3282 *Macromolecules* **1993,** *26,* 3282-3288

The Effect of Swelling on the Elasticity of Rubber: Localization Model Description

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Received August 28, 1992; Revised Manuscript Received March 9, 1993

ABSTRACT: The success of the localization model in describing the elasticity of unswollen natural rubber is reviewed and the model is extended to describe the elasticity of swollen networks. In contrast to the Frenkel–Flory–Rehner modeling of network elasticity, the localization model predicts that the mechanical response of swollen rubbers changes qualitatively in going from low to high cross-link densities. The implications of these predictions are discussed.

1. Introduction

Frenkel[1] and Flory and Rehner[2] introduced some fundamental hypotheses relating to the swelling of rubber and the changes of rubber elasticity associated with this swelling, viz., (1) the free energy of mixing and the elastic free energy in swollen networks are additive and (2) the elastic strain energy density function is *invariant* to swelling. McKenna et al.[3,4] recently evaluated these hypotheses for samples of dicumyl peroxide cross-linked natural rubber. These experimental studies indicated that if the dry rubber free energy density was determined from continuum mechanics theory, rather than from a "molecular" model, then the swollen state compressive properties could be *predicted* directly from the FFR hypotheses. Recently, we have realized that it is difficult to similarly explain the change of rubber elasticity with swelling indicated in the experiments of Gumbrell, Mullins, and Rivlin[5] and Allen et al.[6] Further examination of the FFR hypotheses seems warranted, especially the second hypothesis.

In previous work[7] on characterizing the elasticity of dry rubber we found that the localization model described the dry rubber data well and yielded reasonable magnitudes of the model parameters. This previous work will be summarized as a preliminary to an extension of the model to describe network swelling. The extension of the localization model offers a resolution of the apparent inconsistency between the McKenna et al.[3,4] compression results and the extension results of Gumbrell, Mullins, and Rivlin[5] and Allen et al.[6] in that it predicts two regimes of behavior. At high cross-linking densities the elastic strain energy function is invariant to swelling and, thus, accords with the second Frenkel[1]–Flory–Rehner[2] (FFR) hypothesis. However, at low cross-link densities the model predicts that the second FFR[1,2] hypothesis no longer holds.

In the following section we summarize prior results showing the success of the localization model in describing the dry state properties of peroxide cross-linked natural rubber. We then present the discrepancy between the swollen state compression results of McKenna et al.[3,4,7] and the extension results of Rivlin et al.[5] and Allen et al.[6] In the penultimate section we present an extension of the localization model to describe swollen rubber and we discuss the implications of the model in comparison with experiment. The apparent breakdown of the second FFR hypothesis under certain conditions is perhaps the most important implication of the localization model.

2. Review of the Localization Model

Molecular models of polymeric network elasticity have concentrated on certain minimal aspects of rubber networks. The classical theories focused on the property of network connectivity. Recent theories have stressed "nonideal" contributions to network elasticity. For example, Edwards and co-workers[8,9] have emphasized "topological" interactions associated with the uncrossability of network chains. DiMarzio[10] and Jackson et al.[11] attempted to derive more realistic models by including the chain packing effects in a mean-field approximation.

Gaylord and Douglas[12,13] incorporated these minimal features of a cross-linked network (network connectivity, entanglement interaction, finite chain volume) into a simple theory of rubber elasticity which they call the "localization model". In this model the change in the network free energy with deformation is given by[12,13]

$$\Delta F(\text{elastic})/V_0 = (G_c/2)\sum_{i=1}^{3}(\lambda_i^2 - 1) + G_e\sum_{i=1}^{3}(\lambda_i - 1) \qquad (1)$$

where ΔF(elastic) is the elastic contribution to the free energy of the network, V_0 is the volume of the dry rubber sample, and the λ_i are the principal extension ratios ("stretches"). The variables G_c and G_e are defined below.

The first term in eq 1 is the classical network chain connectivity contribution and the second term is the "localization" contribution. Derivation of eq 1 assumes network incompressibility.[12,13]

In the absence of localization interactions ($G_e = 0$), eq 1 reduces to classical rubber elasticity theory. Although various predictions have been made for the magnitude of the network connectivity modulus G_c, it is proportional to the cross-link density ν

$$G_c = C_0\bar{\nu}k_bT \qquad (2)$$

in all of the classical models. C_0 is a constant related to network structure, k_b is the Boltzmann constant, and T is the absolute temperature.

For an end-linked tetrafunctional network there are various estimates of C_0.[14] Real polymer networks contain dangling ends and various inhomogeneities and the contributions of these imperfections to C_0 are described by Flory.[15] (Dossin and Graessley[16] argue that discrete local "entanglements" may contribute to C_0 so that even in principle an exact specification of the chemical cross-linking might be insufficient to determine C_0 and they therefore take C_0 to be a variable determined by experiment.) Limited specification of network structure also causes some uncertainty in C_0. In the experimental comparisons below we will take C_0 equal to the James and Guth estimate[17] $C_0 \approx 1/2$, lacking perfect information about the network structure. Recent experiments by Gnanou et al.[18] suggest this to be a reasonable presumption.

The localization parameter G_e of eq 1 accounts for the restriction of the configurations of a network chain by surrounding network chains. The basic effect of having a chain "hemmed in" by its surroundings is to reduce the average number of chain degrees of freedom. The physical picture of the network chain "localized" to an irregularity shaped region, defined by the interaction of the network chain with surrounding chains, is similar to Edwards' original formulation of a tube model of network elasticity.[19] Gaylord and Douglas[12,13] take this type of model further by arguing that the *"tube" radius reflects the hard-core cross-sectional radius of the polymer* and thus the tube volume in which the chain is localized is on the order of the chain molecular volume. Since the chain molecular volume is *invariant* to a macroscopic deformation, they argue that the tube volume should also be an invariant. From this constraint they estimate the variation of the chain localization length as a function of deformation to obtain eq 1.

Gaylord and Douglas[13] find that the localization modulus G_e has two contributions

$$G_e = \delta(\bar{\nu} kT) + G_N^* \tag{3}$$

where G_N^* is the cross (cross-link independent) plateau modulus of the polymer melt and δ is a constant. Another implication of the localization model is a rough inverse relation between the melt plateau modulus G_N^* and the average chain cross sectional area σ. This inverse relation also implies that the melt entanglement molecular weight M_e is proportional to the average chain cross sectional area. There are some experimental data which support these relations,[20] i.e., $G_N^* \approx 1/\sigma$ and $M_e \approx \sigma$. Further measurements are necessary to test their quantitative validity.

In the next section we describe our comparison of torsional data for cross-linked natural rubber with the localization model predictions. Some details of the methods of analysis in this comparison are given in Appendix A.

3. Comparison of the Localization Model with Dry Networks Torsional Data

The localization model was fitted successfully to torsion data and to uniaxial and biaxial extension data[7,12] on dry rubber letting both G_c and G_e be free parameters. In each case the quality of fit was good and the magnitudes of the parameters G_c and G_e were found to be reasonable. However, a real test of the theory requires a determination of whether the molecular parameters G_c and G_e vary as predicted. Specifically, we can set G_c to the value estimated from the James and Guth network theory[17] and observe how well we can fit the elasticity data with a single adjustable parameter G_e. The localization model further constrains the variation of G_e so that it is not a "free" parameter. Equation 3 implies that G_e reduces to the plateau modulus of the un-cross-linked rubber in the *formal* limit $\bar{\nu} \to 0$ and that G_e should increase linearly with cross-link density. (The limit $\bar{\nu} \to 0$ is formal since the equilibrium modulus will vanish for $\bar{\nu}$ sufficiently small that the rubber is a liquid.) The model parameters of the theory are evidently highly constrained in terms of direct observables. The only unspecified parameter in the theory is the constant of proportionality in the dependence of G_e on $\bar{\nu}$. McKenna et al.[7] have recently compared the predictions of the localization model with experimental torsion data on dicumyl peroxide cross-linked rubber in the dry state. In the following paragraphs we briefly review this comparison.

Table I. Values of G_e Obtained for Localization Model Determined from Curve Fitting of Equation A.4 to Natural Rubber Torsional Data

	$C_0 = 1/2$		
rubber sample	$\bar{\nu}$ (mol/cm^3)	G_c (Pa)	G_e (Pa)
APHR1	2.09×10^{-5}	2.58×10^{4}	5.94×10^{5}
APHR2	5.22×10^{-5}	6.44×10^{4}	7.24×10^{5}
APHR3	8.35×10^{-5}	1.03×10^{5}	1.09×10^{6}
APHR5	1.46×10^{-4}	1.80×10^{5}	1.67×10^{6}
APHR7.5	2.24×10^{-4}	2.76×10^{5}	2.71×10^{6}
APHR10	3.03×10^{-4}	3.74×10^{5}	2.33×10^{6}
APHR15	4.59×10^{-4}	5.66×10^{5}	3.58×10^{6}

Cross-link densities of their samples are reported in Table I based on the assumption that each dicumyl peroxide molecule decomposes to form a tetrafunctional cross-link. McKenna et al.[7] performed least-squares fits of the derivatives of eq 1 to the torsional data for each cross-link density assuming that $C_0 = 1/2$. (In the original references the reader will see that the fits are very good.) The corresponding estimates of G_c are included in Table I based on this James and Guth[17] estimate for C_0. The curve fits then provide the means to calculate G_e from eq 2 and in Table I it can be seen to increase with cross-link density and that the localization contribution (G_e) to the rubber elasticity *predominates* over the classical term (G_c). Dossin and Graessley[16] and Oppermann and Rennar[21] make similar observations regarding the elasticity of polybutadiene and poly(dimethylsiloane) networks, respectively. A linear regression on the data in Table I shows that G_e is well represented by a linear function of cross-link density

$$G_e(\bar{\nu}) = 5.56 \times 10^5\ (\text{Pa}) + 6.83 \times 10^9\ (\text{Pa cm}^3/\text{mol})\ \bar{\nu} \tag{4}$$

as predicted by the localization model. Moreover, the value of $G_e(\bar{\nu})$ extrapolated to zero cross-link density is close to the reported value of the melt plateau modulus, viz, $G^*_N = 5.77 \times 10^5$ (Pa). This also agrees with localization model predictions. The agreement between the model and experiment exhibited by these measurements is encouraging.

4. Compression and Extension of Swollen Networks—An Apparent Anomaly

In recent work, McKenna et al.[3,4] were able to use the dry rubber strain energy density function obtained from torsion measurements to calculate the compression response of the rubber in the swollen state by applying the concepts of the Frenkel–Flory–Rehner[2] hypothesis and the Valanis–Landel[22] continuum equations of rubber elasticity (see Appendix A). In terms of the volume fraction ϕ of rubber and the elastic contribution to the Helmholtz free energy ΔF, they were able to write

$$\sigma_R = \frac{\sigma_{11} - \sigma_{22}}{\alpha^2 - 1/\alpha} = \phi\,\frac{[\alpha\phi^{-1/3}\Delta F'(\alpha\phi^{-1/3}) - \alpha^{-1/2}\phi^{-1/3}\Delta F'(\alpha^{-1/2}\phi^{-1/3})]}{\alpha^2 - 1/\alpha} \tag{5}$$

$$\sigma_R = \phi^{2/3}\,\frac{[\alpha\Delta F'(\alpha\lambda_s) - \alpha^{-1/2}\Delta F'(\alpha^{-1/2}\lambda_s)]}{\alpha^2 - 1/\alpha} \tag{6}$$

where σ_R is the reduced stress, $\sigma_{11} - \sigma_{22}$ is the principal

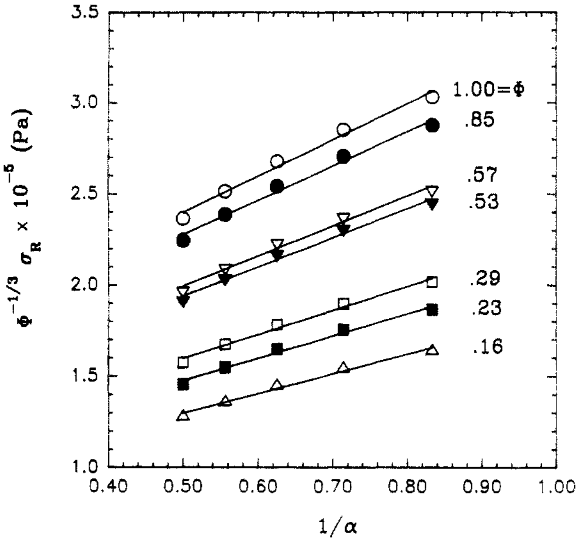

Figure 1. Modified reduced stress $\phi^{-1/3}\sigma_R$ vs $1/\alpha$ for swollen natural rubber calculated from the experimentally determined strain energy function for sample APHR1, in conjunction with the Frenkel[1]–Flory–Rehner[2] hypotheses. Lines represent least-squares fits to Mooney–Rivlin function. (See text for discussion.)

(true) stress difference in the swollen rubber, and α is the mechanical deformation superimposed on the swollen rubber. $\Delta F'(x) = \partial\Delta F/\partial x$ and $\lambda_s = \phi^{-1/3}$ is the swelling deformation. Equation 6 correctly predicted the swollen state response of the cross-linked natural rubbers described in Table I and for solvents having a range of swelling power from poor (acetone) to good (benzene), although some deviation in behavior was apparent at extremely high cross-link densities.

Because eq 6 successfully describes the swollen state compressive properties of natural rubber networks[3,4] and because eq 1 had been found to describe the dry state properties of the rubber, the implication is that the combination of eq 1 and eq 6 would successfully describe the behavior of swollen networks in simple extension. McKenna et al.[3,4] did not perform experiments in simple extension and, therefore, we were unable to make a direct comparison of results and theory. However, for the present illustrative discussion we can use the experimentally determined free energy function of McKenna et al.[3,4] (dry state data) to calculate a *theoretical* stress–strain behavior for swollen natural rubber in simple extension based on the FFR hypotheses (eq 6). The result of such a procedure is shown in Figure 1 in which reduced stress is plotted against $1/\alpha$ over a range of rubber volume fractions ϕ. The values of ϕ are similar to those considered by Gumbrell et al.[5] and Allen et al.[6] in their extension experiments on cross-linked and swollen natural rubber. We see in Figure 1 that the slope of the reduced stress predicted from eq 6 (FFR hypothesis, dry state determined strain energy function) decreases with increasing degree of swelling, as generally observed. However, the decrease is significantly less than that observed in the studies of refs 5 and 6 (see also Treloar[24] for a summary of this classic set of data).

It is conventional to examine deviations from classical rubber elasticity theory in uniaxial extension through the introduction of Mooney–Rivlin[23] parameters. For a swollen rubber we write the reduced stress

$$\sigma_R\phi^{-1/3} = I(\alpha,\phi) = \tau_0/[\phi^{-1/3}(\alpha - 1/\alpha^2)] \qquad (7)$$

$$I(\alpha,\phi) = C_1(\phi) + C_2(\phi)/\alpha \qquad (8)$$

where τ_0 is the stress relative to the dry, undistorted rubber, ϕ is the volume fraction of the rubber, and α is the mechanical deformation in the swollen state. Equation 8 is *empirical* and applies only to *extension* measurements. Nonetheless, it provides a useful means to characterize the elasticity of rubbers if employed properly. We note here that C_1 and C_2 are functions of volume fraction. When C_2 is obtained by fitting straight lines to the predicted results shown in Figure 1 the result is that C_2 varies as $\phi^{1/3}$ as shown in Figure 2. This is dramatically different from the exponent[24] ($C_2 \sim \phi^1$ or $\phi^{4/3}$) often observed in extension experiments on swollen rubber (see section 5). This weaker ϕ dependence of C_2 from previous[5,6] experimental studies is depicted in Figure 2. The large discrepancy for the concentration dependence of C_2 calculated from eq 6 and the free energy function data of McKenna et al.[3,4] (which describes the compressive behavior in the swollen state) and the observations of Gumbrell et al.[5] and Allen et al.[6] is difficult to rationalize in terms of experimental errors. A possible explanation is that one or both of the Frenkel–Flory–Rehner[2] hypotheses are incorrect. Since the compression results of McKenna et al[3,4] are consistent with the FFR hypotheses, outright rejection of the FFR hypotheses is difficult. On the other hand, the data of Gumbrell et al.[5] and Allen et al.[6] were obtained in uniaxial extension and seem inconsistent with the FFR modeling. Could there be something fundamentally different between compression and extension? We see no reason to believe this, but recognize this as a possibility. Another possibility is that there is a difference between the samples used in the experiments of McKenna et al.[3,4] and those used by Gumbrell et al.[5] and Allen et al.[6] In the case of the former the samples were highly cross-linked while in the latter two studies the degree of cross-linking was lower (see Table II). There is some overlap in the ranges, however. In the following section the localization model is extended to swollen rubber and a possible explanation for the discrepancy between the sets of data is discussed.

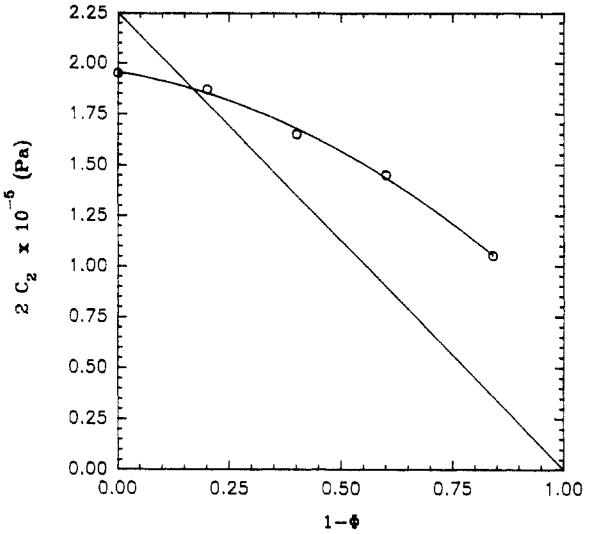

Figure 2. Mooney–Rivlin[23] constant C_2 from modified reduced stress vs $1 - \phi$ for swollen natural rubber. Points represent results calculated from Figure 1 Mooney–Rivlin fits. Curve through points represent $C_2 \propto \phi^{1/3}$. Straight line is representative of literature data for which $C_2 \propto \phi^1$ (or $\phi^{4/3}$). (See text for discussion. Reader is also referred to Allen et al.,[6] Price,[27] and Treloar[24] for extended discussions of the value of the exponent.)

5. Extension of the Localization Model to Swollen Network Elasticity

The swelling of dry polymer networks is a rather unique phenomenon. Lightly cross-linked dry networks can absorb large quantities of certain fluids and increase their volume by orders of magnitude without appreciable change

Table II. Comparison of Degree of Swelling of Natural Rubber in Benzene for Samples Used in Studies of Gumbrell et al.[5] and McKenna et al.[3,4]

study	sample designation	ϕ	$1/\phi$
Gumbrell et al.[5]	A	0.192	5.21
	B	0.181	5.52
	C	0.202	4.95
	D	0.235	4.26
	E	0.223	4.48
	F	0.257	3.89
	G	0.272	3.68
McKenna et al.[3,4]	APHR1	0.158	6.32
	APHR2	0.209	4.78
	APHR3	0.256	3.91
	APHR5	0.334	2.99
	APHR7.5	0.423	2.36
	APHR10	0.405	2.47
	APHR15	0.515	1.94

of shape. The cross-links give these highly swollen materials a remarkable rigidity.

Theoretical prediction of the elasticity of a swollen network from a knowledge of the dry network elasticity is a challenging, unsolved problem. Flory acknowledged[25] that the predictions of the classical rubber elasticity theory are disturbingly inaccurate and suggested that the cause for the observed deviations is also responsible for deviations from classical rubber elasticity theory in the dry state.

Consider a sample of dry cross-linked rubber of volume V_0 which is subjected to an isotropic swelling of dimensions by a factor λ_s. The swollen rubber of volume V is then deformed uniaxially and we measure the stress as a function of swelling and the mechanical deformation α_i.

Extension of eq 1 to describe the elasticity of a swollen network is by no means obvious, but we can progress by following arguments given previously by FFR. The mechanical stretch parameter α_i in the FFR theory is replaced by $\lambda_s\,\alpha_i$ under the presumption that a "stretch is a stretch" regardless of the mode of extension (swelling or mechanical). In the spirit of the FFR theory we replace λ_i in eq 1 by $\alpha_i\lambda_s$ to obtain

$$\Delta F(\alpha_i\lambda_s)/V_0 = (G_c/2)\sum_{i=1}^{3}[(\lambda_s\alpha_i)^2 - 1] + G_e\sum_{i=1}^{3}(\lambda_s\alpha_i - 1) + f(\lambda_s) \quad (9)$$

The unspecified function $f(\lambda_s)$ occurs because swelling is a nonconstant volume deformation (see Appendix B). Assuming network incompressibility allows us to neglect $f(\lambda_s)$ in the consideration of the swollen network elasticity where only the derivative of $\Delta F(\alpha_i,\lambda_s)$ with respect to α_i is required. The free energy density of the swollen network is obtained by multiplying (9) by the polymer volume fraction ϕ as

$$\Delta F(\lambda_s\alpha_i)/V = (G_c/2)\phi\sum_{i=1}^{3}[(\lambda_s\alpha_i)^2 - 1] + (G_e\phi)\sum_{i=1}^{3}(\lambda_s\alpha_i - 1) + f(\lambda_s)\phi \quad (10)$$

The James and Guth[17] network theory should afford a reasonable estimate of G_c, as discussed in section 2, and this value can be compared with estimates of G_c determined from elasticity measurements. G_c should be independent of ϕ and proportional to the network cross-linking density in comparisons of (10) to experiment. The specification of the concentration dependence of G_e is a subtle question on which our extension of the localizatioin model pivots.

To estimate the concentration dependence of G_e we recall eq 3,

$$G_e\phi|_{\phi=1} = G_N(\phi = 1) + \delta(\phi = 1)\bar{\nu}k_BT \quad (11)$$

The variation of the plateau modulus G_N with concentration is estimated using the localization model in the absence of cross-links. Packing arguments similar to those used to estimate the nonclassical term in eq 3 give[12,13]

$$G_N(\phi) \sim G_N{}^*\phi^2, \quad \phi \approx 1 \quad (12)$$

The derivation of eq 12 includes the factor of ϕ indicated in eq 10 and a generalization of eq 12 to d-dimensions is given in Appendix A. This generalization indicates that the origin of the concentration dependence in eq 12 does not arise from binary contacts. Rather it arises from chain packing. Equation 12 accords well with experimental observations on concentrated high molecular weight polymer solutions.[26] Our generalization of (11) involves replacing $G_N(\phi = 1)$ by (12) to obtain (see Appendix A, eq A.5d)

$$G_e\phi \cong [G_N{}^*\phi]\phi + \delta(\phi = 1)\,(\bar{\nu}k_BT)\phi, \quad \phi \equiv \lambda_s^{-3} \quad (13)$$

The factor of ϕ in the second term comes simply from the change in rubber volume with swelling as in the classical term G_c in (10). Note that the δ term in (11) is simply proportional to G_c so it seems natural to treat the δ term in (13) in a similar fashion. Once $G_e\phi$ is fixed as in (13) there are no free parameters in our predictions of the elastic deformation of swollen networks based on (10). We now compare the results of this generalized elasticity model with the swelling experiments mentioned above for lightly cross-linked and highly cross-linked rubbers. Observe that the plateau modulus term and cross-link-dependent term in (13) have different concentration dependencies. This difference could have important implications for the elastic properties of swollen rubbers. For a uniaxial stretch we define the deformation parameters ($\lambda_1 = \alpha$, $\lambda_2 = \alpha^{-1/2}$, $\lambda_3 = \alpha^{-1/2}$) and calculate the tension per unit area as[25]

$$\tau = \mathrm{d}[\Delta F/V]/\mathrm{d}\alpha \quad (14)$$

Inserting (10) with G_e defined by (3), (11), and (13) into (14) gives the tension

$$\tau = G_c\phi^{1/3}(\alpha - 1/\alpha^2) + [\delta(\bar{\nu}k_BT) + G_N{}^*\phi]\phi^{2/3}(1 - \alpha^{-3/2}) \quad (15)$$

A generalization of this expression to d-dimensions is given in Appendix A. The tension τ_0 relative to the dry state cross-sectional area is related to τ,[25] $\tau_0 = \tau/\phi^{2/3}$, and the tension is sometimes written in the "reduced form" shown in eq 7.

A deviation of $I(\alpha,\phi)$ from constancy at a fixed temperature is a measure of the "nonideal" contribution to the rubber elasticity.[5] The reduced tension in (7) is investigated in detail by Gumbrell et al.[5] for uniaxial extension of swollen rubber and (7) is introduced to compare with these data.

Inserting (15) into the definition of $I(\alpha,\phi)$ gives

$$I(\alpha,\phi_s) = G_c + [\delta\bar{\nu}k_BT + G_N{}^*\phi]\phi^{1/3}(1 - \alpha^{-3/2})/\alpha(1 - \alpha^{-3}) \quad (16)$$

For a large uniaxial extension $\alpha \gg 1$ we have $(1 - \alpha^{-3/2})/(1 - \alpha^{-3}) \approx 1$ so that $I(\alpha,\phi_s)$ reduces to

$$I(\alpha,\phi) \sim G_c + B(\phi)/\alpha, \quad \alpha \gg 1 \quad (17)$$

$$B(\phi) = (\delta\bar{\nu}k_BT + G_N{}^*\phi)\phi^{1/3} \quad (18)$$

This is only a *formal* limit since finite extensibility effects become significant for large α. Equations 17 and 18 are introduced for qualitative comparison with experimental studies in the discussion below.

Gumbrell et al.[5], Allen et al.[6], and Price[27] find an empirical correlation of $I(\alpha,\phi)$ identical to (17) for *uniaxial extension* of swollen rubbers. Equation (17) is the Mooney–Rivlin equation (see eq 8 and Appendix A) and this result is actually derived from the localization model along with a specification of the concentration dependence of C_1 and C_2. Equation 8 applies to correlations of uniaxial extension data in a limited range of deformations. Again we emphasize that the Mooney–Rivlin correlation *does not* apply to compression and other geometries of deformation and the localization model does not reduce to this simple form in other types of deformation.

Experimental values of $C_1(\phi)$ obtained by Gumbrell et al.[5] varied very slowly with polymer fraction ϕ and experiments by Allen et al.[6] indicate that $C_1(\phi)$ is "virtually independent of the degree of dilution". Similarly, examination of eq 16 shows that in the limit of infinite extension $I(\alpha,\phi_s)$ reduces to G_c independent of the degree of swelling. G_c is a *network invariant* which apparently can be measured with fair precision.

In contrast to C_1, the C_2 parameter in (8) is found to have a rather strong concentration dependence in the rubbers employed by Gumbrell et al.,[5] Allen et al.,[6] and Price.[27] Gumbrell et al.[5] found that $C_2(\phi)$ for many rubbers (varying cross-link conditions) varied in direct proportion to polymer volume fraction, $C_2 \propto \phi$, to a good approximation. This variation was found to be independent of solvent. Later, experiments by Mullins[28] and Price[27] gave the empirical correlation, $C_2 \propto \phi^{4/3}$, as a slight improvement over the initial correlation of Gumbrell et al.[5] Before comparing with the predictions of the localization model, we emphasize that the large changes of the polymer volume fraction at swelling equilibrium necessitate rather light cross-linking in these rubbers. It is possible that different behavior would be observed in highly cross-linked networks where only modest swelling is possible.

For relatively low cross-linking the δ-dependent term in (17) and (19) is neglected so that the concentration-dependent factor $B(\phi)$, corresponding to $C_2(\phi)$ in (8), reduces to

$$B(\phi) \approx G_N^*\, \phi^{4/3} \quad \text{(low cross-link density, uniaxial extension)} \qquad (19)$$

Equation 18 accords well with the experimental observations of Mullins[28] and Price[27] for the variation of $C_2(\phi)$ in extension. However, the cross-link-dependent contribution to $B(\phi)$ in (17) should dominate for high cross-linking densities to give

$$B(\phi) \approx \delta(\bar{\nu}k_BT)\phi^{1/3} \text{ (high cross-link density, extension)} \qquad (20)$$

This is qualitatively different behavior from eq 19 (see Figures 4 and 5). If we trace this result back to the original form of the free-energy density function $\Delta F(\alpha_i,\lambda_s)$, we find that for high cross-link densities ΔF is given by eq 10 with the high cross-link density limiting form of eq 11

$$\Delta F(\alpha_i,\lambda_s)/V = \phi[(G_c/2)\sum_{i=1}^{3}[(\lambda_s\alpha_i)^2 - 1] + \delta(\bar{\nu}k_BT)\sum_{i=1}^{3}(\lambda_s\alpha_i - 1) + f(\lambda_s)] \qquad (21)$$

$$G_e \sim \delta\bar{\nu}k_BT \propto G_c \qquad (22)$$

The form of the free energy density in (21) is *nonideal* and *invariant* to swelling up to the ϕ scale factor and the $f(\lambda_s)$ term. As described in the previous section, such behavior is calculated from the parameters obtained for cross-linked natural rubber using the Valanis–Landel[22] function and calculating the tensile behavior of swollen rubber using eq 6.

This different concentration dependence of the nonideal contribution to the rubber elasticity in high cross-link and low cross-link density rubbers is a striking prediction of the localization model. The variation of the ΔF with concentration seems to depend on the extent of network cross-linking. Further experimental studies are needed to check this interesting prediction.

The discussion above assumes that the networks are cross-linked in the melt. The localization model suggests that networks of different elasticity might be obtained for networks synthesized from solution. Erman and Mark[29] discuss the effect of varying the concentration at the time of cross-linking on G_c. These arguments indicate that C_0 in eq 2 picks up a dependence on the volume fraction ϕ_x at which the cross-linking occurs. The localization parameter G_e is also expected to reflect the network density at the state of cross-linking. It seems reasonable to replace the "entanglement" G_N contribution to G_e by

$$G_N(\phi_x,\phi) \approx (G_N^*\phi_x)\phi^2 \qquad (23)$$

under the assumption that network drying is not equivalent to a deformation. The ϕ_x term reflects the number of network chains per unit volume under the conditions of cross-linking. Equation 23 would imply that lightly cross-linked rubbers in highly diluted solutions, $\phi_x \ll 1$, would exhibit elasticity similar to an ideal network upon drying, aside from a G_c term which depends on ϕ_x. Some experimental data by Price et al.[30] and Johnson and Mark[31] support this odd possibility, although there is no evidence that (23) holds quantitatively. Networks should evidently exhibit a strong "memory" of the state of cross-linking.[31,45] As another example of this kind, Gaylord et al.[32] apply the localization model to polymer melts which are crosslinked under a strain. Agreement between the localization model and experiment is found to be reasonable given the experimental difficulties involved.

6. Discussion

Frenkel[1] and Flory and Rehner[2] (FFR) assumed that the strain energy density of a rubber is invariant to swelling since the network elasticity has its origin in the cross-links. Swelling changes the number of cross-links per unit volume and stretches the chains. In this view swelling is like any other kind of deformation (i.e., a stretch is a stretch, regardless of its mechanical or thermodynamic origins). The compression experiments of McKenna et al.[3,4] are consistent with this simple picture. However, the FFR hypotheses do not predict the tensile response observed by Gumbrell et al.[5] and Allen et al.[6] for rubbers that were relatively lightly cross-linked, suggesting that the second FFR hypothesis might not be generally valid.

The development of the localization model of rubber networks by Gaylord and Douglas[12,13] and the extension here provides a possible answer to the dilemma posed. There are two ranges of behavior: at high cross-link densities the second FFR hypothesis is valid (see eqs 10, 20, and 21) while at low cross densities the second FFR hypothesis breaks down. This arises because the elastic free energy function in the model contains a term that depends upon the cross-link density and a cross-link-independent term related to the plateau modulus of the un-cross-linked rubber. The latter term becomes relatively small at high cross-linking and the free energy function then depends on the volume fraction of the rubber through the network density, consistent with the FFR hypotheses as applied to obtain eqs 5 and 6. At low cross-link densities the plateau modulus contribution to the confinement term G_e dominates the change of elasticity with swelling and the strain energy function acquires a strong volume fraction dependence. This prediction conflicts with the second FFR hypothesis but seems to be consistent with the available extension data on swollen rubber.[5,6,24,27]

In summary, then, the localization model provides an explanation for the anomalous results of the compression/extension experiments on cross-linked and swollen rubbers. It also suggests that the FFR hypothesis is limited to densely cross-linked networks.

Acknowledgment. Jack Douglas thanks Richard Gaylord and Louis Zapas for many discussions on network swelling and rubber elasticity.

Appendix A. $\partial\Delta F(\lambda)/\partial\lambda$ and Network Tension in d-Dimensions

The continuum formulation[23] of the elasticity of isotropic, incompressible bodies (reasonable approximation for dry rubbers) can be developed without specific reference to an underlying molecular structure. Continuum mechanics stress–strain relations may be expressed in terms of the *invariants* (I_1, I_2) of the deformation tensor and an empirically determined strain energy density function $W(I_1,I_2) \equiv W(\{\lambda_i\})$. Even the crudest formal development of this theory leads to interesting results for rubber elasticity. For example, keeping just the first-order terms in a Taylor series of $W(I_1,I_2)$ about the undeformed state leads to the Mooney–Rivlin[23] equation (8) for uniaxial extension where the strain energy derivatives, $C_1 \propto \partial W/\partial I_1$ and $C_2 \propto \partial W/\partial I_2$ are evaluated in the undeformed state. It is remarkable that this simple version of the continuum model recovers the James and Guth[17] expression for the network tension along with corrections to ideal network elasticity. The continuum formulation of rubber elasticity is also convenient for treating stress–strain relations for complicated deformations. Rewriting a molecular theory in terms of the strain energy density $W(\{\lambda_i\})$ allows us to exploit the continuum mechanics formalism. Transcription from the molecular theory to the continuum formulation is simplified in materials for which $W(\{\lambda_i\})$ is separable in the λ_i.

According to the Valanis–Landel[22] approach to rubber elasticity the elastic strain-energy density function, $W(\{\lambda_i\}) \equiv \Delta F(\text{elastic})/V_0$, is hypothesized to be a separable function of the principal stretches λ_i

$$W(\{\lambda_i\}) \approx \sum_{i=1}^{3} w(\lambda_i) \qquad \text{(A.1)}$$

Classical theories of rubber elasticity belong to the Valanis–Landel[22] class as does the localization model.[12,13] Experimental evidence supports the separability of $W(\{\lambda_i\})$ into a single function of the principal stretches to a very good approximation.[34]

The ability to represent the elastic free energy as a separable function of the $\{\lambda_i\}$ provides us with a means of obtaining the mechanical response of the elastomer in *all deformation geometries* from a series of experiments in a limited number of geometries, e.g., we can describe tensile or compressive responses from the strain energy function derivative determined in torsion. For example, the true stress response to a uniaxial deformation is written as[22]

$$\sigma_{11} - \sigma_{22} = \lambda w'(\lambda) - \lambda^{-1/2}\, w'(\lambda^{-1/2}) \qquad \text{(A.2)}$$

where $w'(\lambda) = \partial w/\partial\lambda$ is the derivative of the Valanis–Landel[22] function w.

Kearsley and Zapas[33a] have shown how to obtain the strain energy derivative function $\partial\Delta F(\lambda)/\partial\lambda \equiv w'(\lambda) - w'(1)/\lambda$ from torsion and normal force measurements on rubber cylinders. Here we simply note their result

$$\partial\Delta F(\lambda)/\partial\lambda = (2/\lambda)(\lambda^2 - 1)[W_1 + W_2/\lambda^2] \qquad \text{(A.3)}$$

where the W_i values represent the derivatives of the strain energy density function, $W_1 = \partial W/\partial I_1$, $W_2 = \partial W/\partial I_2$. (Rivlin and Sawyers[33b] indicate the relations between the Valanis–Landel[22] form of the strain-energy function and the representation in terms of I_1 and I_2.) The strain energy function derivatives are obtained from the torque and normal force measurements at different angular deformations using a mathematical analysis given by Penn and Kearsley.[35]

In previous work McKenna et al.[3,4] obtained values of $\partial\Delta F/\partial\lambda$ for a series of dicumyl peroxide cross-linked natural rubbers and some results are shown in Figure 1. The first derivative of the free energy function of the localization model is given by the simple expression:

$$\partial\Delta F(\lambda)/\partial\lambda = G_c(\lambda - 1/\lambda) + G_e(1 - 1/\lambda) \qquad \text{(A.4)}$$

Values of G_e listed in Table I are obtained[5] from a least-squares fit of the data in Figure 1 to (A.4) where G_c is fixed by the James and Guth[18] prediction.

There has recently been some interest in the elasticity of cross-linked polymer films which can perhaps be idealized as two-dimensional rubbers.[36] Generalization of the localization model to d-spatial dimensions leads to the reduced tension τ

$$\tau = G_c[\alpha - \alpha^{-(d+1)/(d-1)}] + G_e[2/(d-1)][\alpha^{2/(d-1)-1} - \alpha^{-2/(d-1)^2-1}] \qquad \text{(A.5a)}$$

and a generalization of (15) is then given by

$$\tau(\phi,\alpha) = G_c\phi^{(d-2)/d}[\alpha - \alpha^{-(d+1)/(d-1)}] + G_e(\phi)[2/(d-1)]\phi^{(d-1)/d}[\alpha^{2/(d-1)-1} - \alpha^{-2/(d-1)^2-1}] \qquad \text{(A.5b)}$$

$$G_e(\phi) = \delta(\bar{\nu}k_BT) + G_N{}^*\phi^{2/(d-1)} \qquad \text{(A.5c)}$$

Note that (A.5c) implies that in the limit of low cross-linking (formally $\bar{\nu} \sim 0$) that the plateau modulus G_N scales as

$$G_N \sim G_c\phi \sim G_N{}^*\phi^{(d+1)/(d-1)} \qquad \text{(A.5d)}$$

in consistency with previous results.[13c] (A.5a) reduces to (A.4) for $d = 3$ but note that even the ideal elasticity theory is predicted to be quite different in $d = 2$ (i.e., idealized two-dimensional films).[36] Interestingly, the ideal contribution to the tension does not depend on polymer volume fraction in $d = 2$. Observe also that only the classical term remains in the limit of high dimension ($d \rightarrow \infty$)

$$\tau(\phi,\alpha) \sim G_c\,\phi[\alpha - 1/\alpha], \quad d \rightarrow \infty \qquad \text{(A.5e)}$$

and the exponent in A.5d reduces to one for d large rather than the binary contact value of 2. The "entanglement" effect disappears in the infinite dimension limit as expected. We also observe that the classical term in the $d \rightarrow \infty$ limit is the same as in older rubber elasticity theories.[37,38]

Appendix B. Network Stability and the Log Term

The original "single chain" models of network elasticity[38] indicate an additional log term, $A \log (\lambda_x \lambda_y \lambda_z)$, to eq 1 which contributes to the network chain elasticity of compressible rubbers. This term is not obtained in the ideal network model of James and Guth, and in "single chain" theories[37-39] this term is associated with a change of the mean volume occupied by the chain with deformation. This "log term" has been discussed for many years without resolution.

The log term drifts in and out of discussions of network elasticity. Even in continuum mechanics models of network elasticity, where there is no need to invoke the log term, this interesting phenomenon is observed.[22,33] Flory likened this elusive behavior of the log term, its tendency to disappear and reappear later, to the Cheshire Cat of Alice in Wonderland (see McKenna and Hinkley[40]). The usual procedure is to exorcise this term by invoking the assumption of constant volume deformation. However, this is not possible in network swelling. To make matters worse the localization model yields log terms which affect the A term mentioned above.[13]

The log term is evidently tied up with subtle issues, but a reasonable (but not unambiguous) means of determining the log term coefficient might be to invoke the network stability condition indicated by Edwards and Freed[19,41]

$$\partial \Delta F(\lambda_i)/\partial \lambda_i|_{\lambda_i=1} = 0 \qquad (B.1)$$

Heuristic application of (B.1) to swelling ($\lambda_x = \lambda_y = \lambda_z$) with the low cross-link density approximation, $G_e \phi \sim \phi^2 \sim \lambda^{-6}$, leads to the elastic swelling free-energy

$$\Delta F(\lambda_s) \sim 3\phi[G_c \lambda^2/2 + G_N^*/\lambda^2 + A \log \lambda] \qquad (B.2)$$

Equation B.1 would imply

$$A = 2G_N^* - G_c \qquad (B.3)$$

In the absence of localization interactions ($G_e \approx 0$) we obtain the "affine model" result[38]

$$A = -G_c \qquad (B.4)$$

Interestingly, the sign of the log term coefficient can change in (B.3) depending on G_N^*. The magnitude of G_e relative to G_c would be determined by the extent of cross-linking. For example, at high cross-linking $G_e \approx \delta \bar{\nu} k_B T \propto G_c$ and we have a rather different dependence of A on network structure. Preliminary comparisons indicate that (B.2) leads to a swelling activity parameter $S = \lambda_s \ln(a_c/a_u)$ which can have a maximum whose position and height are consistent with observations of Gee et al.[42] (B.2) could help resolve a long standing paradox raised by the maximum which is sometimes observed in the swelling activity parameter.[3,4,42,43]

We note that the ideal network theory of James and Guth[17] and the more recent Flory–Erman theory[44] do not satisfy the stability condition (B.1) and this has significant consequences for the predictions of network swelling in these models.[40]

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