The 'localization model' of rubber elasticity: comparison with torsional data for natural rubber networks in the dry state

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Previously reported results from determinations of the first derivative of the elastic contribution to the free energy density function for dicumyl peroxide crosslinked natural rubber were analysed within the context of the Gaylord–Douglas 'localization model' of rubber elasticity. It was found that the dry state properties of the rubbers are well described by the localization model and that the non-classical contribution to rubber elasticity arising from the confinement of network chains by surrounding chains varies according to the theory. Specifically, a single measure of localization G_e is required to fit the experimental results and the variation of this parameter follows the predictions of the theory, namely, G_e is approximately equal to the rubbery plateau modulus at the limit of zero crosslinking and subsequently follows a linear dependence on crosslink density. The only other parameter in the model, the prefactor to a classical term, was set to the classical phantom value assuming a tetrafunctional network and assuming that each dicumyl peroxide molecule decomposed to form one crosslink.

(Keywords: localization model; natural rubber; networks; rubber elasticity; strain energy function; Valanis–Landel function)

INTRODUCTION

Most molecular theories of rubber elasticity are formulated in such a way that the elastic contribution to the free energy can be represented as a separable function in the principle deformations λ_1, λ_2 and λ_3. Such separable strain energy functions are special cases of the Valanis–Landel (VL)[1] function familiar in continuum mechanics.

In recent work[2–5] we carried out torsional measurements on dicumyl peroxide crosslinked natural rubber in order to evaluate the VL function for a series of networks of differing crosslink density, to compare their responses in the dry and swollen states, and to evaluate the Frenkel[6]–Flory–Rehner[7] (FFR) hypothesis that the elastic and mixing contributions to the free energy are simply additive. By using the VL function to describe the strain energy of the rubber, we were able to strictly avoid the use of a molecular model in our evaluation of the FFR hypothesis.

Here, we take the approach of using the previously obtained dry state data, from which we obtained the first derivative of the free energy function with respect to the deformation λ, to evaluate the Gaylord–Douglas 'localization model' of rubber elasticity[8,9]. According to this model there is a substantial non-classical contribution to the free energy density of the network which is due to the entanglement interaction and the finite volume of the network chains, i.e. local confinement of the chains. There are two salient results which we obtain. First, the ability of the localization model to describe the data using just one adjustable parameter (the confinement modulus G_e) is very good. Second, we find that upon fixing the classical term in the model to its expected value, obtained by assuming one tetrafunctional crosslink per decomposed peroxide molecule, that the non-classical confinement term behaves as expected from the theory[9], i.e. the confinement term is a linear function of the crosslink density and its value extrapolated to zero crosslink density is equal to the plateau modulus of the uncrosslinked polymer.

In this paper we recall the model, describe the previously obtained results, compare the theory with experimental results, and finally discuss the physical significance of the parameters obtained from fitting the model to the data.

LOCALIZATION MODEL

Molecular models of polymeric network elasticity have concentrated on certain minimal aspects of the rubber networks. The classical theories of Wall and Flory[10,11], James and Guth[12], and others focused primarily on the property of network connectivity. Non-classical theories, such as that of Dean and Edwards[13] have emphasized the 'topological interaction' associated with the 'uncrossability' of network chains. DiMarzio[14–16] and Jackson *et al.*[17,18] attempted to derive more realistic models by

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including the physical constraint of finite network chain volume, i.e. packing effects[16].

Gaylord and Douglas incorporated these minimal features of a crosslinked 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[8,9]:

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

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

The first term in equation (1) is the classical network chain connectivity contribution and the second term is the 'entanglement' contribution. Equation (1) assumes a constant volume (incompressibility) deformation.

In previous comparisons of the localization model with experimental results, G_c and G_e were used as adjustable parameters and good agreement was obtained with uniaxial extension data[8]. The model, however, gives specific molecular interpretations to the connectivity and entanglement parameters G_c and G_e, which have not yet been explored in detail. Here we expand the testing of the localization model by varying the crosslink density and observing how the predicted dependences of G_c and G_e compare with the experimental behaviour. Next we briefly review the meaning of G_c and G_e in the localization model.

In the limit of no entanglement interaction ($G_e = 0$), the Gaylord–Douglas model reduces to classical rubber elasticity theory. Although various predictions have been made for the magnitude of the shear modulus G_c, all of the classical models indicate that it is proportional to the crosslink density ν as:

$$G_c = C_0 \nu kT \quad (2)$$

where C_0 is a constant, k is the Boltzmann constant and T is the absolute temperature.

For the ideal (end-linked) tetrafunctional network Wall and Flory and Treloar[19–21] found that $C_0 = 1$, while James and Guth, Dusier and Staverman, and Edwards obtained[19,22] $C_0 = 0.5$. Evidence has been reported in the literature supporting both values, and it is recognized that in the normal situation imperfect networks which may contain dangling ends and various inhomogeneities are studied. Furthermore, experimental evidence that network behaviour is non-ideal and that terms other than the classical term need to be included in the free energy function makes the disputes concerning the magnitude of C_0 somewhat moot. In the experimental comparisons below we will take $C_0 = 0.5$ as the most 'reasonable' estimate lacking perfect information about the network structure. We will also consider values of $C_0 = 1$ and 0.25 to bound the possible values which C_0 might have. We will find that the actual value of C_0 chosen in this range, while affecting the agreement between theory and experiment, does not significantly affect the conclusions of the paper. This insensitivity reflects the predominance of the non-classical contribution to the observed elasticity.

The entanglement parameter G_e of the localization model 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 confined to a random tube, defined by the interaction of the network chain with surrounding chains, is similar to Edwards' original formulation of the tube model[22]. Gaylord and Douglas[8,9] take the model further by arguing that the tube radius reflects the hard core cross-sectional radius of the polymer and thus the tube volume is of the order of the chain molecular volume. Since the chain molecular volume is invariant to a macroscopic deformation Gaylord and Douglas deduce that the tube volume should also be an invariant. From this constraint they estimate the variation of the tube confinement parameters as a function of deformation[8]. The dependence of the confinement parameters on deformation is the origin of the $(\lambda_i - 1)$ terms in equation (1).

A recent calculation[9] by Gaylord and Douglas results in G_e having two contributions:

$$G_e = \gamma(\nu kT) + G_N^* \quad (3)$$

where G_N^* is the crosslink independent plateau modulus of the polymer melt and γ is a constant*.

Another implication of the localization model is a rough inverse relation between the melt plateau modulus G_N^* and the chain cross-sectional area σ. This inverse relation also implies that the melt entanglement molecular weight M_e is proportional to the chain cross-sectional area. There are some experimental data which support these relations[23,24], i.e. $G_N^* \simeq 1/\sigma$ and $M_e \simeq \sigma$. However, further measurements are necessary to test the quantitative validity of these relations. The observation of an inverse relation between G_N^* and σ is important because it supports the picture of packing dominated 'localization interactions' which are the conceptual basis of the localization model.

In the following we describe the methods of analysis and our comparison of torsional data for crosslinked natural rubber with the Gaylord–Douglas model predictions.

METHODS OF ANALYSIS

According to the VL[1] phenomenological approach to rubber elasticity the elastic strain energy density function, $W(\lambda_i) = \Delta F(\text{elastic})/V_0$, is a separable function of the principal stretches λ_i:

$$W(\lambda_i) = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) \quad (5)$$

Classical theories of rubber elasticity belong to the VL class as does the Gaylord–Douglas model[8,9]. Experimental evidence supports the ability to separate $W(\lambda_i)$ into a single function of the principal stretches to a very good approximation[25–28].

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* The melt entanglement molecular weight M_e is defined by the relation $G_N^* = \rho RT/M_e$ so that the entanglement modulus in the localization model equals

$$G_e = \gamma(\rho RT/M_c) + \rho RT/M_e \quad (4)$$

Our considerations are, of course, restricted to crosslink densities above the gelation threshold ($\nu \geqslant \nu^*$). The only free parameter in our comparisons is γ which is predicted to be the slope of a contribution to G_e which is linear in the crosslink density

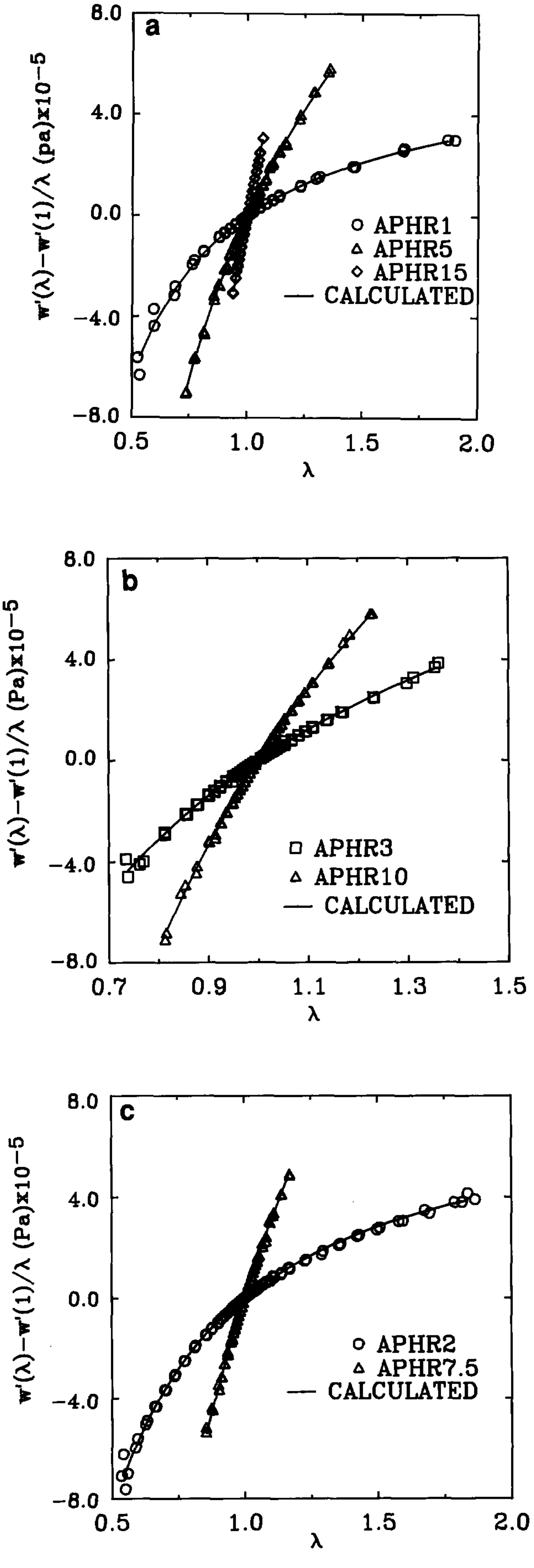

Figure 1 (a)–(c) $w(\lambda)-w'(1)/\lambda$ $(=\partial A/\partial\lambda)$ *versus* λ for peroxide crosslinked natural rubber, as indicated. Data are from references 2–5. Solid lines represent least squares fit to equation (7). Procedure allowed C_0 (or G_c) to float. See also *Table 1*

The ability to represent the elastic free energy as separable in the stretches provides 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. tensile or compressive responses can be described from the strain energy function derivatives determined in torsion. For example the true stress response to a uniaxial deformation is written as:

$$\sigma_{11}-\sigma_{22}=\lambda w'(\lambda)-\lambda^{-1/2}w'(\lambda^{-1/2}) \qquad (6)$$

where $w'(\lambda)=\partial w/\partial\lambda$ is the derivative of the VL function.

Kearsley and Zapas[29] have shown how to obtain the derivative of the VL function $w'(\lambda)-w'(1)/\lambda$ from torsion and normal force measurements on cylinders of dry rubber. Here we simply write their result that:

$$\frac{\partial A(\lambda)}{\partial\lambda}\equiv w'(\lambda)-w'(1)/\lambda=(2/\lambda)(\lambda^2-1)(W_1+W_2/\lambda^2) \qquad (7)$$

where the W_i represent the derivatives of the strain energy density function with respect to the ith invariant of the deformation tensor. Both W_1 and W_2 can be obtained from the torque and normal force measurements at different angular deformations using the Penn and Kearsley scaling approach[30]. We further note that $w'(1)$ can be set to zero without loss of generality. We do this here for purposes of analysis.

In previous work[2–5] we obtained values of $\partial A/\partial\lambda$ in equation (7) for a series of dicumyl peroxide crosslinked natural rubbers and some typical results are shown in *Figure 1*. In order to compare the localization model[8,9] with such results we observe that the first derivative of the elastic free energy function of this model is given by the remarkably simple expression:

$$\frac{\partial A(\lambda)}{\partial\lambda}=G_c(\lambda-1/\lambda)+G_e(1-1/\lambda) \qquad (8)$$

We then fitted the data of reference 2 (*Figure 1*) to equation (8) using a non-linear least squares algorithm[31] assuming that the value of G_c was that given by the classical theories with $C_0=0.5$ (see Introduction), 0.25 and 1. The data were also fitted allowing both G_c and G_e to be floating parameters. The results of these procedures are described below.

RESULTS

Comparison of the Gaylord–Douglas localization model with torsional data for dry networks

In the previous study[2–5] we used the Gaylord–Douglas[8,9] model as a curve fitting device to the VL[1] functions determined from the torsional data for dicumyl peroxide crosslinked natural rubbers. As seen in *Figure 1* the agreement between a general fit to the data and the data themselves is very good. This alone is very impressive because there are only two parameters in the Gaylord–Douglas model. The values for G_c and G_e obtained from these general fits are presented in *Table 1*.

Of more interest than simply carrying out curve fitting of the model was the fixing of the classical term parameter to a reasonable estimate of its theoretical value and consideration of two questions: can the data still be represented by the localization model, now with just one

Table 1 Values of G_c and G_e for the Gaylord–Douglas[8,9] model determined from curve fitting of equation (8) to natural rubber torsional data[2–5]

Rubber sample	ν (mol cm^{-3})	G_c (Pa)[a]	G_e (Pa)[a]
APHR1	2.09×10^{-5}	0	6.43×10^5
APHR2	5.22×10^{-5}	0	8.46×10^5
APHR3	8.35×10^{-5}	2.52×10^5	7.98×10^5
APHR5	1.46×10^{-4}	3.58×10^5	1.32×10^6
APHR7.5	2.24×10^{-4}	7.38×10^5	1.79×10^6
APHR10	3.03×10^{-4}	4.20×10^5	2.23×10^6
APHR15	4.59×10^{-4}	2.33×10^6	5.18×10^3

[a] Equation (8) is $\partial A/\partial\lambda = G_c(\lambda - 1/\lambda) + G_e(\lambda - 1)$; G_c is nominally the 'classical' contribution to rubber elasticity and was used as a fitting parameter, which implies that the C_0 discussed in the text was allowed to float; G_e is the confinement contribution to the network elasticity

Table 2 Molecular masses of natural rubber prepolymer (after milling) and molecular mass between crosslinks, M_c, of samples after crosslinking with dicumyl peroxide

Sample	Dicumyl peroxide (phr)	Prepolymer molecular mass[a] M_w ($\times 10^4$)	M_w/M_n	M_c (g mol^{-1})[b]
APHR1	1	31	2.8	21 800
APHR2	2	31	2.8	8 720
APHR3	3	31	2.8	5 450
APHR5	5	31	2.8	3 115
APHR7.5	7.5	23	2.4	2 020
APHR10	10	31	2.8	1 500
APHR15	15	31	2.8	550

[a] From size exclusion chromatography in toluene using polystyrene calibration of columns. Universal calibration was used assuming the following Mark–Houwink parameters: polystyrene in toluene, $K = 13.4 \times 10^{-3}$ ml g^{-1}, $a = 0.71$; natural rubber in toluene, $K = 50.2 \times 10^{-3}$ ml g^{-1}, $a = 0.667$

[b] Calculated from the formula given by Wood[33]: $1/2M_c = 3.6986(f_p - 0.31) \times 10^{-5}$; M_c is the molecular mass between crosslinks and f_p is the parts per hundred dicumyl peroxide by mass per 100 parts of rubber. This assumes one dicumyl peroxide molecule reacts to form one crosslink. Because the dicumyl peroxide used contains ≈93% peroxide, f_p is 0.93 times the value in the table

adjustable parameter? If so, how does the adjustable parameter (G_e) vary with the network crosslink density, recalling from equation (3) that it should vary linearly and be equal to the rubbery plateau value at zero crosslink density.

The value of the classical term, as discussed earlier, is uncertain both because of disagreement from a theoretical point of view and due to experimental uncertainty as to the actual crosslink density, network imperfections, etc. For the purposes of this work we have assumed that each dicumyl peroxide molecule decomposes to form one tetrafunctional crosslink. This is the basis for the crosslink densities reported in *Table 2*. Furthermore, we have estimated from these values of crosslink density values for G_c which are reasonable based on different values of C_0 which correspond to a theoretical upper bound ($C_0 = 1$), a theoretical lower bound ($C_0 = 0.5$) and finally a very low estimate which might take into account network imperfections ($C_0 = 0.25$). From a subjective standpoint we believe that a value slightly less than 0.5 should provide the most 'reasonable' estimate. *Figures 2–4* show results from fitting with $C_0 = 1$, 0.5 and 0.25, respectively. In all of these results

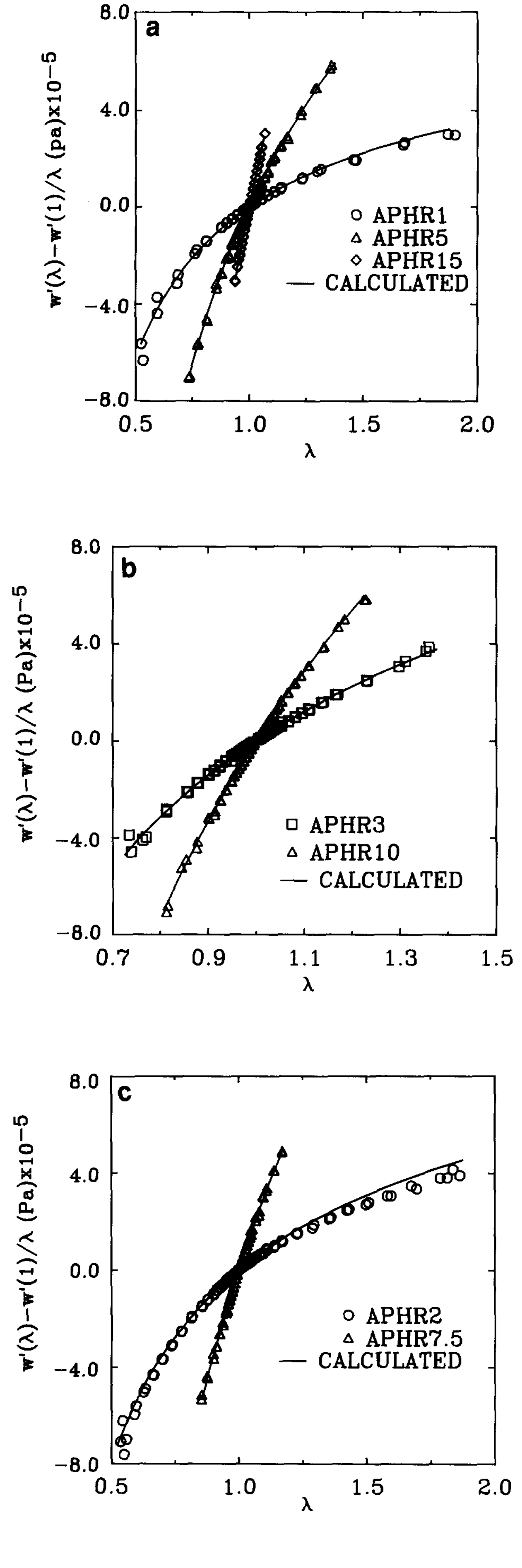

Figure 2 (a)–(c) Same as *Figure 1* but procedure fixed $C_0 = 1.0$. See also *Table 3*

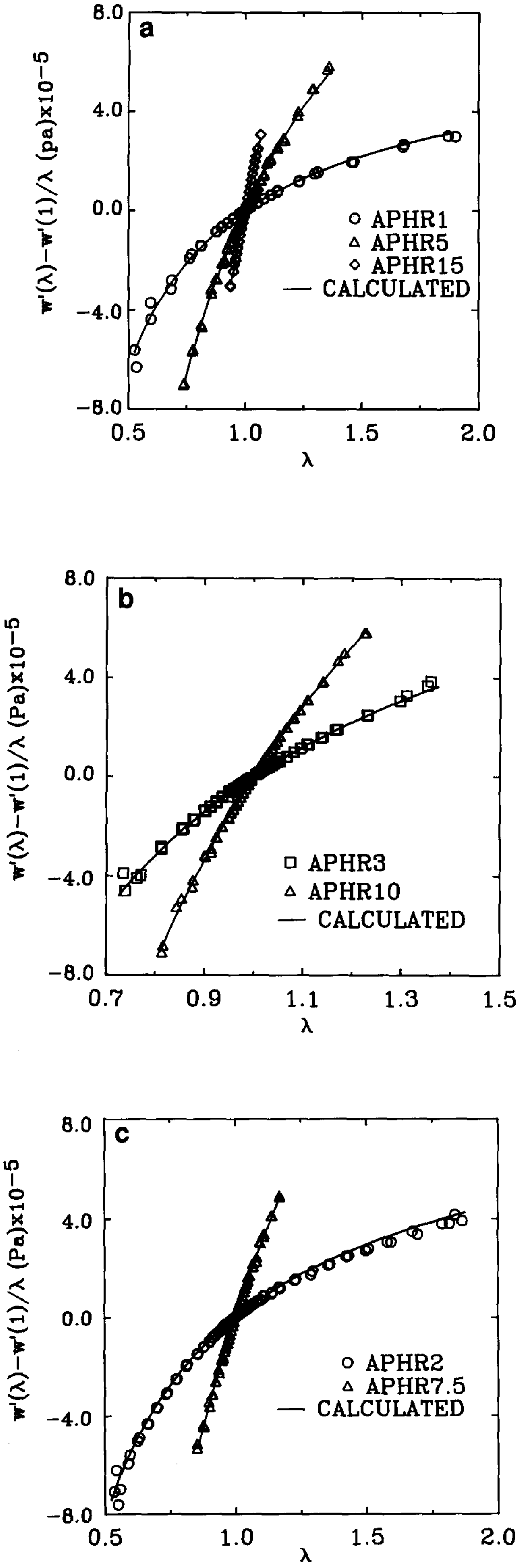

Figure 3 (a)–(c) Same as *Figure 1* but procedure fixed $C_0 = 0.5$. See also *Table 3*

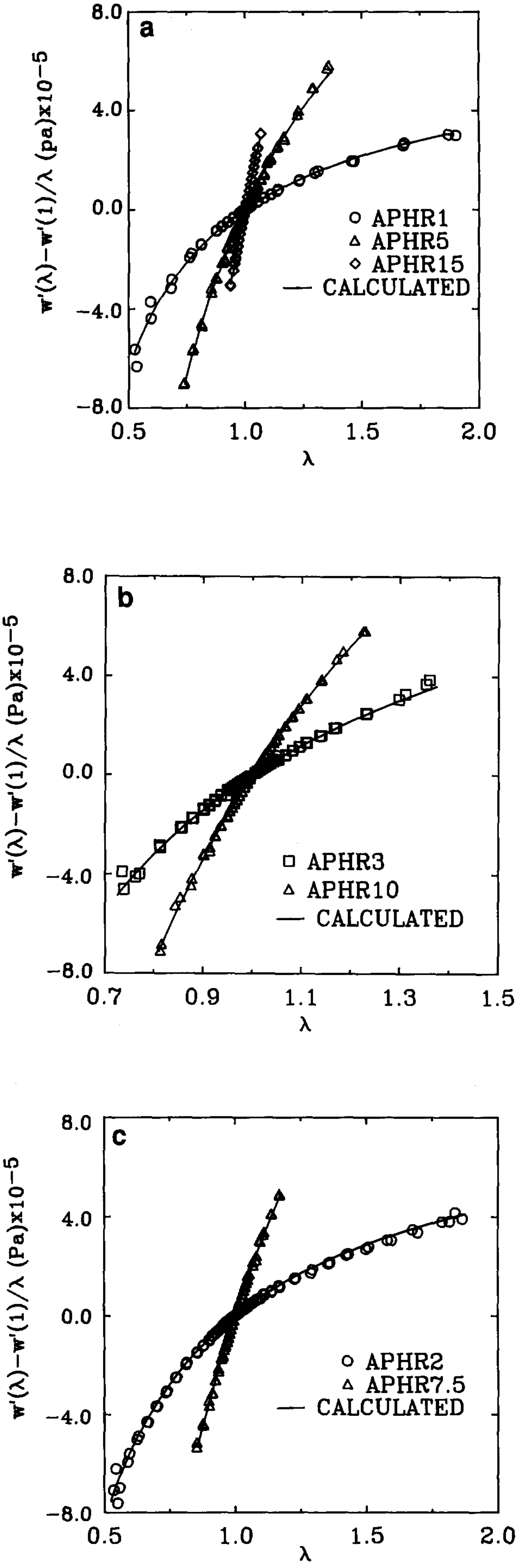

Figure 4 (a)–(c) Same as *Figure 1* but procedure fixed $C_0 = 0.25$. See also *Table 3*

Table 3 Values of G_e obtained for the Gaylord–Douglas[8,9] model determined from curve fitting of equation (8) to natural rubber torsional data

Rubber sample	ν (mol cm^{-3})	$C_0 = 0.5$		$C_0 = 0.25$		$C_0 = 1$	
		G_c (Pa)	G_e (Pa)	G_c (Pa)	G_e (Pa)	G_c (Pa)	G_e (Pa)
APHR1	2.09×10^{-5}	2.58×10^4	5.94×10^5	1.29×10^5	6.18×10^5	5.16×10^4	5.45×10^5
APHR2	5.22×10^{-5}	6.44×10^4	7.24×10^5	3.22×10^4	7.85×10^5	1.29×10^5	6.03×10^5
APHR3	8.35×10^{-5}	1.03×10^5	1.09×10^6	5.15×10^4	1.19×10^6	2.06×10^5	8.89×10^5
APHR5	1.46×10^{-4}	1.80×10^5	1.67×10^6	9.00×10^4	1.85×10^6	3.60×10^5	1.32×10^6
APHR7.5	2.24×10^{-4}	2.76×10^5	2.71×10^6	1.38×10^5	2.98×10^6	5.52×10^5	2.16×10^6
APHR10	3.03×10^{-4}	3.74×10^5	2.33×10^6	1.87×10^5	2.70×10^6	7.48×10^5	1.58×10^6
APHR15	4.59×10^{-4}	5.66×10^5	3.58×10^6	2.83×10^5	4.15×10^6	1.13×10^6	2.45×10^6

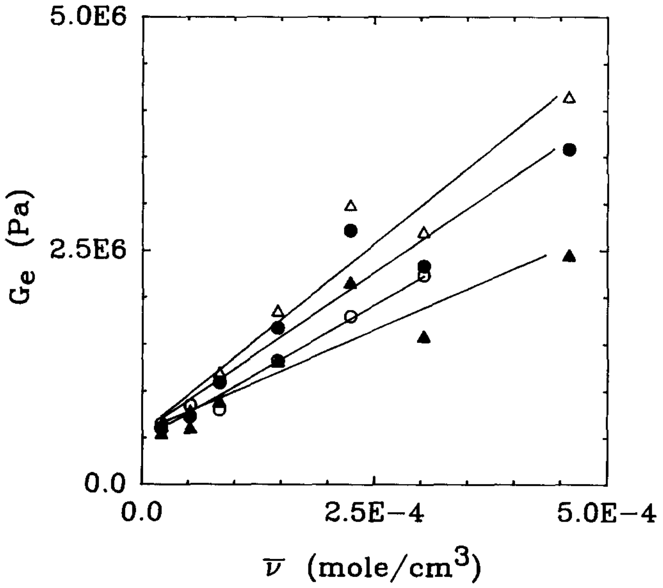

Figure 5 Confinement modulus G_e *versus* crosslink density ν for dicumyl peroxide crosslinked natural rubber. Data groups correspond to different curve fitting procedures. (○) C_0 floating; (▲) $C_0 = 1.0$; (●) $C_0 = 0.5$; (△) $C_0 = 0.25$. Lines represent linear regressions in the data. See *Table 4*

we see that, while the fits are reasonable, there are cases in which they are not as good as obtained upon letting both G_c (or C_0) and G_e float. (All of the curve fits were included here for completeness and in order to show that the fits for the different constraining conditions are not equally good, e.g. cf. *Figures 2c, 3c* and *4c*. It is unclear at this juncture whether this is significant.)

In *Table 3* we present the values of G_e obtained from the curve fits of *Figures 2–4* at the different crosslink densities. As can be seen G_e increases with increasing crosslink density. Furthermore, the values of G_e are generally larger than G_c indicating that the confinement contribution is the dominant contribution to the network elasticity (*Table 1*). In *Figure 5* we see that G_e is well represented as a linear function of crosslink density for all four choices of C_0 (1, 0.5, 0.25 and floating). Notably, the intercept of the data at zero crosslink density in all cases results in an estimate of G_e^* which is near to the actual reported value[32] of the rubbery plateau modulus for natural rubber[8] of 0.75×10^5 Pa. This is best seen in *Table 4* where we report the values from a linear regression on the crosslink density dependence of the confinement parameter G_e for each of the values of C_0 examined.

Table 4 Results from linear least squares determination of the crosslink density dependence of the confinement modulus G_e in the Gaylord–Douglas localization model ($G_e = A + B\nu$)

Curve fitting procedure	$A = G_N^*$ (Pa)	$B = \gamma kT$ (Pa cm^3 mol^{-1})
C_0 floating[a]	4.73×10^5	5.77×10^9
$C_0 = 0.5$	5.56×10^5	6.83×10^9
$C_0 = 0.25$	5.55×10^5	8.06×10^9
$C_0 = 1$	5.62×10^5	4.36×10^9

[a] Value at $\nu = 4.59 \times 10^{-4}$ mol cm^{-3} was not included

DISCUSSION

In previous papers[2–4] we reported on torque and normal force measurements on dicumyl peroxide crosslinked natural rubber and obtained the first derivative of the (elastic) strain energy density function. Classical arguments by Frenkel[6], Flory and Rehner[7] were then followed to predict the elastic properties of swollen rubbers from the dry state and the measured degree of swelling. A comparison of the dry state with a molecular model was strictly avoided since our intention was to check the hypothesis of FFR rather than the adequacy of any particular modular model of rubber elasticity. Here we compared our previously obtained dry state data with the localization model of Gaylord and Douglas[8,9]. This model indicates a substantial non-classical contribution to the elastic free-energy density which is due to the entanglement interaction and the finite volume of the network chains.

Despite the uncertainty in the estimate of the classical contribution to the rubber elasticity arising from experimental and theoretical uncertainties the comparison between theory and our previously obtained torsional data yields good agreement. The fitted parameters follow the predictions of the theory when reasonable estimates of the classical rubber elasticity contribution are made. The confinement modulus is found to vary linearly with crosslink density and extrapolates to the melt plateau modulus in the limit of zero crosslinking. A previous comparison of the localization model to uniaxial data also led to good agreement between theory and experiment[8]. This former study, however, did not explore the effects of crosslink density on the observed moduli G_c and G_e.

Our testing of the localization model of rubber elasticity is part of a longer term goal of characterizing the thermodynamics of polymer networks including mechanical and swelling behaviour. The classical rubber elasticity models are clearly inadequate to describe dry state mechanical data much less describe the swelling of networks. The localization model gives a definite indication of which factors are important in determining the elastic free-energy of a swelling network. The generalization of the model is not trivial, however, because swelling does not correspond to constant volume deformation and new contributions to the rubber elasticity are possible. (The issue of the controversial logarithmic term has to be addressed.) Preliminary calculations indicate that the non-classical confinement contribution to rubber elasticity has a significant influence on the swelling of rubbers. We intend to check these predictions in the near future.

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