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Elastic Contributions from Chain Entangling and Chemical Cross-Links in Elastomer Networks in the Small-Strain Limit

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ABSTRACT: The elastic effects of chain entangling and chemical cross-links in rubber networks are separated experimentally by performing the cross-linking reaction in states of simple extension. The composite network behaves as if composed of two separate networks. Application of Hooke's law to each of the two networks allows calculation of model-independent contributions to Young's modulus of the composite network in the small-strain limit. Analysis of experimental results on 1,2-polybutadiene networks reported by Hvidt, Kramer, Batsberg, and Ferry shows that chain entangling contributes about 75% of the modulus at elastic equilibrium. The entanglement contribution to Young's modulus at 50 °C is 2.1 MPa, approximately equal to the rubber plateau modulus of un-cross-linked 1,2-polybutadiene with a similar microstructure, $E_N{}^\circ = 2.0$ MPa.

A still unsettled question in the understanding of rubber elasticity is whether topological constraints, such as those due to chain entangling, contribute to the equilibrium elastic modulus in cross-linked elastomers and, if so, to what extent. This question is of great experimental consequence: measurements of elastic modulus and swelling behavior are often used in calculating the degree of cross-linking and the extent of reaction in polymer networks. The degree of cross-linking calculated from such measurements may differ by a factor of 4 or more[1-3] when theories with and without a contribution from chain entangling are used.

The constrained junction theory of Flory[4] and Erman and Flory[5,6] has been developed on the basis that topological constraints play no role other than to reduce the fluctuations of the network junctions. Results obtained on end-linked networks seemed to confirm this assumption.[7,8] However, side reactions[9] and the creation of elastically ineffective loops[10] make end-linked networks imperfect in most cases. Other theories assume a constraint contribution adding directly to the total free energy expression in the tradition of the two-network concept of Andrews, Tobolsky, and Hanson[11] and of Flory.[12] Different forms of the constraint contribution have been argued and derived.[13-18] Langley[14] uses the same strain dependence for the entanglement and chemical cross-link contributions and calculates the fraction of trapped entanglements as a function of the degree of cross-linking; Ball, Doi, Edwards, and Warner[15] use a replica slip-link; Higgs and Ball[16] employ hoops; a space filling tube is used by Gaylord and Douglas[17,18] in obtaining a scaling expression for the constraint contribution.

It has proven difficult to make a convincing experiment that decisively answers the question about the entanglement contribution at elastic equilibrium and to interpret the results of unusual experiments in a convincing manner. This paper presents a model-independent analysis of experimental results reported by Hvidt, Kramer, Batsberg, and Ferry,[1] who used Ferry's two-network method to separate the elastic effects of entanglements and cross-links.[19,20] Hooke's law is applied to each of the two elastic contributions, limiting the analysis to small-strain behavior.

Rubber Networks Cross-Linked in Different States

The elastic properties of a rubber network formed from more than one set of cross-links have long been described as a linear combination of the contributions from each set as suggested by Andrews, Tobolsky, and Hanson[11] and later substantiated by Berry, Scanlan, and Watson.[21]

The composite network theory of Flory[12] treats a network of Gaussian chains with one set of cross-links introduced in the isotropic state and a second set introduced in the strained state. For such a seemingly complicated structure, Flory demonstrated for affine motion of the network junctions that the elastic free energy simply separates into two independent contributions

$$\Delta A_{\mathrm{el}} = {}^1\!/_2\nu_1 kT(\lambda_x{}^2 + \lambda_y{}^2 + \lambda_z{}^2 - 3) + {}^1\!/_2\nu_2 kT(\lambda_{x;2}{}^2 + \lambda_{y;2}{}^2 + \lambda_{z;2}{}^2 - 3) \quad (1)$$

where ν_1 and ν_2 are the numbers of network strands per unit volume created in the isotropic and strained states, respectively; k is Boltzmann's constant; T is the absolute temperature; λ_x, λ_y, and λ_z are the extension ratios relative to the reference state for the creation of the first set of network strands (the isotropic state); and $\lambda_{x;2}$, $\lambda_{y;2}$, and $\lambda_{z;2}$ are the extension ratios relative to the reference state for the creation of the second set of network strands. The expression given in Flory's paper[12] also contains a volume term, but this term has been omitted in eq 1 since the volume is constant in the two-network experiments to be described below.

On the basis of this idea, Ferry proposed that the elastic contributions of entanglements and chemical cross-links could be separated experimentally by performing the cross-linking reaction in the strained state.[19]

Ferry's Two-Network Method

The principle of Ferry's two-network method[19,20] is illustrated in Figure 1. An un-cross-linked linear polymer of very high molecular weight is strained at a temperature slightly above the glass transition temperature where large-scale molecular motions are slow. The strained sample is allowed to relax well into the rubber plateau region and then quenched to the glassy state and cross-linked by high-energy radiation, trapping in the topological entanglement structure of the un-cross-linked polymer. After heating and release, the sample retracts to an intermediate length, the so-called state-of-ease, where the original entanglement

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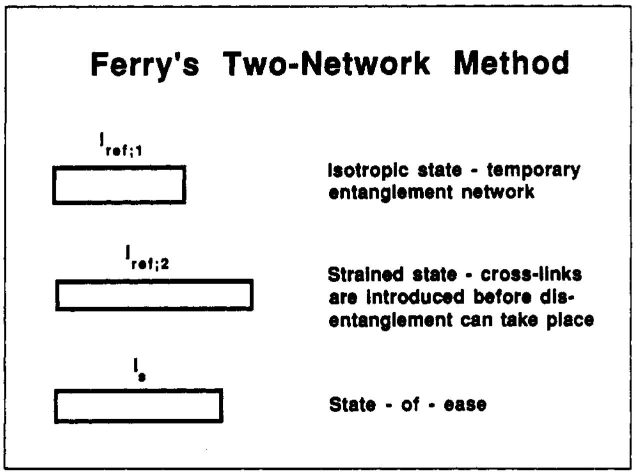

Figure 1. The temporary network of entangled chains is trapped permanently by the introduction of chemical cross-links in the strained state. The entanglement network and the cross-link network oppose each other with equal forces in the state-of-ease with length l_s.

network and the cross-link network created in the strained state balance each other.

Hvidt, Batsberg, Kramer, and Ferry[1] used a polybutadiene with 88% 1,2-structure, a relative molar mass of 291 000, and a glass transition temperature of 255 K. Cross-links were formed by irradiation with 10-MeV electrons, using a dose of 125 kGy. Simple elongational stress–strain behavior from the state-of-ease was measured at 50 °C by hanging weights from the end of the specimen and measuring the change in length with a traveling microscope. The analysis based on eq 1 gave two major results.[1] First, the elastic contribution from chain entangling was found to be greater than that of the chemical cross-links. Second, the entanglement contribution was found to be approximately equal to the rubber plateau modulus of un-cross-linked 1,2-polybutadiene.

The results of Ferry's two-network method have also been analyzed with an empirical two-network Mooney–Rivlin expression[22-24] proposed by Greene, Smith, and Ciferri;[25] with the random tube model of Gaylord and Douglas;[26,27] and with the replica slip-link model of Ball, Doi, Edwards, and Warner.[28] These analyses indicate additionally that the deviations from simple Gaussian behavior, observed at intermediate strains, originate in the elastic contribution from chain entangling.

The inability of eq 1 to describe the two-network data at higher strains and the common rejection of the empirical Mooney–Rivlin equation because of its inability to describe the elastic properties in both extension and compression with the same values of C_1 and C_2[29] have caused skepticism of the results from Ferry's two-network method. However, it is important to point out that these problems are of no consequence for the main conclusions. The results obtained at small strains are completely general, as demonstrated by the present model-independent calculation based on Hooke's law.

Hookean Two-Network Theory

The theoretical expressions developed and used in the present paper are limited to small strains where Hooke's law applies. Hooke's law applies to all solids and states that stress is proportional to strain with Young's modulus E as the constant of proportionality

$$\frac{f}{A} = E\frac{(l - l_{\mathrm{ref}})}{l_{\mathrm{ref}}} \tag{2}$$

where f is the force, positive for simple extension and negative for simple compression; A is the cross-sectional area; l is the length of the deformed sample; and l_{ref} is the undeformed sample length.

For a composite rubber network with two different sets of cross-links, it is assumed that the two sets give independent contributions to the resulting unidirectional force f in the tradition of the work of Andrews, Tobolsky, and Hanson;[11] Berry, Scanlan, and Watson;[21] Flory;[12] Green, Smith, and Ciferri;[25] and Ferry and co-workers.[19,20] Hooke's law is then applied to each of the two networks as shown in eq 3 where subscript 1 refers to the first network

$$f = A_1E_1\frac{(l - l_{\mathrm{ref;1}})}{l_{\mathrm{ref;1}}} + A_2E_2\frac{(l - l_{\mathrm{ref;2}})}{l_{\mathrm{ref;2}}} \tag{3}$$

formed with a reference length of $l_{\mathrm{ref;1}}$ and subscript 2 refers to the second network formed with a reference length of $l_{\mathrm{ref;2}}$.

The resulting force f is equal to zero in the state-of-ease and so

$$0 = A_{\mathrm{ref;1}}\frac{l_{\mathrm{ref;1}}}{l_s}E_1\frac{(l_s - l_{\mathrm{ref;1}})}{l_{\mathrm{ref;1}}} + A_{\mathrm{ref;1}}\frac{l_{\mathrm{ref;1}}}{l_s}E_2\frac{(l_s - l_{\mathrm{ref;2}})}{l_{\mathrm{ref;2}}} \tag{4}$$

where l_s is the length and $A_{\mathrm{ref;1}}(l_{\mathrm{ref;1}}/l_s)$ is the cross-sectional area in the state-of-ease. The reduced expression for the calculation of the ratio of Young's moduli is then

$$\frac{E_2}{E_1} = \frac{l_{\mathrm{ref;2}}(l_s - l_{\mathrm{ref;1}})}{l_{\mathrm{ref;1}}(l_{\mathrm{ref;2}} - l_s)} \tag{5}$$

Thus, only three measurements of length are required to determine the ratio of the moduli.

Young's modulus relative to the state-of-ease, E_s, is derived in terms of E_1 and E_2 by differentiation of eq 3 with respect to l/l_s. The result is

$$E_s = E_1 + E_2 \tag{6}$$

It is calculated from stress–strain measurements in simple extension by plotting the data according to eq 7 where m

$$m\left(\frac{l}{l_s}\right) = \frac{E_sA_s}{gl_s}(l - l_s) \tag{7}$$

is the combined mass of the weight and the lower clamp; g is the gravitational acceleration; A_s is the cross-sectional area in the state-of-ease; and l is the length of the loaded sample.

Results and Discussion

Figure 2 shows the original stress–strain data for sample no. 31[1] plotted according to eq 7. The slope is determined by linear regression to the first four data points only, to ensure compliance with Hooke's law. The precise value of l_s is determined from the intercept of this line with the x-axis.

Table I summarizes the measured and calculated results for six samples cross-linked in states of simple extension. The three moduli E_s, E_1, and E_2 are plotted against the extension ratio during cross-linking in Figure 3. Chain entangling clearly contributes much more to the modulus than the chemical cross-links. The ratio of E_1 to E_2 is equal to 3 when extrapolated to zero strain during cross-linking (corresponding to a traditional, isotropic rubber). This is the same result as that obtained previously from the analysis based on Gaussian chains.[1]

It is perhaps surprising that the contribution from chain entangling calculated from the Hookean analysis depends very little on the extension ratio during cross-linking. This

Table I
Two-Network Results at a Reference Temperature of 50 °C for 1,2-Polybutadiene Cross-Linked in States of Simple Extension[a]

sample no.	$l_{ref;1}$, mm	$l_{ref;2}$, mm	l_s, mm	$l_s/l_{ref;1}$ (=λ_s)	E_s, MPa	E_2/E_1	E_1, MPa	E_2, MPa
31	6.883	7.349	6.992	1.016	2.94	0.33	2.22	0.72
37	6.449	8.321	6.851	1.062	2.89	0.35	2.14	0.75
33	6.127	9.266	6.889	1.124	2.96	0.48	1.99	0.97
36	6.027	11.477	7.108	1.179	3.04	0.47	2.07	0.97
34	4.975	10.412	6.045	1.215	3.07	0.51	2.03	1.04
35	5.842	14.256	7.357	1.259	3.13	0.54	2.04	1.09

[a] The moduli are obtained from Hookean analysis.

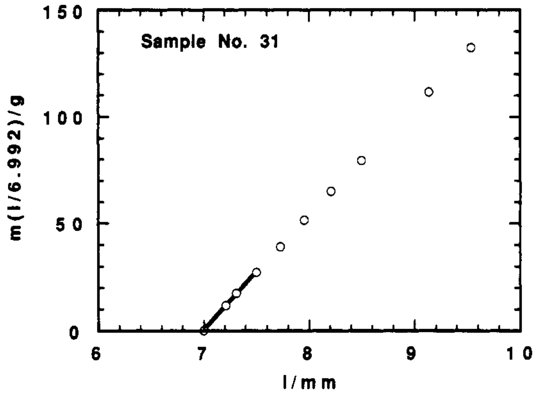

Figure 2. Simple extension measured relative to the state-of-ease at 50 °C and plotted according to eq 7. The lengths between fiducial marks are 6.992 mm unloaded and l when loaded. Open circles are experimental points. Young's modulus is calculated from the slope obtained by linear regression to the first four data points (solid line). The value of Young's modulus is 2.94 MPa.

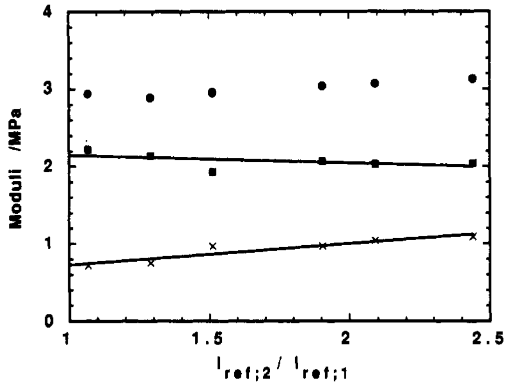

Figure 3. Moduli plotted against the extension ratio during cross-linking: (●) E_s, Young's modulus measured relative to the state-of-ease; (■) E_1, modulus contribution from chain entangling; (×) E_2, modulus contribution from chemical cross-links. The entanglement modulus obtained by linear extrapolation to zero strain is 2.14 MPa; the corresponding value for the chemical cross-links is 0.73 MPa.

is probably due to the small strains on the entanglement network in the state-of-ease.

The modulus contribution from chain entangling is 2.1 MPa when extrapolated to zero strain during cross-linking. This is approximately equal to the rubber plateau modulus of un-cross-linked 1,2-polybutadiene with a similar microstructure, $E_N{}^\circ = 2.0$ MPa at 50 °C.[30] This equality of the elastic contributions from chain entangling before and after cross-linking is also demonstrated by a simplified two-network experiment where the sample is kept at constant length.[31,32]

Conclusions

The model-independent Hookean analysis for a series of 1,2-polybutadiene networks cross-linked in states of simple extension shows unambiguously that 75% of the small-strain equilibrium modulus is due to chain entanglements. Furthermore, the entanglement contribution to the equilibrium modulus is approximately equal to the rubber plateau modulus of the un-cross-linked polymer. Thus, molecular models of rubber elasticity, which neglect independent elastic contributions from chain entangling, must be considered unphysical.

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