Phenomenological aspects of the deformation of elastomeric networks

N. W. Tschoegl
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, Ca 91125, USA

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The application of finite linear viscoelastic theory to elastomeric networks is discussed. It is shown that the time dependent behaviour of rubber-like materials in moderately large deformations can be described successfully by introducing a suitable chosen non-linear strain measure into the Boltzmann superposition integral. A new two-term elastic potential is proposed. The first term is the neo-Hookean potential predicted by the statistical theory of rubber elasticity for a 'perfect' network. The second accounts for contributions arising from the topological constraints which are generally present in real networks. The resulting two-network theory is verified on hand of published data.

INTRODUCTION

General phenomenological theories for the description of the time-dependent mechanical behaviour of rubber-like materials, of which the Green–Rivlin[1] and the Coleman–Noll[2] theories are the best known, require a formidable mathematical apparatus and a prohibitive amount of experimental work. Thus, for example, the theory of Coleman and Noll requires the experimental determination of 15 functions of the invariants, of which 12 are time-dependent. Clearly, the work involved is excessive. Attempts to reduce the number of functions to more manageable size by determining those which assume the lion's share in a given deformation, apparently do not lead to constitutive formulations.

FINITE LINEAR VISCOELASTICITY

Considerable simplification can be achieved by relinquishing the attempt to be quite general. A significant body of experimental evidence[3,4] suggests that the relaxation spectrum of rubber like materials may not be affected significantly by relatively large deformations. The range of strain over which this assumption can be sustained appears to coincide with the range over which the upswing in a plot of the tensile stress, σ, vs. the stretch ratio, λ, does not yet contribute noticeably. A deformation within this range may be called a 'moderately large' deformation. Such a deformation is defined as one in which the relaxation spectrum remains sensibly unchanged. In a moderately large deformation, then, time-shift invariance is preserved just as in infinitesimal deformation and the time-dependence remains well-represented by the Boltzmann superposition integral. The resulting theory has been called *finite linear viscoelasticity*[2,5]. The stress strain non-linearity can be accounted for by any of several formulations which describe the elastic behaviour in near-equilibrium. The so-called BKZ theory[6] is essentially a theory of this type using an elastic potential expressed in terms of the invariants of the deformation tensor. It suffers from the slow convergence of the Taylor expansion of the potential in terms of the invariants.

Chang, Bloch and Tschoegl[7] made use of the elastic potential:

$$W = (2G/n)I_b(n) \tag{1}$$

where G is the shear modulus, n is a material parameter, and $I_b(n)$ is the first invariant of the strain tensor defined, for an incompressible material, by

$$b_{ij} = (B_{ij}{}^{n/2} - \delta_{ij})/n \tag{2}$$

where B_{ij} is Finger's deformation tensor and δ_{ij} is the unit tensor. The elastic potential given by equation (1) had been proposed by Blatz, Sharda and Tschoegl[8] and, independently, by Ogden[9].

For simple tension equations (1) and (2) give the true stress as

$$\bar{\sigma} = (2G/n)(\lambda^n - \lambda^{-n/2}) \tag{3}$$

from which the predictions of the statistical theory of rubber elasticity are regained by setting $n = 2$. Equation (3) represents, with great success, behaviour in simple tension up to about 150–250% elongation, depending on the materials[8]. The strain parameter n may thus be regarded as a measure of the departure of the behaviour of real rubbers (imperfect networks) from that predicted by the statistical theory. Within its range of applicability the elastic potential, equation (1), appears to describe rubber-like behaviour constitutively[8].

Using equation (1) as the non linear measure of strain, Chang, Bloch and Tschoegl[3,4,7] have proposed the model:

$$\bar{\sigma}(t) = (2/3n)\int_0^t E(t - u)\,\mathrm{d}\,[\lambda^n(u) - \lambda^{-n/2}(u)] \tag{4}$$

for moderately large time-dependent tensile deformations of rubber-like materials. The model can be extended to more general time-dependent deformations[3]. Although it was

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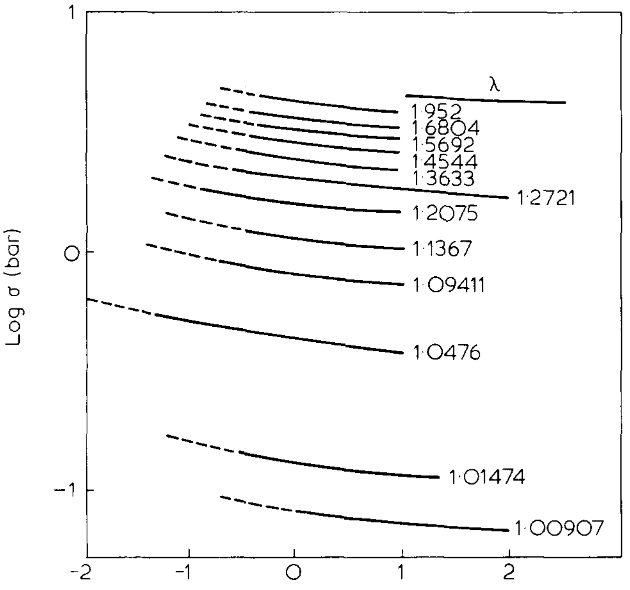

Figure 1 Stress as function of time in stress relaxation at 23° C of SBR at various levels of strain

developed originally for an isotropic, incompressible solid-like (crosslinked) material, it has proved applicable to uncrosslinked rubbers also[7]. It requires only one time-dependent function, the small deformation relaxation modulus, $E(t)$, in addition to the strain parameter, n. For a strain as a step function of time equation (4) takes the form:

$$\bar{\sigma}(t) = (2/3n)E(t)(\lambda^n - \lambda^{-n/2}) \qquad (5)$$

[see equation (3)]. Thus, the model predicts the effects of strain and time factor in a stress relaxation experiment. *Figure 1* shows the stress as a function of time, plotted in logarithmic coordinates, obtained[4] on a specimen of a styrene–butadiene rubber (SBR) at 23°C. The curves are parallel except for the portions indicated by broken lines. The latter reflect 'transient' behaviour arising from the necessity to impose the strain as a ramp function of time with a finite rate of extension. The parallel lines indicate factorizability in accordance with equation (5). The strain parameter n may be obtained conveniently from a series of stress relaxation experiments such as those shown in *Figure 1*. An isochronal time, t_r, is selected and the stresses, σ_r, corresponding to the stretch ratio, λ_r, at the time t_r are cross-plotted to yield an isochronal stress–strain curve. The parameter n is then obtained from a non-linear least squares fit to the data.

Figure 2 shows stress–strain data obtained on the same SBR specimen at four values of the strain rate, $\dot{e}$, spanning 3.5 decades of time. The solid lines were calculated from the model. The fit of the predictions to the experimental data is unprecedently good. The worst deviation, which occurs at the highest strain rate at the highest strains, is still only of the order of 2%. It should be noted that this deviation is not due to the appearance of the upswing in the stress–strain curve because this would have made the experimental points lie above the line, not below it.

Similar excellent agreement was obtained on an uncrosslinked styrene–butadiene copolymer[7]. The full circles in *Figures 3* and *4* show stress–strain data on this sample in the temperature range −20° to 23°C at rates of strain spanning two decades of time. The solid curves again represent the predictions of the model. The agreement is within 2% and may be considered excellent.

Some information on the nature of the strain parameter has been assembled in two earlier publications[4,7]. This work is in progress. At this time it appears that n lies between 1 and 2 for most rubbers at room temperature but may take lower values at lower temperatures. In contrast, for uncrosslinked rubbers, n appears to assume values around 0.5 and seems to be sensibly independent of temperature.

TWO-NETWORK THEORY

From a phenomenological (continuum mechanical) point of view it is perfectly admissable to formulate an elastic potential in which a dimensionless material parameter appears as a non-integral exponent of the deformation tensor[10]. However, it is difficult to assess the molecular significance of such an exponent. The potential, equation (1), has therefore been re-examined in the light of a two-network theory. This is based on the assumption that the observed stress in simple tension can be considered to be a superposition of two stresses, the first representing the contribution of a 'perfect' network obeying the predictions of the theory of rubber elasticity ($n = 2$), and the second reflecting contributions due to an 'imperfect' network for which n assumes values around 0.5. Denoting the strain parameter of the imperfect network by m, the elastic potential becomes:

$$W = G_X I_b(2) + (2G_N/m)I_b(m) \qquad (6)$$

where G_X and G_N are the shear moduli associated with the two networks. The modulus G_N may be considered to represent the contributions made by topological constraints ('entanglements') while G_X represents the modulus which the material would possess in the absence of such constraints. Equation (6) assumes that the two networks are additive. Flory[11] has recently proposed a molecular theory which,

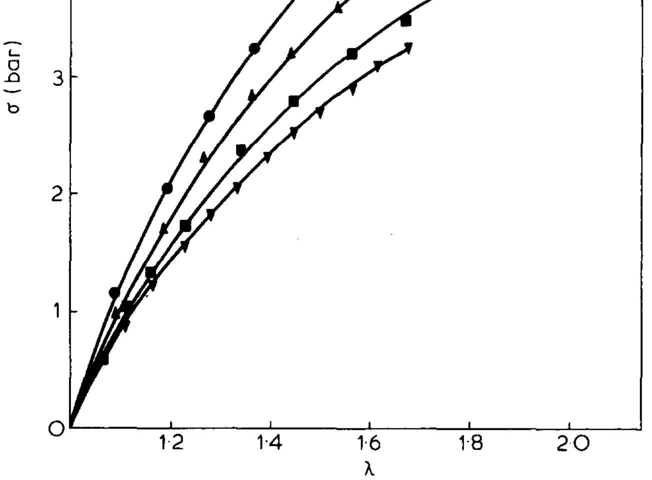

Figure 2 Response of SBR at 23°C to a ramp strain at various rates of extension. ●, 4.536 min^{-1}; ▲, 0.4536; ■, 0.02268; ▼, 0.001134. n = 1.22

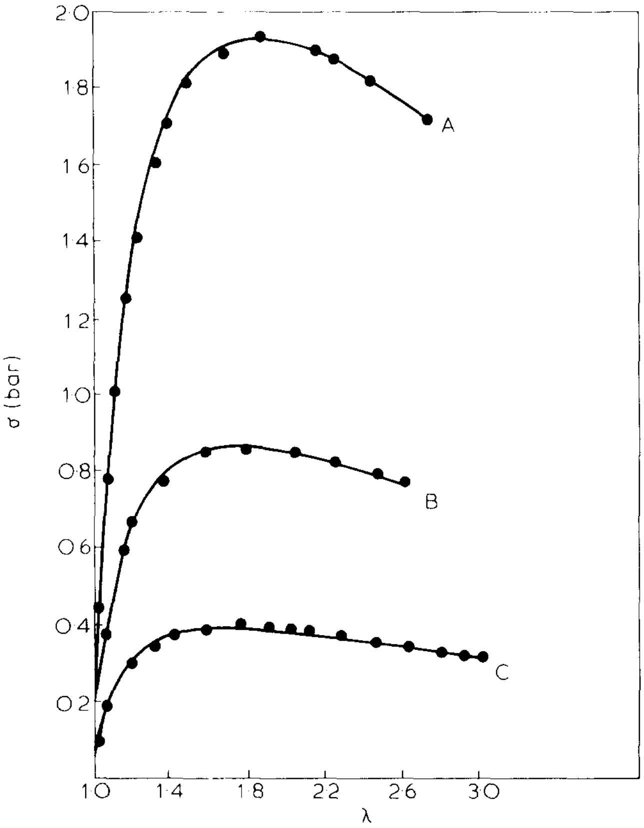

Figure 3 Response of SB copolymer at 23°C to a ramp strain at various rates of extension. A, $\dot{\epsilon}$ = 3.814 min^{-1}; B, 0.3566 min^{-1}; C, 0.04394 min^{-1}. n = 0.4

albeit different in form, is also based on the idea that the observed behaviour can be modelled by the additive contributions of two terms, one of which represents the predictions of the statistical theory for a 'perfect' network while the other represents contributions arising from topological constraints on the movement of the junction points of that network. The work of Ferry and his coworkers, summarized in ref 12, as well as the work of others (see the discussion in ref 13) on two-network systems obtained by irradiating an elastomer in the strained state, provides strong experimental support for the additivity of such networks. Equation (6) therefore appears to be based on a justifiable assumption.

From equation (6) the true stress in simple tension results as:

$$\bar{\sigma} = G_X(\lambda^2 - \lambda^{-1}) + 2G_N(\lambda^m - \lambda^{-m/2})/m \qquad (7)$$

This is easily recast into the form:

$$\sigma_M = G\,[1 - \bar{\nu}_N \Phi_m(\lambda)] \qquad (8)$$

where $\sigma_M = \sigma/(\lambda - \lambda^{-2})$ is the Mooney stress, $G = G_X + G_N$ is the modulus observed in small (infinitesimal) deformation:

$$\Phi_m(\lambda) = 1 - \frac{2(\lambda^m - \lambda^{-m/2})}{m(\lambda^2 - \lambda^{-1})} \qquad (9)$$

and

$$\bar{\nu}_N = \frac{G_N}{G_X + G_N} = \frac{\nu_N}{\nu_X + \nu_N} \qquad (10)$$

where $\nu_N = G_N/RT$, $\nu_X = G_X/RT$, and R and T have their usual significance. Here, ν_N may be considered to be the number of moles per unit volume of 'equivalent pseudo-crosslinks' arising from the topological constraints, and $\bar{\nu}_N$ is the corresponding mole fraction. It is proposed to call ν_X the (*chemical*) *crosslink density*, ν_N the (*equivalent*) *constraint* or *entanglement density*, and $\nu = \nu_X + \nu_N = G/RT$ the *reticulation density*.

It is interesting to note that Heinrich, Straube and Helmis have recently developed a statistical mechanical theory[15,16] based on the ideas of Edwards, Doi and de Gennes, which for simple tension, leads to equation (7) with:

$$G_N = \nu_p RT[m^2/2(6)^{1/2}]\langle R^2\rangle/\rho_0^2 \qquad (11)$$

where ν_p is the number of moles of primary chains in the uncrosslinked polymer from which the vulcanizate is formed, $\langle R^2\rangle$ is the mean-square end-to-end distance of the primary chains, and ρ_0^2 is a parameter related to the strength of the mean square deviation of the actual position of a statistical segment of a primary chain after crosslinking from its original position before vulcanization[16].

Over the range required, a plot of σ_M vs. λ^{-1} according to equation (8) is indistinguishable from a plot according to:

$$\sigma_M = G\frac{2(\lambda^n - \lambda^{-n/2})}{n(\lambda^2 - \lambda^{-1})} \qquad (12)$$

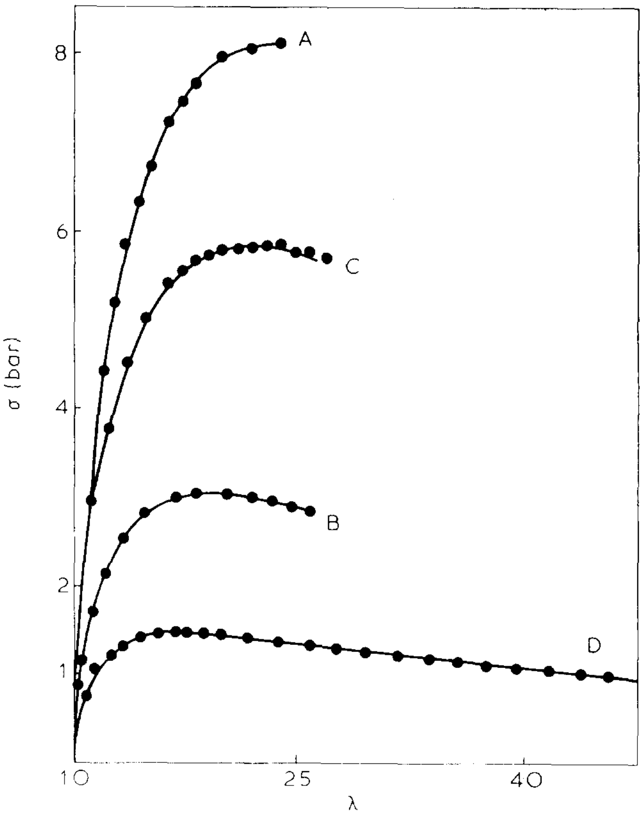

Figure 4 Response of SB copolymer at different temperatures to a ramp strain at various rates of extension. n = 0.4.

Curve	$\dot{\epsilon}$(min^{-1})	T(°C)
A	3.757	–20
B	0.0357	–20
C	3.76	–10
D	0.398	10

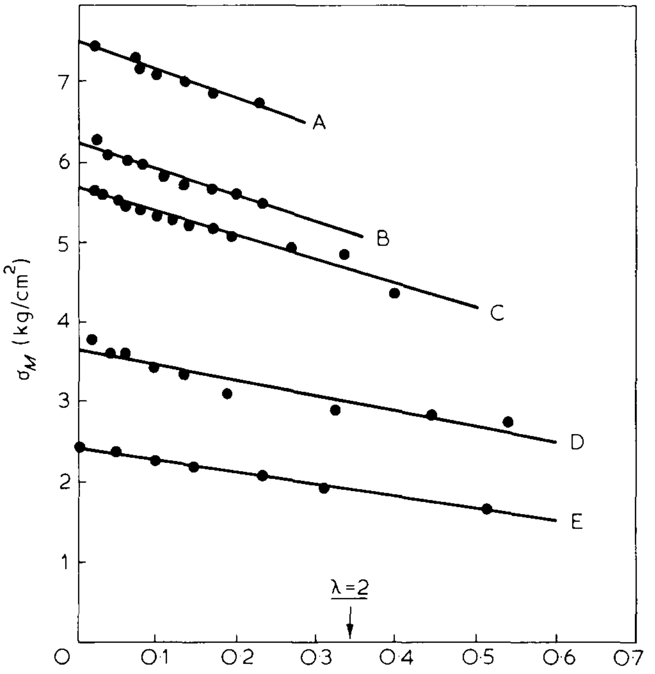

Figure 5 Data of Mullins on natural rubber. See *Table 1* for identification of the curves

if n is chosen appropriately. We infer that the elastic potential given by equation (6) is constitutive whenever that expressed by equation (1) is. Furthermore, introduction of equation (6) into the Boltzmann superposition integral should lead to an equally satisfactory representation of time-dependent moderately large deformations as those derived from equation (1). The tests have not been made yet but there is reasonable hope that the contention should be borne out. Thus, equation (6) would appear to have merit even if $\bar{\nu}_N$ and m are regarded simply as parameters in a phenomenological equation, to be determined by experiment. Its usefulness would be enhanced considerably if m and G_N (or, equivalently, $\bar{\nu}_N$) could be determined by independent measurements.

EXPERIMENTAL VERIFICATION

Unfortunately, the statistical mechanical theory of Heinrich, Straube, and Helmis does not furnish a value for either m or ρ_0. Kramer[17] discusses the possibility of obtaining G_N from the pseudo-equilibrium region of the stress relaxation modulus of the uncrosslinked polymer. He concludes that this should be possible in adequately crosslinked rubbers but that G_N should be less than the plateau modulus, G_N^0, at lower degrees of crosslinking. However, we consider that $\bar{\nu}_N$ (and, hence G_N) can be obtained readily from:

$$\bar{\nu}_N = 1 - \nu_X RT/G \qquad (13)$$

if ν_X and G are known. Published experimental data for which estimates of ν_X have either been given by the authors or could be deduced from the information given in their papers, will be examined presently. First, however, the question of determining a value for m must be addressed. It is tempting to assign to n the value that one would find by determining tensile stress relaxation data obtained on the uncrosslinked polymer[7] in the plateau region where time effects are of minor importance. The published data to be examined do not provide that information. However, the values of m found for the polymers examined so far[7] appear to be close to 0.5 and, furthermore, $\Phi_m(\lambda)$ is not a strong function of m in the range $0.4 < m < 0.6$. Hence, we may attempt to analyse the data by letting:

$$\Phi(\lambda) = \Phi_{1/2}(\lambda) = 1 - \frac{4(\lambda^{1/2} - \lambda^{-1/4})}{\lambda^2 - \lambda^{-1}} \qquad (14)$$

According to equation (8), a plot of σ_M vs. $\Phi(\lambda)$ should yield a straight line with a slope of $\bar{\nu}_N$.

Figures 5 and *6* represent data of Mullins[18] on natural rubber and of van der Hoff and Buckler[19] on polybutadiene rubber, respectively. The data points were read from the plots prepared by Crossland and van der Hoff[20] and represent several crosslink densities for each rubber. It appears that equation (8) describes the observed behaviour at least as well as the Mooney–Rivlin equation, even in its simplified two-parameter form in which $\Phi(\lambda)$ is given by equation (14).

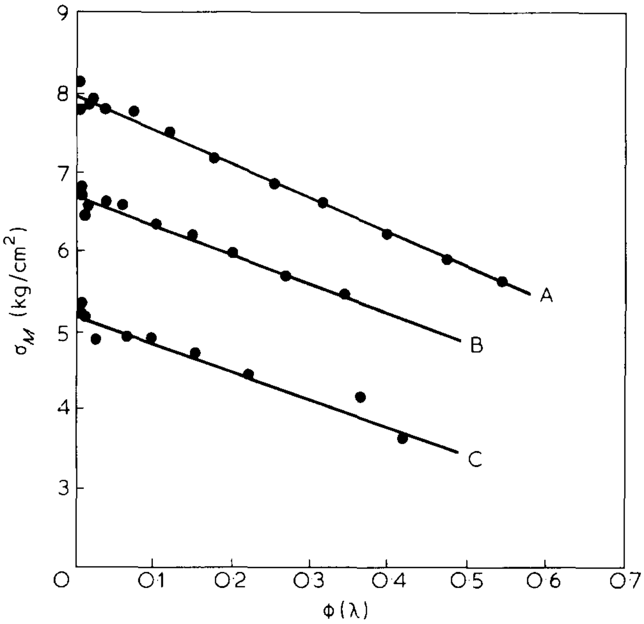

Figure 6 Data of van der Hoff and Buckler on polybutadiene rubber. See *Table 1* for identification of the curves

Table 1 Data on crosslink density

Figure and curve	G (kg/cm^2)	$\nu_X \times 10^{-4}$ (mol cm^{-3})	$\bar{\nu}_N$ (est)	$\bar{\nu}_N$ (slope)
5–A	7.48	1.53	0.312	0.485
5–B	6.24	1.30	0.285	0.531
5–C	5.62	1.14	0.313	0.468
5–D	3.67	0.48	0.560	0.555
5–E	2.45	0.24	0.722	0.685
6–A	7.92	2.29	0.270	0.528
6–B	6.68	0.78	0.705	0.544
6–C	5.16	0.32	0.843	0.667
7–D	4.19	1.15	0.302	0.144
7–E	3.01	0.88	0.264	0.286
7–F	3.65	0.75	0.485	0.470

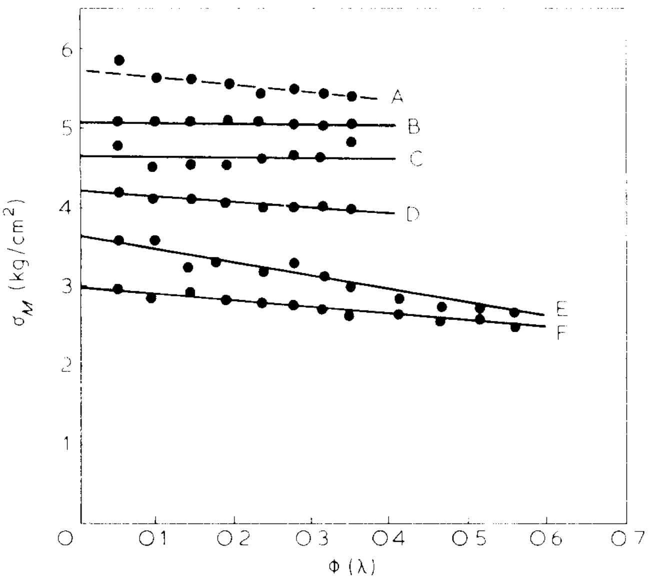

Figure 7 Data of Morton and Rubio on an isocyanate-crosslinked polyisoprene rubber. Curve A; M_{pp} = 3350; Curve B, M_{pp} = 4360; Curve C, M_{pp} = 5980; Curve D, M_{pp} = 7980; Curve E, M_{pp} = 12300; Curve F, M_{pp} = 10480. See *Table 1* for further data

An even more striking verification of the theory can be gleaned from the data of Morton and Rubio[21] on uniform polyisoprene networks synthesized by reaction of α,ω-dihydroxypolyisoprene with triisocyanate. In such rubbers, if one assumes the crosslinking efficiency to be 100%, we should have:

$$\bar{\nu}_N = 1 \quad \rho RT/GM_{pp} \qquad (15)$$

where ρ is the density, and M_{pp} is the molecular mass of the prepolymer. The data are shown in *Figure 7*. Curves B and C represent 'perfect' networks for which $\bar{\nu}_N$ vanishes. In the less highly crosslinked networks represented by curves D, E, and F, $\bar{\nu}_N$ increases with M_{pp}. Note that Curve F is out of order with respect to M_{pp}. The reason for this is not known but the same phenomenon appears in the original data. Curve A represents an anomaly ascribed[21] to the presence of urethane blocks at relatively high crosslink densities.

It is interesting to attempt to correlated $\bar{\nu}_N$ as found from the slopes in *Figures 5*, *6* and *7*, with the same parameter estimated from knowing ν_X. From the data of Mullins, ν_X was obtained as ρ/M_c (chem) where the density, ρ, is 0.910 g/cm^3, and M_c (chem) is calculated from equation (5) of the original publication[18]. The data of van der Hoff and Buckler ν_X is taken directly from the paper. Finally, for the data of Morton and Rubio, ν_X was obtained as ρ/M_{pp}. This was done only for curves D, E and F. Curve A was omitted because of the urethane effect, and $\bar{\nu}_N$ is zero for curves B and C. Values of $\bar{\nu}_N$ were then calculated as $\bar{\nu}_N$ (est) from equation (13), taking G from the intercept of the straight lines in *Figures 5*, *6* and *7*. The data also contains $\bar{\nu}_N$ as obtained from the slope of the lines in the Figures.

In *Figure 8* $\bar{\nu}_N$(est) is plotted as a function of $\bar{\nu}_N$ (slope). The agreement is as good as one could wish in view of the fact that the plot represents at best a rough test of the theory. The slopes from which $\bar{\nu}_N$ (slope) was calculated could change somewhat if a better value of m were known. Furthermore, the scatter of the data points in *Figure 8* is no worse than the scatter in a plot (not shown) of G vs. ν_X, indicating that most of the scatter is probably due to uncertainties or inconsistencies in the determination of ν_X.

The constraint density could also be estimated from the theory of Langley[21–23]. On the basis of this theory, one would have:

$$\nu_X = \nu_e T_e/\nu = \nu_e T_e RT/G = \rho_e T_e RT/GM_e \qquad (16)$$

where ν is the reticulation density, ν_e is the (total) entanglement density in the uncrosslinked polymer, T_e is the probability of trapping entanglements upon crosslinking, ρ_e is the density of the polymer, and M_e is the (average) molecular weight between pseudo-crosslinks. Unfortunately, available data do not contain all the information needed. Further work on the verification and refinement of the theory presented here is planned.

CONCLUSIONS

It appears that the behaviour of elastomeric networks in moderately large deformations can be described satisfactorily by a two-network model in which the first is a 'perfect' network as envisaged by the statistical theory of rubber elasticity, while the second is conceived to be formed through 'equivalent pseudo-crosslinks' modelling the topological constraints (entanglements) which are normally present in real rubbers. The two networks are considered to behave independently and their behaviour is additive.

Several attempts have been made to formulate an elastic potential for the second network. The potential proposed here contains a strain parameter m in addition to a modulus G_N. Reasonable experimental agreement with the theory has been achieved by letting m equal ½. It is conjectured that a slightly better value of m might be obtained from the strain dependence of the modulus of the uncrosslinked polymer in the pseudo-equilibrium plateau region. The modulus, G_N, should be predictable from a knowledge of the chemical crosslink density.

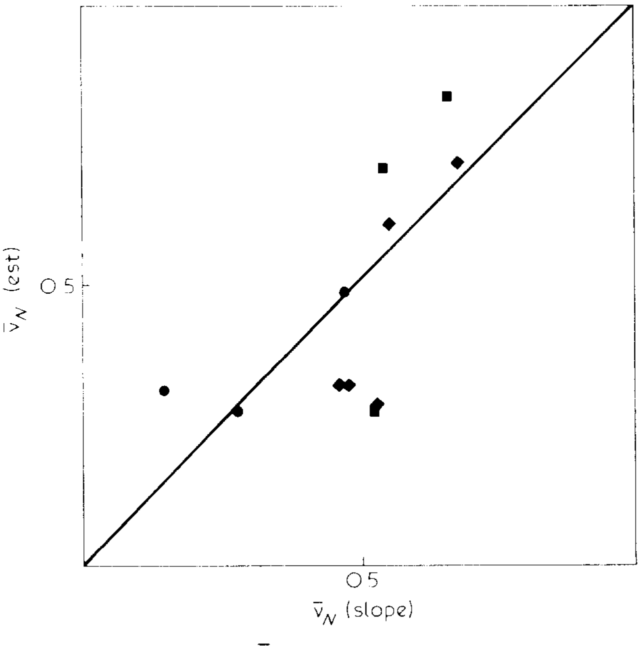

Figure 8 Plot of values of $\bar{\nu}_N$ established from the chemical crosslink density vs. values found from theory. ■, van der Hoff and Buckler; ●, Morton and Rubio; ◆, Mullins

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