A Theory of Large Elastic Deformation

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It is postulated that (A) the material is isotropic, (B) the volume change and hysteresis are negligible, and (C) the shear is proportional to the traction* in simple shear in a plane previously deformed, if at all, only by uniform dilatation or contraction. It is deduced that the general strain-energy function, W, has the form

$$W=\frac{G}{4}\sum_{i=1}^{3}\left(\lambda_i-\frac{1}{\lambda_i}\right)^2+\frac{H}{4}\sum_{i=1}^{3}\left(\lambda_i^2-\frac{1}{\lambda_i^2}\right),$$

where the λ_i's are the principal stretches (1+principal extension), G is the modulus of rigidity, and H is a new elastic constant not found in previous theories. The differences between the principal stresses are $\sigma_i-\sigma_j=\lambda_i\partial W/\partial\lambda_i-\lambda_j\partial W/\partial\lambda_j$.

Calculated forces agree closely with experimental data on soft rubber from 400 percent elongation to 50 percent compression.

Introduction

The fundamental problem in the theory of elasticity is to find the correct expression for the strain energy of a body subjected to a homogeneous strain. If the body is isotropic and the strains are small, it is known that the energy can be expressed in terms of the strains and two constants of the material, the compression modulus and the rigidity modulus. However, the deformations which rubber and similar substances undergo are much too large to be included in the classical theory of small strains, even when the theory is extended to the second and higher approximations. An entirely new approach is required for any adequate theory of the elasticity of rubber.

Hencky[1] recently expressed the strain energy in terms of $\ln(1+e_i)$, instead of the principal strains, e_i. The validity of the theory was thereby extended to much larger deformations, but this treatment of the problem is still incomplete in certain important respects, as will later be shown.

When a sample of soft rubber is stretched by an imposed tension, neither the force-elongation nor the stress-elongation relationship agrees with Hooke's law. On the other hand, if the sample is sheared by a shearing stress, or traction, Hooke's law is obeyed over a very wide range in deformation. In some unpublished measurements in a St. Joe flexometer[2] the shear was found proportional to traction up to 200 percent shear, at which point the cement bond failed between the sample and the supporting steel blocks. Another simplifying feature in the elasticity of rubber lies in the fact that deformations are normally produced without any appreciable change in volume. The most exact data on this point are those by Holt and McPherson.[3]

These two experimental facts constitute the basis for the present theory of elasticity. In Part I strict adherence to Hooke's law in simple shear is assumed. In Part II, Hooke's law is assumed only as a first approximation. Constant volume, or isometric deformation, is assumed in both cases.

Part I. The Linear Case, or Hooke's Law in Simple Shear

It is postulated that the elastic material considered, besides being homogeneous and free from hysteresis, has the following properties within the range of deformations to be considered:

A. The material is isotropic. This signifies not only that the material is isotropic in the undeformed state, but also that after a positive or negative stretch-squeeze it remains isotropic in the plane at right angles to the stretch.

B. The deformations are isometric; that is, occur without change in volume.

C. The traction in simple shear in any isotropic plane is proportional to the shear.

* *Traction* is used in this paper to signify shearing stress, or tangential force per unit area, just as tension is used to signify normal force per unit area.

[1] H. Hencky, J. Rheology **2**, 169 (1931), or Rub. Chem. Tech. **6**, 217 (1933).

[2] R. S. Havenhill and W. B. MacBride, Ind. Eng. Chem. Anal. Ed. **7**, 60 (1935).

[3] W. L. Holt and A. T. McPherson, J. Research Nat. Bur. Stand. **17**, 657 (1936).

This particular combination of properties may conveniently be referred to as "superelasticity." Because of the low modulus of rigidity required by postulate B, superelastics are always relatively soft.

In the analysis which follows we shall make use of the strain energy, or the mechanical work required in a reversible process to produce a particular state of strain. This function has been shown to exist for reversible elastic deformations carried out under either isothermal or adiabatic conditions.[4] The function is different for the two cases; but the difference is apparently not large, at least for rubber, and has not yet been determined in detail by the experimentalist. In the present analysis, therefore, we shall ignore questions as to whether experimental data were obtained under adiabatic or isothermal conditions or under poorly defined conditions intermediate between the two.

It will be convenient to express the strain in terms of the principal stretches rather than the principal extensions. The principal stretch, λ_i, is the ratio of final to initial length in the direction of the i-strain axis.

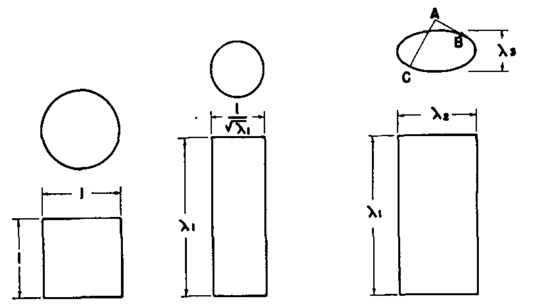

FIG. 1A $W = 0$

FIG. 1B $W = \psi(\lambda_1)$

FIG. 1C $\gamma = AB/AC = \sqrt{\lambda_1}(\lambda_2 - \lambda_3)$
$W = \psi(\lambda_1) + \phi(\lambda_1) \cdot \lambda_1(\lambda_2 - \lambda_3)^2$

FIG. 1.

The condition of constant volume requires

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

The λ's are limited to positive values. A value $\lambda_i < 1$ signifies a reverse stretch, or contraction.

Derivation of the strain-energy function

Consider a cylindrical element of volume in the superelastic material. In the unstrained state let the cylinder be of unit length and unit diameter (Fig. 1A). We shall let the elastic material be deformed, in two steps, so that in its final state it represents the most general deformation of which the material is capable. Each step is itself a possible real deformation in that it is isometric.

The two steps are (a) Fig. 1B, a stretch-squeeze, with stretch λ_1 and uniform squeeze $1/\sqrt{\lambda_1}$, and (b) Fig. 1C, a shear in the plane normal to the stretch, resulting in the final principal stretches λ_2 and λ_3, in this plane. W_b, the work done per unit volume in the first step is some unknown function of λ_1, and we have

$$W_b = \psi(\lambda_1). \quad (2)$$

In order, in the second step, to produce the final stretches λ_2 and λ_3, the stretches produced with reference to the state B must be $\lambda_2\sqrt{\lambda_1}$ and $\lambda_3\sqrt{\lambda_1}$, respectively. The shear is therefore[5]

$$\gamma = (\lambda_1)^{\frac{1}{2}}(\lambda_2 - \lambda_3). \quad (3)$$

Then according to postulate C, the work done per unit volume in this step is

$$W_c = \lambda_1(\lambda_2 - \lambda_3)^2\phi(\lambda_1), \quad (4)$$

where the proportionality factor, ϕ, is an unknown function of λ_1. From Eqs. (2) and (4) we obtain the total work done,

$$W = \Psi(\lambda_1) + (\lambda_2^2 + \lambda_3^2)\Phi(\lambda_1), \quad (5)$$

where

$$\Psi(\lambda_1) = \psi(\lambda_1) - 2\phi(\lambda_1), \quad \Phi(\lambda_1) = \lambda_1\phi(\lambda_1). \quad (6)$$

W must satisfy the condition for zero strain,

$$0 = \Psi(1) + 2\Phi(1). \quad (7)$$

[4] A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, 1920), third edition, p. 92.
[5] Reference 4, p. 69.

Equation (5) is a functional equation. That is, Ψ and Φ are functions of unknown form; and it is their forms that we wish to determine.

The postulate of isotropy requires that W be symmetric in the λ_i. The transformation $\lambda_1 = 1/\lambda_2\lambda_3$ permits a function of λ_1 to be expressed as a function of products of the form $\lambda_1^p \lambda_2^q \lambda_3^q$. But such products or functions of such products can be symmetric only if $p=q$; that is, if the product is unity. We conclude that, except for a constant, $\Psi(\lambda_1)$ cannot in itself be symmetric. Therefore, corresponding to each term in Ψ not a constant, there must be a complementary term in the product $(\lambda_2^2+\lambda_3^2)\Phi(\lambda_1)$. Furthermore, the complementary term must be reducible to the form

$$(\lambda_2^2+\lambda_3^2)\Phi_c(\lambda_1) = \Psi(\lambda_2)+\Psi(\lambda_3)-2C_3, \tag{8}$$

where C_3 is a constant. One obvious solution is $\Phi_c = C_1$, a constant. The relation of Eq. (1) permits one and only one additional solution, $\Phi_c = C_2\lambda_1^2$. Hence

$$\begin{aligned}(\lambda_2^2+\lambda_3^2)\Phi_c &= C_1(\lambda_2^2+\lambda_3^2)+C_2(1/\lambda_3^2+1/\lambda_2^2),\\ \Psi &= C_1\lambda_1^2+C_2/\lambda_1^2+C_3.\end{aligned} \tag{9}$$

We now examine the possible existence of terms Φ_s in Φ which are a self-symmetric and independent of Ψ. If such a term exists, it must be reducible to the equivalent forms

$$\begin{aligned}(\lambda_2^2+\lambda_3^2)\Phi_s(\lambda_1) &= (\lambda_3^2+\lambda_1^2)\Phi_s(\lambda_2)\\ &= (\lambda_1^2+\lambda_2^2)\Phi_s(\lambda_3).\end{aligned} \tag{10}$$

Equating the right members of (10) and applying (1), we find

$$\Phi_s(\lambda_2)-\Phi_s(\lambda_3)+\lambda_2^2\lambda_3^4\Phi_s(\lambda_2)-\lambda_2^4\lambda_3^2\Phi_s(\lambda_3)=0. \tag{11}$$

Since the λ's are subject to one general relation, Eq. (1), we may choose any two of the λ's as independent variables; and any general equation involving only two of the λ's must be an identity in these two. Hence in Eq. (11) we must have

$$\Phi_s(\lambda_2)-\lambda_2^4\lambda_3^2\Phi_s(\lambda_3)=0, \quad \Phi_s(\lambda_3)-\lambda_3^4\lambda_2^2\Phi_s(\lambda_2)=0. \tag{12}$$

Equation (12.1) requires $\qquad \Phi_s(\lambda_3)\equiv C/\lambda_3^2, \quad \Phi_s(\lambda_2)\equiv C/\lambda_2^4. \qquad (13)$

Φ_s is thus required to satisfy two mutually incompatible conditions; and we conclude that no self-symmetric term $(\lambda_2^2+\lambda_3^2)\Phi_s(\lambda_1)$ can exist.

If we choose C_3 in Eq. (9.2) to satisfy Eq. (7), we have

$$W(\lambda_1, \lambda_2, \lambda_3) = C_1(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)+C_2(1/\lambda_1^2+1/\lambda_2^2+1/\lambda_3^2-3). \tag{14}$$

This equation gives the most general solution for W consistent with our three postulates. A more convenient form is obtained by the substitution

$$C_1=(G+H)/4, \quad C_2=(G-H)/4. \tag{15}$$

Then

$$W=\frac{G}{4}\sum_{i=1}^{3}\left(\lambda_i-\frac{1}{\lambda_i}\right)^2+\frac{H}{4}\sum_{i=1}^{3}\left(\lambda_i^2-\frac{1}{\lambda_i^2}\right). \tag{16}$$

In this form G is the modulus of rigidity, as will be evident later. H is a new constant not encountered in previous theories of elasticity.

We seek to understand the significance of H. Let us note, first, that corresponding to any deformation characterized by the principal stretches λ_1, λ_2, λ_3, there exists an isometric *reciprocal deformation* with the principal stretches

$$\lambda_1^* = 1/\lambda_1, \quad \lambda_2^* = 1/\lambda_2, \quad \lambda_3^* = 1/\lambda_3. \tag{17}$$

If $H=0$,

$$W=\frac{G}{4}\sum\left(\lambda_i-\frac{1}{\lambda_i}\right)^2=\frac{G}{4}\sum\left(\lambda_i^*-\frac{1}{\lambda_i^*}\right)^2=W^*, \tag{18}$$

W^* being the strain energy for the reciprocal deformation. If $H \neq 0$, it is a measure of the departure from the symmetry indicated by Eq. (18). If we let

$$\alpha = H/G, \tag{19}$$

we may thus call α the *coefficient of asymmetry*.

It is sometimes useful to have W, given by Eq. (16), reduced to the form (8), originally considered. It is easily verified that

$$W = \frac{G}{4}\left[\lambda_1^2 + \frac{1}{\lambda_1^2} + 2\left(\lambda_1 + \frac{1}{\lambda_1}\right) - 6\right] + \frac{H}{4}\left[\lambda_1^2 - \frac{1}{\lambda_1^2} - 2\left(\lambda_1 - \frac{1}{\lambda_1}\right)\right] + \left[\frac{G}{4}\left(\lambda_1 + \frac{1}{\lambda_1}\right) - \frac{H}{4}\left(\lambda_1 - \frac{1}{\lambda_1}\right)\right]\gamma^2, \tag{20}$$

where γ, defined by Eq. (3) is the shear in the 2, 3 plane after a uniform stretch-squeeze with stretch λ_1.

General stress relations

Since the strain-energy is independent of the mean tension or hydrostatic pressure, it is not to be expected that the absolute stresses can be deduced from the strain-energy function. However, we can deduce the difference between any pair of principal stresses. Let σ_i be the tension on a surface normal to the i-strain axis. Then

$$\begin{aligned} dW &= \sigma_1\lambda_2\lambda_3 d\lambda_1 + \sigma_2\lambda_3\lambda_1 d\lambda_2 + \sigma_3\lambda_1\lambda_2 d\lambda_3, \\ &= \sigma_1 d\lambda_1/\lambda_1 + \sigma_2 d\lambda_2/\lambda_2 + \sigma_3 d\lambda_3/\lambda_3. \end{aligned} \tag{21}$$

In this equation we may not treat the $d\lambda_i$ as three independent variables, since they are subject to the relation, deduced from Eq. (1),

$$d\lambda_1/\lambda_1 + d\lambda_2/\lambda_2 + d\lambda_3/\lambda_3 = 0. \tag{22}$$

We may, however, set one of the $d\lambda_i = 0$, say

$$d\lambda_1 = 0, \tag{23}$$

and then

$$dW = \frac{\partial W}{\partial \lambda_2} d\lambda_2 + \frac{\partial W}{\partial \lambda_3} d\lambda_3 = \sigma_2 \frac{d\lambda_2}{\lambda_2} + \sigma_3 \frac{d\lambda_3}{\lambda_3}. \tag{24}$$

By using Eqs. (22) and (23) with (24), we find

$$\begin{aligned} \sigma_3 - \sigma_2 &= \lambda_3 \frac{\partial W}{\partial \lambda_3} - \lambda_2 \frac{\partial W}{\partial \lambda_2}, \\ &= \frac{G}{2}\left[\left(\lambda_3^2 - \frac{1}{\lambda_3^2}\right) - \left(\lambda_2^2 - \frac{1}{\lambda_2^2}\right)\right] + \frac{H}{2}\left[\left(\lambda_3^2 + \frac{1}{\lambda_3^2}\right) - \left(\lambda_2^2 + \frac{1}{\lambda_2^2}\right)\right]. \end{aligned} \tag{25}$$

In the rubber industry stresses are frequently expressed as force per unit area in the initial, undeformed state. If we represent these specific forces by T_i, then $\sigma_i = \lambda_i T_i$ and

$$\lambda_3 T_3 - \lambda_2 T_2 = \frac{G}{2}\left[\left(\lambda_3^2 - \frac{1}{\lambda_3^2}\right) - \left(\lambda_2^2 - \frac{1}{\lambda_2^2}\right)\right] + \frac{H}{2}\left[\left(\lambda_3^2 + \frac{1}{\lambda_3^2}\right) - \left(\lambda_2^2 + \frac{1}{\lambda_2^2}\right)\right]. \tag{26}$$

It can easily be shown that Eq. (25) requires no change in form if the σ_i's are interpreted, not as absolute stresses, but as impressed stresses superimposed on a hydrostatic pressure system. The like is true of Eq. (26) if the T_i's are interpreted as impressed forces.

Particular stress equations

If the stretch-squeeze prior to shearing is omitted, $\lambda_1 = 1$; and Eq. (20) reduces to

$$W = G\gamma^2/2, \tag{27}$$

and the traction is

$$\tau = \partial W/\partial \gamma = G\gamma. \tag{28}$$

G is therefore the modulus of rigidity, as was stated above.

TABLE I.

$E(\lambda)=\lambda^2+1/\lambda^2+2(\lambda+1/\lambda)-6=E(1/\lambda).$
$F(\lambda)=\lambda^2-1/\lambda^2-2(\lambda-1/\lambda)=-F(1/\lambda).$
$P(\lambda)=\lambda-1/\lambda^3+1-1/\lambda^2=(\lambda+1)(1-1/\lambda^2)=-(1/\lambda^2)P(1/\lambda).$
$Q(\lambda)=\lambda+1/\lambda^3-1-1/\lambda^2=(\lambda-1)(1-1/\lambda^3)=(1/\lambda^2)Q(1/\lambda).$
$\lambda P(\lambda)=\lambda^2-1/\lambda^2+\lambda-1/\lambda=-(1/\lambda)P(1/\lambda).$
$\lambda Q(\lambda)=\lambda^2+1/\lambda^2-\lambda-1/\lambda=(1/\lambda)Q(1/\lambda).$

λ	E	F	P	Q	λP	λQ
1.0	0	0	0	0	0	0
1.1	0.055	0.002	0.522	0.025	0.5745	0.027
1.2	.201	.012	.927	.084	1.112	.101
1.3	.420	.037	1.253	.164	1.629	.212
1.4	.699	.078	1.525	.254	2.136	.356
1.5	1.028	.139	1.759	.352	2.639	.528
1.6	1.401	.219	1.965	.454	3.144	.726
1.7	1.812	.320	2.150	.558	3.656	.948
1.8	2.260	.443	2.320	.663	4.176	1.193
1.9	2.740	.585	2.477	.768	4.706	1.460
2.0	3.250	.750	2.625	.875	5.250	1.750
2.2	4.356	1.142	2.900	1.087	6.379	2.392
2.4	5.567	1.620	3.154	1.299	7.570	3.117
2.6	6.877	2.181	3.395	1.509	8.828	3.923
2.8	8.282	2.827	3.627	1.718	10.155	4.810
3.0	9.778	3.556	3.852	1.926	11.556	5.778
4.0	18.562	8.438	4.922	2.953	19.688	11.812
5.0	29.440	15.360	5.952	3.968	29.760	19.840
6.0	42.361	24.306	6.968	4.977	41.806	29.861
7.0	57.306	35.265	7.977	5.982	55.837	41.878
8.0	72.266	48.234	8.982	6.986	71.859	55.891
9.0	93.235	63.210	9.986	7.989	89.876	71.901
10.0	114.210	80.190	10.989	8.991	109.890	89.910

It is to be noted that in finite deformation the strain axes do not lie at 45° with the direction of shear. Hence the traction on a plane parallel to the shearing displacement, given by Eq. (28), is not the maximum traction, τ_m, which by the general theory of stress is $(\sigma_2-\sigma_3)/2$. Thus, by Eq. (25),

$$\tau_m=\tau(\lambda_2+\lambda_3)/2. \tag{29}$$

Isometric simple stretch

We define an isometric simple stretch as a stretch combined with uniform contraction in the normal plane, such that the volume remains constant. Then

$$\lambda_2=\lambda_3=1/(\lambda_1)^{\frac{1}{2}}. \tag{30}$$

Therefore, $\gamma=0$; and, if we omit subscripts, Eq. (20) reduces to

$$W=\frac{G}{4}E(\lambda)+\frac{H}{4}F(\lambda), \tag{31}$$

where

$$E(\lambda)=\lambda^2+\frac{1}{\lambda^2}+2\left(\lambda+\frac{1}{\lambda}\right)-6,$$

$$F(\lambda)=\lambda^2-\frac{1}{\lambda^2}-2\left(\lambda+\frac{1}{\lambda}\right).$$

If the deformation is produced by an imposed tension in the direction of stretch, the specific tensile force is

$$T=\frac{G}{2}P_2(\lambda)+\frac{H}{2}Q_2(\lambda), \tag{32}$$

where

$$P_2(\lambda)=(\lambda+1)(1-1/\lambda^3),$$
$$Q_2(\lambda)=(\lambda-1)(1-1/\lambda^3),$$

and the tension is

$$\sigma=\lambda T=\frac{G}{2}\lambda P_2+\frac{H}{2}\lambda Q_2. \tag{33}$$

The functions P_2, Q_2, λP_2 and λQ_2 are tabulated in Table I. P_2 and Q_2 are shown graphically in Fig. 2. This figure shows that the function P_2 is closely similar to experimental force-elongation curves of rubber from 0 up to 200 or 400 percent elongation ($\lambda=3$ or 5). The Q_2 function gives an added term with which the slope in the straight portion of the curve can be adjusted.

The close fit to experimental data that can be obtained with Eq. (32) is shown by the dashed

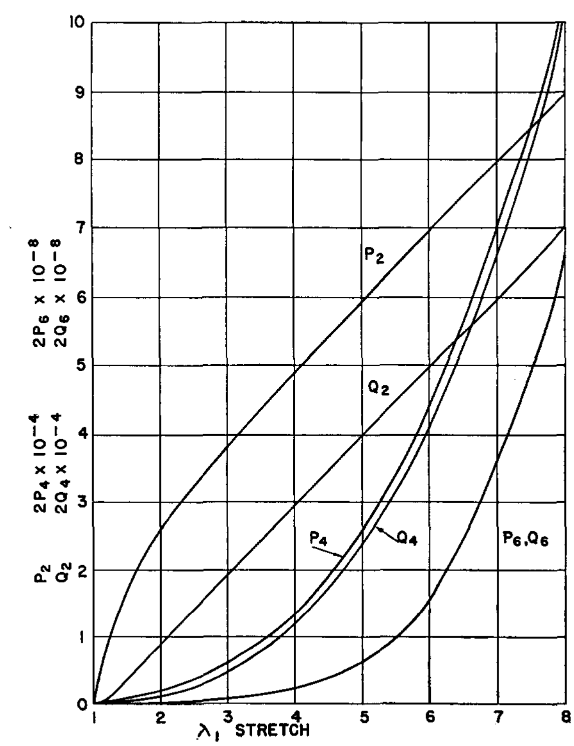

FIG. 2.

curves in Fig. 3. The data used are those published by R. H. Gerke,[6] together with similar, unpublished data on a tread, or high carbon-black, stock. These data were obtained by the equilibrium stress-strain technique developed by Gerke. They are probably less affected by hysteresis than any other stress-strain data on rubber that have so far been published. The data for the second elongation cycle only were used, and the two lengths at each stress were averaged, as indicated in Table II. In order to allow for the set, all stretch data were calculated to the basis $\lambda=1$ for the mean measured length at zero tension.

The dotted curves in Fig. 3 were obtained by applying Hencky's formula.[1] It is seen that these curves depart sooner from the experimental data than do the curves derived by the present theory.

Equation (33) has been applied to the data published by Hencky[1] and used by him to test his own formula. The results are given in Table III. The agreement of Eq. (33) with the experimental data is nearly but not quite as close as that obtained with Hencky's formula.

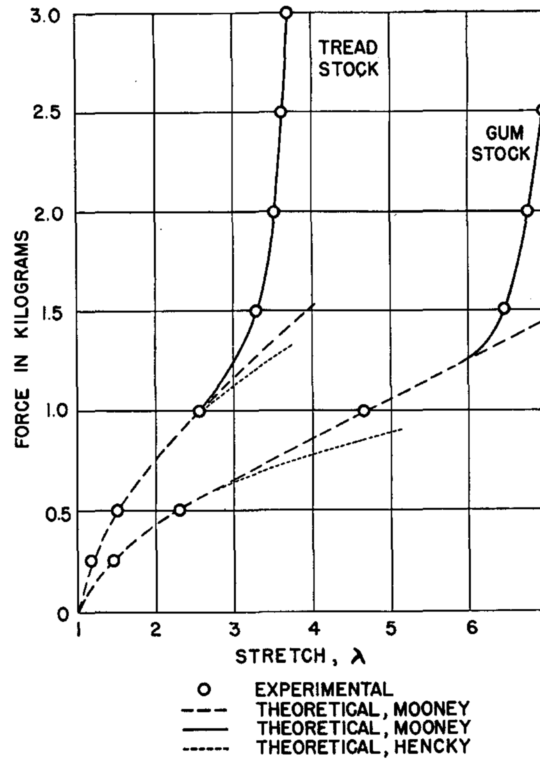

FIG. 3.

Other applications

The preceding equations can be applied wherever the state of strain is homogeneous or, if variable, is known as a function of position. For example, it is possible to calculate the energy of a cylindrical cord subjected to combined stretch and twist. On the other hand, more complex problems involving the general field equations governing stress-strain relationships cannot be solved until these general equations are developed for superelastic material.

TABLE II.

GUM STOCK

Load, g	0	250	500	1000	1500	2000	2500
Stretching Length, in.	1.02	1.48	2.30	4.75	6.55	6.95	7.10
Retracting Length, in.	1.03	1.50	2.40	4.75	6.60	6.85	—
Mean Length	1.02	1.49	2.35	4.75	6.58	6.90	7.10
Stretch, λ	1.00	1.46	2.30	4.66	6.45	6.77	6.96

TREAD STOCK

Load, g	0	250	500	1000	1500	2000	2500	3000
Stretching Length, in.	1.24	1.41	1.79	3.03	4.15	4.45	4.64	4.78
Retracting Length, in.	1.33	1.60	2.08	3.56	4.36	4.65	4.73	—
Mean Length	1.29	1.50	1.94	3.30	4.25	4.55	4.68	4.78
Stretch, λ	1.00	1.16	1.50	2.56	3.30	3.53	3.63	3.71

a_0, initial cross section, approximately 0.10×0.125 inch $=2.5\times 3.2$ mm.
Initial length between bench marks, 1 inch.

Curves in Fig. 3 given by:

	G DYNES/CM^2	G LB./IN.^{2}	α	G(HENCKY) LB./IN.^{2}
Gum stock—$a_0T(g)=138P(\lambda)+61.7Q(\lambda)$	3.33×10^6	48.6	0.448	46.7
Tread stock—$a_0T(g)=271P(\lambda)+60.6Q(\lambda)$	6.65×10^6	95.8	0.223	82.4

[6] R. H. Gerke, Ind. Eng. Chem. **22**, 73 (1930); Rub. Chem. Tech. **3**, 304 (1930).

TABLE III.

λ	LN λ	TENSION (LB./IN.²) Measured	Calculated (Hencky)	Calculated* (Mooney)
2.718	1.0	410.0	405	408.1
2.226	.8	270.8	275	275.5
1.822	.6	171.0	176	170.9
1.492	.4	100.7	101.8	96.9
1.221	.2	44.5	44.8	42.4
1.000	0	0	0	0
.819	−.2	−37.3	−36.8	−35.9
.670	−.4	−72.7	−68.7	−69.4
.549	−.6	−103.7	−98.5	−103.7
.449	−.8	−129.8	−128.0	−142.2
.368	−1.0	−162.4	−160.0	−189.5

* σ(lb./in.²) $=31.98\lambda P(\lambda)+26.86\lambda Q(\lambda)$; $\alpha=0.84$; $G=53.3$ lb./in.² (Mooney); $G=67$ lb./in.² (Hencky).

Discussion

The foregoing theory has led to expressions involving two constants of the material. Various other authors, including Hencky, have suggested empirical formulas for the load-elongation curve of rubber which contain only one constant. However, it would be a mistake to infer that Eq. (32) represents merely a better approximation, obtained by including another term in the formula.

If we assume that the postulates A to C are necessary and sufficient to describe a superelastic material, then we may state the conclusion:

Just as two constants, the modulus of rigidity and Poisson's ratio, are required to characterize the infinitesimal deformation of a hard, or moderately elastic material, so two constants, the modulus of rigidity and the coefficient of asymmetry, are required to characterize the moderate deformation of a soft, or superelastic material.

That Hencky's one-parameter formula fits experimental data so well is apparently a happy accident, depending in part upon the value of the coefficient of asymmetry of the sample used to test the formula. No matter what the asymmetry is, the exact representation of Hooke's law in simple shear would require the addition of an infinite number of terms in Hencky's present formula.

It is frequently pointed out that in elongation under tension the cross-sectional area decreases from its initial value; and it is suggested that the elongation-tension curve should be linear, or nearly so, even though the elongation-force curve is not. This is true. But even the elongation-tension curve departs appreciably from linearity, as has been emphasized by Shacklock.[7] Equation (33) shows that this is to be expected.

Various molecular explanations have been offered[8] for the shape of the force-elongation curve of rubber up to 100 or 200 percent elongation. These explanations depend upon certain assumed molecular structures and mechanisms of elasticity which are supposed to be different in rubber from what they are in harder and less superelastic materials. The present theoretical analysis shows that these theories really explain the mere fact that rubber has a linear traction-shear curve. Since in this respect rubber is not at all peculiar, the shape of the elongation-force curve requires no molecular peculiarities of rubber for its explanation.

There is no conflict between the present theory and the recent thermodynamic theories of the elasticity of rubber.[9] Rather, the two theories are supplementary. The thermodynamic theory offers an explanation for the existence of the modulus of rigidity and how it varies with temperature. The present theory, assuming the modulus, predicts how it will be manifested in different kinds of deformations.

Part II. The General or Nonlinear Traction-Shear Relation

When rubber or a similar superelastic material is strained in any manner to the point of rupture, there is observed a tightening or stiffening before rupture. That is, the derivative of the stress with respect to strain shows a marked and continuous increase. Hence, in order to extend our analysis to large deformations, we must assume that the traction-shear relation is linear only as a first approximation and departs from linearity at sufficiently large shears. We therefore replace postulate C, Part I, with postulate D:

[7] C. W. Shacklock, Trans. Ind. Rub. Inst. **8**, 568 (1933); **9**, 94 (1933); also Rub. Chem. Tech. **6**, 486 (1933).
[8] R. Houwink, Ind. Rub. J. **92**, 455 (1936), a review article.
[9] H. Mark, Oesterr. Chem. Zeitg. **40**, 321 (1937); W. Kuhn, Kolloid Zeits. **76**, 258 (1936). E. Guth, Kautschuk **13**, 201 (1937).

D. The traction in simple shear is an analytic function of the shear.

Considering again the deformation shown in Figs. 1A, 1B, 1C, we must now write the strain-energy density in the form

$$W=\sum_1^\infty \psi_{2n}(\lambda_1)+\sum_1^\infty \lambda_1{}^n(\lambda_2-\lambda_3)^{2n}\phi_{2n}(\lambda_1), \quad W(1, 1, 1)=0. \tag{34}$$

Odd powers of $(\lambda_2-\lambda_3)$ must be excluded in order to satisfy the condition of symmetry with respect to λ_2 and λ_3. It is found that the condition of symmetry with respect to λ_1, λ_2 and λ_3 requires that, corresponding to each term $(\lambda_2-\lambda_3)^{2n}$, $n>1$, there must be also additional terms of lower degree, $(\lambda_2-\lambda_3)^{2m}$, $m=1, 2, \cdots, n-1$. The necessity for these additional terms and the way they fit into the solution will be illustrated in the case $n=2$. Let

$$W_4=\psi_4(\lambda_1)+\lambda_1{}^2(\lambda_2-\lambda_3)^4\phi_{40}(\lambda_1)+\lambda_1(\lambda_2-\lambda_3)^2\phi_{42}(\lambda_1), \tag{35}$$

which, by Eq. (1), may be written

$$W_4=\psi_4+6\phi_4-2\phi_{42}+\lambda_1{}^2(\lambda_2{}^4+\lambda_3{}^4)\phi_{40}+\lambda_1(\lambda_2{}^2+\lambda_3{}^2)[-4\phi_{40}+\phi_{42}]. \tag{36}$$

By the same argument as that given in connection with Eq. (5), we must now have

$$\phi_{40}=A_4\lambda_1{}^2+B_4/\lambda_1{}^2. \tag{37}$$

With these powers of λ_1 as the only admissible terms in ϕ_{40}, the symmetry condition requires, again by the same argument, that

$$-4\phi_{40}+\phi_{42}=0. \tag{38}$$

The solution is then completed by setting

$$\psi_4=A_4\left(\frac{1}{\lambda_1{}^4}+2\lambda_1{}^2-3\right)+B_4\left(\lambda_1{}^4+\frac{2}{\lambda_1{}^2}-3\right), \tag{39}$$

and we have

$$W_4=A_4\left(\frac{1}{\lambda_1{}^4}+\frac{1}{\lambda_2{}^4}+\frac{1}{\lambda_3{}^4}-3\right)+B_4(\lambda_1{}^4+\lambda_2{}^4+\lambda_3{}^4-3). \tag{40}$$

As before, if we let

$$A_4=(G_4-H_4)/8, \quad B_4=(G_4+H_4)/8, \tag{41}$$

Eq. (37) becomes

$$W_4=\frac{G_4}{8}\sum_1^3\left(\lambda_i{}^4+\frac{1}{\lambda_i{}^4}-2\right)+\frac{H_4}{8}\sum_1^3\left(\lambda_i{}^4-\frac{1}{\lambda_i{}^4}\right). \tag{42}$$

The treatment for higher values of n proceeds in a like manner. Thus, for any positive, integral n we may expand

$$[(\lambda_1)^{\frac{1}{2}}(\lambda_2-\lambda_3)]^{2n}$$

and regroup the terms, as in Eq. (36), in the forms

$$\lambda_1{}^{n-p}\frac{(2n)!}{p!(2n-p)!}(\lambda_2{}^{2n-2p}+\lambda_3{}^{2n-2p}), \quad p=0, 1, \cdots, (n-1). \tag{43}$$

We set

$$\phi_{2n,\,0}=A_{2n}\lambda_1{}^n+B_{2n}/\lambda_1{}^n. \tag{44}$$

Then we add to the solution, terms of the form

$$C_{2n,\,p}\lambda_1{}^{n-p}(\lambda_2{}^{2n-2p}+\lambda_3{}^{2n-2p})(A_{2n}\lambda_1{}^n+B_{2n}/\lambda_1{}^n), \quad p=1, \cdots, (n-1). \tag{45}$$

By the proper choice of the $C_{2n,\,p}$, we cause all terms to cancel except the one for which $p=0$. Finally, by the suitable choice of ψ_{2n}, we reduce W_{2n} to the form

$$W_{2n}=A_{2n}\left(\frac{1}{\lambda_1^{2n}}+\frac{1}{\lambda_2^{2n}}+\frac{1}{\lambda_3^{2n}}-3\right)+B_{2n}(\lambda_1^{2n}+\lambda_2^{2n}+\lambda_3^{2n}-3). \tag{46}$$

The complete solution for W may therefore be written

$$W=\sum_{n=1}^{\infty}\frac{G_{2n}}{4n}\sum_{i=1}^{3}\left(\lambda_i^{2n}+\frac{1}{\lambda_i^{2n}}-2\right)+\sum_{n=1}^{\infty}\frac{H_{2n}}{4n}\sum_{i=1}^{3}\left(\lambda_i^{2n}-\frac{1}{\lambda_i^{2n}}\right). \tag{47}$$

W is here written as an infinite series, but it may terminate at some finite n.

As was done in Part I, the Eq. (47) can be converted to the form (34.1), in which the energy is divided into two portions, that due to the stretch-squeeze and that due to the shear in the plane normal to the stretch. In this case the transformation leads* to

$$\begin{aligned}W=&\sum_{n=1}^{\infty}\frac{G_{2n}}{4n}\left[\lambda_1^{2n}+\frac{1}{\lambda_1^{2n}}+2\left(\lambda_1^{n}+\frac{1}{\lambda_1^{n}}\right)-6\right]+\sum_{n=1}^{\infty}\frac{H_{2n}}{4n}\left[\lambda_1^{2n}-\frac{1}{\lambda_1^{2n}}-2\left(\lambda_1^{n}-\frac{1}{\lambda_1^{n}}\right)\right]\\&+\sum_{q=1}^{\infty}\frac{\gamma^{2q}}{(2q)!}\sum_{n=q}^{\infty}\left\{\frac{G_{2n}}{2n}\left(\lambda_1^{n}+\frac{1}{\lambda_1^{n}}\right)-\frac{H_{2n}}{2n}\left(\lambda_1^{n}-\frac{1}{\lambda_1^{n}}\right)\right\}n^2(n^2-1^2)\cdots[n^2-(q-1)^2],\end{aligned} \tag{48}$$

in which γ is the shear, as defined by Eq. (3).

If the deformation is a simple shear applied to a sample not previously deformed, $\lambda_1=1$, and Eq. (48) reduces to the form

$$W=\sum_{q=1}^{\infty}\frac{\gamma^{2q}}{2q(2q-1)!}\sum_{n=q}^{\infty}G_{2n}n(n^2-1^2)\cdots[n^2-(q-1)^2]. \tag{49}$$

Stress equations

The tensile force at stretch λ in isometric simple stretch is obtained from Eq. (48) by setting $\gamma=0$ and differentiating. Thus we find for the force per unit initial area,

$$T=\sum_{1}^{\infty}\frac{G_{2n}}{2}P_{2n}(\lambda)+\sum_{1}^{\infty}\frac{H_{2n}}{2}Q_{2n}(\lambda), \tag{50}$$

where

$$P_{2n}(\lambda)=\frac{1}{\lambda}\left(\lambda^{2n}-\frac{1}{\lambda^{n}}\right)\left(1+\frac{1}{\lambda^{n}}\right),\quad Q_{2n}(\lambda)=\frac{1}{\lambda}\left(\lambda^{2n}-\frac{1}{\lambda^{n}}\right)\left(1-\frac{1}{\lambda^{n}}\right). \tag{51}$$

* The proof rests upon the identities, valid for all-positive, integral n,

$$\begin{cases}\lambda_2^{2n}+\lambda_3^{2n}-\dfrac{2}{\lambda_1^{n}}=\dfrac{2}{\lambda_1^{n}}\displaystyle\sum_{q=1}^{n}\gamma^{2q}\frac{n^2(n^2-1)\cdots[n^2-(q-1)^2]}{(2q)!},\\[2ex]\dfrac{1}{\lambda_2^{2n}}+\dfrac{1}{\lambda_3^{2n}}-2\lambda_1^{2n}=2\lambda_1^{n}\displaystyle\sum_{q=1}^{n}\gamma^{2q}\frac{n^2(n^2-1)\cdots[n^2-(q-1)^2]}{(2q)!}.\end{cases}$$

To establish these identities, the following theorem is used: Let

$$J(n,q)\equiv\sum_{r=0}^{q}\frac{q!}{r!(q-r)!}\frac{(2n-1)(2n-3)\cdots(2n-2r+1)}{1\cdot3\cdots(2r-1)}.$$

Then for all positive, integral values of q, the equation

$$J(n,q)=0$$

has the roots

$$n=0,\ -1,\ -2\cdots-(q-1);$$

and J is the product of the factors,

$$J(n,q)\equiv\frac{2^qn(n+1)(n+2)\cdots[n+(q-1)]}{1\cdot3\cdot5\cdots(2q-1)}.$$

The theorem can be proved by mathematical induction.

The tension, or force per unit actual area, is

$$\sigma=\lambda T=\sum_1^{\infty}\frac{G_{2n}}{2}\lambda P_{2n}+\sum_1^{\infty}\frac{H_{2n}}{2}\lambda Q_{2n}. \tag{52}$$

These equations for T and σ apply, of course, not only to elongation but also to compression, or stretch less than unity.

The traction as a function of shear in the plane normal to a stretch is, from Eq. (48),

$$\tau(\gamma,\lambda_1)=\sum_{q=1}^{\infty}\frac{\gamma^{2q-1}}{(2q-1)!}\sum_{n=q}^{\infty}\left\{\frac{G_{2n}}{2n}\left(\lambda_1{}^n+\frac{1}{\lambda_1{}^n}\right)-\frac{H_{2n}}{2n}\left(\lambda_1{}^n-\frac{1}{\lambda_1{}^n}\right)\right\}\{n^2(n^2-1)\cdots[n^2-(q-1)^2]\}. \tag{53}$$

If the shear is applied to a sample not previously stretched,

$$\tau(\gamma,1)=\sum_{q=1}^{\infty}\frac{\gamma^{2q-1}}{(2q-1)!}\sum_{n=q}^{\infty}G_{2n}n^2(n^2-1^2)\cdots[n^2-(q-1)^2]. \tag{54}$$

The stresses in other situations can be obtained by applying Eq. (23) to the general expression for W, Eq. (48).

If the $H_{2n}=0$, it is easily shown, as in the linear case, that two deformations reciprocal to each other have the same energies.

Some of the functions P_{2n}, Q_{2n}, λP_{2n} and λQ_{2n} are shown in Fig. 2. The graphs show that for large values of n and λ, we have approximately $P_{2n}\doteq Q_{2n}$. By referring to Eq. (51) we see that for $\lambda>3$ and $n\geqq 3$, we have approximately

$$P_{2n}\doteq Q_{2n}\doteq\lambda^{2n-1} \tag{55}$$

and for $\lambda\leqq\frac{1}{3}$, $n\geqq 3$,

$$-P_{2n}\doteq Q_{2n}\doteq 1/(\lambda_{2n+1}). \tag{56}$$

We consider the general problem of determining the G_{2n} and H_{2n} from appropriate experimental data. Owing to the limitations of current experimental techniques, there is only one practically feasible method. By Eq. (52) we form expressions for the sum and the difference in the tension in pairs of simple isometric extension and contraction reciprocal to each other. Thus we obtain

$$\begin{aligned}\sigma(\lambda)+\sigma(1/\lambda)&=\sum H_{2n}\lambda Q_{2n}(\lambda),\\ \sigma(\lambda)-\sigma(1/\lambda)&=\sum G_{2n}\lambda P_{2n}(\lambda).\end{aligned} \tag{57}$$

If we have a set of experimental values of σ extending both to large elongations and large compressions, we can obtain from Eq. (57) a set of linear algebraic equations for the G_{2n} and H_{2n}. The number of terms required to obtain a satisfactory fit will doubtless vary from one set of data to another. If the G_{2n} obtained from Eq. (57.2) are substituted into Eq. (54), the resulting expression for τ should agree with an experimental traction-shear curve. This check would constitute a simple but fairly complete test of the theory.

Applications

Unfortunately there are no published data that are sufficiently extensive and free from hysteresis to determine both the G_{2n} and H_{2n} beyond the linear case. The curves and data published by Sheppard and Clapson[10] apply to the first deformation of the samples. Their results are therefore considerably affected by hysteresis. Consequently, although their data can be satisfactorily represented by the Eqs. (57), any theoretical interpretation of the equations in this application would be of doubtful validity, since the theory does not include hysteresis.

However, we can get a partial test of the suitability of our general equations for representing departures from the linear case. To do so, we treat the complete force-elongation curves discussed in Part I. We cannot use Eqs. (57), since the compression data are lacking; and shall be able to determine only the sum of certain $G_{2n}+H_{2n}$, not their separate values.

If we define a residue, R, as the difference between the experimental curve and the linear theoretical curve given by Eq. (32) in Part I, then it is found that R can be closely represented by the equation

$$R=C\lambda^m. \tag{58}$$

[10] J. R. Sheppard and W. J. Clapson, J. Ind. Eng. Chem. **24**, 782 (1932).

For the two stocks considered, we have

Stock	C	m
Gum	9.1×10^{-19}	25
Tread	3.33×10^{-7}	17.

The full lines in Fig. 3 are drawn in accordance with these values. We thus see that these particular experimental data are completely represented by an equation of the form

$$T=\frac{G_2}{2}P_2(\lambda)+\frac{H_2}{2}Q_2(\lambda)+C\lambda^m. \tag{59}$$

When $\lambda=1$, T reduces, not to zero, as it should, but to the value C. However, in the two cases cited, the error is extremely small. From the approximation (55) it follows that

$$(G_{2n}+A_{2n})/2n=C, \tag{60}$$

where $2n=m+1$.

The large values of m required in the examples given suggest that the term $C\lambda^m$ does not have any simple theoretical interpretation, and the evaluation of the exponent m should be considered essentially as an empirical feature of the equation. Also, it would be premature, if not incorrect, to conclude at present that a single term of the type $C\lambda^m$ will suffice in all cases.

It is possible from Eq. (53) to predict some interesting effects of stretch on the modulus of rigidity in the plane normal to the stretch. However, no data are available for testing the predictions.

The theory of superelastic deformations would be made more useful if hysteresis effects were included; but present knowledge of the laws of hysteresis in rubber is insufficient to indicate the appropriate modifications of the equations.

Glossary

C_1, C_2, C_3 = constants.
G = modulus of rigidity in the linear case.
H = modulus characterizing asymmetry of reciprocal deformations.
$P_2(\lambda)=(\lambda+1)(1-1/\lambda^3)$.
$Q_2(\lambda)=(\lambda-1)(1-1/\lambda^3)$.
γ = shear in a plane normal to the stretch in a previous isometric simple stretch.
T = specific tensile force, or force per initial (unstrained) unit area.
W = strain-energy density.
$\alpha=H/G$ = coefficient of asymmetry.
λ_i = principal stretch = 1 + principal extension.
τ = traction, or shearing stress.
σ = tension.

Breakdown Potentials of Gases Under Alternating Voltages

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Starting potentials for hydrogen, nitrogen, helium, and argon of commercial purity at frequencies up to one million cycles per second were investigated using a discharge tube with spherical electrodes. Five gap distances were employed, ranging from 10 mm to 50 mm. The slope of the log pressure *versus* log distance curve was found to be independent of frequency and also of the gas for small gap distances.

Introduction

Comparatively few studies have been made of breakdown potential in gases under alternating voltages. Reukema[1] found that for 6.25 cm diameter spheres in air with gap lengths ranging from 0.25 to 2.5 cm the sparking potential began to lower, below that at 60 cycles, when the frequency approached 20,000 cycles and that the lowering continued to frequencies as high as 60,000 cycles, after which no further change occurred up to 425,000 cycles. Hutton, Mitra, and Ylostalo[2] made some studies on the value of starting potentials as a function of frequency but the most work in this field has been done by J. Thomson.[3] He compared the alternating and

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[1] L. E. Reukema, Trans. Am. Inst. Elect. Eng. **45**, 38 (1928).
[2] Hutton, Mitra, Ylostalo. Comptes rendus **176**, 1871 (1923); **178**, 476 (1924).
[3] J. Thomson, Phil. Mag. **10**, 280 (1930); **18**, 696 (1934); **23**, 1 (1937).