

A Determination of Crosslink Density from Compression Modulus Data

R. E. MELLELY and J. E. STUCKEY,
University of Aston in Birmingham, England

Synopsis

A comparison of the crosslink densities calculated from compression modulus and stress-strain measurements is made for a series of natural rubber vulcanizates. Errors resulting from the use of accepted approximations and the effect of sample dimensions are also investigated.

INTRODUCTION

Calculation of the crosslink density of an elastomer vulcanizate from extension stress-strain measurements is dependent upon the experimental determination of the C_1 constant of the Mooney, Rivlin, Saunders equation,^{1,2}

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

and the modification for highly swollen networks,

$$f = 2A_0\nu_r^{-1/3}(\lambda - \lambda^{-2})C_1. \quad (1a)$$

The constant C_1 is related to the intercrosslink molecular weight, M_{cphys} , which includes a contribution due to entanglements and makes no allowance for molecule ends. The exact significance of the constant C_2 is still a matter of controversy, but it has been shown³ to become effectively zero at high degrees of swelling ($\nu_r \approx 0.2$). The values of C_1 obtained from compression stress-strain determinations reported here used rubbers swollen in some cases to $\nu_r \approx 0.3$ and correlated well with those obtained from dry extension stress-strain measurements. This has been previously reported by others.^{4,5}

Although C_1 determinations on natural rubber vulcanizates can be made quite conveniently by the tension stress-strain method, there are considerable experimental difficulties associated with some synthetic rubbers. The compression modulus technique, initiated by Cluff, Gladding, and Pariser⁶ and extended by others,^{5,7,8} does not suffer from this restriction and is becoming increasingly popular. When considering the deformation of a swollen rubber in compression using the approximations introduced by the previous workers,⁵⁻⁷ eq. (1) may be rewritten in the following form:

$$C_1 = \frac{f}{\Delta h} \cdot \frac{h_0}{6A_0} \quad (2)$$

where f is the load producing a deformation Δh , and h_0 and A_0 are the initial height and area of the sample, respectively.

Using a more refined approximation, Khadim and Smith⁹ arrived at the following expression:

$$C_1 = \frac{f}{\Delta h} \cdot \frac{h_0}{6A_0} \left[\frac{1}{1 + \nu_r^{1/3} \Delta h h_0^{-1}} \right] \quad (3)$$

Kay, Moore, and Thomas⁸ and Moore and Thomas¹⁰ derived an exact equation involving no approximations from which it is possible to calculate C_1 from a single compression measurement, i.e.,

$$C_1 = \frac{f h_0 h_d^2}{2A_0(h_d^3 - h_s^3)} \quad (4)$$

where h_s and h_d are the height of the swollen undeformed sample and of the swollen deformed sample, respectively. This expression has been rewritten using parameters that are more suitable for the microcompression technique now commonly used:

$$C_1 = \frac{f \nu_r^{1/3}}{2A_0} \left[\frac{3h_s \Delta h^2 - 3h_s^2 \Delta h - \Delta h^3}{h_s^3 - 2h_s^2 \Delta h + h_s \Delta h^2} \right]^{-1} \quad (5)$$

Equations (2) to (5) vary in the extent of mathematical approximation. To test the validity of these approximations, the four equations were used to calculate values of C_1 from compression data obtained from swollen samples over a range of crosslink densities. In addition, the effect of sample area and thickness was investigated.

MATERIALS AND EXPERIMENTAL METHODS

Yellow Circle natural rubber (RSSI) and dicumyl peroxide of 99% purity (mp 39°C) were used to prepare four formulations, A, B, C, and D, containing 1, 2, 3, and 4 parts of peroxide per hundred parts of rubber, respectively. These were milled to a Wallace plasticity of 18.5 and press-cured at 140°C for 120 min.

The values of C_1 were determined on each of the four vulcanizates using the extension stress-strain method described by Greensmith¹¹ and the microcompression technique of Smith.⁵ (In the former case, dry samples were used; in the latter, the samples were swollen to equilibrium in benzene.) The test samples used for the two determinations were cut from adjacent parts of the sheets to guard against possible variations of crosslink density.

For the evaluation of the effect of sample size upon compression modulus results, vulcanizates were prepared from compound C using a stepped mould. Specimens varying from 0.18 to 0.29 cm in thickness (h_0) and 0.1

TABLE I
 C_1 Tension Results Compared with C_1 Compression Results^a

Formulation	Peroxide content	C_1 (tension), (g/cm ²) × 10 ⁻³	ν_r	C_1 (compression), (g/cm ²) × 10 ⁻³				
				eq. 2	eq. 3	eq. 4	eq. 5	
A	1	0.98 ± 3%	0.173	1.10 ± 2%	1.06 ± 4%	1.05 ± 4%	1.05 ± 4%	
B	2	1.79 ± 3%	0.228	2.03 ± 7%	1.98 ± 8%	1.97 ± 8%	1.97 ± 8%	
C	3	2.46 ± 3%	0.261	2.65 ± 3%	2.60 ± 3%	2.60 ± 3%	2.58 ± 2%	
D	4	(too brittle)	0.310	3.72 ± 4%	3.65 ± 4%	3.59 ± 9%	3.65 ± 3%	

^a Calculated using eqs. (2), (3), (4), and (5) over a range of crosslink densities.

to 0.6 cm²/in area (A_0) were used. All determinations were carried out in triplicate.

RESULTS AND DISCUSSION

The C_1 tension results and the four sets of C_1 compression results calculated from eqs. (2) to (5) are shown in Table I. The maximum per cent variation in each set of triplicate results is included. The C_1 compression results derived from eqs. (3), (4), and (5) give better correlation with C_1 tension, although the discrepancy shown by eq. (2) is less than the variation within some sets of compression triplicate results. The discrepancy between the two methods is greatest for the samples of lower crosslink density.

TABLE II
 C_1 Compression Results for Test Pieces of Various Dimensions (A_0 and h_0)^a

h_0 , cm	A_0 , cm ⁻²			
	0.13	0.23	0.42	0.62
0.18	2.41	2.71	2.64	2.48
0.25	2.69	2.59	2.40	2.48
0.29	2.53	2.61	2.64	2.53

^a Calculated using eq. (5). Formulation C, vulcanized 120 min at 140°C; $\nu_r = 0.265 \pm 3\%$.

Table II compares the C_1 compression results obtained from samples of the same crosslink density (from compound C) but varying in area and thickness. Equation (5) was used to calculate the results. The overall variation is $\pm 6\%$, which is less than the variation found in some sets of triplicate results for the same sample dimensions. The ν_r values of the samples, swollen to equilibrium in benzene at 25°C, were determined by weighing and found to be $0.265 \pm 3\%$.

CONCLUSIONS

The simple microcompression technique for the determination of C_1 gives results that correlate well with those obtained by the extension stress-strain method. The mathematical approximations used in deriving eqs. (3), (4), and (5) make no practical difference to this correlation, and those used in eq. (2) have very little effect. The effect of the variation of sample dimensions in the compression technique over the range studied is negligible.

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