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Approximate Calculation of Equilibrium Modulus Factors for Rubber Networks from Swollen Compression Data

It is generally accepted that, in contrast to unidimensional extension data, compression stress/strain measurements on partially or fully swollen rubber networks can be fitted by the gaussian expression

$$f=A_0G_cv_r^{-\frac{1}{3}}(\lambda^{-2}-\lambda) \tag{1}$$

where f is the compressive force with reference to the unswollen cross-sectional area (A_0), v_r is the volume fraction of rubber in the swollen network, G_c is the compression modulus factor, and λ represents the actual compression ratio of the swollen sample, defined by

$$\lambda=\frac{\text{Compressed swollen height }(h_c)}{\text{Uncompressed swollen height }(h_s)}$$

The compressive strain, Δh, is defined by $\Delta h = h_s - h_c$, so that

$$\lambda^{-2} - \lambda = (1 - \Delta h/h_s)^{-2} - (1 - \Delta h/h_s)$$

Since λ in compression is less than unity, the first term of the RHS can be expanded binomially giving

$$\lambda^{-2} - \lambda = \left[1 + 2\frac{\Delta h}{h_s} + 3\left(\frac{\Delta h}{h_s}\right)^2 + 4\left(\frac{\Delta h}{h_s}\right)^3 + \ldots\right] - (1 - \Delta h/h_s) \qquad (2)$$

Since Δh is small in comparison with h_s,

$$\lambda^{-2} - \lambda \approx 3\Delta h/h_s \qquad (3)$$

an approximation first proposed by Cluff, Gladding and Pariser[1].

Substituting the approximation (3) in equation (1), since $v_r^{1/3} = h_0/h_s$,

$$G_c \approx (f/\Delta h)\,(h_0/3A_0) \qquad (4)$$

where h_0 is the unswollen height.

It is not easy to measure h_s accurately. Approximation (4) is therefore convenient experimentally, since $f/\Delta h$ is obtained as the slope of a compression/deflection plot and h_0 and A_0 are readily measured on the *dry* test-piece, for instance by use of a projection microscope. The approximation (4) was proposed as valid for use in the region $1{\cdot}00 \geqslant \lambda \geqslant 0{\cdot}95$, and has been used on this basis by Loan[2] and by ourselves[3,4].

In practice it may be difficult to obtain usable experimental data while remaining within the five per cent deflection restriction. The reason for this is the imperfect surface flatness of moulded specimens which results in less than the full area of the swollen test-piece contacting the compressor foot during the earliest part of the loading cycle. It is, therefore, often preferable to obtain data at rather higher deflections, up to perhaps 10 to 15 per cent, and to reject the lowest strain measurements.

Although the linear approximation (4) often appears to fit experimental data, comparison with a plot of equation (1) shows serious deviations from this 'exact' gaussian expression even at low strains. A better approximation may be computed by retaining the second term of the binomial expansion, equation (2), giving an expression for the modulus factor.

$$G_c = \frac{f v_r^{1/3}}{A_0(\lambda^{-2} - \lambda)} \approx \frac{f h_0 h_s^{-1}}{A_0 \,.\, 3\left[\dfrac{\Delta h}{h_s} + \left(\dfrac{\Delta h}{h_s}\right)^2\right]}$$

$$\approx \frac{f h_0 h_s}{3A_0 \Delta h\,(h_s + \Delta h)} \approx \frac{f h_0^2}{3A_0 \Delta h\,(h_0 + v_r^{1/3}\Delta h)} \qquad (5)$$

Table 1

v_r	G_c *dyne* $cm^{-2} \times 10^{-6}$		
	Eqn (1)	*Eqn (4)*	*Eqn (6)*
0·2900	3·460	3·920	3·431
0·3200	3·658	4·014	3·647
0·3276	3·956	4·602	4·004

Equation (5) involves v_r but the Reticulometer technique[3,4] normally combines swelling with modulus measurements and so a value of this parameter is available.

For comparison with equation (4), equation (5) may be rewritten

$$G_c \approx \frac{f}{\Delta h} \cdot \frac{h_0}{3A_0} \cdot \frac{1 + v_r^{1/3} \Delta h\, h_0^{-1}}{1} \qquad (6)$$

Measurements made with NR gum vulcanizates[5] using approximations (4) and (6) in comparison with 'exact' results using the gaussian equation (1) show that (6) fits the data well over the required strain range, the approximate values of G_c being within two per cent of the exact values (*Table 1*).

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Complex Formation between Silver Perchlorate and Azo-bis-isobutyronitrile

In an earlier communication[1] we reported that the rate of thermal decomposition of azo-bis-isobutyronitrile (AZO) at 70°C is considerably enhanced by silver perchlorate and that the rate of initiation of the free-radical polymerization of methyl methacrylate by AZO shows a corresponding increase in the presence of the salt. At constant AZO concentration, it is found that the rate of polymerization increases initially with increasing [$AgClO_4$], but eventually reaches a plateau value independent of [$AgClO_4$]. Under these conditions the rate of initiation is approximately four times as great as that holding in the absence of silver perchlorate. Further, we showed that kinetic observations on the polymerization are consistent with the formation of a 1:1 $AgClO_4$–AZO complex which decomposes more rapidly at a given temperature than does pure AZO. Although a 2:1 complex could not be definitely excluded, this appeared less likely.