

Assessment of the sliding link model of chain entanglement in polymer networks

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The stress-strain relations derived from the sliding link model of chain entanglement proposed by Ball *et al.* (*Polymer* 1981, **22**, 1010) are compared with experimental results. There is good agreement with Ogden's empirical treatment of several results obtained previously from general pure strain tests on rubber vulcanizates. New uniaxial data for random polyisoprene networks at various stages from the gel point indicate that a significant fraction of trapped entanglements does not behave as the sliding links of the model but gives the same contribution to the stress as the chemical cross-links.

(Keywords: Network elasticity; chain entanglement; sliding link)

INTRODUCTION

The deviations from the classical statistical elasticity theory for undiluted elastomer networks are currently attributed to the presence of chain entanglements. According to the theory proposed by Ball *et al.*¹, these topological constraints can be modelled by links which make a sliding contact between the network strands. Here, the corresponding stress-strain relations for pure strains are derived and compared with the elastic response of polyisoprene vulcanizates.

Deformation dependent part of the model free energy

In accord with the Valanis-Landel symmetry postulate², the replica formalism used to calculate in ref. 1 the contribution of a sliding link to the strain dependence of the free energy of shear \bar{F} of a Gaussian network leads to a sum of the same functions of each extension ratio $\lambda_1\lambda_2\lambda_3$ (equation (58), ref. 1):

$$\frac{\bar{F}}{K_B T} = \frac{1}{2}N_c \sum \lambda_i^2 + \frac{1}{2}N_s \sum \left[\frac{(1+\eta)\lambda_i^2}{1+\eta\lambda_i^2} + \log(1+\eta\lambda_i^2) \right] \quad (1)$$

K_B is the Boltzmann constant, T the temperature, N_c the number of cross-links, N_s the number of sliding links and η a relative measure of the freedom of a link to slide.

For $\eta=0$, the N_s entanglements would induce the same strain dependence as the N_c cross-links and equation (1) would predict the usual free energy of a phantom network, a result previously obtained by Deam and Edwards³ for the cross-links' contribution to the free energy. An argument minimizing \bar{F} leads to conjecture that $\eta=0.2343$ if each slip link can on average slide as far as the centres of its topologically neighbouring links¹. Though physical freedom restriction of slip is probably close to this case, η is considered here as a material parameter, the actual value of which should be determined by comparing equation (1) with experimental evidence, similar to the

two other parameters N_c , N_s directly related to the network's structure.

For this purpose the result of the spatial derivations of the model free energy for pure strains are presented in a form yielding the stress contribution of the sliding links relative to that of the cross-links. These calculations imply the usual incompressibility condition $\lambda_1\lambda_2\lambda_3=1$.

Pure shear strain

For pure shear maintained by principal stresses t_1 and t_2 with $t_3=0$, then $\lambda_1=1/\lambda_3$ if $\lambda_2=1$ and the stress difference t_1-t_2 along the directions of λ_1 and λ_2 resulting from the derivation of equation (1) with respect to λ_1 is given by:

$$\frac{t_1-t_2}{\lambda_1^2-1} = K_B T \left[N_c + \frac{N_s}{(\eta\lambda_1^2+1)^2} \right] \quad (2)$$

which decreases monotonically with λ_1 .

Uniaxial extension or compression

For uniaxial deformation maintained by a single positive or negative stress $t=t_1$ along the direction of $\lambda=\lambda_1$, $\lambda_2=\lambda_3=\lambda^{-1/2}$ and for the reduced modulus $\Phi = t/(\lambda^2-\lambda^{-1})$ of the model:

$$\frac{t}{\lambda^2-\lambda^{-1}} = K_B T [N_c + N_s H(\lambda, \eta)] \quad (3)$$

with a strain dependent term H expressing again a deviation from the classical elasticity theory:

$$H(\lambda, \eta) = \frac{\lambda^2}{\lambda^2 + \lambda + 1} \left[\frac{1}{(\lambda + \eta)^2} + \frac{\lambda + 1}{\lambda(1 + \eta\lambda^2)^2} \right] \quad (4)$$

This modulus, which decreases with λ in extension, attains in the compression zone a maximum value larger

than the linear shear modulus

$$\Phi(\lambda \rightarrow 1) = K_B T [N_c + N_s / (1 + \eta)^2]$$

The response of the model differs radically in this respect from the Mooney–Rivlin stress–strain relation which usually describes the tensile properties of undiluted rubber networks at medium extensions:

$$\frac{t}{\lambda^2 - \lambda^{-1}} = 2C_1 + 2\frac{C_2}{\lambda} \quad (5)$$

Numerical calculations show, however, that the strain dependences in the extension zone are not significantly different for equations (3)–(5), owing to a long inflection approximately centred on $\lambda = 2$ in the plots of $H(\lambda, \eta)$ against $1/\lambda$.

To assess the applicability of the model to actual rubber networks, it is necessary to refer first to investigations reported previously which include pure strains of various types.

DETERMINATION OF η BY FITTING WITH OGDEN EXTENSIONS POWER SERIES

Ogden⁴ proposed to express the strain energy function W of incompressible materials by a power series of principal extensions consistent with the Valanis–Landel postulate:

$$W = \sum_n \frac{\mu_n}{\alpha_n} (\lambda_1^{\alpha_n} + \lambda_2^{\alpha_n} + \lambda_3^{\alpha_n} - 3) \quad (6)$$

Once the coefficients α_n, μ_n are obtained from an accurate identification of the results of general strain tests, this empirical formula completely describes the whole non-linear elastic response of a network⁵. The pure shear stress difference is, for example, given by:

$$t_1 - t_2 = \sum_n \mu_n (\lambda_1^{\alpha_n} - \lambda_2^{\alpha_n}) \quad (7)$$

and the tensile stress in uniaxial extension or compression by:

$$t = \sum_n \mu_n (\lambda^{2\alpha_n} - \lambda^{-2\alpha_n/2}) \quad (8)$$

In particular, a three-term series with the following coefficients was found⁴ to account for the data of Treloar⁶ in uniaxial and biaxial extensions for an elastic, non-strain crystallizing network, prepared by curing natural rubber with 8% sulphur (equation (22), ref. 7):

$$\alpha_1 = 1.3 \quad \alpha_2 = 5.0 \quad \alpha_3 = -2.0$$

$$\mu_1 = 0.618 \quad \mu_2 = 0.00118 \quad \mu_3 = -0.0098 \quad \text{MPa}$$

These figures have been used in equations (7) and (8) to analyse three values of η : 0.2343, 0.40, 0.60, the pure shear and uniaxial deformation behaviours of the vulcanizate, shown by plots of $(t_1 - t_2)/(\lambda^2 - 1)$ against $1/(\eta\lambda_1^2 + 1)^2$ in Figure 1 and Φ against $H(\lambda, \eta)$ in Figure 2. Both figures clearly indicate a better fit with the linear correlations predicted by the theory for $\eta = 0.40$, in spite of relatively small differences between the values of η . They also yield for $\eta = 0.40$ the same values for the other material

parameters: $RTN_c = 0.270$ MPa, $RTN_s = 0.275 \pm 0.005$ MPa.

As expected, differences appear at large deformations. The marked increase of the stress terms for $\lambda \geq 3$ probably reflects the finite chains extensibility. Non-Gaussian effects should also ultimately contribute to the progressive upward deviations found at $\lambda \leq 0.6$. The latter discrepancy seems, however, mainly due to the indirect extrapolation procedure used to investigate the compression zone, and to higher correlation of links, neglected in the model¹, which then would be more influential than in the extension zone.

The same treatment has been applied to the results of Jones and Treloar⁷ for the equilibrium shear strain response of a natural rubber vulcanizate cross-linked by a sulphur-accelerator system (equation (21), ref. 7), and to

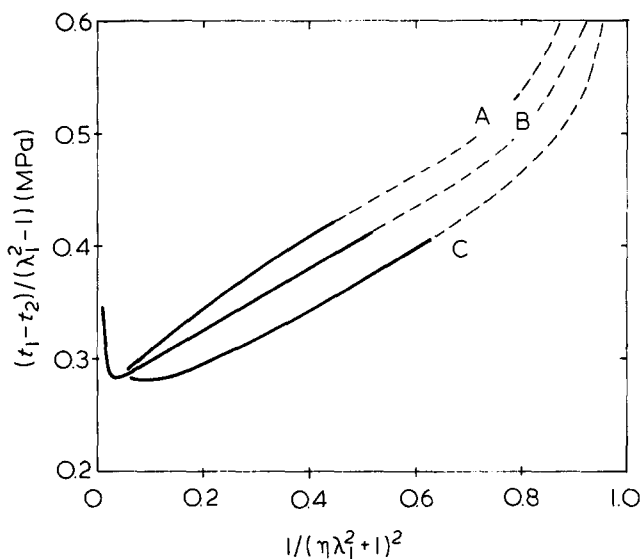


Figure 1 Assessment of equation (2) using the pure shear behaviour of a natural rubber vulcanizate for different sliding freedom coefficients, η : A, 0.6; B, 0.4; C, 0.2343. Data derived from empirical equation (22), ref. 7. —, extension zone; ---, compression zone

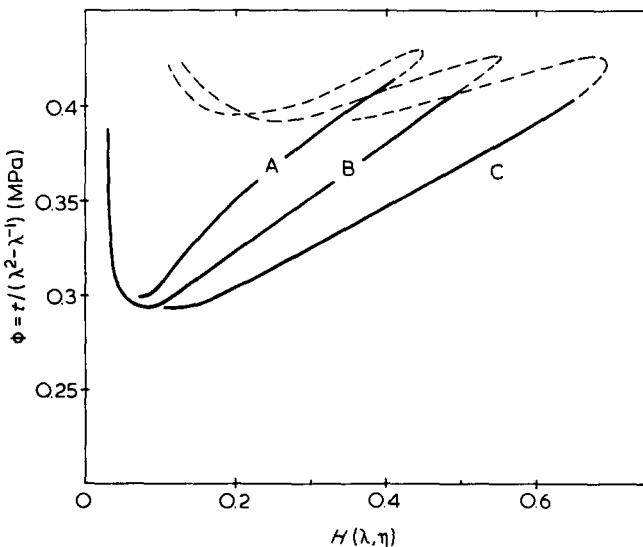


Figure 2 Assessment of equations (3) and (4) using the uniaxial deformation of the network of Figure 1 for different sliding freedom coefficients, η : A, 0.6; B, 0.4; C, 0.2343. Data derived from empirical equation (22), ref. 7. —, extension zone; ---, compression zone

those of Arentz and Landel for the stress at 10 min relaxation of a series of styrene-butadiene vulcanizates (Table 4, ref. 8). Best agreement was also obtained for $\eta^* = 0.40$, apparently almost insensitive to the networks' cross-link density or even to the polymer microstructure.

RELATION OF N_c , N_s TO NETWORKS' CHEMICAL PARAMETERS

To establish the relation of the model material parameters N_c and N_s with the actual structural characteristics of polymer networks, equilibrium data for better-defined systems were needed in a range of cross-link densities approaching the gel point. In the present case of rubber networks prepared from long-chain precursors, large hysteresis effects occur at low cross-link density and precise determinations of the stress relaxation kinetics in the domain of the strains examined become necessary. Independent determinations of the number of chemical cross-links and trapped entanglements are also required.

For this study of the significance of N_c and N_s , similar vulcanizates to the previous ones were used, tested in uniaxial extension only, with the assumption that $\eta^* = 0.40$ deduced from the preceding general strain results.

Materials

Twelve networks have been prepared by cross-linking a commercial 92% *cis* 1-4 polyisoprene, a highly pure non-crystallizing elastomer, with *C* parts dicumyle peroxide per weight of polymer: $0.002 < C < 0.01$. Press curing for 30 min at 170°C ensured complete decomposition of the peroxide which is known to react stoichiometrically with polyisoprene with negligible chain scission⁹. The cross-linking probability, q , of a randomly chosen monomer can then be calculated from the peroxide initial content in the mix by $q = 2C68/271$, the average number γ of cross-linked units per chain from q and the number-average molecular weight M_n of the precursor by $\gamma = qM_n/68$ (68 and 271 being the respective molecular weights of a monomer and of the peroxide). This evaluation of γ was confirmed by sol fraction determinations ω_s in accord with the Charlesby-Pinner relation between γ and ω_s (ref. 10).

Thus, the molecular weight $M_c = 68/q$ between cross-links was obtained in the range 13 600–68 000 for two different molecular weight distributions of the precursor controlled by gel permeation chromatography:

$$M_n = 390\,000 \quad \text{and} \quad M_w = 1\,200\,000 \quad \text{for code A}$$

$$M_n = 250\,000 \quad \text{and} \quad M_w = 630\,000 \quad \text{for code B}$$

These values of M_c are larger than the 'entanglement distance' $M_c = 6700$ of the polyisoprene deduced from

dynamic measurement of its shear plateau modulus at 30°C: $G_N^0 = 0.34$ MPa. Table 1 gives for five networks together with M_n , C , q and γ , the number of effective strands ν , chemical junctions μ and the fraction T_e of trapped entanglements calculated by the relations derived by Miller *et al.*¹¹ for randomly cross-linked systems with non-uniform distribution.

Test method and results

The stress relaxation of samples (70 × 4 × 2 mm) stored at -15°C is recorded at constant extension and 30°C for 20–60 min, after stretching in less than 0.1 s in a maximum range of extension λ between 1.25 and 3. The same sample is used for tests at different elongations to avoid the dispersion due to cross-section errors, a reproducibility better than 1% being obtained in these conditions.

Virtual equilibrium stresses, t , have been calculated by extrapolating at long times the relaxation data, using the Chasset-Thirion equation¹²:

$$F(\lambda, \tau) = F_c(\lambda) \left[1 + \left(\frac{\tau}{\tau_0} \right)^{-m} \right] \quad (9)$$

where F and F_c represent the force per unit unstrained section at time τ and at equilibrium, m and τ_0 two constants.

The reduced stress $\Phi = t/(\lambda^2 - \lambda^{-1})$ found for the five networks of Table 1 is plotted against $H(\lambda, \eta^*)$ in Figure 3 and against $1/\lambda$ in Figure 4 where the data fit equally well equations (3) and (5), with correlation coefficients all better than 0.96 relative to the theoretical linear regressions. The model parameters N_c , N_s and the Mooney-Rivlin coefficients so frequently quoted in the square analysis are given in Table 2.

The results indicate an approximate equivalence between $2C_1/RT$ and N_c and $2C_2/RT$ and N_s for $N_c/(2C_1/RT) \approx 1.10$ and $N_s/(2C_2/RT) \approx 1.40$ for $\eta^* = 0.40$. This fortuitous proportionality might confer a more fundamental meaning to the phenomenological Mooney-Rivlin coefficients to frequently quoted in the literature.

To investigate the connection of N_c and N_s with the networks structure by means of equation (3) without a front factor correction affecting N_c , it is necessary to assume first that the mean square end-to-end distance of the strands in the unstrained state is the same as for a corresponding set of free chains, a condition probably almost fulfilled for these randomly cross-linked networks occupying their as-formed volume. The theory of Ball *et al.*, which implies that the topological entanglements all behave as sliplinks and that the chemical junctions are free to fluctuate about their mean position, leads then to predict $N_s = G_N^0 T_e / RT$ and $N_c = \mu$.

A comparison of the data in Tables 1 and 2, as well as

Table 1 Characterization of polyisoprene-peroxide networks

Code	$C \times 10^2$	$M_n \times 10^{-3}$	$q \times 10^3$	γ	$\nu \times 10^5$ (cm ³)	$\mu \times 10^5$ (cm ³)	T_e
A4	0.8	390	4.01	23	5.17	2.67	0.859
A5	1.0	390	5.02	29	6.53	3.36	0.887
B8	0.35	250	1.76	6.5	1.94	1.07	0.560
B10	0.6	250	3.01	11	3.64	1.95	0.706
B11	0.8	250	4.01	15	4.99	2.64	0.769

the plots of N_s and $N_c - \mu$ against T_c in Figure 5, shows, however, that this is definitely not confirmed by the present experiments. The density of entanglements behaving as sliplinks when trapped, $\bar{N}_s = N_s/T_c$, remains effectively constant but its mean value, $8.2 \times 10^{-5} \text{ cm}^{-3}$, is significantly lower than the number deduced from the plateau modulus of the uncross-linked polymer $G_N^0/RT = 13.5 \times 10^{-5} \text{ cm}^{-3}$. N_c is systematically much larger than μ and this compensates somehow the deficiency relative to the expected number of effective sliplinks.

To interpret analogous discrepancies between the chemical characteristics of various types of entangled polymer networks and their neo-Hookean behaviour, Dossin and Graessley¹³, and Ferry and Kan¹⁴ have postulated a phantom network contribution to the elastic modulus equal to νRT , approximately twice as large as μRT for tetrafunctional cross-links in imperfect networks. The fluctuations of the cross-links, therefore, was assumed

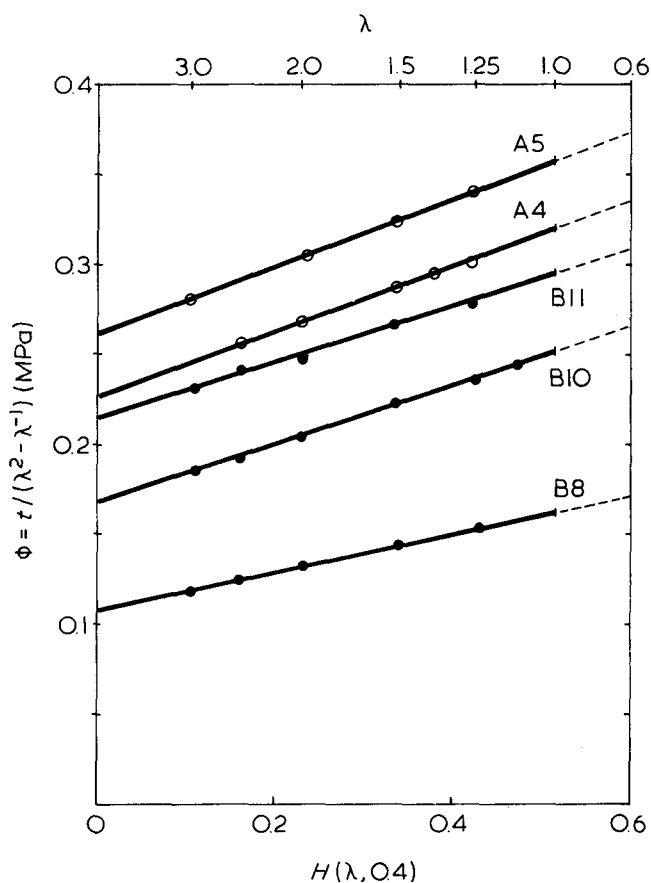


Figure 3 Plot of the tensile reduced modulus Φ against the strain term $H(\lambda, \eta^*)$ for uniaxial extension of five polyisoprene vulcanizates. $\eta^* = 0.40$; —, extension zone; ---, extrapolation in the compression zone. Peroxide content, C: A5, 1; A4, 0.8; B11, 0.8; B10, 0.6; B8, 0.35%

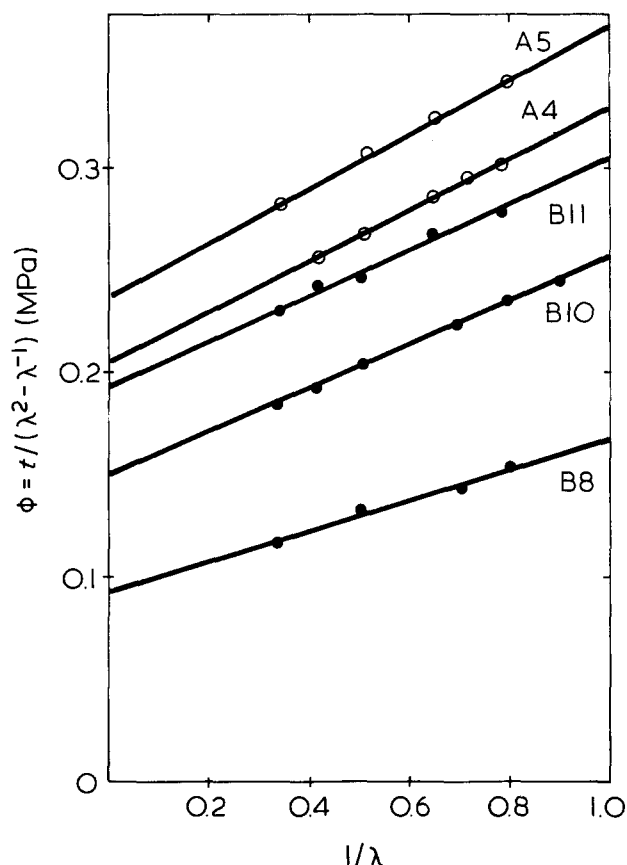


Figure 4 Mooney-Rivlin plot of the tensile reduced modulus Φ against $1/\lambda$ for uniaxial extension of the same networks as in Figure 3. Peroxide content, C: A5, 1; A4, 0.8; B11, 0.8; B10, 0.6; B8, 0.35%

to be largely suppressed by configurational involvement with neighbouring strands. The conclusions suggest, moreover, that the trapped entanglements can behave either as sliplinks or as pseudo-cross-links, the former accounting for the C_2 and the latter for part of the C_1 Mooney-Rivlin coefficients.

This assumption is used here but at this stage the still disputable questions concerning the magnitude of the phantom network contribution to the modulus and an *a priori* possible increase of the proportion α of potential pseudo-cross-links with μ or T_c , still remain. Such variation of α with the cross-link density could explain a faster increase of $N_c - \mu$ with T_c in Figure 5 than for $N_c - \nu$. The proposed splitting of the trapped entanglements leads to the following formulations of N_c and N_s in terms of the structural parameters:

$$RTN_c = \gamma RT + \alpha G_c^{\text{max}} T_c \quad (10)$$

$$RTN_s = (1 - \alpha) G_c^{\text{max}} T_c \quad (11)$$

Table 2 Stress-strain parameters of polyisoprene-peroxide networks ($RT = 2.52 \times 10^3 \text{ J}$; $\eta^* = 0.40$)

Code	$2C_1/RT \times 10^5$ (cm^3)	$2C_2/RT \times 10^5$ (cm^3)	$N_c \times 10^5$ (cm^3)	$N_s \times 10^5$ (cm^3)	$N_{c\nu} \times 10^5$ (cm^3)	$N_{c\mu} \times 10^5$ (cm^3)	$N_s \times 10^5$ (cm^3)
A4	8.15	4.97	9.05	7.00	4.50	7.43	8.15
A5	9.40	5.23	10.36	7.40	4.30	7.89	8.34
B8	3.75	2.89	4.28	4.12	4.17	5.73	7.36
B10	5.92	4.35	6.65	6.45	4.28	6.66	9.13
B11	7.71	4.35	8.52	6.10	4.57	7.65	7.93

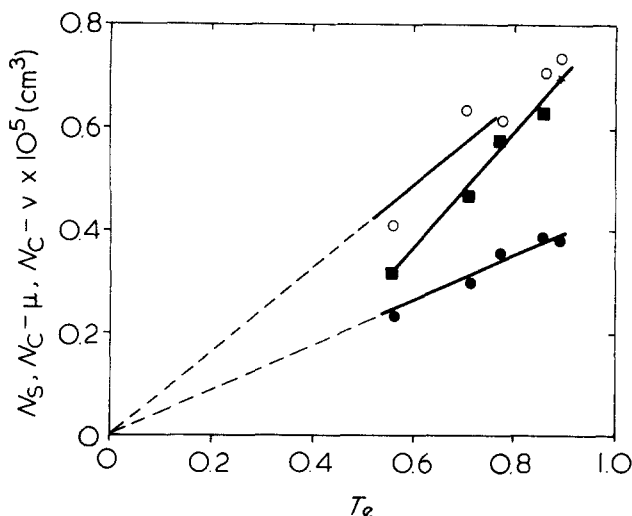


Figure 5 Influence of the trapping factor T_e on the number of sliplinks N_s and of pseudo-cross-links $N_c - \mu$ or $N_c - \nu$ for the same networks as in Figure 3: \circ , N_s ; \blacksquare , $N_c - \mu$; \bullet , $N_c - \nu$

where γ represents either μ or ν , G_e^{\max} the maximum possible topological contribution to the elastic modulus, i.e. the total density of entanglements, and α the partition coefficient eventually depending on the cross-link density.

With these notations, equation (3) can be rearranged to the form:

$$\frac{\Phi}{RT \cdot T_e} = \frac{\gamma}{T_e} + \frac{G_e^{\max}}{RT} [\alpha + (1 - \alpha)H(\lambda, \eta^*)] \quad (12)$$

which entails a rectilinear relation with slope unity for constant λ between $\Phi/T_e RT$ and γ/T_e provided that α remains an invariant parameter.

The corresponding Langley plots of $\Phi/T_e RT$ against γ/T_e , previously restricted to network analysis of very small deformations, also become significant at large strains by means of equation (12). This method has been applied, therefore, both to the vanishing strain modulus of the five networks of Table 2 and to the equilibrium modulus $\Phi(\lambda) = t/(\lambda^2 - \lambda^{-1})$ at constant extension ratio $\lambda = 1.5$ of the whole set of 12 networks. (The vanishing strain modulus is deduced from N_c and N_s by $\Phi(\lambda \rightarrow 1) = RT[N_c + N_s/(1 + \eta^{*2})]$.) In Figure 6, which shows the four correlations obtained in this way with μ/T_e or ν/T_e as the chemical variable, the points seem to occur along straight lines at least for $\lambda = 1.5$. Owing to equation (12), this implies that $d\alpha/d(\gamma/T_e)$ is constant. More precisely: (1) if $\gamma = \nu$, the slope is close to 1 (1.04 according to a least square analysis), $\bar{N}_{cv} = (N_c - \nu)/T_e$ should be constant in Table 2; if $\gamma = \mu$, the slope is close to 2, then

$$\alpha = \frac{RT}{G_e^{\max} [1 - H(1.5, \eta^*)]} \frac{\mu}{T_e}, \quad \text{if } \bar{N}_{c\mu} = \frac{N_c - \mu}{T_e}$$

$\bar{N}_{c\mu} T_e / \mu$ should be constant in Table 2.

The assertion $\gamma = \nu$ fits better with the results: $\Delta \bar{N}_{cv} \approx 4\%$, $\Delta(\bar{N}_{c\mu} T_e / \mu) \approx 14\%$. However, α will be shown to be independent of ν/T_e (and $\gamma = \nu$) if more complete data show that the Langley plot of Figure 6 yields straight lines for other values of λ than $\lambda = 1.5$, as it seems to be true for $\lambda \rightarrow 1$.

Assuming that this is the case:

$$A(\alpha, \lambda) = \frac{G_e^{\max}}{RT} [\alpha + (1 - \alpha)H(\lambda, \eta^*)] \quad (13)$$

The value of the coefficient $\alpha = 0.328$ has then been calculated from the ratio:

$$\frac{A(\alpha, 1)}{A(\alpha, 1.5)} = \left[\alpha + \frac{1 - \alpha}{(1 + \eta^{*2})} \right] / [\alpha + (1 - \alpha)H(1.5, \eta^2)] \quad (14)$$

where $A(\alpha, 1) = 7.35 \times 10^{-5} \text{ cm}^{-3}$, $A(\alpha, 1.5) = 8.75 \times 10^{-5} \text{ cm}^{-3}$, $H(1.5, \eta^*) = 0.350$, $(1 + \eta^{*2}) = 1.96$.

Its substitution in equation (13) leads to a value of $G_e^{\max} = 0.329 \text{ MPa}$ very close to the polymer plateau modulus $G_N^0 = 0.34 \text{ MPa}$ and to the potential number of entanglements $G_e^{\max}/RT = 13.04 \times 10^{-5} \text{ cm}^{-3}$ in the networks.

These determinations of the topological parameters α and G_e^{\max} are corroborated by the small variations of the density $\bar{N}_{cv} = (N_c - \nu)/T_e$ of the entanglements which seem to behave on this basis as pseudo-cross-links. The mean value of $\bar{N}_{cv} = 4.2 \times 10^{-5} \text{ cm}^{-3}$ leads to other estimations of α by $\bar{N}_{cv}/(\bar{N}_{cv} + \bar{N}_s) = 0.35$ and of G_e^{\max}/RT by $\bar{N}_{cv} + \bar{N}_s = 12.5 \times 10^{-5} \text{ cm}^{-3}$ in satisfactory agreement with the previous ones.

CONCLUSIONS

This verification of the sliding model of chain entanglements in entangled networks confirms the direct association indicated previously on the basis of the Mooney-Rivlin equation, by Ferry and Hsin-Chia Kan¹⁴

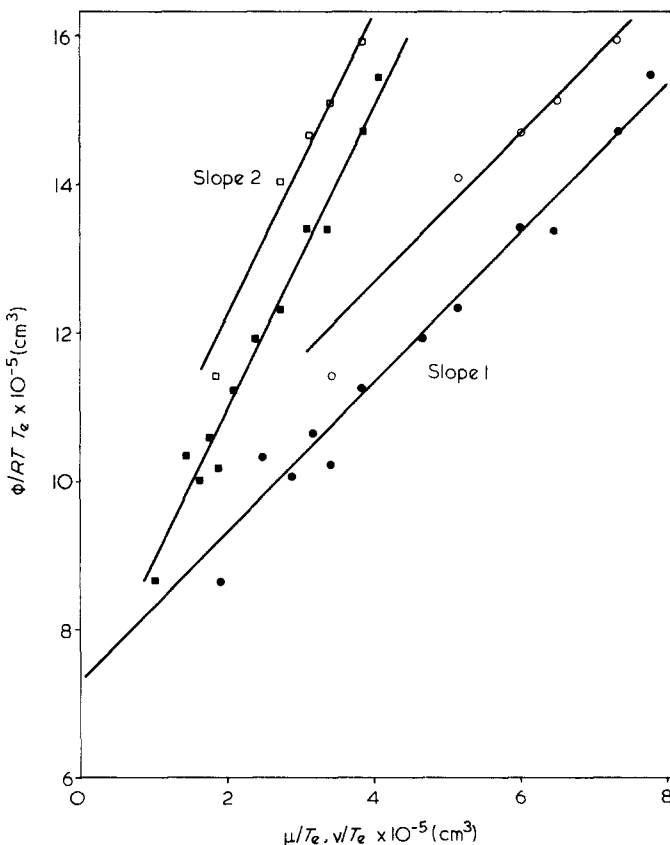


Figure 6 Langley plots extended to large extensions for a set of polyisoprene-dicumyle peroxide vulcanizates cross-linked in bulk and including the networks of Figures 3 and 4; for μ/T_e as chemical variable: \square , $\lambda \rightarrow 1$; \blacksquare , $\lambda = 1.5$. For ν/T_e : \circ , $\lambda \rightarrow 1$; \bullet , $\lambda = 1.5$

between the deviations of the statistical elasticity theory and the relative concentrations of cross-links and trapped entanglements. Except for compressive deformations, quantitative agreement with the model is found using general shear strain results of the literature for a value of the sliding freedom coefficient almost compatible with a theoretical topological condition.

Uniaxial extension tests with polyisoprene vulcanizates treated on this theoretical basis indicate a uniform repartition, with a ratio of $\approx 2/3, 1/3$ between the trapped entanglements which seem to actually behave as sliding links and those giving the same stress-strain dependence as that of the chemical cross-links. This conclusion is in qualitative agreement with a previous study of the elastic behaviour of well-characterized polybutadiene networks¹³.

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