

The Characterization of Elastomer Networks

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The most satisfactory methods for characterizing unfilled elastomer network structures are shown to be those involving stress/strain measurements in tension or compression on highly swollen rubbers. In practice compression techniques are simpler to use, and in those cases where the fraction of soluble material in the vulcanizate is low a single deflection measurement can lead to an exact value for the elastic constant C_1 .

STUDIES of heat ageing mechanisms in rubber vulcanizates necessarily involve some consideration of the effect of network chain concentration, i.e. crosslink density, on heat stability. This leads to a requirement for well founded and preferably rapid techniques for the characterization of rubber vulcanizate structures. The techniques used at present are based upon the relationship between stress, strain and network structure derived from the kinetic theory of rubberlike elasticity¹, and upon a modification of this relationship by (Mooney and) Rivlin².

From a practical standpoint the most interesting development in recent years has been the work of Cluff *et al.*³ in which compression modulus measurements on swollen rubbers have been used, in conjunction with the kinetic theory relationship, to give estimates of network chain concentration. This technique is attractive in that it is simple to operate and it allows the use of highly swollen rubbers without the difficulties encountered in tensile experiments.

In the present work the results of compression modulus measurements are analysed along with those of tensile stress/strain measurements on dry and swollen rubbers. It is shown that the approximations made by Cluff, and subsequently by Loan⁴ and Smith⁵ place unnecessary constraints upon the compression technique, which, under certain conditions can be used as a 'single point' method for evaluating network chain concentration.

EXPERIMENTAL

Materials

The polymers used in this work were an ethylene propylene (EP) copolymer (Dutral N35), a trifluoropropyl methyl vinyl silicone (Dow Corning Silastic LS 420), and a methyl vinyl silicone (I.C.I. E302). The EP copolymer was vulcanized with recrystallized dicumyl peroxide, the fluoro-silicone with 2,5-dimethyl-2,5-ditertiary butyl peroxy-hexane, and the methyl silicone with bis-1,4-dichlorobenzoyl peroxide. No fillers were used.

Compounding and vulcanization

All compounds were mixed on a 6 in. × 2 in. laboratory roll mill. Thin sheets of thickness 0.010 to 0.015 in. were moulded under pressure for swelling measurements and tensile stress/strain experiments. Discs of

thickness 0.25 in. and diameter 0.5 in. were moulded individually for compression experiments. In all cases the rubber compounds were heated for a sufficient time to decompose virtually all of the peroxide vulcanizing agent.

Stress/strain measurements in tension

The technique used for dry rubbers has been described previously⁶. When using swollen rubbers modifications were made in the method of applying and measuring the load so that the specimen could remain immersed in the solvent throughout the experiment (see *Figure 1*). The strip of rubber was

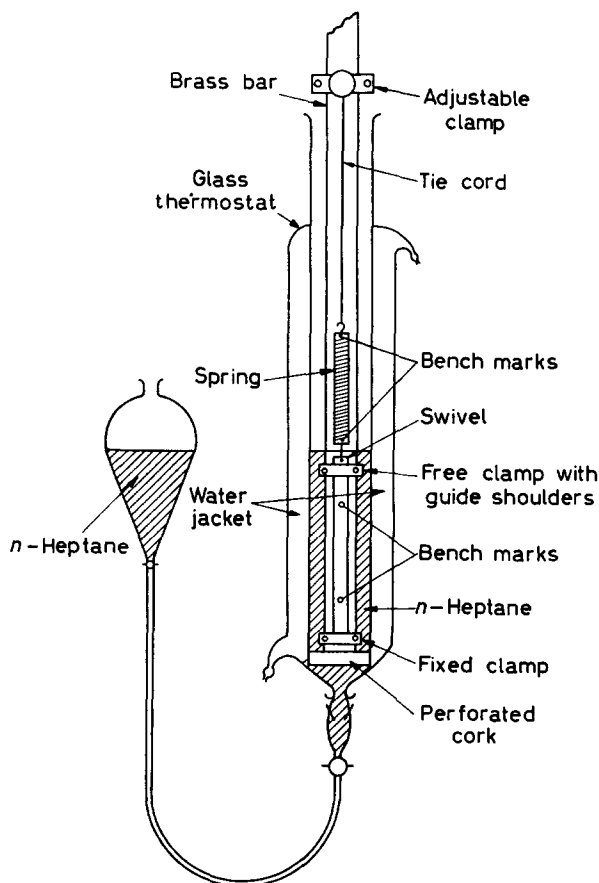


Figure 1—Swollen tension apparatus

first swollen to equilibrium outside the apparatus, then mounted in the clamps in the swollen state and bench marks placed on the already dry surface. It was then introduced into the apparatus and the level of solvent raised to cover the specimen completely. A period of 12 to 18 hours elapsed before measurements were begun. The load was applied through the helical spring and measured after a period of three minutes.

Stress/strain measurements in compression

Compression measurements were only performed on rubbers swollen to equilibrium. The apparatus was essentially that used by Cluff *et al.* and Loan. Deflections were measured with a Wallace dial gauge reading directly to 0.002 mm, and the time required to reach a steady reading at a given load ranged from three to five minutes. To obtain precise values for the undeformed height of the dry specimen (h_0) and swollen specimen (h_s) small increments of load were made over a limited range of stress. h_0 and h_s were then determined by extrapolating the load/deflection curve to zero load. In all these experiments a 'spring load' correction, which varied with dial gauge reading, had to be applied to the nominal load.

RESULTS AND DISCUSSION

Measurements in tension on dry rubbers

The results of tensile stress/strain measurements are usually analysed by means of the Mooney-Rivlin equation,

$$f = 2A_0(C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}) \quad (1)$$

where f is the applied force, A_0 the cross-sectional area of the unstrained specimen, C_1 the elastic constant, λ the extension ratio, and C_2 an empirical constant. When the plot of $\frac{1}{2}fA_0^{-1}(\lambda - \lambda^{-2})^{-1}$ against λ^{-1} is linear, this leads to a reliable extrapolated value for the elastic constant C_1 . The slope of the line is equal to C_2 . The results obtained for EP copolymer at various levels of crosslink density are shown in *Table 1*.

Table 1. Values of C_1 and C_2 from tensile stress/strain measurements on dry EP copolymer vulcanizates at 25°C

Weight per cent dicumyl peroxide	$C_1 \times 10^{-6}$ dyne cm ⁻²	$C_2 \times 10^{-6}$ dyne cm ⁻²	$\frac{C_2}{C_1}$
2	0.30	1.16	3.89
3.5	0.57	1.60	2.82
4	0.77	1.55	2.00
6	1.35	1.39	1.03

Preliminary experiments with EP copolymer vulcanizates showed that for a given load the approach to equilibrium strain was exceptionally slow. The period of ten minutes that elapsed between loading and measurement of strain, although adequate for the more highly crosslinked vulcanizates, undoubtedly leads to substantial errors in the measured strain for lightly cured systems. Such errors will result in artificially high values for the measured crosslink density, i.e. C_1 will be too high. It is possible that this unfavourable long term 'creep' is also responsible for the high values obtained for C_2 and the ratio C_2/C_1 . If the vulcanizates were swollen in a suitable solvent, such as *n*-heptane, approach to equilibrium strain would be much more rapid. Changes in the observed value for C_2 could then be taken as an indication of the extent to which it is determined by failure to reach true equilibrium conditions.

Preliminary experiments in tension with dry fluorosilicone rubbers showed that approach to equilibrium strain was far more rapid than with EP co-

polymer vulcanizates. Experiments were carried out with three minute intervals between loading and measuring the strain, and the results obtained from the Mooney-Rivlin equation are shown in *Table 2*.

Table 2. Values for C_1 and C_2 from tensile stress/strain measurements on fluorosilicone vulcanizates at 25°C

Weight per cent peroxide curative	$C_1 \times 10^{-6}$ dyne cm^{-2}	$C_2 \times 10^{-6}$ dyne cm^{-2}	$\frac{C_2}{C_1}$
1.0	0.65	0.20	0.30
1.5	0.70	0.20	0.28
2.0	0.70	0.21	0.30
2.5	0.80	0.12	0.15

The relatively low values obtained for C_2 and the C_2/C_1 ratio reinforce the view that ability to approach true equilibrium strain conditions has an important bearing on the magnitude of C_2 .

Measurements in tension on swollen rubbers

For swollen rubbers the Mooney-Rivlin equation becomes

$$f = 2A_0 (C_1 + C_2\lambda^{-1}) (\lambda - \lambda^{-2}) V_r^{-\frac{1}{3}} \quad (2)$$

where V_r is the volume fraction of rubber in the vulcanizate swollen to equilibrium. When the experimental data for EP copolymer vulcanizates were plotted in the form $\frac{1}{2}fA_0^{-1}(\lambda - \lambda^{-2})^{-1}V_r^{\frac{1}{3}}$ against λ^{-1} , horizontal straight lines were obtained (see *Figure 2*). Therefore C_2 was zero in all cases and

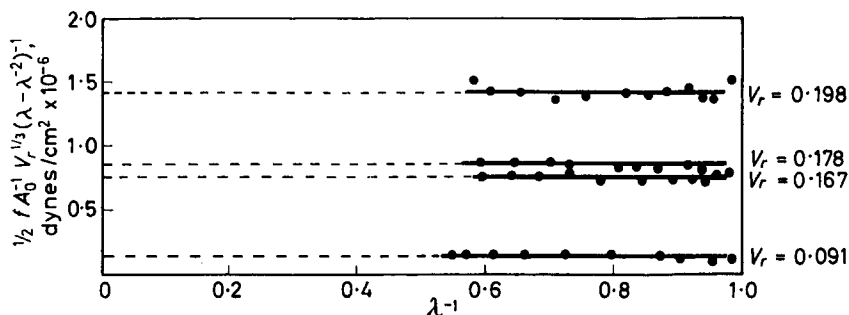


Figure 2—Stress/strain measurements on swollen rubbers at 25°C

swollen EP copolymer vulcanizates meet the requirements of the kinetic theory of rubberlike elasticity completely in respect of their stress/strain behaviour in uniaxial tension. The values of C_1 obtained in this way are shown together with those from dry tension experiments in *Figure 3*, and it is apparent that agreement is acceptable only at the highest crosslink densities. At all other levels experiments on dry rubbers lead to considerably higher estimates of crosslink density, and this is attributed to a failure to achieve equilibrium strain in these experiments.

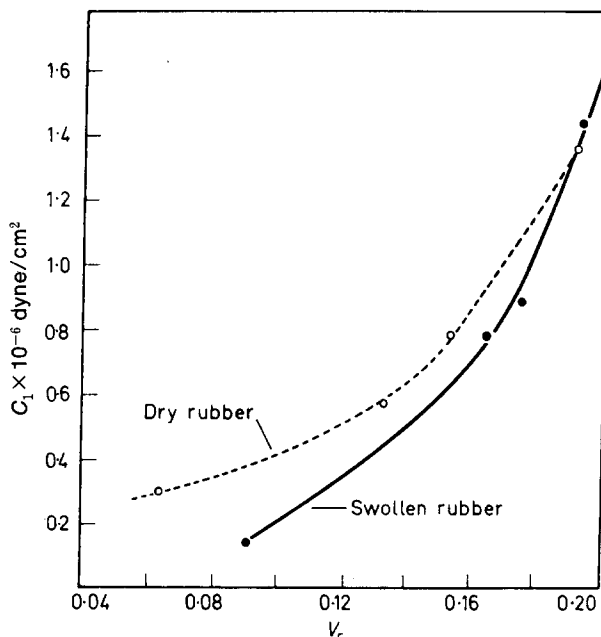


Figure 3— C_1 from tension experiments on Dutral vulcanizates

Measurements in compression on swollen rubbers

Experiments carried out in uniaxial compression with freedom of movement in other directions are formally equivalent to those carried out in uniaxial tension. According to the kinetic theory of rubberlike elasticity, the relationship between stress, strain and network structure in compression should therefore be

$$f = 2A_0C_1(\lambda - \lambda^{-2})V_r^{-1/3} \quad (3)$$

In a plot of $\frac{1}{2}fA_0^{-1}(\lambda - \lambda^{-2})^{-1}V_r^{1/3}$ against λ there should be continuity through $\lambda = 1$, and the values of C_1 obtained from tensile and compression measurements on swollen rubbers should fall on a common curve when plotted against V_r .

The results of measurements in compression on swollen EP copolymer vulcanizates are shown in Figure 4, and, as with the tensile experiments on swollen rubbers, C_2 is zero. The continuity of behaviour in tension and compression is shown by the plot of C_1 against V_r in Figure 5. It follows that the expression derived from the kinetic theory of rubberlike elasticity provides a complete description of the equilibrium stress/strain behaviour of swollen EP copolymer rubbers in uniaxial tension and compression in the range of λ from 1.82 to 0.75.

With fluorosilicone and methyl vinyl silicone gum vulcanizates exactly the same situation arises. The stress/strain behaviour in uniaxial compression is again described completely by equation (3).

Practical application of compression modulus techniques

Analysis of compression modulus measurements by means of equation

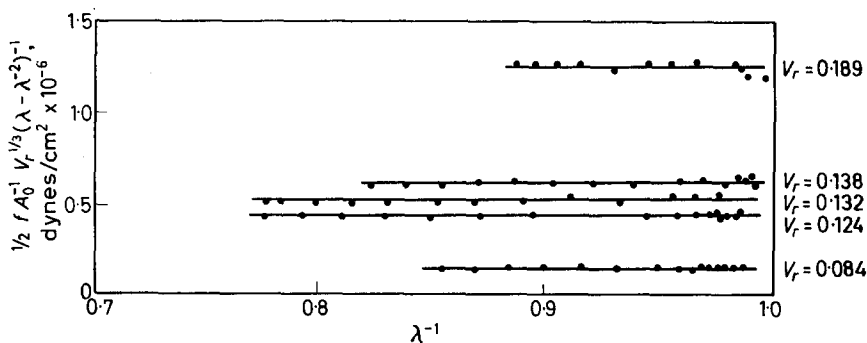


Figure 4—Stress/strain properties of swollen Dutral vulcanizates in uniaxial compression

(3) is a tedious process, and it is possible to derive a relationship which is more convenient in practice. The kinetic theory equation can be re-arranged in the form

$$C_1 = \tau V_r^{1/2} / 2 (\lambda - \lambda^{-2}) \tag{4}$$

where τ is the force per unit cross-sectional area of the unswollen specimen and λ the compression ratio. If the experiment is conducted on a cylindrical specimen of initial swollen height h_s , and the application of a uniaxial stress τ deflects it to height h_D it can be shown that

$$(\lambda - \lambda^{-2}) = (h_D^3 - h_s^3) / h_s h_0^2 \tag{5}$$

Again, assuming isotropic swelling of the specimen of unswollen height h_0

$$V_r^{1/3} = h_0 / h_s$$

Substituting in equation (4) gives

$$C_1 = \tau h_0 h_D^2 / 2 (h_D^3 - h_s^3) \tag{6}$$

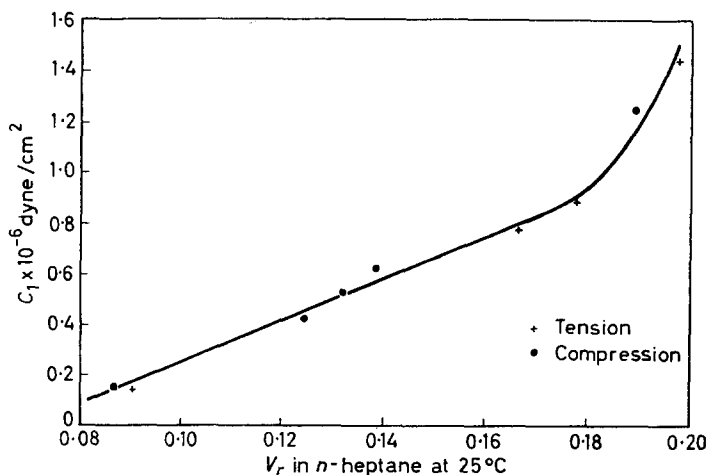


Figure 5—Values from measurements in compression and tension on swollen rubbers

and C_1 is now represented in terms of the directly measured quantity h_D and the applied stress τ . This equation allows C_1 to be determined from a single deflection measurement. All vulcanizates used in the present work showed isotropic swelling and the values of V_r calculated from h_0 and h_s agreed well with those measured. It is feasible, therefore, to calculate h_s from the known value of V_r and the measured value of h_0 . It only remains to apply a stress τ and measure the deformed height h_D to calculate C_1 . In cases where there is a significant (i.e. more than five per cent) fraction of soluble material in the vulcanizate it will be necessary to make a correction to the measured value for h_0 .

This single-point technique has been applied to EP copolymer, fluorosilicone, and methyl vinyl silicone rubbers and the results are shown in Table 3. In all these systems the fraction of soluble material in the vulcanizates was low and it was permissible to use the measured value for h_0 .

Table 3. C_1 values from single point measurements and from full kinetic theory treatment

Rubber	Weight per cent peroxide	$C_1 \times 10^{-6}$ dyne cm^{-2} single point	$C_1 \times 10^{-6}$ dyne cm^{-2} kinetic theory	Per cent compression used
EP copolymer	4.0	0.55	0.546	6.7
Methyl vinyl silicone	2.0	0.44	0.46	6.0
Fluorosilicone	1.0	0.63	0.66	11.0

Other methods of evaluating C_1 from compression modulus measurements

Use of equation (6) is the most exact method of analysing compression modulus data, and in those cases where the soluble fraction is low and where isotropic swelling occurs it can be used as a single point method.

Other workers have preferred to use approximations to equation (6), but in so doing have placed what appear to be unnecessary constraints upon the method. For example Cluff *et al.* use the expression

$$C_1 = \tau h_0 / 6\Delta h \quad (7)$$

and Smith uses an expression equivalent to

$$C_1 = \tau h_0 (h_s - 2\Delta h) / 6\Delta h \cdot h_s \quad (8)$$

where Δh is the measured deflection.

Both equations are arrived at by making assumptions regarding the magnitude of Δh relative to h_s which limits their usefulness to regions of low compression. These approximations arise in the expression relating $(\lambda - \lambda^{-2})$ with h_s and Δh (see equation 5). If the cubic and quadratic terms in this equation are expanded and all terms containing Δh to the power two or more are neglected, one arrives at equation (8). If only third powers of Δh are neglected the equation becomes

$$C_1 = \tau h_0 (h_s - \Delta h) / 6\Delta h \cdot h_s \quad (9)$$

When a further approximation, that $(h_s - \Delta h) \simeq h_s$, is made one arrives at equation (7). The particular attraction of equations (7) and (8) presumably arises from the fact that in the initial stages of compression plots of τ against Δh and τ against $\Delta h/(h_s - 2\Delta h)$ may give reasonable straight lines, the slopes of which can be fed directly into the equations for C_1 . In the present work plots of τ versus Δh were found to give well defined linear regions up to five per cent compression, but because of the approximations inherent in equation (7) the values of C_1 were in error (see Table 4).

Table 4. C_1 values from kinetic theory treatment and from the approximate method of Cluff

Rubber	Weight per cent peroxide	$C_1 \times 10^{-6}$ dyne cm^{-2} kinetic theory	$C_1 \times 10^{-6}$ dyne cm^{-2} method of Cluff
EP copolymer	4.0	0.546	0.59
Methyl vinyl silicone	2.0	0.46	0.50
Fluorosilicone	1.0	0.66	0.74

In the same systems plots of τ against $\Delta h/(h_s - 2\Delta h)$ showed less certain linear regions in the low deflection range, and despite the fact that equation (8) is reasonably accurate uncertainties in estimating the slope rendered this method unsuitable in this form. Undoubtedly the best of the approximate methods would be one based upon equation (9). This could be used either as a single point method or as a graphical method in which τ is plotted against $\Delta h \cdot h_s/(h_s - \Delta h)$ and the slope inserted into the equation for C_1 .

The authors are indebted to Mr R. Sinnott and Mr J. Day for preparing the vulcanizates used in this work.

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(Received February 1968)

REFERENCES

- ¹ TRELOAR, L. R. G. *The Physics of Rubber Elasticity*, p 56. Clarendon: Oxford, 1949
- ² RIVLIN, R. S. *Phil. Trans. A*, 1948, **240**, 459
- ³ CLUFF, E. F., GLADDING, E. K. and PARISER, R. *J. Polym. Sci.* 1960, **45**, 341
- ⁴ LOAN, L. D. Society of Chemical Industry, *Monograph* No. 17, 1963, 24
- ⁵ SMITH, D. A. *J. Polym. Sci. C*, 1967, **16**, 525
- ⁶ THOMAS, D. K. *Polymer, Lond.* 1964, **5**, 463