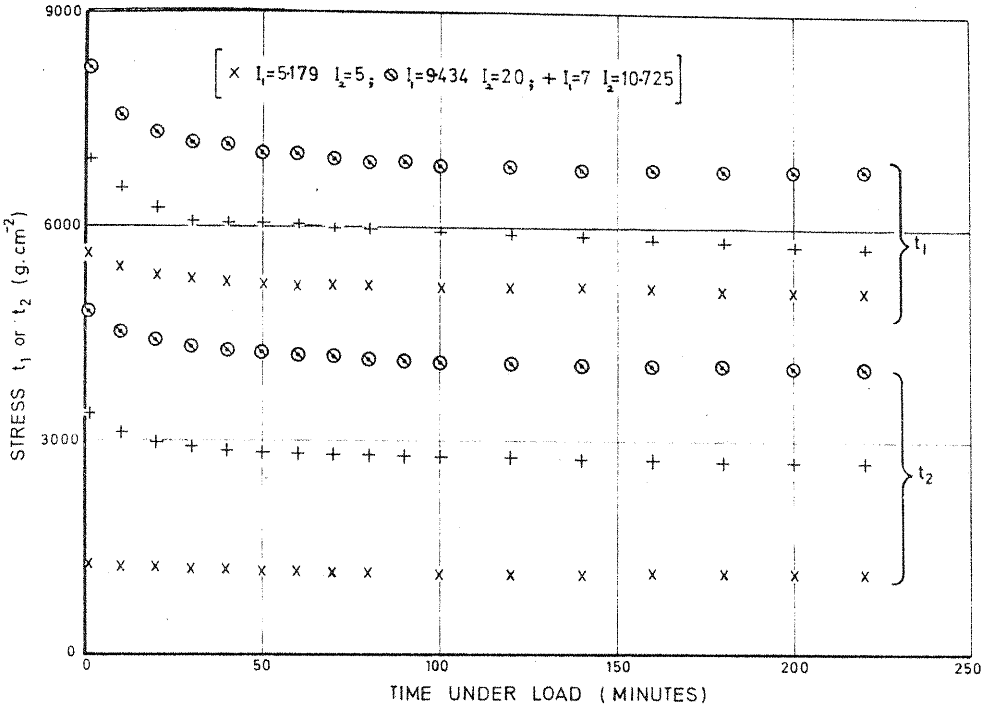


FIGURE 6. RELAXATION OF THE PRINCIPAL STRESSES t_1 and t_2 FOR NATURAL RUBBER AT 25°C

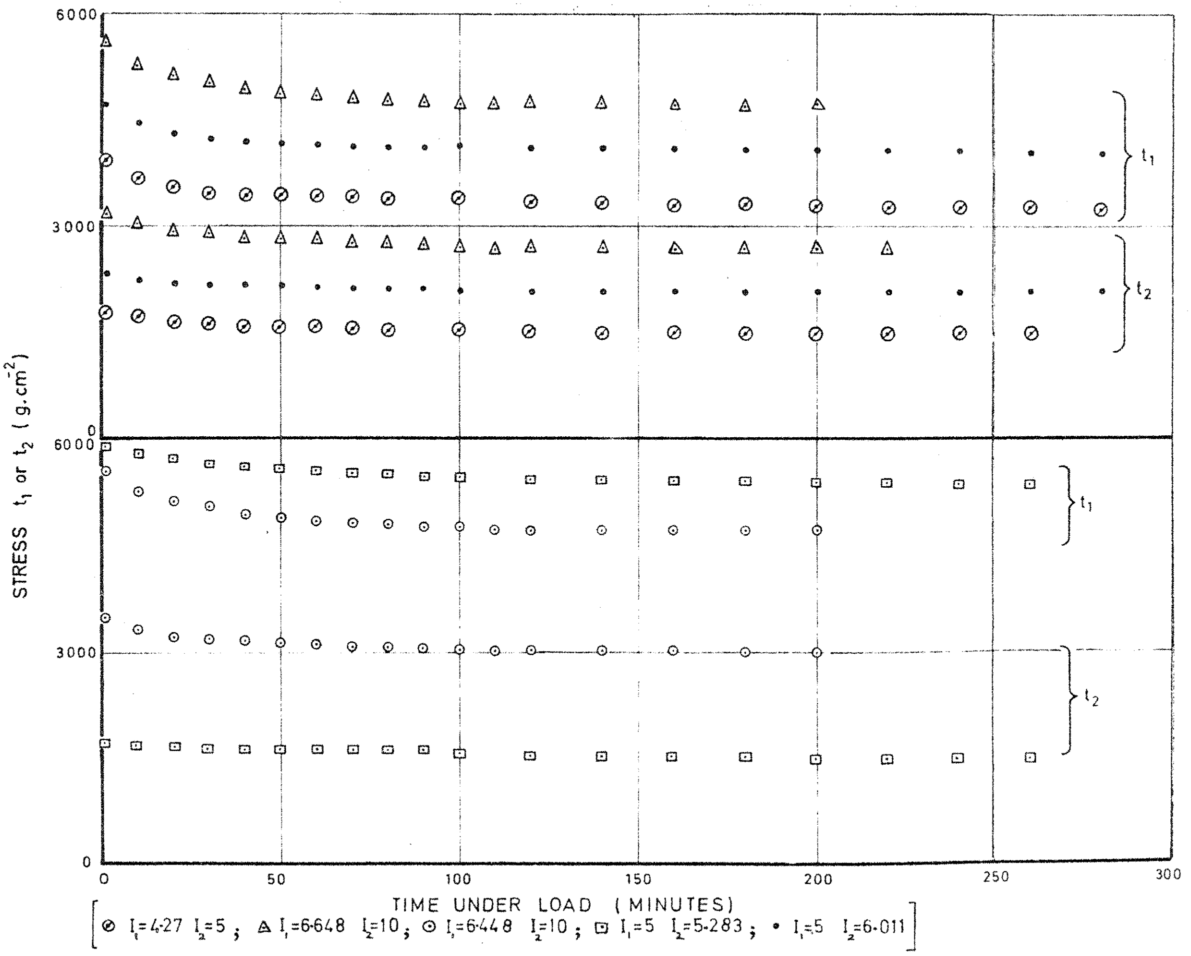


FIGURE 7. RELAXATION OF THE PRINCIPAL STRESSES t_1 AND t_2 FOR NATURAL RUBBER AT 25° C.

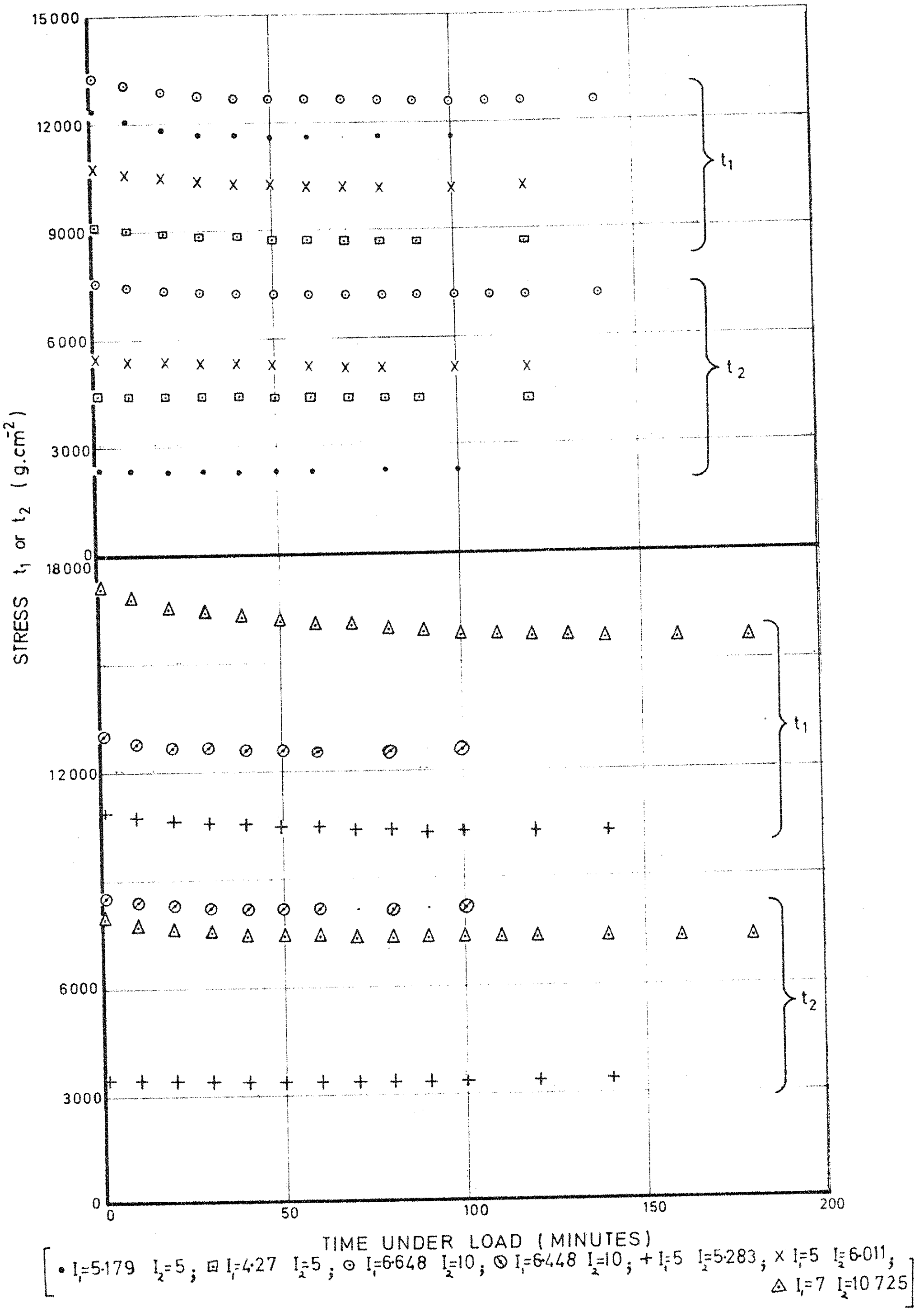


FIGURE 8 RELAXATION OF THE PRINCIPAL STRESSES t_1 and t_2 FOR BUTYL RUBBER AT 0°C

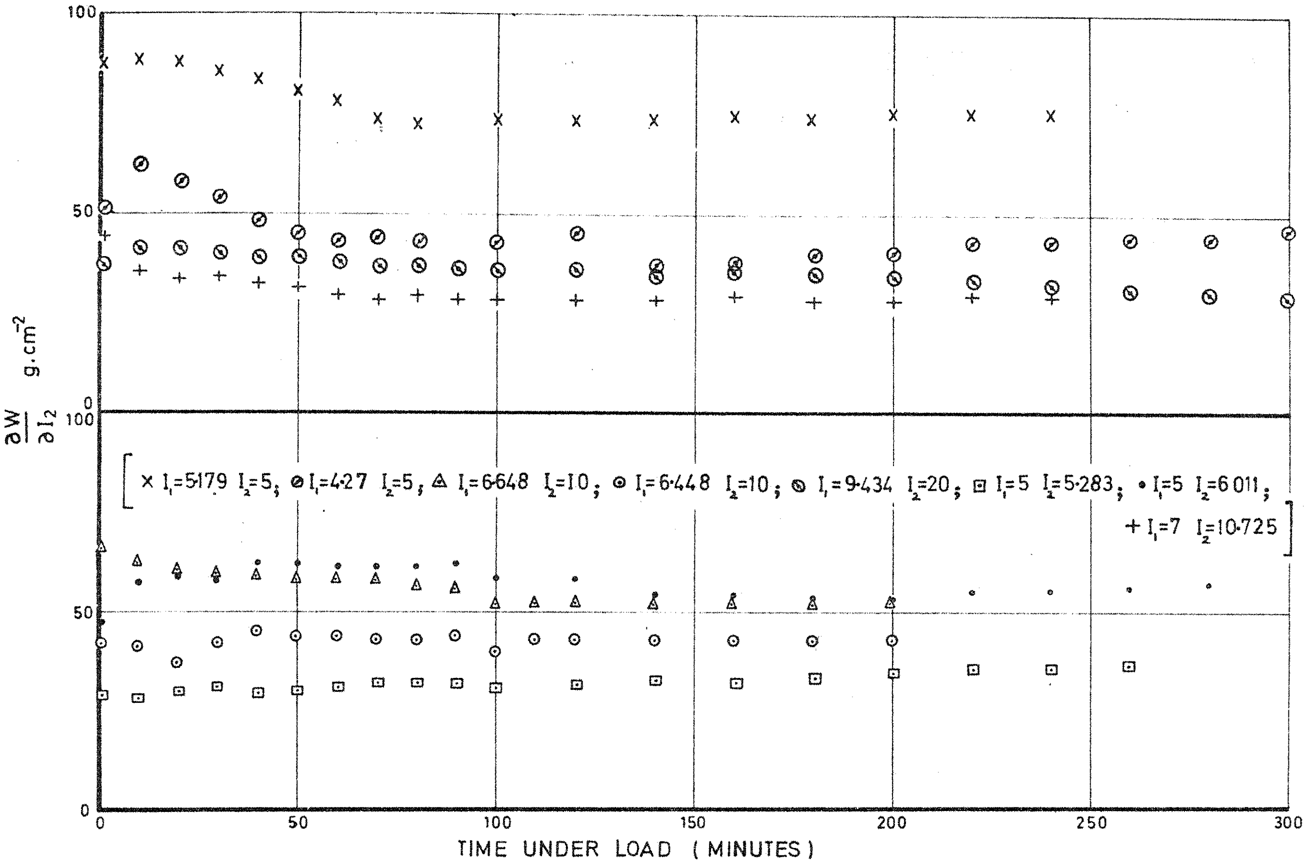


FIGURE 9. $\frac{\partial W}{\partial I_2}$ AS A FUNCTION OF THE RELAXATION TIME, FOR NATURAL RUBBER AT 25°C

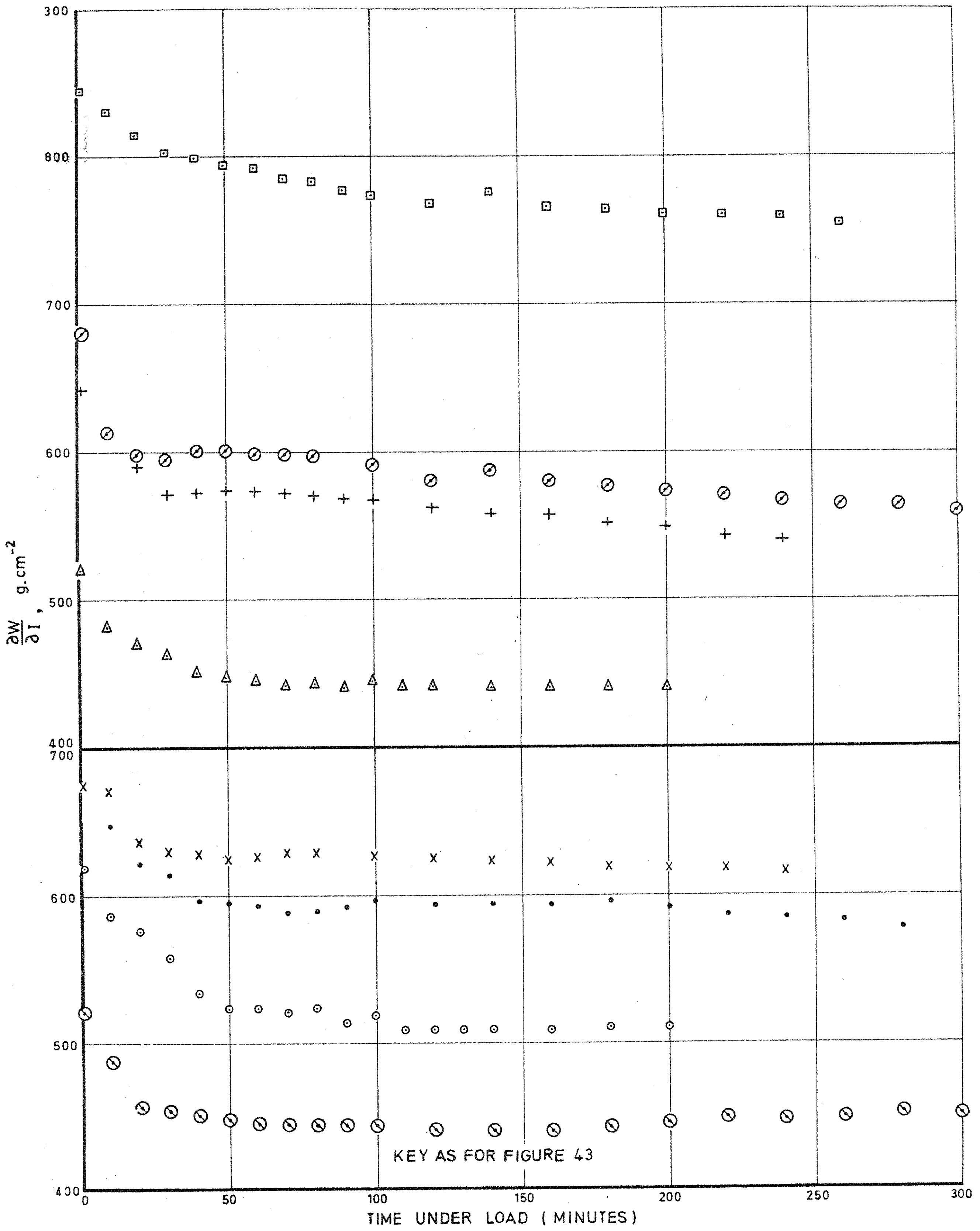


FIGURE 10. $\frac{\partial W}{\partial I_1}$ AS A FUNCTION OF THE RELAXATION TIME, FOR NATURAL RUBBER AT 25°C.

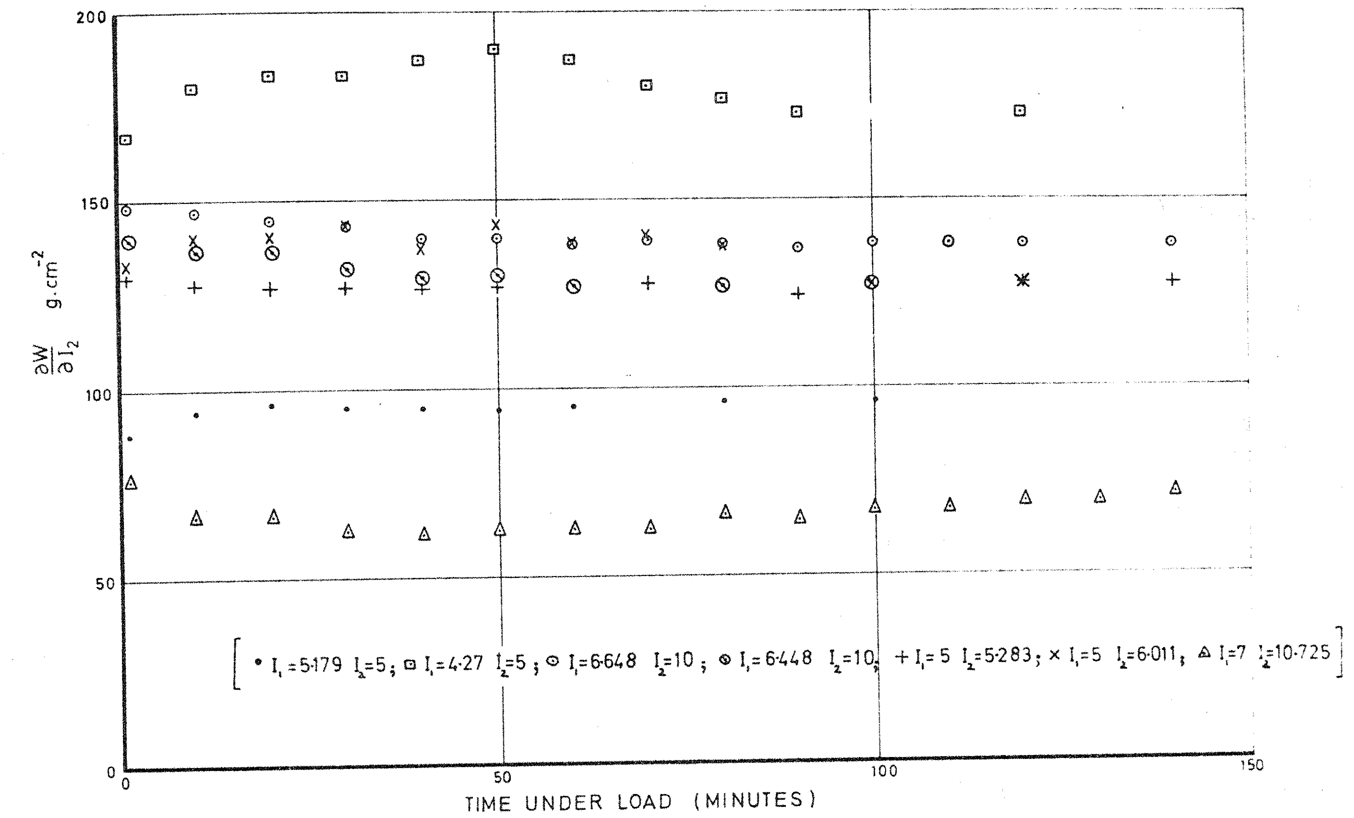


FIGURE 11. $\frac{\partial W}{\partial I_2}$ AS A FUNCTION OF THE RELAXATION TIME, FOR BUTYL RUBBER AT 0°C

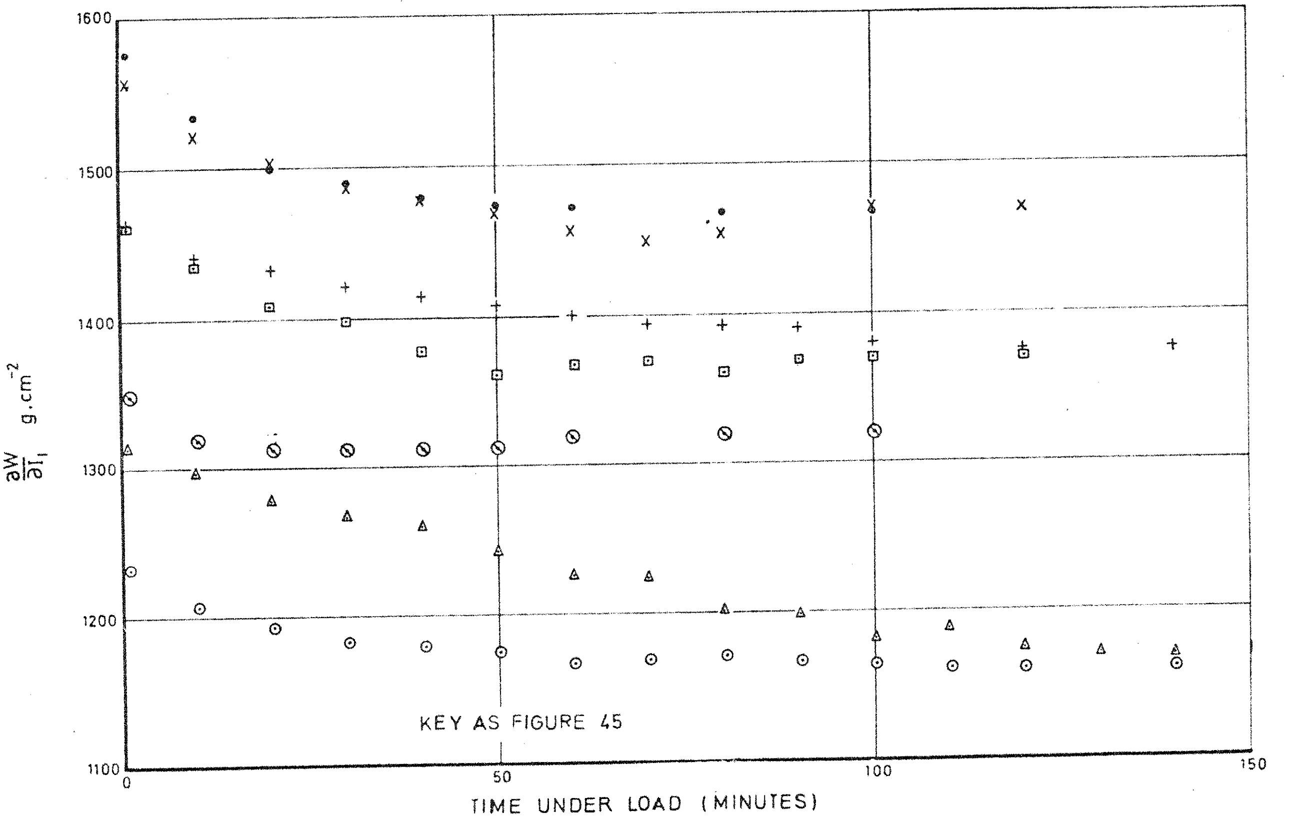


FIGURE 12. $\frac{\partial W}{\partial I_1}$ AS A FUNCTION OF THE RELAXATION TIME, FOR BUTYL RUBBER AT 0°C

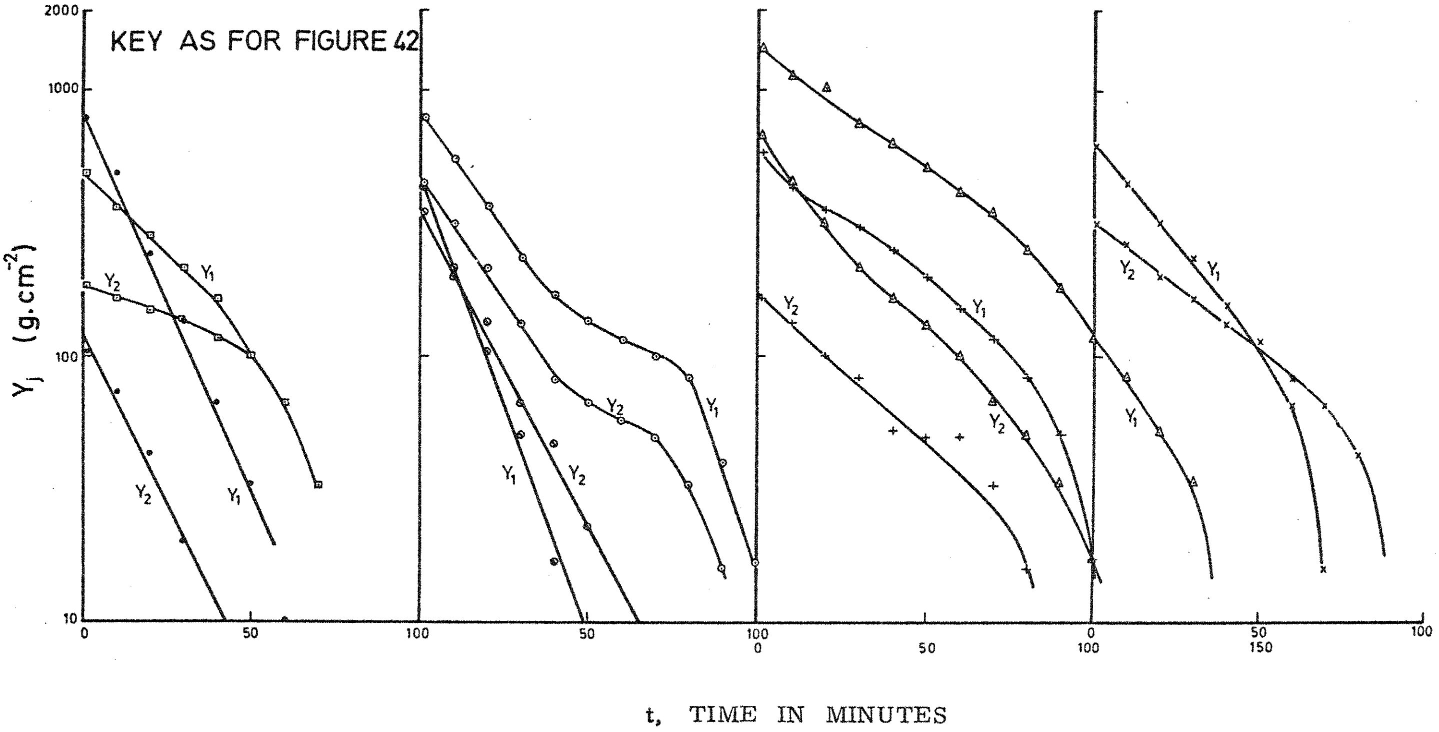


FIGURE 13 AN EXAMINATION OF 7.11 FOR BUTYL RUBBER AT 0°C