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STRESS-STRAIN DATA FOR VULCANISED RUBBER UNDER VARIOUS TYPES OF DEFORMATION.

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Introduction.

In a previous paper [1] the statistical method developed by Wall [2] for treating the problem of the elasticity of a 3-dimensional network of long-chain molecules was extended to cover the case of a homogeneous deformation of the most general type. The result was expressed by an equation representing the work of deformation per c.c. of the material (W) as a function of the three principal strains, namely

$$W = \tfrac{1}{2}G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad . \quad . \quad . \quad (1)$$

where λ_1, λ_2 and λ_3 are the semi-axes of the strain ellipsoid, and G is a physical constant of the material which is related to N, the number of molecules per c.c.

It is hardly necessary to emphasise the importance of this result, both in connection with the theory of large deformations of matter in general, and of rubbers in particular, and also as a means for elucidating more clearly the structure of rubber from the molecular standpoint, and the mechanism of its elasticity. The experiments described in this paper were undertaken with the two-fold purpose firstly, of obtaining further evidence as to the validity of the molecular-kinetic theory as an explanation of the elasticity of rubber, and secondly, in order to find out whether equation (1) could usefully be employed for the calculation of the stress-strain properties of rubber in cases of practical interest.

Scope of the Work.

The types of deformation studied were (1) 2-dimensional extension of a sheet, as in a balloon, (2) simple elongation, (3) pure shear, and (4) elongation combined with shear in a plane at right angles to the elongation. Two types of rubber were studied, one of a type which was expected to give the closest approximation to ideally elastic behaviour, and the other of a type more commonly used in the industry. These rubbers were compounded according to the following formulæ :—

[1] Treloar, *Trans. Faraday Soc.*, 1943, **39**, 241.
[2] Wall, *J. Chem. Physics*, 1942, **10**, 132 and 485.

8 % S RUBBER.

	Parts by Weight.
Rubber (smoked sheet)	100
Sulphur . . .	8
Vulcanised 3 hours at 50 lbs. steam pressure (147° C.)	

LATEX RUBBER.

	Parts by Weight.
Rubber	100
Sulphur	2
ZnO	2·5
Piperidine pentamethylene dithiocarbamate	1
Vulcanised 30 mins. at 100° C.	

The 8 % S rubber was chosen because it is of a type known to show highly reversible elastic behaviour, and absence of crystallisation on stretching up to 400 % extension at least.[3] It has been shown by the study of the stress-temperature relations for this rubber,[3, 4] that its elasticity is determined quantitatively by the entropy effect, as required by the kinetic theory. It appeared therefore to be the most suitable rubber for testing the theoretical stress-strain formulæ. Technically, the 8 % S rubber has certain disadvantages, notably a low tensile strength, and it seemed desirable to study also a rubber having good properties from the practical standpoint, namely a latex rubber.

The latex rubber showed very marked creep and hysteresis effects, probably due mainly to crystallisation. These effects were much less noticeable at 50° C. than at room temperature. For this reason the data on this rubber were all obtained at the higher temperature, the experiments being carried out in an air thermostat. The experiments on the 8 % S rubber were made at a room temperature of 20 ± 1° C. In this respect the data for the two rubbers are not strictly comparable.

All the experiments on each of the rubbers were made on specimens cut from a single sheet.

2-Dimensional Extension.

For the production of a 2-dimensional extension the method employed was the inflation into the form of a balloon of a circular sheet clamped round its circumference. A detailed study has been made of the state of strain over the surface of such an inflated sheet; the results of this study, as well as a number of experimental details relevant to the present work, will be published elsewhere.[5] It was found that the strain was substantially uniform over an area in the neighbourhood of the centre or "pole" of the inflated sheet; in the present experiments the measurements of extension were made on two marked points lying on opposite sides of a circle of 2 mm. radius with the pole as centre, the diameter of the unstretched sheet being 25 mm. Besides the extension, it was necessary to measure also the radius of curvature of the polar region (r), and the air pressure in the balloon (P), so that the tension T in the sheet might be obtained from the usual relation

$$P = 2T/r \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

The region of the balloon over which the shape could be considered approximately spherical covered a larger area than the region of uniform strain.[5] The measurement of r was therefore made by observation of points at a greater distance from the pole than the marked points used for the calculation of the extension ratio. This procedure gave an improvement in accuracy, particularly at low extensions.

In carrying out the experiments air was admitted to the balloon at a convenient rate until the desired degree of distension had been reached. The air supply was then cut off while measurements of the extension and of P and r, were made. The process was repeated at successively higher

[3] Meyer and Ferri, *Helv. Chim. Acta*, 1935, **18**, 570.
[4] Anthony Caston and Guth, *J. Physic. Chem.*, 1942, **46**, 826.
[5] Treloar, *Trans. I.R.I. in press.*

distensions. The reverse part of the curve with decreasing distension, was obtained as the air was allowed to escape by stages. The time between successive points was not controlled, but was about 4 minutes.

It has often been observed with rubbers exhibiting imperfect elastic behaviour that the first stress-strain curve differs noticeably from the second and later curves. For this reason the sheet was subjected to an *initial distension* for about 2 minutes at the operating temperature, before measurements were begun. This introduced a slight non-recoverable strain. The extension ratios were calculated on the basis of the new (strained) marked length, and the figure for the thickness was corrected accordingly.

If P is measured in mm. of mercury, and r in cm., the tension T in kg. per cm. of the sheet (analogous to surface tension), taking the density of mercury at 20° C. to be 13·56 g./c.c., is, from (2),

$$T = 0{\cdot}678 \text{ kg./cm.}$$

It is convenient to refer the measurements to a sheet of initial thickness 1 cm., hence if t is the tension for such a sheet, and d_0 is the initial thickness of the actual sheet in cm.,

$$t = 0{\cdot}678\, Pr/d_0 \text{ kg./cm.} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

per cm. of original thickness.

Compressive Force. Since a 2-dimensional extension may be considered to be equivalent to a unidirectional compression at right angles to the plane of the sheet,[1] it is possible to calculate the equivalent compressive force f from the experimental data, f representing the force on a surface of original area 1 cm². The compression ratio α is obtainable from the measured linear extension ratio $1/\sqrt{\alpha}$ (assuming no volume change on extension).* The tensile *stress* in the sheet is t/α, and the equivalent compressive stress is αf. Since these two are equal,

$$f = t/\alpha^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Table I gives the relevant experimental data, and the calculated values of f and t, for the 8 % S rubber.

TABLE I.—TENSION IN SHEET (t) AND EQUIVALENT FORCE OF COMPRESSION FOR 8 % S RUBBER AT 20° C. ORIGINAL THICKNESS 0·82 MM.

Air Press. P (mm.).	Radius of curvature r (cm.).	Linear Extension ratio $1/\sqrt{\alpha}$.	Compression Ratio α.	Tension in Sheet t (kg./cm. per cm.).	Equivalent Compressive force, f (kg./cm.²).
31	$3{\cdot}6_1$	$1{\cdot}02_7$	0·95	0·92	1·02
71	$2{\cdot}5_6$	$1{\cdot}06_5$	0·88	1·50	1·93
125	2·10	$1{\cdot}11_5$	0·80	2·17	3·90
164	1·69	1·14	0·77	2·30	5·76
210	$1\ 59_6$	1 20	0·69	2·77	—
270	$1{\cdot}51_6$	1·31	0·58	3·38	10·0
304	$1{\cdot}45_4$	1·42	0·49	3·65	14·9
335	$1{\cdot}41_6$	1·68	0·35	3·93	31·3
341	$1{\cdot}42_2$	1·94	0·265	4·01	57·0
332	1·43	2·49	0·161	3·93	153
316	1·60	3·03	0·109	4·17	352
303	1·71	3·43	0·085	4·28	596
293	1·92	3·75	0·071	4·64	910
285	2·10	4·07	0·060	4·94	1360
280	2·28	4·26	0·055	5·27	1740
276	2·44	4·45	0·050	5·54	2180

* For the validity of this assumption see Holt and McPherson, *Nat. Bur. Stds. J. Res.*, 1936, **17**, 657.

The experimental data for the two rubbers are represented in Figs. 1 and 2, which show the tension in the sheet (t) as a function of the linear extension ratio $1/\sqrt{\alpha}$. In Fig. 1, which refers to the 8 % S rubber, curve (a) shows the points obtained with extensions up to the bursting point, whilst curve (b) shows the degree of agreement between the curves obtained with increasing and with decreasing extensions. The continuous curve in (a) represents the theoretical relation [1]

$$t = G(1 - \alpha^3) \quad (5)$$

when G has the value 4·0 kg./cm². For this rubber the data are in agreement with the form predicted by the theory up to an extension ratio of 3·0 ; thereafter there is a progressive departure from the theoretical curve.

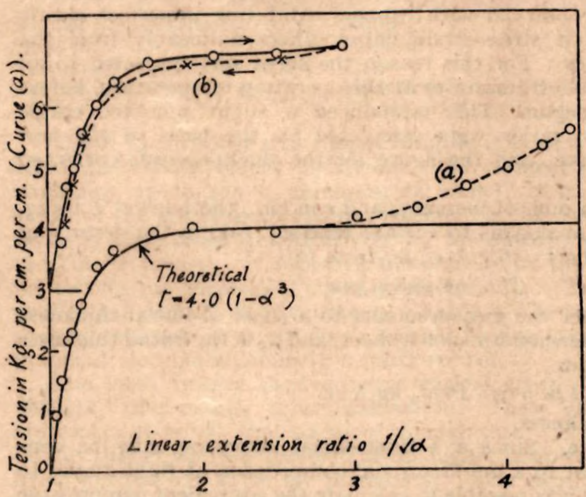

FIG. 1.—2-dimensional extension. 8 % S rubber, 20° C.

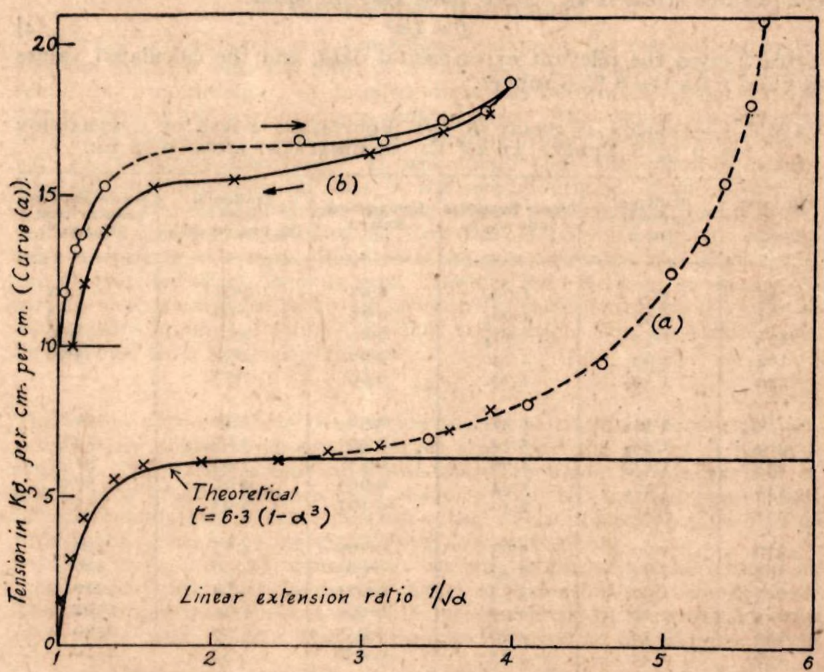

FIG. 2.—2-dimensional extension. Latex rubber, 50° C. For curve (a), × with glass clamp, O with metal clamp.

The latex rubber showed a much less perfectly reversible type of behaviour (Fig. 2 (*b*)), but the data show a similar approach to the theoretical curve up to an extension ratio of 3·0 (Fig. 2 (*a*)), and a similar departure above this point. Owing to the greater strength of this rubber it was possible to continue the curve to greater extensions before bursting occurred.

(To obtain the curve (*a*) two different clamps were used, of which details are given in reference (5). The first, an open-ended glass tube on which the rubber was bound, enabled the small distensions to be measured, but was unsatisfactory at high tensions, whilst the sceond, a metal clamp, was suitable at higher extensions only. The rubber was removed from the first clamp, and placed in the second in the middle portion of the curve. The points obtained with each clamp are separately indicated in Fig. 2.)

Simple Elongation.*

The specimens used for the simple elongation had a width of 3 mm., a thickness of about 0·8 mm., and a marked length of 10 mm. The cross-sectional area was determined either by weighing, or by measurement with a microscope and thickness gauge. The stretched lengths were measured with a travelling microscope, while weights were added to the lower clamp. The rate of extension was not controlled, but the time taken for each reading was about 1 minute. The samples were given an initial extension of about 400 % before readings were taken, and as in the 2-dimensional extension the initial length and cross-sectional area were corrected for any non-recoverable strain thus introduced.

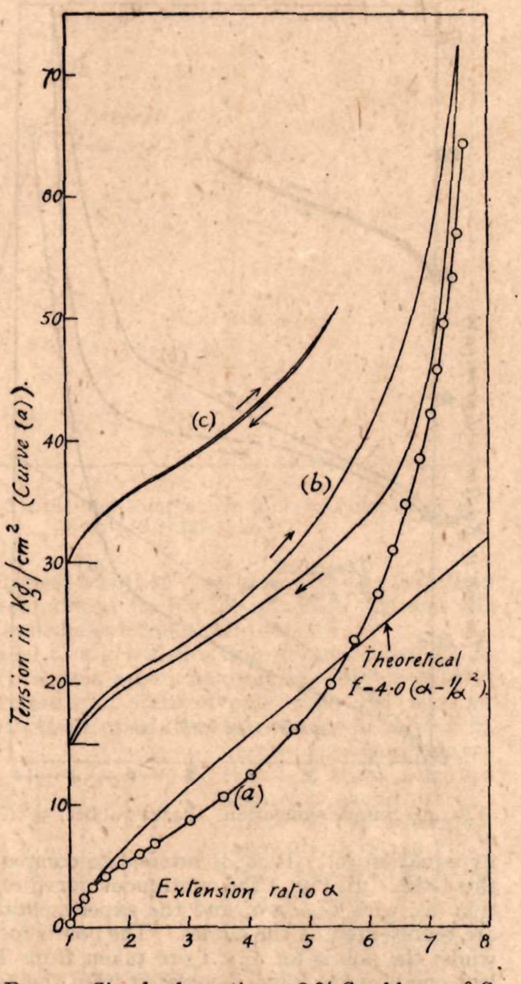

FIG. 3.—Simple elongation. 8 % S rubber, 20° C.

The extension was continued until breaking occurred, but the breaking point thus determined did not represent the highest extension that might have been obtained if dumb-bell shaped specimens had been employed.

Fig. 3 represents the data for the 8 % S rubber. Curve (*a*) shows the

* By "simple elongation" is meant an extension in one direction, accompanied by free contraction in directions at right angles.

complete stress-strain curve obtained with increasing extensions. Curves (*b*) and (*c*) show that the curve is reversible up to at least 450 % extension, but is not accurately reversible when the maximum extension is approached.

The theoretical form of the elongation curve is [1]

$$f = G(\alpha - 1/\alpha^2) \quad . \quad . \quad . \quad . \quad (6)$$

If G is given the value 4·0 kg./cm². which was obtained from the 2-dimensional extension, it is seen from Fig. 3 that the experimental curve begins to fall below the theoretical at about 40 % extension, the departure becoming greater and reaching a maximum at about 250 % extension, where the difference between the theoretical and experimental tension is 24 %. Thereafter the experimental curve turns upwards, crosses the theoretical, and finally departs from it at an increasing rate.*

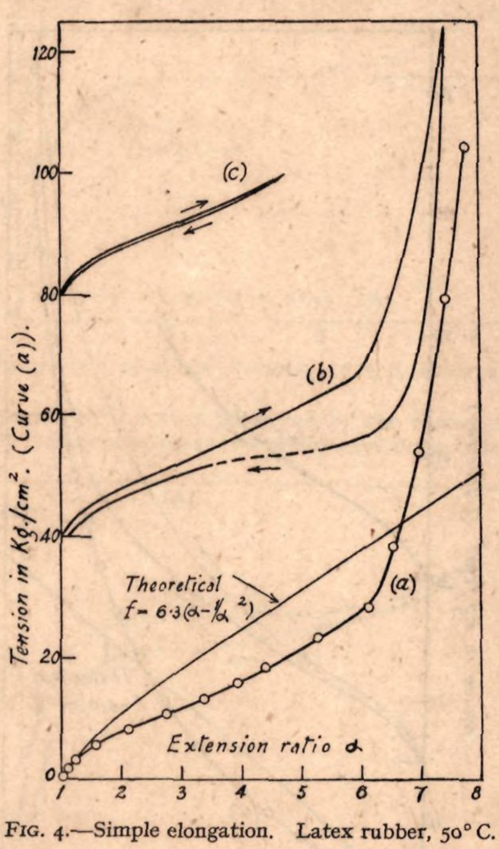

FIG. 4.—Simple elongation. Latex rubber, 50° C.

In the case of the latex rubber (Fig. 4) the same general phenomena were observed, but the discrepancies between the experimental and theoretical curves were more serious. The maximum difference (excluding the high-elongation end) was 35 %. The curve (*b*) shows that hysteresis was more serious than with the 8 % S rubber, and it was observed in taking the readings that slow drift or "creep" effects were much more noticeable.

Compression and Elongation. Theoretically the elongation and compression curves form a continuous curve represented by equation (6). It is of interest to compare the experimental data on this basis. In Fig. 5 the continuous curve represents the theoretical relation (6), with $G = 4·0$, and the experimental data for the 8 % S rubber are represented by the circles. The points for $\alpha > 1$ are taken from Fig. 3, whilst the points for $\alpha < 1$ are taken from Table I, in which the equivalent compressive force, calculated from the 2-dimensional extension data,

* The author's attention has been drawn to an early paper by Baker (*Proc. Physic. Soc.*, 1899, **17**, 107), in which the approximate constancy of frequency of vibration of a stretched rubber cord over a wide range of extension is discussed. A calculation on the basis of formula (6) yields the result $n = k\sqrt{1 - 1/\alpha^3}$, n being the frequency of vibration and k a constant. Thus n becomes substantially independent of frequency for extensions higher than about 100 %. Moreover, at lower extensions Baker's experimental data agree more closely with this formula than with the formula suggested by him, *i.e.* $n = k'\sqrt{1 - 1/\alpha}$, based on the assumption of a linear stress-strain relation.

is given. The continuity between the extension and compression branches of the curve is satisfactorily exhibited.

Pure Shear.

A convenient method of applying a large shear to rubber is to stretch a short wide strip between clamps. The form of the sheet under these conditions is illustrated in Fig. 6. The strip had a width of 75 mm. and an unstretched "length," between clamps, of 5 mm. It was stretched by applying weights to the lower clamp. To determine the state of strain in the stretched sheet vertical lines were marked on the unstretched sheet at distances of 7·5 mm. The position of these lines on the stretched sheet was then measured with the travelling microscope. The result is reproduced in Fig. 6, in which AB and CD represent the clamped edges, and the extension ratio was 6·2.

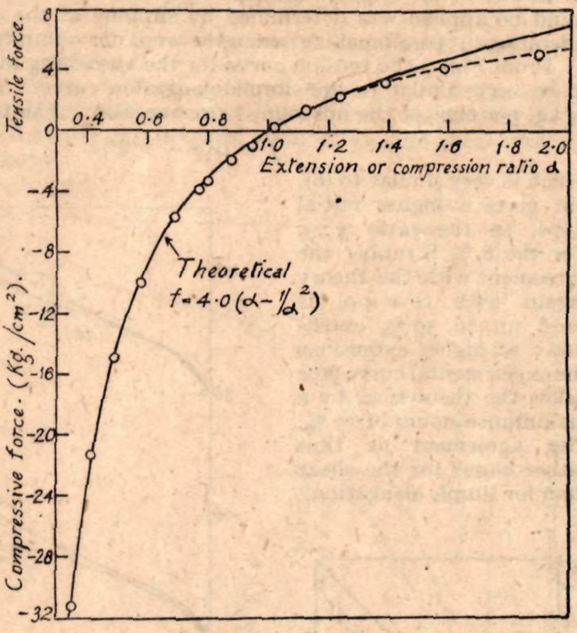

FIG. 5.—Tensile and compressive force as function of α. 8 % S rubber, 20° C.

In a pure shear lines parallel to a given direction (in this case AB) do not change their length.[1] To a first approximation the stretched strip represented in Fig. 6 is therefore in a state of pure shear, for with an extension of 520 % in the vertical direction there is a change of only 12 % in the horizontal direction. A more accurate approach would be obtained if the outermost segments shown in Fig. 6 could be removed; this may be done, in effect, by working with two strips of different widths and subtracting the tension on the narrower from the tension on the wider strip to obtain the tension on the middle portion. This was not done in the present experiment, because the correction was found to be insignificant, whilst the operation of subtraction multiplied the experimental error. But it was done in the case of combined shear and elongation (section 6), where the curvature of the edges was much greater.

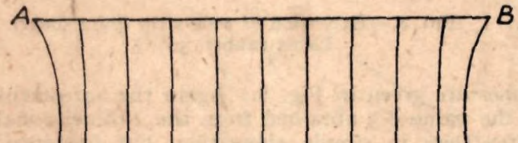

FIG. 6.—State of strain in wide sheet at $\alpha = 6{\cdot}2$.

It should be pointed out that the stretching of a wide strip gives a pure shear only if the volume remains unchanged.

The experimental technique employed in the stretching of the wide strip was the same as in the simple elongation. Measurements were made on marks at an original distance of 4 mm. The maximum load which could be applied was determined by slipping at the clamp or other considerations ; true breaking strengths were not obtained.

From Fig. 7 the tension curve for the stretching of a wide strip is seen to be very similar to the simple elongation curve. The tension is given in kg. per cm². of the unstrained cross-section. The theoretical relation is

$$f = G(\alpha - 1/\alpha^3) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which is very similar to (6), but gives a higher initial slope, in the ratio 4 : 3. For the 8 % S rubber the agreement with the theory (again with $G = 4{\cdot}0$) is good up to 50 % extension ; at higher extensions the experimental curve falls below the theoretical by a maximum amount of 17 %. The agreement is thus rather closer for the shear than for simple elongation.

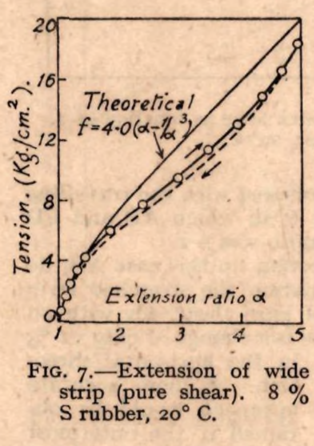

FIG. 7.—Extension of wide strip (pure shear). 8 % S rubber, 20° C.

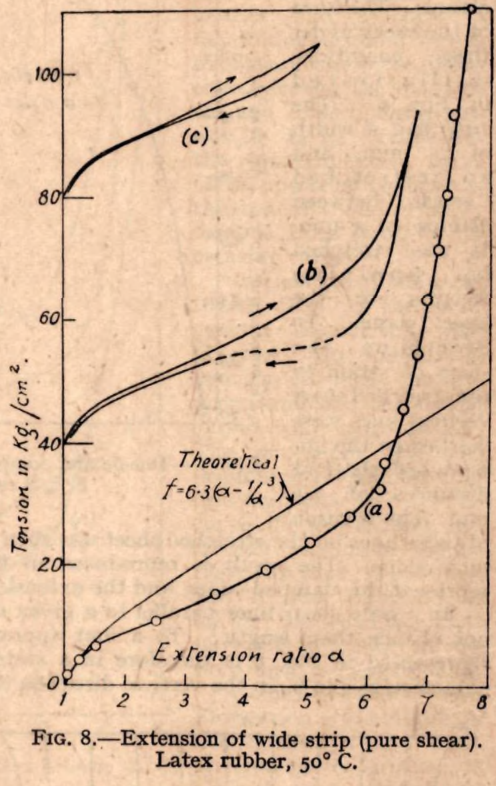

FIG. 8.—Extension of wide strip (pure shear). Latex rubber, 50° C.

Data for the latex rubber are given in Fig. 8. Again the agreement with theory, when G has the value 6·3 obtained from the 2-dimensional extension, is slightly better than in simple elongation, but hysteresis effects (curve (*b*)) are considerable.

The Shear Stress. Thus far the principal tension in the direction of stretching only has been considered. The shear stress and shear strain will now be derived. The shear strain σ is given by the relation

$$\sigma = \alpha - 1/\alpha \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where α is the principal extension ratio. To find the shear stress F_σ, use is made of the work of deformation per c.c., W. We have then for the tensile force f,

$$f = \mathrm{d}W/\mathrm{d}\alpha,$$

and for the shear stress

$$F_\sigma = \mathrm{d}W/\mathrm{d}\sigma.$$

Hence,

$$F_\sigma = f \cdot \frac{d\alpha}{d\sigma} = f \cdot \frac{\alpha^2}{1 + \alpha^2} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

from (8). Equations (8) and (9) enable the relation between shear stress and shear strain to be obtained.

The results are shown in Figs. 9 (curve (*a*)) and 10. These curves were obtained from the smooth curves in Figs. 7 and 8 respectively. The theory requires a linear relation between shear stress and shear strain, as indicated in the figures.

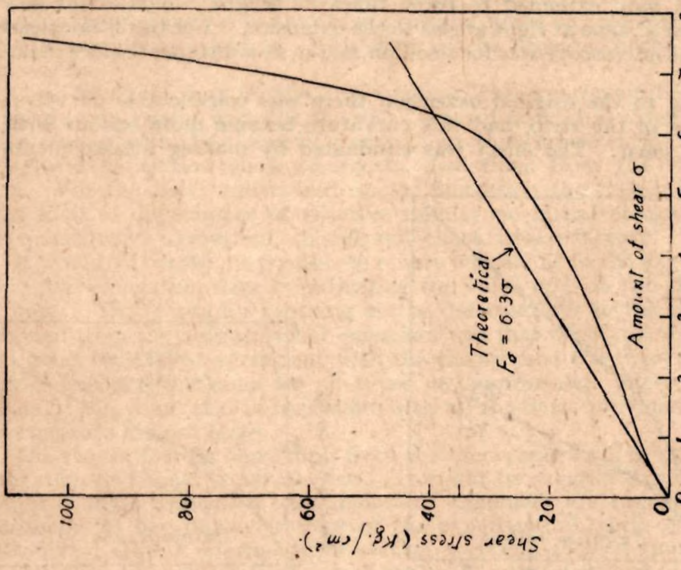

FIG. 10.—Shear stress *vs.* shear strain. Latex rubber, 50° C.

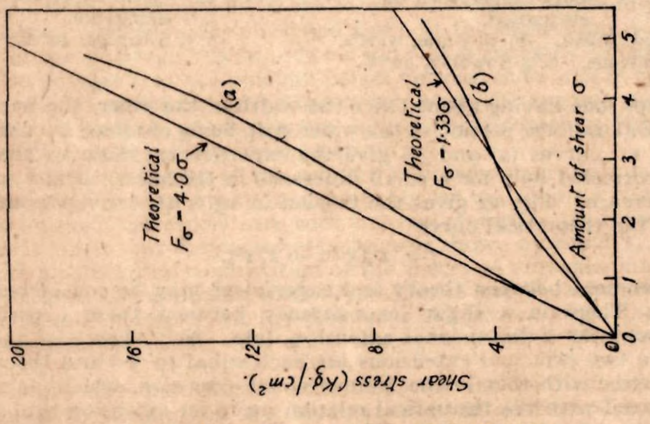

FIG. 9.—Shear stress *vs.* shear strain. (*a*) Pure shear. (*b*) Shear superposed on elongation. 8 % S rubber, 20° C.

Combined Elongation and Shear.

The experiment described in this section was designed to test the theoretical expectation in the case of a shear applied in a plane at right angles to an initial simple elongation. The theory shows that the effective rigidity to shear should be inversely proportional to the original extension ratio.[1] The experiment involved stretching a wide strip, as described in section 5, with the difference that the rubber was stretched parallel to AB (Fig. 6) before clamping.

The experiment was performed on the 8 % S rubber. A strip of rubber, suitably marked, was first extended to as nearly as possible three times its original length, then clamped along its edges in clamps of width 75 mm. The edges of the clamps lay along lines originally separated by 5 mm., the distance between clamps before the application of the shear was therefore $5/\sqrt{3}$ mm. The protruding ends of the stretched strip were then cut off along a marked line with scissors. The result was a strip of width 75 mm. extended to three times its length, which could now be sheared in a plane at right angles to the extension. For the shear measurements the microscope was focussed on marks at a distance (before shearing) of 3 mm.

Owing to the original extension there was considerable curvature at the edges of the strip, and this curvature became more serious with increasing shear. The effect was eliminated by making measurements on

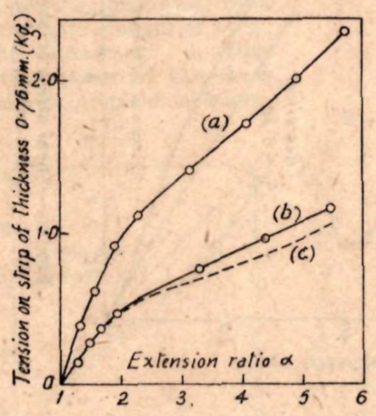

FIG. 11.—Shear superposed on elongation.
(*a*) 75-mm. width. (*b*) 38·5-mm. width. (*c*) Difference. 8 % S rubber, 20° C.

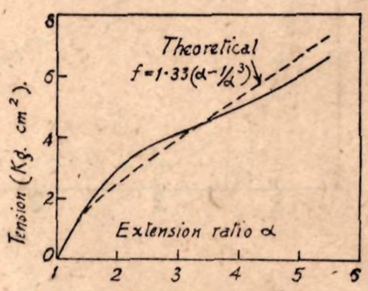

FIG. 12.—Shear superposed on elongation.
8 % S rubber, 20° C.

two strips, one having about twice the width of the other, the tension on the central uniform portion of the wider strip being obtained by difference. In Fig. 11, curves (*a*) and (*b*) give the experimental data for these two strips (corrected only for a small difference in thickness), whilst (*c*) gives the difference. Fig. 12 gives the tension in kg./cm². derived from (*c*), as well as the theoretical curve

$$f = 1{\cdot}33\,(\alpha - 1/\alpha^2).$$

The agreement between theory and experiment may be considered satisfactory. There is a slight inconsistency between these experimental results and the 2-dimensional extension data. For when $\alpha = 3\sqrt{3}$ (*i.e.* 5·20) the two principal extensions are each equal to 3·0 and the tension should agree with that in the 2-dimensional extension, which, as already seen, agreed with the theoretical relation up to an extension ratio of 3·0. In the present experiment the difference amounts to about 10 %. If this difference were genuine it would suggest that the stresses are not independent of the way in which strains are superposed to produce a given final strain. However, the experimental errors are greatly increased by the process of subtraction of the two sets of data, and it is felt that the difference of 10 % is not sufficiently outside the probable error in this particular experiment, to justify such a conclusion.

In Fig. 9, curve (*b*) represents the shear stress-strain relationship, calculated as in section 5, for the shear superimposed on an elongation of 200 %. The theoretical line has a slope of one-third that for the pure shear.

Discussion.

It has already been pointed out [1] that in the derivation of equation (1) from the molecular network theory, it is assumed that the molecules do not approach a condition of full extension. It is this approach to full extension which is responsible for the strong upward curvature shown by the experimental curves in the three principal types of deformation when the deformation is very large. This effect will be neglected in the following discussion.

Considering the data for the 8 % S rubber, the experimental curves are in general agreement with the theory. The 2-dimensional extension data agree closely with the theoretical curve, but the experimental curves for shear and elongation show significant deviations from the theoretical form. For the shear superposed on an elongation the theory gives the right kind of dependence of effective rigidity on initial elongation, and the quantitative agreement, though not exact, is satisfactory.

It would, of course, be possible to obtain a closer fit to the experimental shear and elongation data by adjusting the value of G in the theoretical formulæ. The reason for referring all the deformations to the value of G obtained from the 2-dimensional extension was that this type of deformation gives the closest agreement with the theory, and the theory requires that G shall be the same for all types of deformation. Moreover, this choice of the value of G is consistent with all the data, provided that the deformations are not large.

The reason for the departures from the theoretical form in the cases of elongation and shear is not obvious. It might be suggested that internal energy changes associated with molecular alignment are responsible, but this seems to be unlikely in view of the experimental work of Anthony Caston and Guth [4] referred to in section 2, which showed that internal energy changes were relatively small to 350 % extension, and in any case were in the wrong direction to account for the present deviation. It is possible that the assumptions of the theory with regard to the distribution of molecular lengths in the stretched state, or the assumption of a single value for the molecular weight between junction points may be inadequate. It is also possible that the junction points between molecules in the actual rubber are not as definite as the theory requires ; for example, there may be effective junction points akin to entanglement-cohesions, which may break down under certain states of strain.

The statistical theory of the network is based on certain fundamental assumptions of a very general and probably far too simple a character to lead to an exact correspondence with any real material. In these circumstances it is felt that the degree of agreement shown by the 8 % S rubber provides a substantial confirmation of the theory as an explanation of the physical basis of rubberlike elasticity. This is particularly true for the 2-dimensional extension and the shear plus elongation, where the form of the experimental results was quite unsuspected when the theory was developed.

It is probable that Mooney's formula [6] for the work of deformation, derived on the assumption of a linear stress-strain relation in shear, might lead to a closer fit to the experimental stress-strain curve for elongation than the form (6). This application of Mooney's formula is, however,

[6] Mooney, *J. Appl. Physics*, 1940, **11**, 582.

inadmissible, since the present work shows that the departure from linearity in shear is of the same order of magnitude as the discrepancy in the elongation curve.

Turning now to the latex rubber data, the agreement is less good. Evidently the structure of this rubber approximates less closely to the ideal elastic network; indeed, the elastic behaviour is obviously farther from the ideal, as the hysteresis loops show. This is probably due partly to the effects of crystallisation, which occurs more readily in this rubber than in the 8 % S compound.

Deviations of the observed magnitude lead to the conclusion that from the practical standpoint the utility of the theoretical formulæ is likely to be somewhat limited. This limitation arises to a considerable extent from the imperfectly definable properties of technical rubbers, and to this extent would apply to any theoretical relations that might be obtained. Nevertheless, it is felt that the theory may have value in revealing the general character of the stress-strain relations for the various types of deformation of rubber and in providing a sound, if not strictly quantitative basis for further practical development.

Summary.

Stress-strain data are given for two types of vulcanised rubber: (1) an 8 % S rubber, and (2) a latex rubber. The types of deformation studied were simple elongation, 2-dimensional extension (or compression), pure shear, and combined elongation and shear. Comparison with the theoretical relations based on the molecular-network model shows the agreement to be good for the 2-dimensional extension, but less good for simple elongation and shear. The effect of combined elongation and shear is satisfactorily accounted for. It is concluded that the theory provides a satisfactory explanation of rubberlike elasticity, and forms a useful basis for the description of the mechanical properties of rubber subjected to large deformations of any type.

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