Applications of a two -network model for crosslinks and trapped entanglements

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The dependence of stress and birefringence on strain in uniaxial extension of crosslinked rubbers can accurately be described by a model in which the properties of a network of crosslinks and a network of trapped entanglements are additive. The crosslink network is neo-Hookean and the entanglement network can conveniently be described by the Mooney–Rivlin equation. When the crosslinks are introduced in a state of strain near the glass transition temperature, the two networks have different reference undeformed states; they can be distinguished by appropriate measurements in the state of ease where their associated stresses are equal and opposite and in the state of deformation where the crosslinks were introduced and make no contribution to the stress. When partial relaxation is permitted before crosslinking, trapping probabilities can be calculated for both relaxed and unrelaxed entanglements and compared with the Langley theory. The results are consistent with the terminal mechanism of relaxation in the tube theory of Doi and Edwards.

INTRODUCTION

Many viscoelastic properties of uncrosslinked polymers are consistent with a network of strands which are defined by some kind of topological restraint; the restraints can be represented by entanglements or slip links or confinement within a virtual tube of a certain radius[1,2]. The restraints are released by long-range motions, for example by reptation along the molecular contour[3], within a characteristic time that is very long compared with the time scale of more local motions corresponding to configurational rearrangements between entanglements or within the virtual tube radius. When crosslinks are introduced, some entanglements are trapped so their restraints cannot be released and there is considerable evidence that the corresponding network strands contribute to the equilibrium modulus[4,5]. The trapping probability is related to the average number of crosslinked points per molecule by the theory of Langley[6].

The entire network can be regarded as the superposition of two networks – one whose strands run between crosslinks, the other whose strands run between trapped entanglements. The concept of a dual network was introduced by Andrews and Tobolsky[7] to describe the effects of two stages of crosslinking in different states of strain; the elastic properties on the basis of Gaussian statistics were treated by Berry, Scanlan and Watson[8] and in more detail by Flory[9]. In our model there is only one stage of crosslinking but the trapped entanglements correspond to the first set of crosslinks in the classical theory. If the crosslinks are introduced in a strained state (near T_g so the entanglements do not rearrange during the crosslinking), the two networks have different reference states for defining strain. If the crosslinking is done in the unstrained state, the two networks have the same reference state but can be distinguished by different stress strain relations. From analysis of stress, strain, and birefringence relations of both types of networks, information is obtained on trapping probabilities of entanglements in various stages of relaxation, which can be interpreted qualitatively by the tube model of topological restraint. Thus it is convenient to invoke both tube and entanglement representations to explain the observed behaviour. Deviations from Gaussian elasticity, as approximately described by the Mooney–Rivlin equation, for example, can be related to the relative proportions of crosslinks and trapped entanglements. In this discussion, only deformation in uniaxial extension is considered. Application of a two-network model to polymers crosslinked in other types of deformation is referred to in another paper at this conference by Kramer[10].

CLASSICAL TWO-NETWORK MODEL

In the classical two-stage experiment, crosslinks are introduced in the unstrained state to form ν_1 moles of elastically effective strands per cm^3, the sample is deformed in uniaxial extension to a stretch ratio λ_0, and ν_2 moles of additional strands per cm^3 are introduced by further crosslinking. Upon release, the sample seeks a state of ease with stretch ratio λ_s in which the strain free energy is a minimum. If the distribution of strand configurations is Gaussian (neo-Hookean elasticity), the dependence of free energy on strain corresponds[8,9] to the superposition of two independent networks with ν_1 moles of strands whose reference undeformed state is $\lambda = 1$ and ν_2 moles of strands whose reference undeformed state is $\lambda = \lambda_0$; at $\lambda = \lambda_s$, the stresses associated with the two networks are equal and opposite. The ratio ν_2/ν_1 can be obtained from λ_0 and λ_s:

$$\nu_2/\nu_1 = \lambda_0^2(\lambda_s^3 - 1)/(\lambda_0^3 - \lambda_s^3) \tag{1}$$

and the absolute values of ν_2 and ν_1 can be obtained by combining equation (1) with stress measurements; for

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Table 1 Characterization of 1,2-polybutadienes

Polymer	A	B	C
$\bar{M}_n \times 10^{-5}$	1.52	2.36	0.96
$\bar{M}_w \times 10^{-5}$	1.90	2.91	1.61
% vinyl (1,2)	95	88	96
T_g(°C)	−10 ± 2	−18	(−10)

example, at $\lambda = \lambda_0$, where the strands of the second-stage crosslinks do not contribute, the true tensile stress is

$$\sigma = \nu_1 RT(\lambda_0^2 - 1/\lambda_0) \tag{2}$$

and, after ν_1 is obtained from this equation, ν_2 can be calculated from equation (1). Alternatively, Young's modulus can be measured in small deformations from the state of ease[9]. This calculation assumes a front factor of unity, appropriate to affine motions of the crosslinks[11]; that assumption is made throughout this paper, although it may be necessary to modify it subsequently[11–14].

A modification of the classical two-network model was made by Greene, Smith and Ciferri[15] to take into account deviations from Gaussian elasticity in terms of the Mooney–Rivlin formulation of the relation of stress to strain in uniaxial extension.

TWO-NETWORK MODEL FOR A POLYMER CROSSLINKED NEAR THE GLASS TRANSITION IN UNIAXIAL EXTENSION

If an uncrosslinked polymer is deformed in uniaxial extension, held near the glass transition temperature (T_g) so the long-range topological restraints are immobilized, and subjected to crosslinking, some of the entanglements are trapped with their strands in deformed configurations. The densities of strands between trapped entanglements (ν_N) and between crosslinks (ν_X) correspond to ν_1 and ν_2 in the classical two-network model. Upon release and warming above T_g, the sample seeks a state of ease $\lambda = \lambda_s$ in which the stresses associated with the two individual networks are equal and opposite[16]. (If a trapped entanglement is less effective than a crosslink in contributing to strain energy, the effectiveness factor is absorbed into the definition of number of effective strands, as in the treatment of Langley[6] and in any similar method of counting entanglements[1].)

In the experiments reviewed in this paper, 1,2-polybutadiene ('high vinyl') has been crosslinked near T_g by γ-irradiation. Similar experiments with crosslinking by electron irradiation are reviewed by Kramer[10]. The polymers used have slightly different microstructures, and their characterizations are summarized in *Table 1*, including the number- and weight-average molecular weights $\bar{M}_n$ and $\bar{M}_w$. Experimental details are given in a series of papers[17–21].

These experiments provide for the first time the opportunity of calculating the ratio of trapped entanglements to crosslinks, and with the assumption of a specific front factor the absolute density of trapped entanglements, from equilibrium mechanical measurements alone. Previously, entanglement densities have been available only from transient or dynamic viscoelastic measurements[1], or from analysis of the additivity of trapped entanglements and crosslinks in which equilibrium mechanical measurements were combined with sol–gel ratio data[4,22,23] or chemical analysis of the crosslinking reaction[5].

In calculating ν_N and ν_X from these experiments, consistent results are obtained from crosslinking at different stretch ratios λ_0 and from detailed stress–strain relations in deformation of the two-network samples from the state of ease only if deviations from Gaussian elasticity are taken into account. For this purpose, the Mooney–Rivlin formulation is used[23]; although its inconsistencies and shortcomings are well known[24–26], it serves well empirically to describe behaviour in uniaxial extension. A large number of data[14,18–21] show that the crosslink network can be taken as Gaussian (no Mooney–Rivlin C_2) but the trapped entanglement network requires both Mooney–Rivlin terms.

The relative magnitudes of C_{1N} and C_{2N} for the trapped entanglement network are expressed by the parameter $\psi_N = C_{2N}/(C_{1N} + C_{2N})$ and this is determined from stress relaxation measurements on the uncrosslinked polymer[20,27]. Isochronal stress–strain data in uniaxial extension during relaxation can be fitted to the Mooney–Rivlin equation and described by a time-dependent ψ_N. In applying this information to the trapped entanglement network, a value of ψ_N is selected corresponding to the relaxation history up to the time the crosslinks were introduced. It varies from 0.50, if essentially no relaxation occurs before crosslinking, to as high as 0.89 if substantial prior relaxation is deliberately permitted. (It may be remarked that the non-linear stress relaxation of the uncrosslinked polymer is described very well by a modification of the Doi–Edwards theory of molecular dynamics[2] which is free of the Mooney–Rivlin inconsistencies but is mimicked by conventional Mooney–Rivlin formuation both in extension and in compression where C_2 is observed empirically to be zero[28].)

ADDITIVITY OF STRESS AND BIREFRINGENCE FOR TWO-NETWORK MODEL CROSSLINKED IN UNIAXIAL EXTENSION

If the two-network model applies, the tensile stress σ measured at any stretch ratio λ should be the sum of the stresses σ_X and σ_N associated with the crosslink network and trapped entanglement network, respectively. These may be formulated as follows, σ_X being the same as that for the second stage of crosslinking in the classical theory:

$$\sigma_X = \nu_X RT[\lambda^2/\lambda_0^2 - \lambda_0/\lambda] \tag{3}$$

$$\sigma_N = \nu_N RT[(1 - \psi_N)(\lambda^2 - 1/\lambda) + \psi_N(\lambda - 1/\lambda^2)] \tag{4}$$

$$\sigma = \sigma_X + \sigma_N \tag{5}$$

whereas equation (1) is modified by the Mooney–Rivlin character of the trapped entanglement network to give

$$\nu_X/\nu_N = \lambda_0^2(\lambda_s^3 - 1)[\psi_N + (1 - \psi_N)\lambda_s]/(\lambda_0^3 - \lambda_s^3)\lambda_s \tag{6}$$

Equation (5) can be tested as follows. (a) The measured stress at λ_0 is σ_N because $\sigma_X = 0$; equation (4) gives ν_N. (If the sample cannot be stretched to λ_0 without breaking, there is a more complicated calculation involving stress measurements at several λ.) (b) The ratio ν_X/ν_N is obtained from equation (6) and hence ν_X. (c) The total stress σ is calculated by equations (3)–(5) at various λ and compared with experiment. This has been done for numerous networks crosslinked under conditions where very little prior relaxation occurs[18,20]. An example is shown in *Figure 1* (Polymer C, $\lambda_0 = 1.567$, $\lambda_s = 1.140$)[20]. The agreement is very good

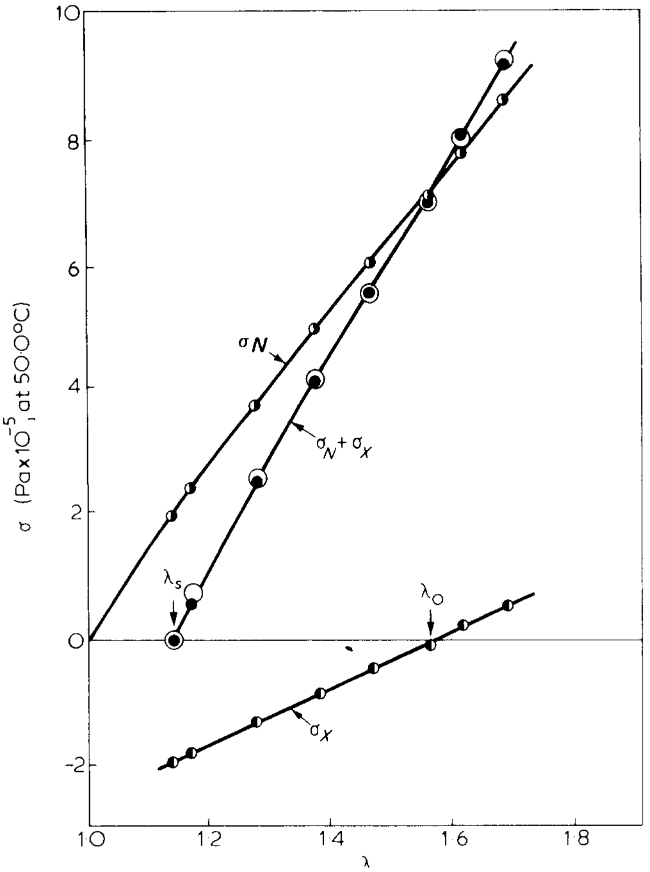

Figure 1 Stress–strain curves calculated for crosslink network, trapped entanglement network, and their sum; also experimentally measured (○, exp; ●, calc.) for polymer C at 50.0°C. $\nu_X = 0.86 \times 10^{-4}$, $\nu_N = 1.85 \times 10^{-4}$ mol cm^{-3}; $\lambda_0 = 1.567$, $\lambda_s = 1.140$, $\psi_N = 0.57$

both for $\lambda < \lambda_0$ where the X-network is in compression and for $\lambda > \lambda_0$ where both networks are in elongation. Other examples are equally good.

Stress birefringence can be treated similarly. Additivity of the two networks implies:

$$\Delta n = \mathscr{C}_N \sigma_N + \mathscr{C}_X \sigma_X \tag{7}$$

where Δn is the birefringence at stretch ratio λ and the $\mathscr{C}$s are the respective stress–optical coefficients. For most polymers, $\mathscr{C}_N$ and $\mathscr{C}_X$ are expected to be equal, since $\mathscr{C}$ is not affected by crosslinking. For polybutadiene of high 1,2 content, they may differ because of an anomaly which will be mentioned below, but equation (7) can be tested in any case as follows. (a) At $\lambda = \lambda_0$, $\sigma_X = 0$, so the X-network contributes no birefringence and $\mathscr{C}_N = \Delta n_0/\sigma_0$. (b) In the state of ease, $\sigma_{Ns} = -\sigma_{Xs}$, so if there is a residual birefringence it is $\Delta n_s = \sigma_{Ns}(\mathscr{C}_N - \mathscr{C}_X)$. A residual birefringence is actually observed, and with σ_{Ns} available from equation (4), we obtain $\mathscr{C}_X = \mathscr{C}_N - \Delta n_s/\sigma_{Ns}$. (c) Δn is calculated at various λ from equation (7) and compared with experiment. This has been done for various networks including those from Polymer B in which the residual birefringence in the state of ease is quite small and from Polymer C in which it is rather large[20]. An example is shown in *Figure 2*, Polymer B, $\lambda_0 = 1.624$, $\lambda_s = 1.166$, $\mathscr{C}_N = 4.40 \times 10^{-10}$, $\mathscr{C}_x = 4.54 \times 10^{-10}$ Pa^{-1}. Very good agreement is found for this and for other cases in which the two $\mathscr{C}$ values differ much more and are sometimes actually of opposite sign. The two-network model appears to be very successful.

For Polymers A and C in which $\mathscr{C}_N$ and $\mathscr{C}_X$ differ and depend in a complicated manner on the extent of irradiation[20], it is believed that these anomalies are due to a side reaction of cyclization of the vinyl groups which is important when the vinyl content is nearly 100% and creates stiff segments of ladder structure as concluded by von Raven and Heusinger[29]. This does not appear to influence the additivity of stress and birefringence.

EFFECTIVENESS OF ENTANGLEMENT TRAPPING

If there are ν_e mol/cm^3 of entanglement strands in the uncrosslinked polymer, ν_N may be less than ν_e, and the difference represents untrapped entanglements which may contribute to transient stress but not to stress at equilibrium. The theory of Langley[6] predicts the trapping probability $T_e \equiv \nu_N/\nu_e$ in terms of γ, the average number of crosslinked points per original molecule, on the basis of a random tetrafunctional crosslinking process. It increases monotonically with γ and approaches unity.

The density of (unrelaxed) entanglements ν_e at the time of introduction of crosslinks can be estimated from the non-linear stress relaxation measurements on the uncrosslinked polymer[20,27]. Young's modulus $E(t)$ can be obtained from the time-dependent Mooney–Rivlin coefficients as $E(t) = 6C_1(t) + 6C_2(t)$, and with the usual assumption of a front factor of unity, $\nu_e(t) = E(t)/3RT$. A value is selected corresponding to the relaxation history up to the time the crosslinks were introduced; for Polymers B and C, if essentially no relaxation prior to crosslinking occurs, it is about 2.4×10^{-4} mol/cm^3. The number of crosslinked points per original molecule, γ, is approximately $\bar{M}_n\nu_X/\rho + 1$, where ρ is the polymer density and ν_X is available from the two-

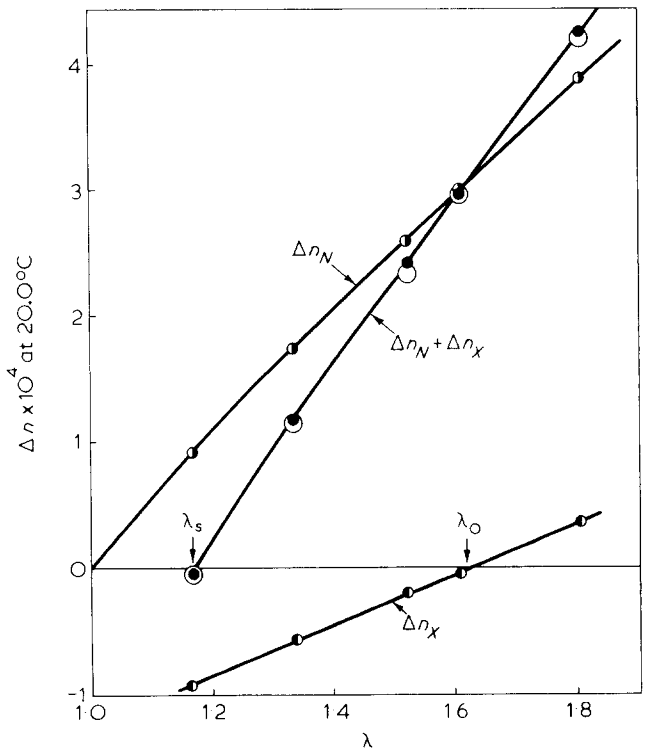

Figure 2 Birefringence–strain curves calculated for crosslink network, trapped entanglement network, and their sum; also experimentally measured (○, exp; ●, calc.), for Polymer B at 20.0°C. $\nu_X = 0.97 \times 10^{-4}$, $\nu_N = 1.85 \times 10^{-4}$ mol cm^{-3}; $\lambda_0 = 1.624$, $\lambda_s = 1.166$; $\mathscr{C}_N = 4.40 \times 10^{-10}$ Pa^{-1}, $\mathscr{C}_X = 4.54 \times 10^{-10}$ Pa^{-1}, $\psi_N = 0.625$

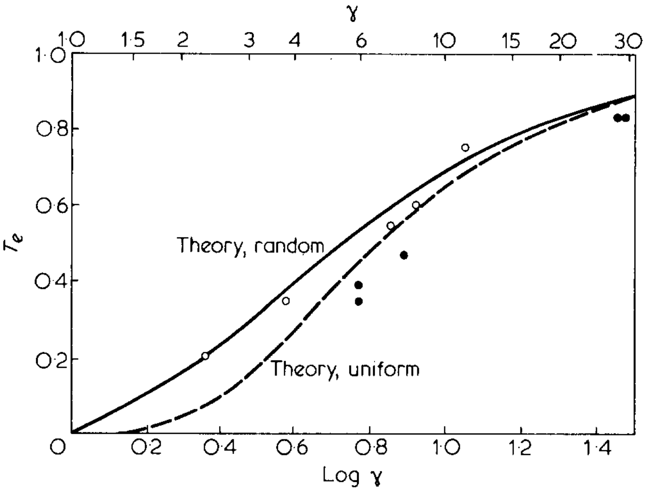

Figure 3 Entanglement trapping probability plotted against log γ. Points, experimental; curves, Langley theory for uniform and most probable molecular weight distribution of original linear polymer. ○, C, $\bar{M}_n = 96\,000$, $\bar{M}_w/\bar{M}_n = 1.68$; ●, B, $\bar{M}_n = 236\,000$, $\bar{M}_w/\bar{M}_n = 1.23$

network analysis. The experimentally determined ratio ν_N/ν_e can then be compared with the calculation of the Langley theory, as shown in *Figure 3* for Polymers B and C with different molecular weights and molecular weight distribution. The agreement is fairly good with the respective curves for uniform and most probable molecular weight distributions and gives further support to the concept of entanglement trapping.

RELAXED AND UNRELAXED TRAPPED ENTANGLEMENTS

If relaxation at $\lambda = \lambda_0$ is deliberately permitted before crosslinks are introduced, the value of ν_N is found to be abnormally small, even for high degrees of crosslinking where γ is large and T_e approaches unity. This occurs because some of the entanglement strands have rearranged and some entanglements are trapped in relaxed configurations for which the reference undeformed state is $\lambda = \lambda_0$, not $\lambda = 1$.

In this case the contribution of the trapped relaxed entanglement strands (density ν_{NR}) adds to that of the crosslink strands. The foregoing equations 3 to 6 hold with ν_Y substituted for ν_X and σ_Y for σ_X; $\nu_Y = \nu_X + \nu_{NR}$ and σ_Y is the stress associated with the network of crosslinks plus trapped relaxed entanglements (Y network).

To distinguish the trapping of relaxed and unrelaxed entanglements, a series of experiments was performed[21] in which samples of Polymer C were stretched to $\lambda_0 = 1.6$ and held at 0°C. (about 10° above T_g) for controlled periods (t_R) from 3 min to 8.8 h, then cooled to -10°C and crosslinked. The values of ν_N, and ν_Y were obtained by the same procedures as before, with Y substituted for X. The additivity of stresses associated with the N and Y networks was again accurately confirmed as illustrated in *Figure 4*. The total density of entanglements $\nu_e(t_R)$ at the time of crosslinking was obtained from stress relaxation data on the uncrosslinked polymer[20].

Figure 5 shows plots of $\nu_e(t_R)$, $\nu_N(t_R)$, and $\nu_Y = \nu_X + \nu_{NR}$ plotted against log t_R, for a series of samples crosslinked with constant irradiation dose and therefore (nearly) constant ν_X. Both the total and trapped unrelaxed entanglements decrease as the relaxation progresses. The sum $\nu_X + \nu_{NR}$ is constant at first and then increases; it is concluded

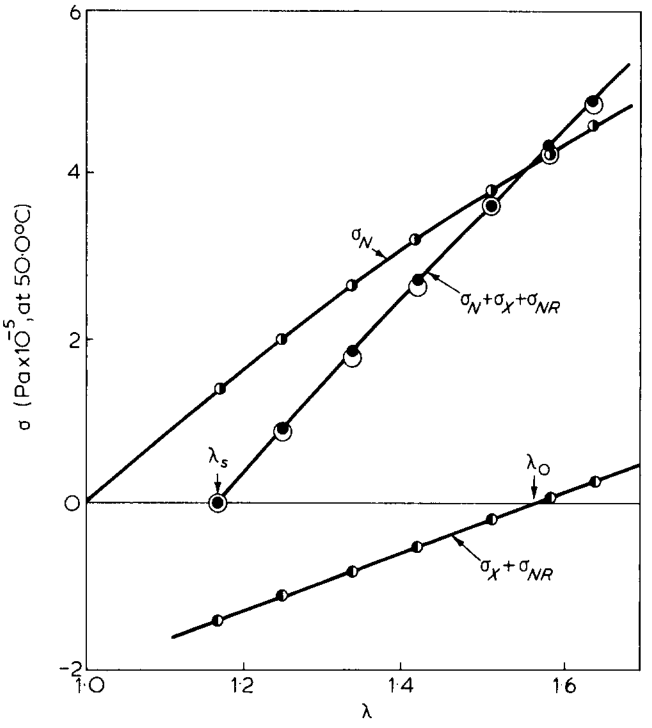

Figure 4 Stress–strain curves calculated for N network, Y network, and their sum; also experimentally measured: ○, exp.; ●, calc., for Polymer C, log t_R (sec) = 3.5, dose 3.0×10^{20} eV/g. $\lambda_0 = 1.560$ $\lambda_s = 1.166$, $\nu_N = 1.164 \times 10^{-4}$ mol cm^{-3}, $\nu_Y = 0.673 \times 10^{-4}$ mol cm^{-3}, $\psi_N = 0.725$

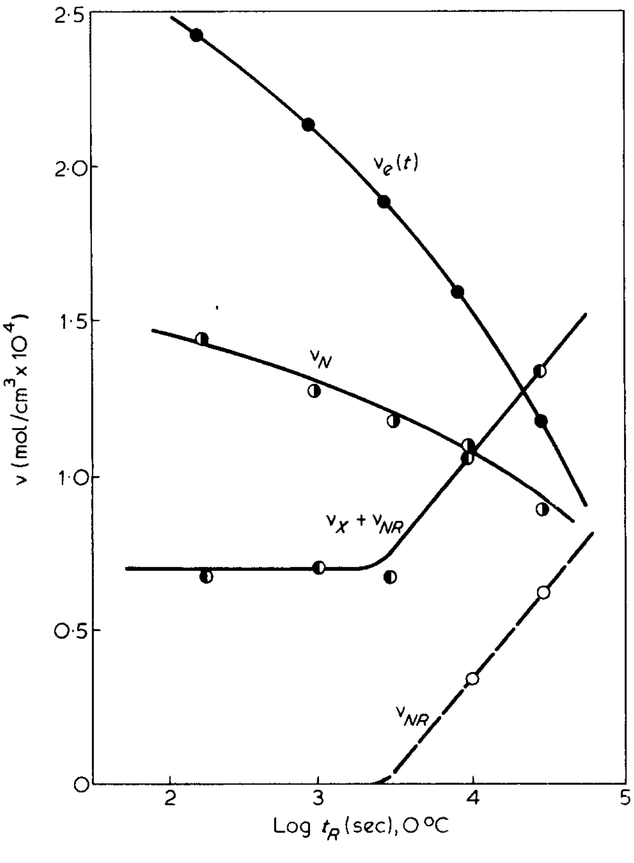

Figure 5 Concentrations of unrelaxed entanglement strands $\nu_e(t)$, trapped unrelaxed entanglement strands ν_N, and crosslink strands plus trapped relaxed entanglement strands $\nu_Y = \nu_X + \nu_{NR}$, plotted against log t_R in sec. (Dose 3.0×10^{20} eV/g, $\lambda_0 \cong 1.6$)

that ν_X remains constant at 0.70 x 10^{-4} mol/cm^3 and ν_{NR} increases steadily after an initial lag, shown as ν_Y – 0.70 x 10^{-4} by the dashed curve.

Individual trapping probabilities may now be calculated for the two classes of entanglements. For this purpose, it is assumed that the total density of entanglement strands ν_e^0 remains constant during the relaxation, so the density of relaxed strands at any time is $\nu_e^0 - \nu_e(t_R)$. Estimation of ν_e^0 is rather arbitrary, but has been taken as 2.6 x 10^{-4} mol/cm^3. Then for the unrelaxed entanglements $T_{e,u} = \nu_N/\nu_e(t_R)$ and for the relaxed $T_{e,r} = \nu_{NR}/[\nu_e^0 - \nu_e(t_R)]$. These values are plotted in *Figure 6* and compared with the Langley theory (for this degree of crosslinking, $\gamma = 8.6$ and T_e interpolated from *Figure 3* for $\bar{M}_w/\bar{M}_n = 1.7$ is 0.62).

When the initial relaxation is slight, $T_{e,u}$ is independent of t_R and agrees with the Langley theory, as in *Figure 3*. After longer relaxation periods, the trapping probability of the unrelaxed entanglements increases. The trapping probability of the relaxed entanglements, $T_{e,r}$, is zero up to the point where $T_{e,u}$ begins to increase, and then increases but remains smaller than the Langley prediction.

This behaviour can be understood qualitatively in terms of the alternative tube model for the topological restraints of an entangled molecule[2,3]. The final stage of relaxation in an uncrosslinked polymer involves the escape of a molecule from its tube by diffusing back and forth along its contour. In a state of strain, the ends regain a random configurational distribution finding new tube paths, progressing from the ends inwards, while a steadily shrinking central portion remains confined in the deformed tube. The relaxed and unrelaxed entanglements can be identified with constraints on the ends and centre, respectively. Whereas the Langley theory provides an average trapping probability, it is evident that the probability will be greater near the centre of a molecule than near the ends. In fact, there is essentially no chance of trapping a relaxed entanglement until the randomized ends become longer than the average entanglement spacing and also longer than the average spacing between crosslinked points. (This description ignores the possibility that some constraints even near the centre of the molecule can be relieved by escape of other molecules from *their* tubes, with resulting reorganization of the tube itself[30], but no attempt is made to take that complication into account at the present time.)

TWO-NETWORK MODEL FOR TRAPPED ENTANGLEMENTS IN ORDINARY NETWORKS

The success of the two-network model with a neo-Hookean X-network and a Mooney–Rivlin N-network for samples crosslinked in strained states suggests its application to conventional networks crosslinked unstrained. In many investigations, the stress–strain relations for such networks in uniaxial extensions (e.g. from $\lambda = 1.1$ to 2) have been described by the Mooney–Rivlin equation and values of the coefficients C_1 and C_2 are available in the literature. In previous compilations, the dependence of C_2 on the degree of crosslinking has been puzzling since it may increase, decrease or remain nearly constant[31,32]. Now, by analogy with the networks discussed above, the deviations from neo-Hookean elasticity may be attributed to the trapped entanglement network *only*. The degree of deviation, as measured again by $\psi = C_2/(C_2 + C_1)$ where these coefficients refer to the entire sample (not just the entanglement network), should be a single function of the relative proportions of trapped entanglements and crosslinks, as expressed by the ratio $f_N = \nu_N/(\nu_N + \nu_X)$. This ratio depends not only on the degree of crosslinking but also on the entanglement spacing characteristic of a particular polymer and the initial molecular weight prior to crosslinking. Taking all these variables into account, a rather simple relation is obtained.

Data in the literature which provide C_1 and C_2 can be analysed as follows[33]. The total concentrations of strands contributing to the modulus of elasticity is

$$\nu_X + \nu_N = E/3RT = 2(C_1 + C_2)/RT \qquad (8)$$

With a preliminary estimate of T_e, ν_X is obtained as:

$$\nu_X = 2(C_1 + C_2)/RT - \nu_e T_e \qquad (9)$$

where ν_e for a given polymer is estimated from the plateau modulus as derived from viscoelastic measurements[1]. From this ν_X, γ is estimated as $\nu_X \bar{M}_n/\rho + a$, where $\bar{M}_n$ is the number-average molecular weight before crosslinking, ρ is density and a is between 1 and 2. Then a revised value of T_e is obtained from the Langley theory, and the process is iterated to give a final value of T_e and eventually f_N. Data for five different polymers have been analysed in this way, covering a 4-fold range in ν_e, ranges of $\bar{M}$ (not necessarily $\bar{M}_n$, however) up to 3-fold, and ranges of ν_X up to 10-fold. The results are plotted in *Figure 7* and show the expected dependence of ψ on f_N, which corresponds to $\psi = f_N - 0.275$. The value extrapolated to $f_N = 1$, i.e. entanglements only, is near the maximum observed for uncrosslinked polymers[27,34–36] although in this case ψ is time dependent and the entanglements are of course untrapped.

It follows from this relation that, with increasing crosslinking, C_2/C_1 is at first nearly constant, then C_2 is nearly constant as C_1 increases, and finally C_2 decreases as C_1 increases[33]. Different portions of this progressive behaviour have been observed by different investigators covering a narrower range of ν_X and $\bar{M}_n$[31,32,37].

Of course, deviations from neo-Hookean elasticity ought to be described by a better relation than the Mooney–Rivlin equation, to provide a proper constitutive equation as well as a molecular interpretation of the parameters involved. However, any theory should take into account dependence on initial molecular weight and differences among polymers such as represented by different values of ν_e, as well as on crosslinking density.

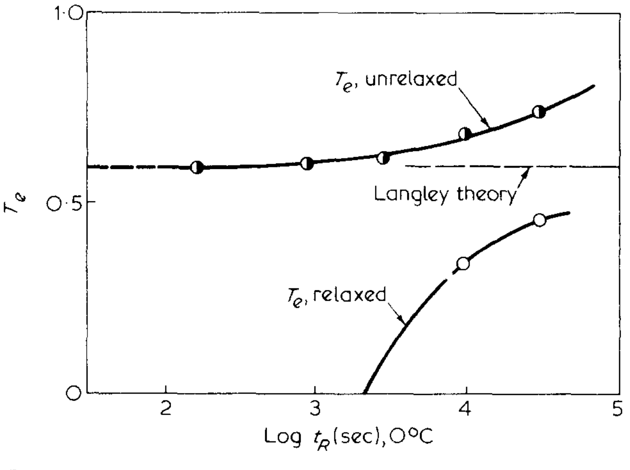

Figure 6 Entanglement trapping probabilities $T_{e,u}$ for unrelaxed and $T_{e,r}$ for relaxed entanglements, calculated from data of *Figure 5* and compared with Langley theory

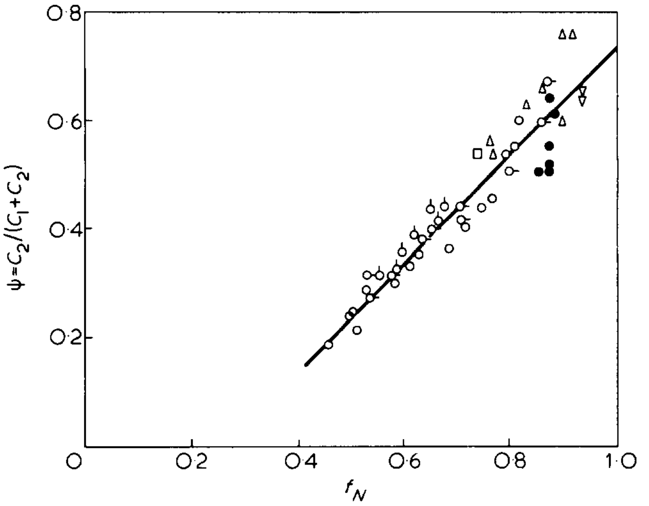

Figure 7 Plot of ψ against f_N for conventional crosslinked networks of five rubbers[33]:

Symbol	Rubber
○	Natural rubber, *cis*-polyisoprene
△	Polybutadiene, *cis–trans*
▽	Polybutadiene, high *cis*
□	Polybutadiene, high vinyl
●	Poly(dimethyl siloxane)

CONCLUSIONS

The concept of a two-network model of crosslinks and trapped entanglements, the first with neo-Hookean stress–strain relations and the second with deviations from neo-Hookean elasticity that can be approximately represented by the Mooney- Rivlin formulation is useful in describing stress and birefringence, which are precisely additive when the reference undeformed states of the two networks are different. The interaction of crosslinks with the topological restraints existing before crosslinking, in networks prepared under various conditions of strain and prior relaxation, can be analysed to permit distinction between entanglements trapped before and after relaxation. The former correspond to portions of molecules that have not escaped from their deformed virtual tubes and the latter to those that have escaped and found new tube paths.

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