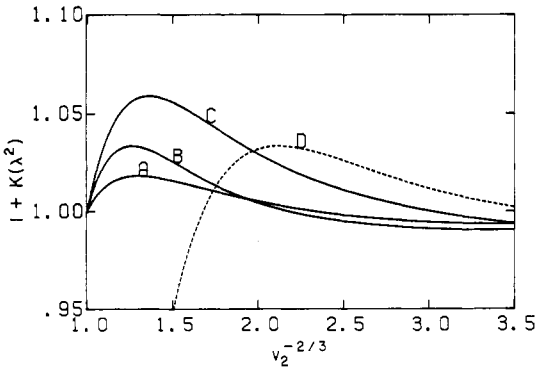

Figure 7. Calculations of $1 + K(\lambda^2)$ vs. $v_2^{-2/3}$ for bulk-cured (solid lines) and solution-cured (dotted line) networks: curve A, $v_2^0 = 1.0$, $\kappa = 3.0$, $\zeta = 0.6$; curve B, $v_2^0 = 1.0$, $\kappa = 10.0$, $\zeta = 0.6$; curve C, $v_2^0 = 1.0$, $\kappa = 10.0$, $\zeta = 0.4$; curve D, $v_2^0 = 0.46$, $\kappa = 10.0$, $\zeta = 0.6$.

are apparent from the bulk-cured curves (curves A, B, and C). First, as κ increases the maximum increases while its location is shifted to slightly lower dilutions, and second, as ζ decreases (κ constant) the maximum becomes more prominent and occurs at higher dilutions. Comparison between solution- and bulk-cured curves (κ and ζ constant) demonstrates that a broader maximum occurs at higher dilutions for the solution-cured case.

Conclusions

This investigation allows comparison of the elastic component of the solvent chemical potential for bulk- and solution-cured PDMS + cyclohexane systems. It reveals that a sharper maximum occurs at a slightly lower dilation for the bulk-cured sample but that numerical values of $\lambda \ln (a_{1,c}/a_{1,u})$ for each system are nearly the same.

The diluent dependence of $\lambda \ln (a_{1,c}/a_{1,u})/V_1$ has been tested. As Figure 6 shows, curves for the PDMS + cyclohexane and PDMS + benzene systems fail to coalesce. This illustrates that $\lambda\mu_{1,el}/V_1$ is not only a function of dilution, but that there are also specific solvent effects. This anomaly cannot be attributed to differences between χ_c and χ_u or to changes of chain dimensions. This leads us to the inevitable conclusion that the elastic and mixing free energies are not strictly separable.

The newest version of Flory's theory is clearly an improvement over the old. The theory not only shows qualitative agreement with experiment but also is quantitatively more accurate than its predecessor. The experimental maxima occur in the predicted region, and the expected differences between bulk- and solution-cured samples are experimentally confirmed. Hence, apart from the solvent dependence, the theory accounts remarkably well for the swelling behavior of these poly(dimethylsiloxane) samples. Further swelling measurements to test the effect of network topology will be reported.

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On the Suppression-of-Junction-Fluctuations Parameter in Flory's Network Theory

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ABSTRACT: The concept of suppression of junction fluctuations in polymer networks is quantified by means of κ in Flory's recent network elasticity theory. The same concept is also measured by the h parameter in Dossin and Graessley's expression for the small-strain modulus. In this work an analytical relationship between these two physically related parameters is obtained for the case of a perfect, incompressible, unswollen network.

A new theory of rubber elasticity has been recently put forward by Flory.[1-3] According to this theory, the fluctuations of network junctions (cross-links) are restricted by the presence of neighboring network strands. The magnitude of constraints depends on network structure, topology, and strain. In a strained phantom network (a model in which network topology is ignored) junction fluctuations give rise to deformation of network strands

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such that the instantaneous junction positions are nonaffine with the macroscopic strain. Limitation of these fluctuations tends to make the strand deformation more affine. A key parameter in characterizing real network behavior, according to Flory's theory, is κ, a measure of the severity of constraints imposed by neighboring chains on network junctions relative to those imposed by the network of phantom chains[3] ($0 < \kappa < \infty$).

Dossin and Graessley[4] have used the suppression-of-junction-fluctuations concept in the formulation of an expression for the small-strain modulus (excluding entanglement contribution):

$$G_0 = (\nu - h\mu)kT/V \tag{1}$$

Here ν and μ are the number of strands and junctions in the network and h is an empirical constant that measures the severity of constraints on junction fluctuations and varies between 0 (complete suppression) and 1 (phantom network).

It is obvious from the discussion above that κ and h are intimately related. Equation 1 has been used to correlate small-strain data from several elastomeric networks and h values for different polymers have been reported.[4-10] Other workers[3,11-13] have published experimental κ values for similar systems. It seems to be of interest to relate h and κ in order to eliminate the ambiguity resulting from the usage of these two separate definitions of the severity-of-junction-constraints parameter. In what follows we will demonstrate the relationship between the two for a perfect network formed in bulk.

The ratio of force due to entanglement constraints on junctions to that of a phantom network in the case of uniaxial deformation is (cf. ref 2, eq 62)

$$f_c/f_{ph} = (\mu/\xi)[\alpha K(\lambda_1) - \alpha^{-2}K(\lambda_2)](\alpha - \alpha^{-2})^{-1} \tag{2}$$

where α is the relative elongation, ξ is the network cycle rank, and $K(\lambda_t)$ is a function of the principal extension ratios defined below. For uniaxial deformation the extension ratios are $\lambda_1 = \alpha$, $\lambda_2 = \lambda_3 = \alpha^{-1/2}$.

For a perfect network (i.e., a network free of dangling ends and ineffective loops) of functionality ϕ (ref 2, eq 6 and 7)

$$\xi = \mu(\phi - 2)/2 = \nu - \mu \tag{3}$$

The function $K(\lambda_t)$ in eq 2 is computed by (ref 3, eq 13)

$$K(\lambda_t) = \frac{B}{1+B}\frac{\partial B}{\partial(\lambda_t^2)} + \frac{D}{1+D} + \frac{\partial D}{\partial(\lambda_t^2)} \tag{4}$$

B and D above depend on $\mathcal{S}(\Delta x_t)$, the a priori probability of a displacement Δx_t from the center of constraint in the direction of the t axis, or, more specifically, on the nature of the dependence of the domain of constraint on the strain (assumption iii in ref 2).

$$\mathcal{S}(\Delta x_t) = (\sigma_0\lambda_t^{-p}/\pi)^{1/2}\exp[-\sigma_0\lambda_t^{-p}(\Delta x_t)^2] \tag{5}$$

$$\langle(\Delta x_t)^2\rangle = \lambda_t^p\langle(\Delta x_t)^2\rangle_0 \tag{6}$$

where the subscript 0 denotes the reference state. Flory[2] gives an expression for B and D for the case $p = 2$. The more general expression[3] contains an error in the relations for B and D. The appropriate equations are

$$B = \kappa(\lambda_t^p + \kappa)^{-2}[\kappa(\lambda_t^2 - 1) + \lambda_t^2 - \lambda_t^p] \tag{7}$$

$$D = (\lambda_t^p + \kappa)^{-2}\lambda_t^p[\kappa(\lambda_t^2 - 1) + \lambda_t^2 - \lambda_t^p] = B\lambda_t^p/\kappa \tag{8}$$

It is important to realize that in its corrected form the contribution of constraints to the free energy, ΔA_c, does not vanish at the limit of $\kappa = 0$ for any $p \neq 2$. Brotzman and Eichinger[14] have attempted to correct this problem by setting $p = 2$ in eq 6 but retained eq 5 as shown above. Although their arbitrary model does yield $\Delta A_c = 0$ for $\kappa = 0$, an incorrect limiting value is obtained for $\kappa \to \infty$.[15]

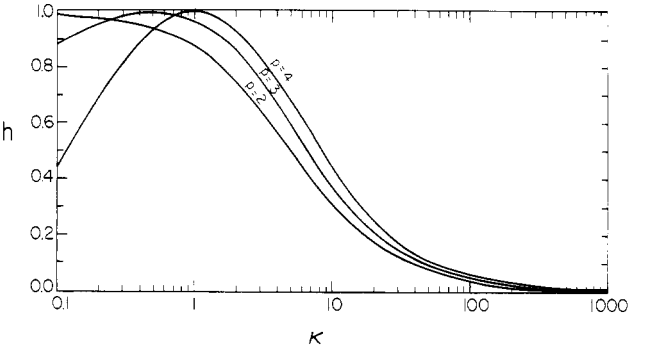

Figure 1. Flory's κ junction-fluctuation-suppression parameter against Dossin and Graessley's h parameter.

The tensile force for an incompressible unswollen network ($V/V^0 = 1$) can be written as (cf. eq 1 of ref 2 and eq 2 above)

$$f = f_{ph}(1 + f_c/f_{ph}) = \xi\left(\frac{kT}{L^0}\right)(\alpha - \alpha^{-2}) \times \left\{1 + \left(\frac{\mu}{\xi}\right)[\alpha K(\alpha) - \alpha^{-2}K(\alpha^{-1/2})](\alpha - \alpha^{-2})^{-1}\right\} \tag{9}$$

or in terms of σ, the tensile force per unit unstretched area ($A^0 = V^0/L^0$):

$$\frac{\sigma}{\alpha - \alpha^{-2}} = \frac{kT}{V}\{\xi + \mu[\alpha K(\alpha) - \alpha^{-2}K(\alpha^{-1/2})](\alpha - \alpha^{-2})^{-1}\} \tag{10}$$

Using the definition of G_0

$$G_0 = \lim_{\alpha\to 1}\left(\frac{\sigma}{\alpha - \alpha^{-2}}\right) \tag{11}$$

and equating to eq 1, we obtain for a "perfect" network

$$1 - h = \lim_{\alpha\to 1}[\alpha K(\alpha) - \alpha^{-2}K(\alpha^{-1/2})](\alpha - \alpha^{-2})^{-1} \tag{12}$$

It now follows from eq 4, 7, 8, and 12 that

$$h = 1 - (\kappa^2 + 1)(\kappa + 1 - \tfrac{1}{2}p)^2(\kappa + 1)^{-4} \tag{13}$$

Equation 13 is depicted in Figure 1, where h is shown as function of κ for several commonly used[2,3,14] values of p. At the limit of $\kappa = 0$ (i.e., no entanglement contribution) $h = (4 - p)p/4$. Hence, only for $p = 2$ the phantom network value, $h = 1$, is recovered. Furthermore, for any $p > 4$ negative values are obtained for h, resulting in small-strain modulus values $G_0 > \nu kT/V$, which is in disagreement with the basic model.[2,15] It should be stressed again that the entire analysis presented above holds only for incompressible, unswollen, perfect networks.

Finally, it is comforting to note that the value $h \simeq 0.5$, $p = 2$ reported by Gottlieb et al.[9] for a randomly cross-linked PDMS network is in fair agreement with values suggested by Flory[3] for similar systems (κ = 10–20).

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Modified Gaussian Model for Rubber Elasticity. 2. The Wormlike Chain†

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ABSTRACT: The modified Gaussian model for the wormlike chain is applied approximately to a three-chain model of rubber elasticity. A closed-form expression for the network free energy is obtained and equations governing the uniaxial extension and solvent swelling are derived. Numerical results for the stress–strain behavior in uniaxial extension are presented.

I. Introduction

In the first paper in this series[1] the modified Gaussian model of the freely jointed chain was applied to a simple model of an elastic network. A simple closed-form expression for the network free energy was obtained and equations governing network behavior in uniaxial extension and in solvent swelling were derived. The solvent swelling equation has proven to be useful in interpreting experimental data on the swelling of bituminous coals.[2]

In this paper the use of the modified Gaussian model in rubber elasticity is extended to the case of the wormlike chain of Porod and Kratky.[3] The wormlike chain allows more freedom in the treatment of non-Gaussian chain statistics because the chain length and the chain stiffness can be varied independently. It also provides a treatment of chain statistics that avoids the use of the concept of statistical segments. This is an advantage for short chains, where the division into statistical segments can be arbitrary and unrealistic. This work has been motivated by three considerations: (1) to see whether the modified Gaussian model could provide useful closed-form expressions for the network free energy for this more complicated chain model; (2) to provide a preliminary theoretical basis for experimental measurements of the elastic properties of networks in which chain stiffness is varied systematically; (3) to provide a more realistic model for interpretation of solvent swelling measurements on bituminous coals.[4]

A variety of non-Gaussian effects have been included in the theory of rubber elasticity but the effect of chain stiffness seems not to have been previously considered explicitly. In this paper we focus only on the effects of single-chain statistics using a simple three-chain affine deformation model and ignore all the complicated and important network effects. Therefore, the equations derived and numerical results presented can only be used for qualitative or semiquantitative comparison with experiment. The results, however, should provide some insight as to where the effects of chain stiffness will be important. In the future we hope to apply the modified Gaussian model to coupled chains in a network to provide a more realistic model. For the present the simple theory presented here must suffice.

II. Modified Gaussian Model

In this section the development of the modified Gaussian model is reviewed briefly and the essential equations presented. For a detailed presentation of the reader is referred to the original paper.[6]

The polymer chain is assumed to contain $N + 1$ identical backbone atoms connected by N bond vectors $\vec{b}_i$, $i = 1, 2, \ldots, N$. The true backbone potential V is a function of $\{b\}$ and is expressed in units such that $kT = 1$. The chain is subjected to an equilibrium force $\vec{f}$ acting on the end-to-end vector $\vec{R}$

$$\vec{R} = \sum_{i=1}^{N} \vec{b}_i \tag{1}$$

The exact distribution function of the set $\{b\}$ is

$$\psi_V(f) = \exp(\vec{R}\cdot\vec{f} - V)/Z_V(f) \tag{2}$$

$$Z_V(f) = \int \exp(\vec{R}\cdot\vec{f} - V)\, \mathrm{d}\{b\} \tag{3}$$

In the presence of $\vec{f}$ the mean end-to-end vector $\langle\vec{R}\rangle_f$ does not vanish and is calculated

$$\langle\vec{R}\rangle_f = \int \vec{R}\psi_V(f)\, \mathrm{d}\{b\} \tag{4}$$

$$= \mathrm{d} \ln Z_V(f)/\mathrm{d}\vec{f} \tag{5}$$

The idea of the modified Gaussian model is that the exact distribution function can be expanded in a series of Hermite-like polynomials orthogonal with respect to a weight function $e^{-\xi}$, where

† J.K. dedicates this paper to the memory of Arthur F. Scott, Professor Emeritus of Chemistry at Reed College, who was an inspiration for generations of students.

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