Contribution of entanglements to rubber elasticity

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Uncrosslinked polymers show rubber-like properties above the glass transition temperature and at times short enough to prevent flow. This effect is thought to be due to a temporary entanglement network. Several studies indicate large entanglement contributions to the equilibrium elastic modulus of crosslinked networks. Three methods are discussed in greater detail: stoichiometric crosslinking with a suitable peroxide, the Langley method, and the two-network method. The two latter methods give equilibrium entanglement modulus contributions which are equal to the pseudo-equilibrium modulus of the uncrosslinked polymer. They also indicate that the entanglement contribution to the stress is responsible for departures from neo-Hookean behaviour observed in simpler extension.

INTRODUCTION

Uncrosslinked polymers exhibit a number of properties which indicate the existence of a temporary network[1,2] above a certain molecular weight; for example, the viscosity–molecular weight relationship shows a change in exponent from 1 to about 3.4 at a certain critical molecular weight; dynamic mechanical measurements show a pseudo-equilibrium rubber plateau; and the recovery is nearly complete for short time deformations. *Figure 1* shows storage modulus plotted against frequency in a double logarithmic plot for a series of polystyrenes with different molecular weights. For samples of high molecular weight, the plateau is very pronounced, covering nearly 6 decades on the frequency scale. The recovery is nearly complete in the plateau region, while plastic flow takes place at low frequencies where the modulus decreases rapidly. The above properties are in agreement with the behaviour of uncrosslinked elastomers. They bounce when dropped on the floor and flow like highly-viscous liquids when left on a table. The thermoelastic measurements on india rubber reported by Gough[4] in 1805 actually were performed on raw rubber, i.e. uncrosslinked natural rubber which exhibited considerable irreversibility.

Polymer chains in amorphous polymers are random coils in their unperturbed configurations. The mean density contribution of a particular polymer coil in the effective volume occupied by it is of the order of 1%. This means that a very large number of other coils pervade the occupied volume of the first coil[5]. Although there are no chemical crosslinks in the system, the entangled chains are thought to form a network because of the inability of the strands to cross. Upon deformation, the constraints of the entanglement network should cause a reduction in conformational entropy, and thus a retractive force. However, the network is of a temporary nature; there are no permanent links to prevent the chains from slowly diffusing away from each other. A more detailed discussion of the evidence for a so-called entanglement network in uncrosslinked polymers has been given in reviews by Ferry[1], Graessley[2] and Smith[2].

The contribution of entanglements to the equilibrium elasticity after the introduction of chemical crosslinks is the subject of the present paper. If the temporary nature of the entanglement network of an uncrosslinked polymer carries over to the crosslinked system, no entanglement contribution should be expected at elastic equilibrium. Many workers have assumed simple additivity of the contributions from chemical crosslinks and entanglements[1,6,7], while Flory[8] recently has suggested a different mechanism. Comparing a phantom network with a real network, he suggests that the presence of the other chains in a real network should reduce the junction fluctuations and make the fluctuations change nearly affinely upon deformation of the network. For a network with tetrafunctional junctions, this should raise the front factor from one half (phantom network) towards one (real network), i.e. the modulus is increased by a factor of up to two. Flory[9] also derived stress–strain ex-

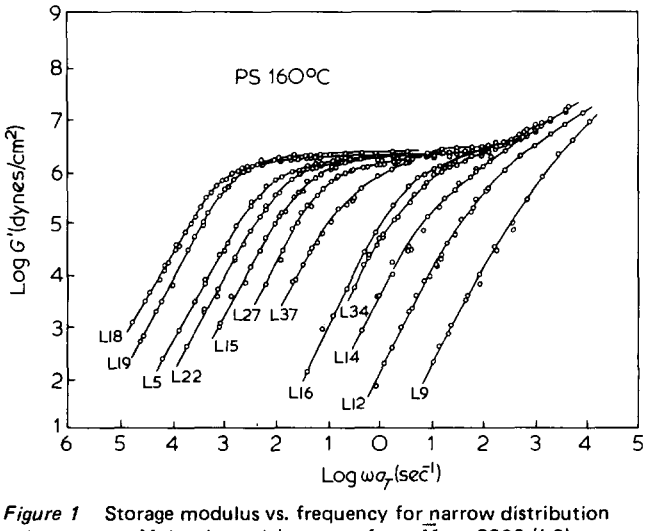

Figure 1 Storage modulus vs. frequency for narrow distribution polystyrenes. Molecular weights range from $\bar{M}_W$ = 8900 (L9) to $\bar{M}_W$ = 581 000 (L18). Data of Onogi, Masuda, and Kitawaga[3]. [Reproduced by kind permission of Marcel Dekker Inc. from *Macromolecules* 1970, **3**, 109 ©]

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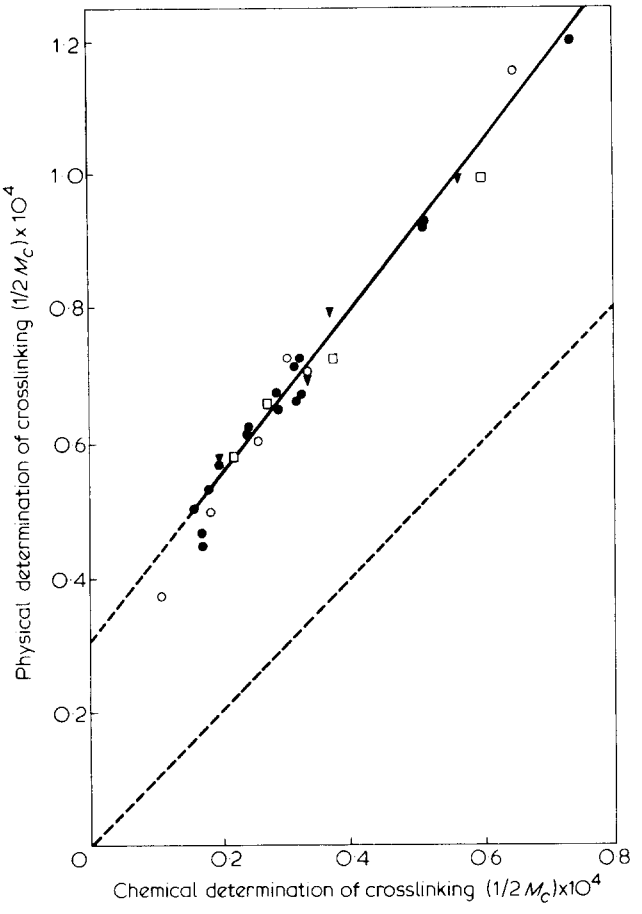

Figure 2 Comparison of physical and chemical estimates of crosslinking. Data of Moore and Watson[21]. [Reproduced by kind permission of John Wiley and Sons from *J. Polym. Sci.* 1956, **19**, 237 ©]

pressions which qualitatively reproduced departures from the expression for a phantom network.

Evidence will be presented which supports the idea of topological contributions from so-called trapped entanglements, and it will be shown that the entanglement contribution to the modulus in highly crosslinked rubbers is equal to the pseudo-equilibrium modulus of the uncrosslinked polymer.

ENTANGLEMENT THEORIES FOR UNCROSSLINKED POLYMERS

For short time deformations, uncrosslinked polymers behave very much like crosslinked rubbers: the material may be deformed several hundred percent without breaking and with complete recovery. The modulus is of about the same magnitude as for a crosslinked rubber. This has led to the application[1] of the Gaussian molecular theory of rubber elasticity, although it may be difficult to define what is meant by a network strand for an entanglement network. Thus, from the plateau modulus, apparent concentrations of strands terminated by entanglements may be calculated.

To describe the properties under flow, Lodge[10] and Yamamoto[11] modified the Gaussian network theory by introducing temporary junctions with a distribution of lifetimes. They made the assumption that the concentration of junctions is constant and that each strand is created in a stress-free state. Bueche *et al.*[12], Eyring *et al.*[13] and Graessley[14] have developed theories based on the idea that entanglement effects can be represented by an increase in the molecular friction coefficient.

In spite of an overwhelming number of entanglement studies, the precise nature of an entanglement coupling has not yet been established. One approach is to view an entanglement coupling as an interaction between only two chains. The above-mentioned use of the Gaussian network theory with tetrafunctional junctions is an example of this. Another example is the calculations of Ziabicki[15] who approximates the two chains by two pairs of half-lines with variable apex angle. A different approach is to view each polymer chain as being effectively restricted to a tube-like region as used in the calculations by de Gennes[16], Edwards[17] and Doi and Edwards[18]. When the polymer is deformed, the tubes are deformed, resulting in an entropy change of the system.

THEORY OF RUBBER ELASTICITY

The statistical molecular theory[5,19] for a network consisting of Gaussian phantom chains (formed and tested in the undiluted state) gives the following expression for the engineering stress σ:

$$\sigma = gRT\frac{\rho}{M_c}(\lambda - \lambda^{-2}) \qquad (1)$$

where g is the front factor, R is the gas constant, T is the absolute temperature, ρ is density, M_c is the mean molecular weight of effective network strands and λ is extension ratio. The statistical theory has been amazingly successful in predicting stress–strain properties of real rubbers. However, minor discrepancies are found. In simple extension, the experimental curve drops below the theoretical curve at larger strains[19], and the predicted modulus seems to be somewhat too low.

The front factor, g, for a phantom network is equal to $(f-2)/f$[20] where f is the functionality of the chemical crosslinks. In a real network both the strands and the junctions are highly restricted in their motions. As mentioned in the introduction, Flory[8,9] has suggested that this might cause the junction fluctuations to change nearly affinely, making g approach one in real networks.

A number of studies indicate apparent front factors which are several times higher than predicted by Flory's modified theory. The following sections will give a more detailed discussion of three types of studies, all of which indicate large entanglement contributions in crosslinked rubbers.

Results of Moore and Watson

Moore and Watson[21] studied di-t-butyl peroxide-cured natural rubber. The crosslinking mechanism is well-known and is thought to proceed practically without side reactions for this system. Thus, by varying the amount of crosslinking agent, different but known degreees of crosslinking should be obtained. From swelling measurements, a physical estimate of crosslinking could be made. *Figure 2* compares the physical determination of crosslinking with the chemical determination, the latter being estimated from the amount of crosslinking agent. The physical values are clearly higher than the values estimated from the amount of crosslinking agent. The crosslinks are thought to be tetrafunctional which means that the front factor for a phantom network should be equal to one half. However, the authors assumed

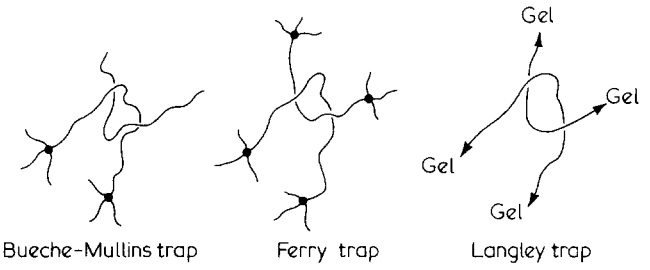

Figure 3 Various entanglement entrapment criteria. Black dots indicate chemical crosslinks. Reproduced by kind permission of Springer–Verlag from Graessley, *Adv. Polym. Sci.* 1974, **16**, 111 ©]

g equal to one, and even with this value, the observed moduli for the lower degrees of crosslinking are about two times the predicted values (shown with dashes).

Extrapolation of the experimental values to zero crosslinking gives an appreciable finite intercept independent of the value of the front factor. Moore and Watson suggested that these results indicate a modulus contribution originating in the presence of 'physical' crosslinkages in the uncrosslinked polymer, i.e. an entanglement contribution to the modulus.

It should now be possible, at least in principle, to calculate the entanglement contribution in the crosslinked network at any degree of crosslinking. However, there are several problems in applying equation (1). The numerical value of the front factor for a real network, formed and tested in the undiluted state, has not been properly established. Experimental determinations of the front factor give values of about 0.5 for networks prepared in the dilute state[22,23] while the Langley method gives values closer to one for networks prepared in the undilute state[7,24,25]. The contribution of elastically effective network strands created by the crosslinking process may be difficult to assess. Some of the problems which could be mentioned are the possibilities of side reactions, a distribution of crosslink functionalities and network defects such as intrachain loops and elastically ineffective chain ends. And finally, it is also unclear whether the Flory[26] method or the Scanlan[27] method should be used in counting the number of effective network strands terminated by chemical crosslinks. The two counting methods give different values at small crosslink densities. At high degrees of crosslinking, there is no difference between the two methods.

ENTANGLEMENT ENTRAPMENT CRITERA

With increasing degrees of crosslinking in a system of linear polymer chains, disentanglement of the chains becomes increasingly difficult. As soon as a chain is connected to another chain, it can no longer disentangle by the reptation mechanism proposed by de Gennes[16] for linear chains. Disentanglement may now have to take place by a slow diffusion of the chain end[28] towards the crosslinked point. In *Figure 3*, an entanglement is viewed as a constraint involving only two chains. Various entrapment criteria have been proposed for this simplified picture of an entanglement coupling, as shown in *Figure 3*. The Bueche–Mullins trap does not prevent the upper chain from diffusing away, thereby causing disentanglement. In a Langley trap, each of the four strands is connected to the gel structure, permanently trapping the entanglement.

Langley method

Langley[29] has developed a method for calculating the total concentration of elastically effective network strands, ν, assuming additivity of the contributions from chemical crosslinks and entanglements. His method takes into account molecular weight, molecular weight distribution, functionality of the crosslinks, and chain scission. Data at low degrees of crosslinking is needed, and it therefore makes a difference whether the Flory[26] or the Scanlan[27] criterion for counting elastically effective strands is used. With the Flory criterion:

$$\nu = \nu_c w_g T_e^{1/2} + \nu_e T_e \tag{2}$$

With the Scanlan criterion

$$\nu = \tfrac{1}{2}\nu_c T_e^{1/2}(3 w_g - T_e^{1/2}) + \nu_e T_e \tag{3}$$

where ν_c is the concentration of network strands terminated by chemical crosslinks, w_g is the gel fraction, ν_e is the concentration of potential entanglement strands and T_e is the fraction of potential entanglements which have become trapped by the crosslinking process. T_e depends on functionality of the crosslinks, initial molecular weight and molecular weight distribution, and on the fraction of repeating units which have undergone crosslinking, g, or scission, p.

When the functionality of crosslinks is known, sol extraction measurements give w_g, q, and p, allowing calculation of T_e. A further determination of the elastic modulus, allows determination of the concentration of potential entanglements, ν_e, and the front factor, g. Dossin *et al.*[7] have recently published results from a very extensive study on polybutadiene (~8% vinyl) and ethylene–propylene copolymer (~60 mol % ethylene). *Figure 4* shows a Langley plot of the initial moduli, G_0. The intercept on the ordinate axis gives the potential entanglement modulus contribution, G_e^{max}, and the slope gives the front factor, g. *Table 1* summarizes the results for three different studies, using the

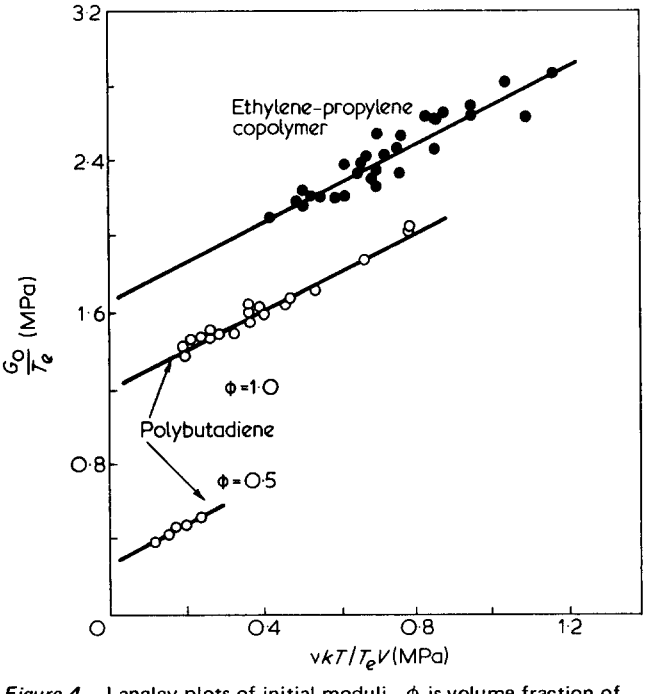

Figure 4 Langley plots of initial moduli. ϕ is volume fraction of polymer during crosslinking. Data of Dossin *et al.*[7]. [Reproduced by kind permission of the American Chemical Society from *Polym. Prepr.* 1979, **20**, 224 ©]

Table 1 Results from the Langley method for poly(dimethyl siloxane), polybutadiene (~8% vinyl), and ethylene–propylene copolymer. Moduli are given at 298K

Polymer	g	G_e^{max} (MPa)	G_N^0 (MPa)
Poly(dimethyl siloxane)	0.81	0.23[a]	0.30[c]
(Langley and Polmanteer[24])	0.60	0.26[b]	
Polybutadiene (Pearson *et al.*[25])	1.22	0.45[a]	1.3
Polybutadiene, $\phi = 1.0$	1.0	1.2	1.3
Polybutadiene, $\phi = 0.5$	~1.0	0.26	0.24
Ethylene–propylene copolymer (Dossin *et al.*[7])	1.1	1.6	1.7

ϕ is the volume fraction of polymer during crosslinking
[a] Flory criterion. [b] Scanlan criterion. [c] Ref 1, p 406

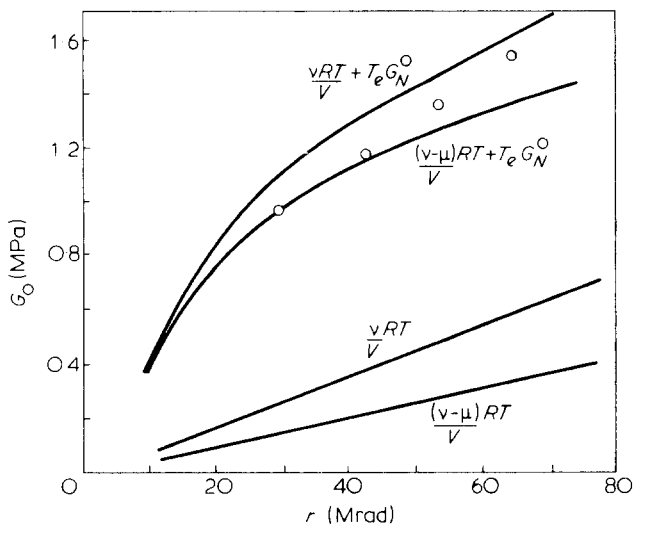

Figure 5 Initial moduli for polybutadiene ($\bar{M}_W$ = 210 000) crosslinked in bulk vs. radiation dose. Full lines show predicted behaviour with and without junction point fluctuations and a topological contribution based on plateau modulus. Data of Dossin *et al.*[7] [Reproduced by kind permission of the American Chemical Society from *Polym. Prepr.* 1979, **20**, 224 ©]

Langley method. Except for the study by Pearson *et al.*[25], excellent agreement between G_e^{max} and the stress relaxation modulus G_N^0 is obtained. The study by Dossin *et al.*[7], which includes a very large number of samples, clearly points to g = 1.0 whereas the study by Langley and Polmanteer[24] gives somewhat lower values.

Figure 5 is a plot of initial modulus in simple extension, G_0, *versus* irradiation dose. The full lines show predicted behaviour for a number of cases. Starting from the bottom, the first curve shows the predicted modulus for a phantom network, g = ½; the second curve is for a network with greatly reduced junction fluctuations, g = 1; the third curve is for a phantom network plus a topological (entanglement) contribution. The last curve is for a network with greatly reduced junction fluctuations plus a topological contribution. The circles are experimental points. It can be seen that, regardless of the junction fluctuation effect, the chemical contribution is a small part of the modulus in these networks. As stated by the authors, there appears to be no way to account for the observed behaviour without invoking something in addition to a chemical contribution.

Dossin *et al.*[7] also determined the Mooney–Rivlin parameters for their samples *Figure 6* is a plot of $2C_2$ *versus* the topological contribution, $T_e G_N^0$. The solid line corresponds to $2C_2 = \frac{1}{2} T_e G_N^0$. The interpretation given by the authors is that departures from the ideal Gaussian stress–strain relation are entirely dependent on the topological (entanglement) contribution. The other half of the effective topological contribution should then be included in C_1.

Two-network method

For a Gaussian network crosslinked in the strained undiluted state, the elastic free energy, ΔA_{el}, of the composite network may be expressed as the sum of two terms[30]:

$$\Delta A_{el} = \tfrac{1}{2} G_1 (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + \tfrac{1}{2} G_2 (\lambda_{x2}^2 + \lambda_{y2}^2 + \lambda_{z2}^2 - 3) \quad (4)$$

where G_1 is the modulus of the original network and G_2 is the modulus of the network formed in the strained state. The extension ratios λ_x, λ_y and λ_z are taken relative to the initial state while λ_{x2}, λ_{y2} and λ_{z2} are taken relative to the strained state.

By crosslinking entanglement networks of 1,2-polybutadiene in strained states, Ferry and coworkers have developed a method[31] to determine the entanglement contribution to the moduli of crosslinked polymers, using the two-network fomalism. After crosslinking and release, the composite network retracts to a state of ease. Stress–strain measurements relative to the state of ease allow determination of the two moduli, G_N due to entanglements and G_X due to chemical crosslinks introduced in the strained state. The entanglement modulus contribution, G_N, determined this way may be compared directly with G_N^0, determined from measurements in the rubber plateau region of the uncrosslinked polymer.

In the two-network method, the only assumption made is that the contributions from entanglements and chemical crosslinks, are separable and of the form shown in equation

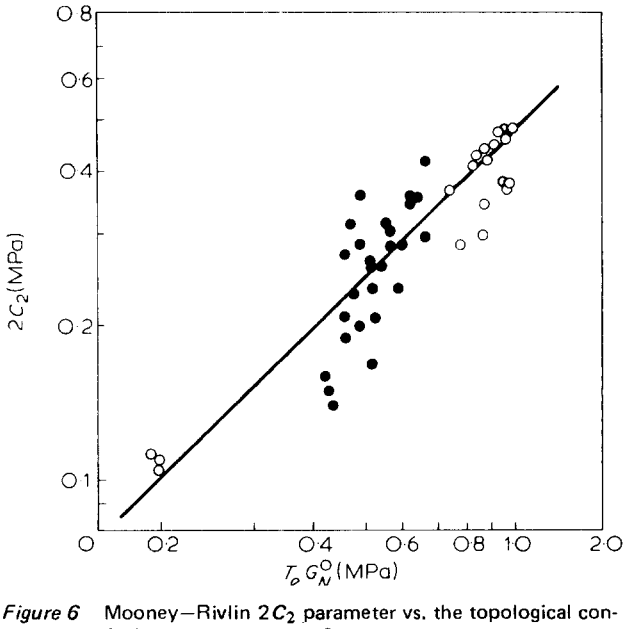

Figure 6 Mooney–Rivlin $2C_2$ parameter vs. the topological contribution. ○, Polybutadiene data; ●, ethylene–propylene copolymer data. Data of Dossin *et al.*[7]. [Reproduced by kind permission of the American Chemical Society *Polym. Prepr.* 1979, **20**, 224 ©]

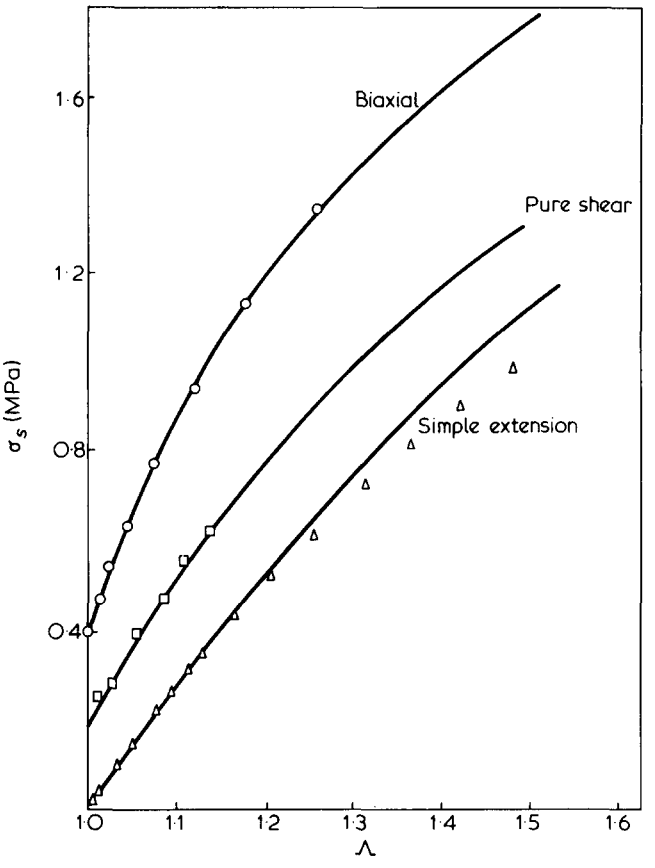

Figure 7 Stress–strain data at 323K for samples crosslinked and tested in three different types of deformation. Full lines are predictions from Gaussian theory. Scale for simple extension. (Unpublished data by Hvidt, Kramer, Batsberg and Ferry)

(4). The functionality of the chemical crosslinks, the value of the front factor, and whether to use the Flory or the Scanlan criterion need not be known. More details on the two-network method are given in another paper at this conference by Ferry[32].

Most of the work has been done on samples crosslinked in states of simple extension[31–35]. In the latest experiments[36], 2-polybutadiene was strained in different types of deformation at only 8K above the glass transition temperature, cooled to well below T_g, and then crosslinked in the strained state with 10 MeV electrons.

Figure 7 shows three samples, each of which have been crosslinked and subsequently stress–strain tested in the same geometry – starting from the top: equibiaxial extension, pure shear, and simple extension. Full lines are theoretical curves, using the ideal Gaussian theory. The well-known departure in simple extension is also observed here. Unfortunately, the samples break at rather low extension ratios when tested in equibiaxial extension or pure shear, but in no case were significant departures from theory observed.

Thin strips were cut from the composite networks and then tested in simple extension. *Figure 8* shows the results for samples crosslinked in simple extension, pure shear, and undeformed during crosslinking. It is clear that the so-called C_2 effect is found in simple extension irrespective of sample geometry. The departure from ideal behaviour for simple extension samples may be described using the Mooney–Rivlin expression for the entanglement contribution[33,34,37,38]. For samples which have experienced negligible relaxation prior to crosslinking in the strained state, it is found[38] that $C_{1N} \simeq C_{2N}$, i.e. the entanglements contribute roughly equally to the C_1 term and to the C_2 term of the crosslinked network. Strands terminated by chemical crosslinks contribute only to the C_1 term. These results are in agreement with the results of Dossin *et al.*[7].

Figure 9 shows the modulus contribution from chemical crosslinks, G_x, calculated from the two-network theory. G_s is the composite network modulus measured directly on thin strips at small strains. It is clear that the chemical contribution calculated from the two network theory accounts for only about 25%of the observed modulus. This is also in agreement with the results of Dossin *et al.*[7], see *Figure 5*.

Figure 10 shows the entanglement modulus contribution, G_N, calculated from the ideal two-network theory. There is very good agreement between the results from different types of strain, G_N^0 is the pseudo-equilibrium shear modulus in the viscoelastic plateau region[1]. These results show that $G_N^0 \simeq G_N$ from the two-network method. This means that the topological constraints which cause the pseudo-equilibrium rubber plateau become permenently trapped by the crosslinks, as assumed in the Langley method.

Front factor

It should be possible, at least in principle, to calculate the number of strands terminated by chemical crosslinks

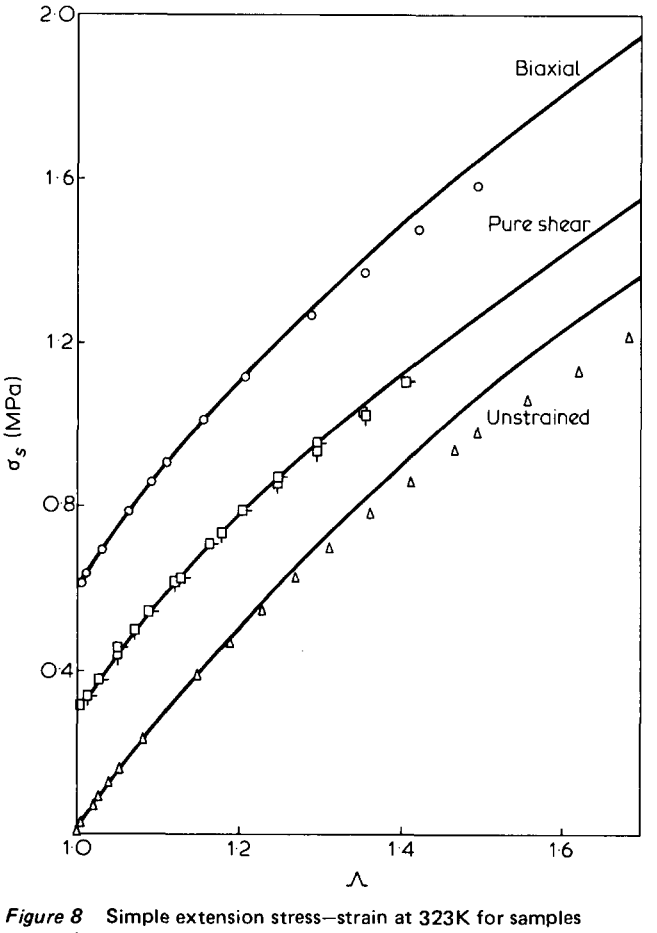

Figure 8 Simple extension stress–strain at 323K for samples crosslinked in unstrained, pure shear, and equibiaxial states as indicated. Solid lines for biaxial and pure shear are calculated from Gaussian theory, using moduli determined by inflation experiments. Scale for unstrained. (Unpublished data by Hvidt, Kramer, Batsberg and Ferry)

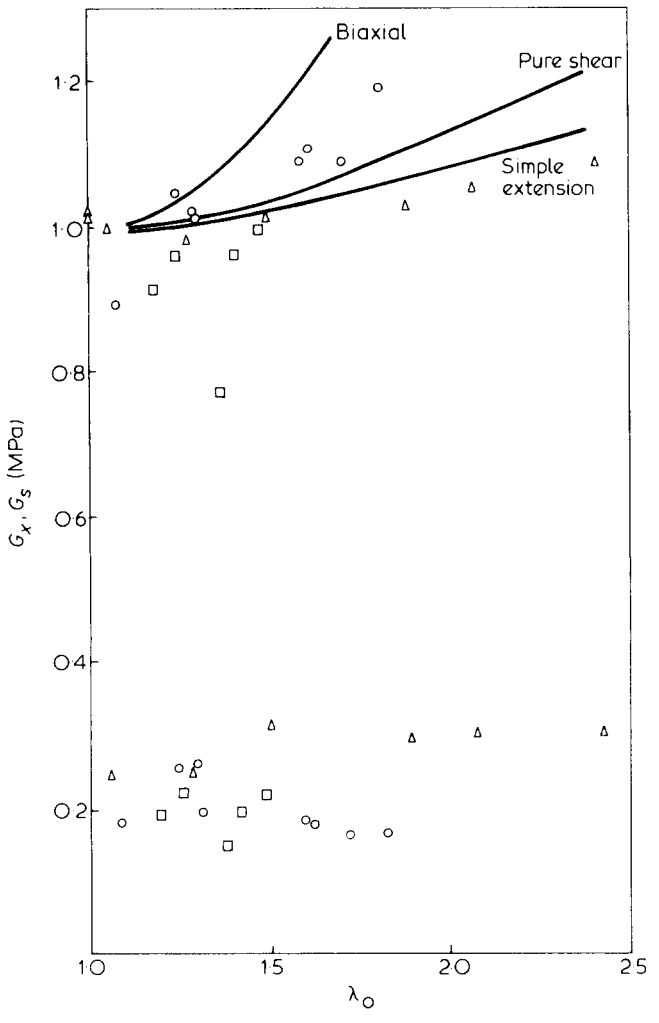

Figure 9 Composite network modulus, G_s, and modulus contribution from chemical crosslinks, G_X (●), vs. extension ratio during crosslinking, λ_0. Solid lines are predictions from the two-network theory, calculated with $G_X = 0.26$ MPa and $G_N = 0.73$ MPa. ○, Equibiaxial; □, pure shear; △, simple extension sample. (Unpublished data by Hvidt, Kramer, Batsberg and Ferry)

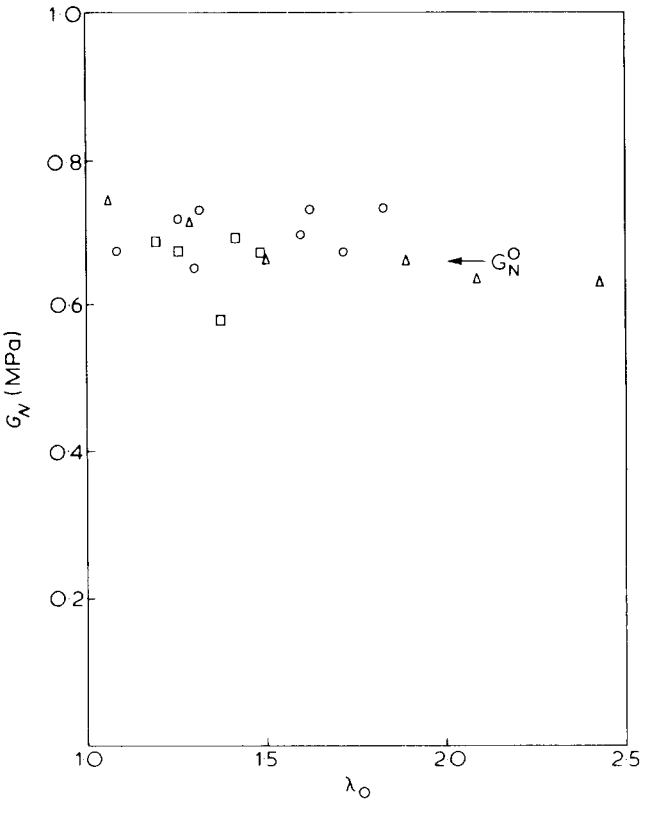

Figure 10 Entanglement contribution to the equilibrium modulus, G_N, vs. extension ratio during crosslinking, λ_0. G_N^0 is the pseudo-equilibrium stress relaxation modulus at 323K. ○, Equibiaxial; □, pure shear; △, simple extension sample. (Unpublished data by Hvidt, Kramer, Batsberg, and Ferry)

from the gel dose. The two-network method should therefore allow a rather direct determination[36] of the front factor for the modulus contribution from strands terminated by chemical crosslinks.

However, the functionality of the crosslinks must be known and should preferably be uniform. This is unfortunately not the case for high-vinyl polybutadiene, since the crosslinks may partly be formed by a chain reaction, involving several vinyl groups[25,39]. The mean functionality should therefore be expected to be higher than four. For the sake of illustration, the front factor was calculated for two cases. Assuming tetrafunctional crosslinks, $g = 0.6$; assuming hexafunctional crosslinks, $g = 1.2$. Experiments with other polymers have been planned.

CONCLUSION

In highly corsslinked rubbers, the entanglement network structure is made permanent by the chemical crosslinks. In this case, the entanglement contribution to the equilibrium modulus, G_N, is found to be equal to the pseudo-equilibrium modulus of the uncrosslinked polymer, G_N^0. At lower degrees of crosslinking or if chain scission has taken place, the entanglement contribution is less than G_N^0. This is due to rearrangement of the entanglement network structure or complete disentangling of part of the network.

Both the Langley method and the two-network method indicate that the entanglement contribution to the stress is responsible for departures from neo-Hookean behaviour observed in simple extension.

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