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Interpretation of Stress-Strain Isotherms for Elastomers Cross-Linked in Solution

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ABSTRACT: Stress-strain isotherms exhibited by elastomeric networks in elongation differ in form from the predictions of the simplest molecular theories. Specifically, the reduced stress $[f^*]$ generally shows an unexpected large decrease with increase in elongation α, and, in the approximation that $[f^*]$ is linear with α^{-1}, the decrease is characterized by the ratio $2C_2/2C_1$ of phenomenological elasticity constants, where $2C_1$ is an approximate measure of the high-deformation modulus. Experimental studies have shown that cross-linking polymers in solution gives networks having greatly reduced values of $2C_2/2C_1$. The more recent and more realistic constraint theory of rubberlike elasticity is found to give a good account of these results when the important constraint parameter κ is varied with volume fraction v_{2C} of polymer present during the cross-linking. However, the dependence of κ on v_{2C} is significantly stronger than that suggested by theory. The values of κ thus obtained are within the range of values obtained in other comparisons of theory and experiment, as are the values of the heterogeneity parameter ζ. The values of κ generally decrease with decrease in v_{2C} and with increase in degree of cross-linking $(2C_1)$, according to the relation $\kappa = 2(2C_1)^{-1/2}v_{2C}{}^{4/3+m}$. Treatment of experimental data by two independent methods led to $m = {}^2/_3$ and ${}^8/_9$, in contrast to a value of $m = 0$ expected from theory. Deviation of m from zero indicates a particularly strong effect of dilution on the degree of network chain interpenetration.

Introduction

The quantity of foremost importance in characterizing the elastomeric properties of rubberlike materials in elongation is the reduced stress of modulus. It is defined by[1,2]

$$[f^*] \equiv f v_2{}^{1/3}/[A^*(\alpha - \alpha^{-2})] \tag{1}$$

where f is the equilibrium retractive force, v_2 the volume fraction of polymer in the stretched network, A^* the undeformed cross sectional area of the dry sample, and α its elongation (ratio of length in the stretched state to the length in the unstretched state at the same volume). In the simplest molecular theories it is given by [2-6]

$$[f^*] = \nu k T v_{2C}{}^{2/3} \tag{2}$$

where ν is the number density of network chains relative to the dry network, k the Boltzmann constant, T the absolute temperature, and v_{2C} the volume fraction of polymer chains in the system being cross-linked which are successfully incorporated in the network structure. These theories thus predict that once a network is formed and a temperature chosen for its characterization, its reduced stress should be independent of elongation.

Experimental values of $[f^*]$, however, generally show a strong dependence on α, with $[f^*]$ decreasing with increase in α.[2,7] Over the typical range of elongations studied the relationship can be represented by the simple phenomenological equation[2,7-9]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{3}$$

within experimental error, where $2C_1$ and $2C_2$ are independent of α. If $2C_1$ represents the molecular contribution given in eq 1, then the normalized quantity $2C_2/2C_1$ is a measure of the discrepancy between experiment and the simplest molecular theories.[7]

A number of experimental studies[6,10-14] have shown that cross-linking polymers in solution gives networks which, even when dried, have very small and frequently negligible values of $2C_2/2C_1$. Typical results from one of the most extensive studies of this type, on poly(dimethylsiloxane) (PDMS), are shown in Figure 1.[13] They were obtained by interpolations or limited extrapolations of the results given in the first four columns of Table I. The decreases in $2C_2/2C_1$ are seen to be particularly pronounced at lower values of v_{2C} (higher dilutions). Unfortunately, very little is known about the origin of this interesting effect.

In one study[13] it was suggested that solution cross-linked networks have "simpler topologies", without any elaboration beyond the assumption that the degree of entangling among network chains was diminished. An alternative explanation[15] was based on the fact that if a network is formed in the undiluted state but studied swollen, its value of $2C_2/2C_1$ is also unusually small.[2,7] In this interpretation, imperfections even in an unswollen network would act as diluent, thus decreasing $2C_2/2C_1$ in the usual manner. Such imperfections would be expected to be more numerous in networks formed in solution because of the increased probability of intramolecular cross-linking, which leads to loops that can be elastically ineffective.[15] If the cross-linking was carried out by using high-energy radiation, as is frequently the case, then chain scission[16,17] could cause the formation of dangling chains, and such irregu-

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Table I
Experimental Values of the Ratio $2C_2/2C_1$ and the Constraint Theory Parameters Reproducing Them

				parameters					
				first scheme			second scheme		
	exptl results[a]								
sample	v_{2C}[b]	$2C_1$, N mm^{-2}	$2C_2/2C_1$	κ	$(\xi kT/V^0)v_{2C}^{-1/3}$, N mm^{-2}	ζ	κ	$(\xi kT/V^0 v_{2C}^{-1/3}$, N mm^{-2}	ζ
B-1	0.879	0.0306	1.20	8.84	0.0388	0.09	6.50	0.0424	0.20
B-2	0.893	0.0337	1.54	8.69	0.0512	0.18	8.70	0.0516	0.20
B-3	0.901	0.0358	1.74	8.58	0.0580	0.18	10.10	0.0581	0.20
B-4	0.914	0.0566	0.995	7.02	0.0683	0.08	5.80	0.0748	0.20
B-5	0.914	0.0583	1.06	6.92	0.0734	0.10	6.08	0.0775	0.18
B-6	0.920	0.0534	1.42	7.33	0.0796	0.18	8.47	0.0789	0.18
B-7	0.927	0.0769	0.771	6.20	0.0843	0.05	4.62	0.0936	0.18
B-8	0.934	0.0839	0.993	6.02	0.1074	0.14	5.99	0.1096	0.18
S1-1	0.669	0.0232	1.50	5.88	0.0372	0.15	4.50	0.0345	0.34
S1-2	0.684	0.0435	1.10	4.49	0.0545	0.14	3.67	0.0580	0.34
S1-3	0.702	0.0592	0.961	4.05	0.0718	0.14	3.46	0.0757	0.32
S1-4	0.698	0.0692	1.02	3.70	0.0883	0.22	3.58	0.0901	0.32
S1-5	0.701	0.0931	0.889	3.22	0.1152	0.24	3.22	0.1166	0.32
S2-1	0.565	0.0272	1.78	3.87	0.0421	0.34	3.62	0.0428	0.52
S2-2	0.577	0.0436	1.38	3.19	0.0616	0.38	3.13	0.0620	0.50
S2-3	0.581	0.0590	0.988	2.78	0.0738	0.38	2.48	0.0752	0.46
S2-4	0.586	0.0799	0.884	2.43	0.0973	0.30	2.33	0.0988	0.46
S2-5	0.583	0.0855	0.863	2.33	0.1039	0.34	2.27	0.1051	0.46
S2-6	0.583	0.0916	0.898	2.25	0.1140	0.42	2.33	0.1137	0.46
S3-1	0.496	0.0295	1.44	2.86	0.0406	0.30	4.45	0.0386	0.74
S3-2	0.547	0.0355	1.23	3.18	0.0460	0.21	2.58	0.0482	0.54
S3-3	0.507	0.0482	1.05	2.34	0.0598	0.25	2.02	0.0618	0.62
S3-4	0.508	0.0517	1.19	2.27	0.0685	0.44	2.20	0.0689	0.64
S3-5	0.514	0.0724	0.933	1.96	0.0894	0.44	1.91	0.0900	0.60
S3-6	0.515	0.0895	0.679	1.77	0.1001	0.22	1.57	0.1034	0.58
S3-7	0.516	0.0992	0.628	1.69	0.1092	0.21	1.50	0.1129	0.58
S4-1	0.465	0.0553	0.784	1.84	0.0622	0.17	1.45	0.0653	0.70
S4-2	0.439	0.0507	1.32	1.71	0.0690	0.94	0.0640	0.44	1.78
S4-3	0.441	0.0655	0.920	1.52	0.0796	0.52	1.46	0.0799	0.80
S4-4	0.449	0.0741	0.763	1.48	0.0853	0.36	1.35	0.0867	0.75
S4-5	0.449	0.0858	0.513	1.38	0.0887	0.10	1.08	0.0937	0.70
S4-6	0.469	0.0920	0.569	1.45	0.0982	0.17	1.22	0.1023	0.68
S4-7	0.469	0.1068	0.385	1.35	0.1047	0.00	0.970	0.1129	0.60
S5-1	0.377	0.0361	1.06	1.50	0.0440	0.36	1.22	0.0450	1.05
S5-2	0.377	0.0449	0.873	1.34	0.0520	0.30	1.11	0.0533	1.00
S5-3	0.382	0.0542	0.723	1.25	0.0600	0.25	1.03	0.0618	0.95
S5-4	0.378	0.0625	0.541	1.14	0.0646	0.10	0.873	0.0680	0.90
S5-5	0.380	0.0689	0.491	1.10	0.0702	0.06	0.836	0.0740	0.90
S5-6	0.381	0.0876	0.358	0.98	0.0854	0.00	0.709	0.0911	0.85
S6-1	0.281	0.0449	0.437	0.75	0.0444	0.00	0.534	0.0468	1.30
S6-2	0.280	0.0390	0.868	0.79	0.0450	0.72	0.717	0.0449	1.50
S6-3	0.280	0.0438	0.749	0.75	0.0490	0.64	0.674	0.0490	1.50
S6-4	0.280	0.0585	0.536	0.65	0.0617	0.54	0.584	0.0622	1.40
S6-5	0.285	0.0841	0.163	0.56	0.0768	0.00	0.299	0.0847	1.00
S6-6	0.282	0.100	0.122	0.50	0.0908	0.00	0.209	0.1015	0.80

[a] Reference 13. [b] Samples B1 and S1-S6 were prepared at volume fractions v_{2S} of polymer of 1.00, 0.75, 0.62, 0.55, 0.48, 0.40, and 0.30, respectively. Values of the volume fraction v_{2C} remaining after extraction are somewhat lower because of the presence of a small amount of uncross-linked (soluble) polymer.

larities should be particularly numerous at the high doses required to cross-link a polymer diluted by large amounts of solvent.[13] Recent computer simulations of radiation-cured networks of PDMS,[17] however, indicate that the elastically ineffective material present in such networks cannot possibly explain the much decreased values of $2C_2/2C_1$.

In the time since the relevant experiments were carried out, the molecular theory of rubberlike elasticity has been greatly improved.[18,19] It now takes into account some aspects of network topology, specifically the degree of chain entangling around the cross-links or junctions. The more severe the entangling and constraints, the closer the deformation should be to the affine limit (at which the junctions move linearly with the macroscopic deformation). The ratio $2C_2/2C_1$ is then interpreted simply as the increase in nonaffineness with increase in elongation, as the stretched chains become less entangled in the vicinity of the junctions. The increased fluctuations in the direction of the elongation brought about by the decreased entangling cause the decrease in $[f^*]$ characterized by $2C_2/2C_1$.[18,19]

The purpose of the present investigation was to adopt this constraint theory to networks cross-linked in solution and to carry out calculations attempting to reproduce the experimental values[13] of $2C_2/2C_1$ reported for PDMS networks in Table I.

Theory

The more important of the two parameters in the theory is κ, which serves as a measure of the severity of the entanglement constraints relative to that in a "phantom network", where such constraints are absent.[19] If κ is taken to be proportional to the degree of chain interpenetration, then[20]

$$\kappa = I(N_A d/2)^{3/2}(\langle r^2\rangle_0/M)^{3/2}(\xi/V^0)^{-1/2} \tag{4}$$

where I is the interpenetration proportionality constant

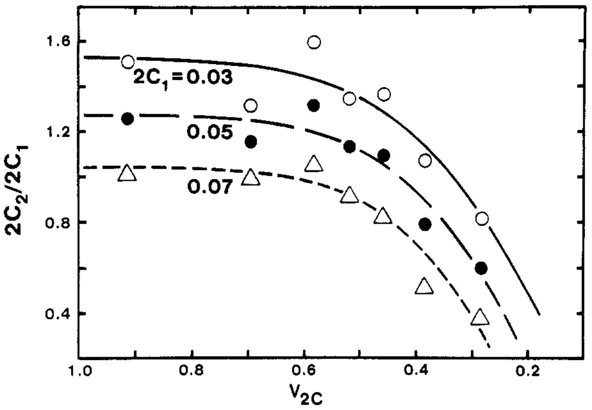

Figure 1. Experimental values[13] of the ratio $2C_2/2C_1$ of phenomenological elasticity constants which represents the normalized elongation dependence of the reduced stress $[f^*]$. The networks were obtained by cross-linking poly(dimethylsiloxane) at the values shown for the volume fraction v_{2C} of the polymer in solutions with cyclohexane. The measurements were in elongation at 25 °C and were carried out on the dried networks. The values of $2C_2/2C_1$ are for the specified values of $2C_1$, which is approximately the high deformation limit of $[f^*]$.

and N_A is Avogadro's number. In the case of cross-linking in solution, the density of the polymer becomes its concentration

$$d = d_0 v_{2C} \tag{5}$$

where d_0 is its density in the undiluted state.[20] The factor $\langle r^2\rangle_0$ is the unperturbed dimension[21] of a network chain of molecular weight M, ξ is the cycle rank of the network, and V^0 is the reference volume obtained in the state of cross-linking. The phenomenological parameter $2C_1$ is related to ξ by

$$2C_1 = (\xi kT/V^0)v_{2C}^{-1/3} \tag{6}$$

The expression on the right-hand side of eq 6 is the "front factor" or modulus of the network obtained by extrapolation of stress-strain data to $\alpha^{-1} \rightarrow 0$. The derivation of eq 6 is given in the Appendix.

Combining these three equations gives

$$\begin{aligned}\kappa &= I(N_A d_0/2)^{3/2}(\langle r^2\rangle_0/M)^{3/2}(kT)^{1/2}(2C_1)^{-1/2}v_{2C}^{4/3} \\ &= A(2C_1)^{-1/2}v_{2C}^{4/3}\end{aligned} \tag{7}$$

Previous results on PDMS indicate $A = 2.0$,[20] and thus

$$\kappa = 2(2C_1)^{-1/2}v_{2C}^{4/3} \tag{8}$$

which is the prediction of how κ should vary with the concentration of polymer present during cross-linking.

If advantageous, the above dependence of κ on v_{2C} can be generalized to

$$\kappa = 2(2C_1)^{-1/2}v_{2C}^{4/3+m} \tag{9}$$

where m takes into account heterogeneities in network structure. The best value of m would be that making the ratio

$$\psi = \kappa(2C_1)^{1/2}/2v_{2C}^{4/3+m} \tag{10}$$

independent of v_{2C}, with a constant value of unity.

The expressions for $[f^*]$ at any specified reciprocal elongation in the constraint theory and in the phenomenological representation, respectively, are[19]

$$[f^*(\alpha^{-1})]_1 = (\xi kT/V^0)v_{2C}^{-1/3}(1 + f_c/f_{ph}) \tag{11}$$

$$[f^*(\alpha^{-1})]_2 = 2C_1 + 2C_2\alpha^{-1} \tag{12}$$

where

$$f_c/f_{ph} = [\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)]/(\alpha - \alpha^{-2}) \tag{13}$$

$$\lambda_1 = v_{2C}^{1/3}\alpha \tag{14}$$

$$\lambda_2 = v_{2C}^{1/3}\alpha^{-1/2} \tag{15}$$

$$K(\lambda^2) = B[\dot{B}(B + 1)^{-1} + g(\dot{g}B + g\dot{B})(gB + 1)^{-1}] \tag{16}$$

$$B = (\lambda - 1)(1 + \lambda + \zeta\lambda^2)/(1 + g)^2 \tag{17}$$

The quantity $\zeta > 0$ is the other parameter in the constraint theory and increases with increase in heterogeneity in the network structure.[19] It is less important than κ and, since it is generally quite small,[20,22] is frequently set equal to zero. The remaining quantities are given by[19]

$$g = \lambda^2[\kappa^{-1} + \zeta(\lambda - 1)] \tag{18}$$

$$\begin{aligned}\dot{B} = B\{&[2\lambda(\lambda - 1)]^{-1} + (1 - 2\zeta\lambda) \times \\ &[2\lambda(1 + \lambda - \zeta\lambda^2)]^{-1} + 2\dot{g}(1 + g)^{-1}\}\end{aligned} \tag{19}$$

$$\dot{g} = g\lambda^{-2} + (\zeta/2)\lambda \tag{20}$$

Numerical Calculations

In the first scheme employed, the basic goal was to determine whether varying κ with the $^4/_3$ power of v_{2C} (eq 8) would give values of $2C_2/2C_1$ in good agreement with experiment. Since the dependence of $[f^*]$ on α^{-1} in the constraint theory is nonlinear, the comparisons were made over the most reliable experimental range of elongation, that corresponding to $\alpha^{-1} = 0.6 - 0.8$. (Lower values of α are too uncertain because of problems in measuring lengths in the unstretched state, and higher values of α can give rise to non-Gaussian effects.)

For each network, κ was obtained from eq 8. The front factor $(\xi kT/V^0)v_{2C}^{-1/3}$ of the constraint theory was initially identified with $2C_1$ (eq 6), and an initial, small value was arbitrarily assigned ζ to begin the calculations. Both the constraint theory (eq 11) and phenomenological representation (eq 12) were used to calculate values of $[f^*]$ at $\alpha^{-1} = 0.6$ and 0.8. The value of $(\xi kT/V^0)v_{2C}^{-1/3}$ in eq 11 was then adjusted to bring the two isotherms into coincidence at $\alpha^{-1} = 0.6$; i.e., $(f^*(0.6)]_1 = [f^*(0.6)]_2$. The approximate slope of the theoretical isotherm was calculated from $\{[f^*(0.8)]_1 - [f^*(0.6)]_1\}/0.2$ and the ratio of it to $2C_1$ compared to the experimental value of $2C_2/2C_1$. If the two values of $2C_2/2C_1$ differed, ζ was varied in an attempt to bring the theoretical value into agreement with the experimental. Exact agreement between the data and the calculated results for the exponent $m = {}^4/_3$ was not possible for all samples, so the entire series of calculations was repeated for different values of m. Exact agreement for all networks was possible only for $m = {}^2/_3$. The resulting values of κ are listed in column five of the table. The corresponding values of $(\xi kT/V^0)v_{2C}^{-1/3}$ are given in column six, and the values of ζ giving the best agreement for each network are listed in column seven.

The second scheme employed was based on the generalized equations (9) and (10). In it, an initial value of ζ was chosen for each isotherm, and, from it, the values of the front factor and κ that fit the experimental values of $[f^*(0.6)]$ and $[f^*(0.8)]$ were obtained. Additional values of ζ were then chosen and the similarly successful values of the front factor and κ again calculated. Plots of κ against ζ were then used to obtain the *minimum* successful value of κ, since cross-linking in solution should decrease chain interpenetration[13] and thus decrease κ.[20] All such curves did exhibit minima, and these values of κ and the corresponding values of the front factor $(\xi kT/V^0)v_{2C}^{-1/3}$ and ζ

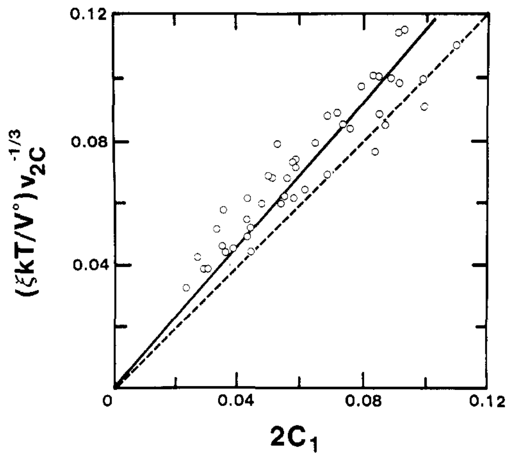

Figure 2. Comparison of the calculated $(\xi kT/V^0)v_{2C}^{-1/3}$ values with the experimental $2C_1$ values. The dashed line is at an angle of 45° (corresponding to equality of the two quantities), and the solid line is the least-squares fit to the points.

are given in the last three columns of Table I.

Results and Discussion

The values of κ obtained from the first scheme are all well within the range found to reproduce the elastomeric properties of networks prepared from PDMS and other polymers.[20,22] The decrease in κ with decrease in v_{2C} (increase in dilution during cross-linking) reflects a decrease in entanglement constraints due to diminished chain interpenetration. In topological terms, high dilutions during cross-linking make it more likely that cross-links which are topological neighbors will also be spatial neighbors in the dried network. This parameter also decreases with increase in cross-linking (increase in $2C_1$) due to decrease in interpenetration as the network chain length decreases. The values of ζ do not appear to show any significant trend. The values giving the best agreement with experiment were generally very small, as expected.

The values of the front factor $(\xi kT/V^0)v_{2C}^{-1/3}$ appearing in the constraint theory should equate to $2C_1$ according to the present treatment. Results of calculations of this factor are compared with experimental $2C_1$ values in Figure 2. The solid straight line is the least-squares fit to the points, and the dashed line is the 45° line which would obtain if eq 6 were exact. The slope of the solid line is 15% larger than the theoretically expected value. Within the approximations introduced by the present analysis, the front factor of the constraint theory may therefore be replaced by $2C_1$.

In the second interpretative scheme, the minimum successful values of κ (column eight) are again seen to decrease with decrease in v_{2C} and increase in $2C_1$, as would be expected from decrease in chain interpenetration. It is also important to note that the values of ζ that minimize κ are now found to be approximately constant for samples prepared at approximately the same value of v_{2C}. These values of ζ are shown as a function of v_{2C} in Figure 3. The strong increase in ζ with decrease in v_{2C} indicates increased heterogeneity in the networks cross-linked in solution, as might be expected.

Values of the test ratio ψ calculated for $m = 0$ are shown as a function of v_{2C} in Figure 4. They are not independent of v_{2C} and reach the expected value of unity only in the limit $v_{2C} \rightarrow 1.0$ (where the exponent on v_{2C} becomes irrelevant). Thus, $m = 0$ is not an acceptable assignment in this analysis of the data. The value of m that was found, by least-squares analysis, to make ψ independent of v_{2C} was $^8/_9$. These results, shown in Figure 4, are gratifying in that the constant value of ψ, specifically 1.08, is close to the expected value of unity.

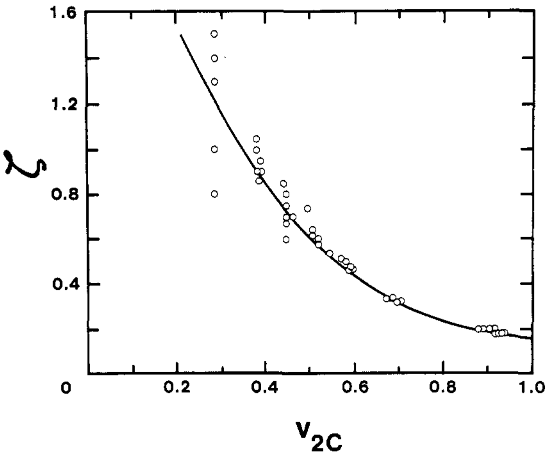

Figure 3. Dependence of the heterogeneity parameter ζ (last column of Table I) on v_{2C}.

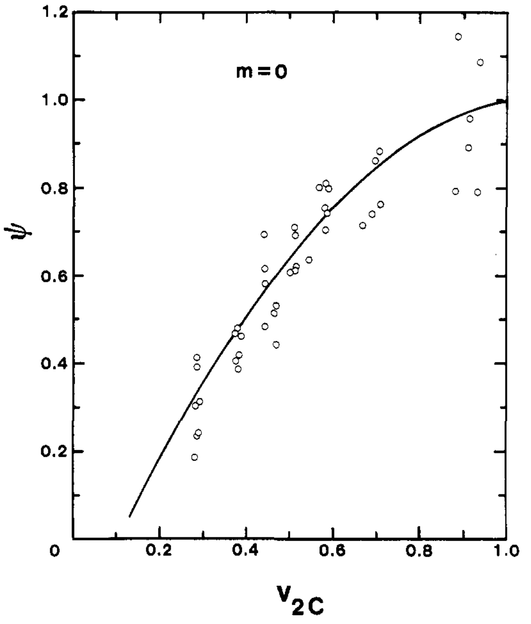

Figure 4. Values of the ratio $\psi = \kappa(2C_1)^{1/2}/2v_{2C}^{4/3+m}$ shown as a function of v_{2C} for $m = 0$. The best value of the parameter m is that giving constant ψ, which should then be unity.

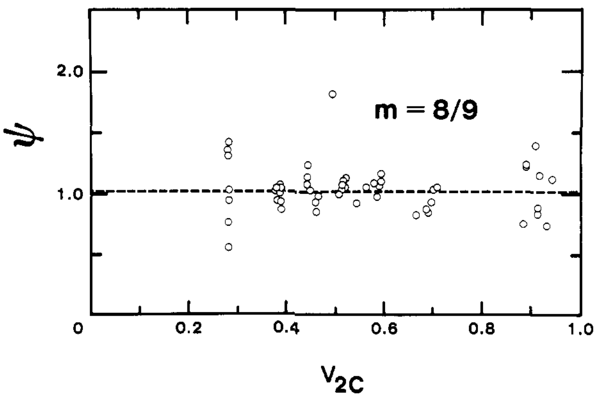

Figure 5. Values of ψ using $m \approx {}^8/_9$, which makes ψ independent of v_{2C}. The constant value of ψ thus obtained, 1.08, is very close to the expected value of 1.00.

Values of κ and $(\xi kT/V^0)v_{2C}^{-1/3}$ calculated according to the two different schemes are in approximate agreement, irrespective of the differences in the less important ζ parameter. Similarly, the values $m = {}^2/_3$ and $^8/_9$ obtained independently do not differ significantly. A mean value from the two schemes may be assessed as $m = {}^7/_9 \pm {}^1/_9$. It would, of course, be important to use other polymer networks to test this prediction of the effect of dilution during cross-linking. Networks prepared from polymers having higher values of the plateau modulus would be of particular interest to those looking for possible effects of chain entanglements on elastomeric properties.

In any case, the present investigation does represent another instance of the constraint theory of rubberlike elasticity giving a consistent interpretation[20,22-29] of the elastomeric properties of polymer networks.

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Appendix

The elastic free energy of a phantom network is given by

$$\Delta A = (\xi kT/2)(\textstyle\sum \lambda_i^2 - 3) \qquad \text{(A-1)}$$

where λ_i is the ratio of the final length of the sample in the ith principal direction to the length in the state of reference obtained during cross-linking. Letting λ denote the extension ratio in uniaxial deformation, eq A-1 may be written

$$\Delta A = (\xi kT/2)[\lambda^2 + 2(V/V^0)\lambda^{-1} - 3] \qquad \text{(A-2)}$$

where V and V^0 are the volumes in the final and reference states, respectively. The force f acting on the network is obtained by

$$f = \partial \Delta A/\partial L = \partial \Delta A/L_0 \partial \lambda \qquad \text{(A-3)}$$

where L and L_0 are the final and reference lengths, respectively. Equations A-2 and A-3 yield

$$f = (\xi kT/L_i)(v_{2C}/v_2)^{2/3}(\alpha - \alpha^{-2}) \qquad \text{(A-4)}$$

where L_i is the initial length, i.e., the swollen undistorted length, and $\lambda = \alpha(V/V^0)^{1/3}$ is the ratio of the final length to the initial length. Inasmuch as the volume of the network during the stress-strain experiment is in general different from that during cross-linking, L_i will differ from L_0.

Substituting eq A-4 in eq 1 leads to the definition of the reduced force in the limit as $\alpha^{-1} \to 0$ as

$$\lim_{\alpha^{-1}\to 0} [f^*] = (\xi kT/V_i) v_{2C}^{2/3} v_2^{-1} \qquad \text{(A-5)}$$

where V_i is the initial volume of the network at L_i. In terms of the reference volume V^0, eq A-5 becomes

$$\lim_{\alpha^{-1}\to 0} [f^*] = (\xi kT/V^0) v_{2C}^{-1/3} \qquad \text{(A-6)}$$

Comparison of eq A-6 with eq 3 in the limit as $\alpha^{-1} \to 0$ establishes eq 6.

According to the constraint theory, the reduced force at finite α is given by[20]

$$[f^*] = (\xi kT/V^0) v_{2C}^{-1/3}(1 + f_c/f_{ph}) \qquad \text{(A-7)}$$

where f_c and f_{ph} are the contributions to the force by the constraints and by the phantom network, respectively. The contribution f_c tends to zero as α increases, and eq A-7 reduces to eq A-6, as required by the definition.

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