

Swelling in crosslinked natural rubber: experimental evidence of the crosslink density dependence of χ

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Mechanical and swelling measurements were carried out on samples of dicumyl-peroxide-crosslinked natural rubber. The balance of the elastic free energy and the mixing free energy at swelling equilibrium was used to calculate the value of the Flory–Huggins χ parameter for a series of crosslinked rubbers swollen in an excess of different solvents. The results show that χ for the crosslinked rubber is greater than that of the uncrosslinked counterpart. Other evidence from the literature, based on swelling activity parameter measurements, which supports this conclusion, is discussed. We also find that the value of χ in the crosslinked rubber is a linear function of the crosslink density. We examine these results in the context of the Freed and Pesci lattice model.

(Keywords: dilatational modulus; Flory–Huggins interaction parameter; rubber elasticity; strain energy function; swelling; swelling activity parameter; Valandis–Landel function)

INTRODUCTION

The Frenkel–Flory–Rehner hypothesis^{1,2} states that in swelling of crosslinked networks the elastic contribution and the mixing contribution to the free energy are equal and additive. Then the chemical potential difference between the rubber–solvent system and the pure solvent is written as^{2–5}:

$$(\mu_1 - \mu_1^\circ) = (\mu_1 - \mu_1^\circ)_{\text{mix}} + (\mu_1 - \mu_1^\circ)_{\text{el}} \quad (1a)$$

At swelling equilibrium $(\mu_1 - \mu_1^\circ)$ vanishes so that:

$$(\mu_1 - \mu_1^\circ)_{\text{mix}} = -(\mu_1 - \mu_1^\circ)_{\text{el}} \quad (1b)$$

It is generally accepted that the appropriate expression for the mixing term is the Flory–Huggins expression^{6,7}:

$$(\mu_1 - \mu_1^\circ)_{\text{mix}} = RT[\ln(1 - v_2) - v_2 + \chi v_2^2] \quad (2)$$

where v_2 is the volume fraction of rubber, χ is the Flory–Huggins polymer–solvent interaction parameter, R is the gas constant and T is the absolute temperature. An important point to be made here is that χ is generally assumed to be the same for the crosslinked and uncrosslinked rubbers, i.e. $\chi_c = \chi_u$. The major objective of this paper is to show that this is not the case and that χ is a function of the crosslink density of the rubber. This is an extension and elaboration of work communicated previously⁸.

The elastic contribution to the chemical potential is usually expressed in terms of a molecular theory^{1–5,9–13}. Here, we avoid assuming a specific molecular model and simply measure the elastic strain energy density function of the crosslinked networks. There are two assumptions that we will need in doing this. First, we will assume the

validity of the Valanis–Landel¹⁴ hypothesis, that the strain energy density of the dry rubber can be represented as a separable function in the principal stretches:

$$W(\lambda_1, \lambda_2, \lambda_3) = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) \quad (3)$$

where the λ_i are the principal stretches, W is the strain energy density function and we will refer to w as the Valanis–Landel (VL) function. The VL function has been found to be an excellent representation of the dry state properties of rubber networks in a broad range of deformations and deformation geometries^{15–18}. The second assumption is that the elastic strain energy density function which represents the properties of the rubber in the dry state also represents its properties in the swollen state at the appropriate state of stretch. This latter assumption is one of the fundamental premises of the Frenkel–Flory–Rehner (FFR) hypothesis^{1,2} and has been shown to be consistent with the experimental observations made in recent studies conducted in this laboratory^{19,20}. In terms of the Valanis–Landel¹⁴ strain energy function we can express the elastic contribution to the chemical potential as:

$$(\mu_1 - \mu_1^\circ)_{\text{el}} = V_1 w'(\lambda_s) / \lambda_s^2 \quad (4)$$

where V_1 is the molar volume of the solvent, w' is the derivative of the VL function and $\lambda_s = v_2^{-1/3}$ is the swelling deformation.

In what follows we will describe experiments in which the elastic properties of the rubber in the dry state are determined from torsion and normal force measurements and the values of χ_c are calculated by equating equation (2) with equation (4) and solving for χ_c . The resulting values of χ_c are dependent on the crosslink density of the rubber and it is found for six different solvents that this

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dependence can be represented by the following linear equation:

$$\chi_c = \chi_0 + \alpha_1 v \quad (5)$$

where χ_0 is the value of χ in the uncrosslinked rubber at the dilute solution limit for good solvents and at the limit of miscibility for poor or non-solvents. Furthermore, over the range of parameters studied we will show that the relation that describes the crosslink dependence of the value of χ in the crosslinked systems can be written in a 'universal' form, viz.:

$$(\chi_c - \chi_0)/\chi_0 = \alpha v \quad (6)$$

where $\alpha = \alpha_1/\chi_0$ is independent of the solvent. These findings will be discussed in terms of a recent theory of Freed and coworkers²¹⁻²⁵, which predicts a crosslink-dependent χ .

Finally, we will also discuss the importance of the swelling activity parameter (defined as $S = \lambda_s \ln(a_c/a_u)$, where λ_s is as defined above and a_c and a_u are the activities in the crosslinked and uncrosslinked rubbers, respectively) in testing theories of rubber elasticity and show that the data for S in the literature support the finding that χ for crosslinked rubber is different from χ for uncrosslinked rubber.

EXPERIMENTAL METHODS

Samples of natural rubber from National Bureau of Standards SRM 385 were mixed with dicumyl peroxide (Di-Cup T, Hercules Inc.)* by milling on a two-roll mill. The samples were then placed in a cylindrical mould 1.27 cm in diameter by 7 cm in length and cured at 149°C for 2 h. Crosslink density was varied by changing the amount of dicumyl peroxide added during milling. This varied from one part peroxide per hundred parts rubber (1 phr) to 15 phr. Crosslink density was calculated using Wood's²⁶ equation relating the amount of decomposed peroxide to the molecular weight between crosslinks. The

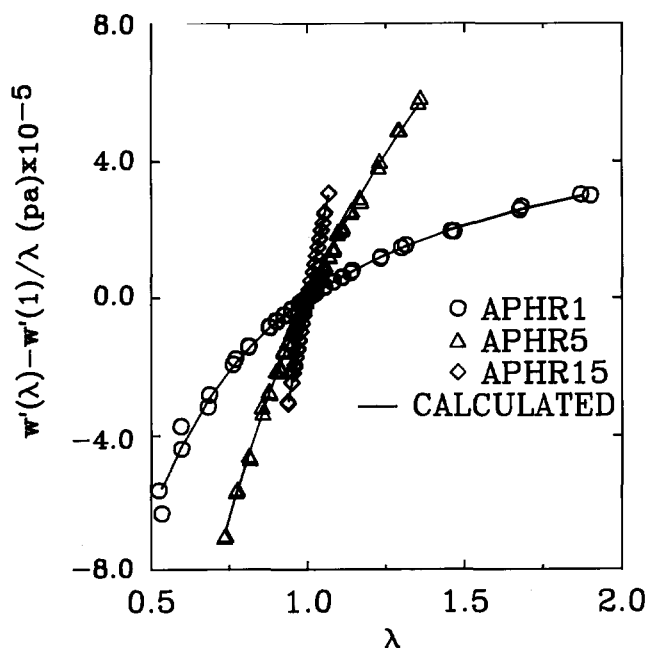


Figure 1 Typical data for dicumyl-peroxide-crosslinked natural rubbers showing variation of Valanis-Landel function derivative $w'(\lambda) - w'(1)/\lambda$ with deformation λ (from ref. 20)

Table 1 Molecular weights of natural rubber prepolymer (after milling) and molecular weight between crosslinks, M_c , of samples after crosslinking with dicumyl peroxide

Sample designation	Dicumyl peroxide (phr)	Prepolymer molecular weight ^a		M_c^b (g mol ⁻¹)
		M_w (g mol ⁻¹)	M_w/M_n	
APHR1	1	310 000	2.8	21 800
APHR2	2	310 000	2.8	8 720
APHR3	3	310 000	2.8	5 450
APHR5	5	310 000	2.8	3 115
APHR7.5	7.5	230 000	2.4	2 020
APHR10	10	310 000	2.8	1 500
APHR15	15	310 000	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: $K = 13.4 \times 10^{-3} \text{ ml g}^{-1}$, $a = 0.71$. Natural rubber in toluene: $K = 50.2 \times 10^{-3} \text{ ml g}^{-1}$, $a = 0.667$

^b Calculated from the formula given by Wood²⁶:

$$1/(2M_c) = 3.6986(f_p - 0.31) \times 10^{-5}$$

M_c is the molecular weight between crosslinks and f_p is the parts 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 $\approx 93\%$ peroxide, f_p is 0.93 times the value in the table

molecular weight of each milled rubber sample was obtained prior to crosslinking using size exclusion chromatography in toluene. The characteristics of the different samples are presented in Table 1.

The cylindrical samples were further machined to final dimensions using a grinding procedure developed previously^{27,28}, which ensures flat ends, end surfaces that are perpendicular to the central axis of the cylinder and centring of the sample in the test fixtures. For the torsional testing the samples were held to the platens of a Rheometrics RMS-7200* rheometer using a cyanoacrylate adhesive. The cylinders were 1–1.2 cm in diameter by 0.7–1.5 cm in height. The actual geometries were measured using a caliper accurate to 0.0025 cm. The RMS-7200 configuration used the standard rotary transducer for angular measurements and the 10 000 g cm/2000g load cell for torque and normal force measurements. The whole is interfaced with a personal computer for data acquisition and control. Single-step stress relaxation experiments were performed by applying a step in torsion and monitoring the torque and normal force responses. All data are reported as 131 s isochronal values for the torque and normal force. The step time was less than 0.5 s.

All tests were performed at $24 \pm 1^\circ\text{C}$. The solvents were acetone, methyl ethyl ketone (MEK), ethyl acetate, 1,2-dichloroethane, n-decane and benzene, thus covering the range from non-solvent to good solvent for natural rubber.

ANALYSIS

Determination of the elastic contribution to the chemical potential

There is good empirical evidence¹⁵⁻¹⁸ for the validity of the Valanis-Landel¹⁴ proposition that the elastic free

* Certain commercial materials and equipment are identified in this article to specify the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the materials and equipment identified are necessarily the best available for the purpose

energy function of rubber networks can be expressed as a separable function in the principal stretches. The assumption that this is true is essential to the analysis of the FFR hypothesis that we will use in this paper.

The Valanis–Landel¹⁴ strain energy function can be written as follows (equation (3)):

$$W(\lambda_1, \lambda_2, \lambda_3) = w_1(\lambda_1) + w(\lambda_2) + w(\lambda_3)$$

where $W(\lambda_1, \lambda_2, \lambda_3)$ is the elastic contribution to the free energy of the network and we will refer to the $w(\lambda_i)$ as the Valanis–Landel (VL) function. Importantly, the ability to represent successfully the elastic free energy term as separable in the stretches provides us with a means of obtaining the mechanical response of a network in all deformation geometries from a series of experiments in a limited number of geometries, e.g. we can describe tensile or compression responses from experimental results in torsion. The true stress response to a uniaxial deformation is, for example, written as¹⁴:

$$\sigma_{11} - \sigma_{22} = \lambda w'(\lambda) - \lambda^{-1/2} w'(\lambda^{-1/2}) \quad (7)$$

where $w'(\lambda) = \partial w / \partial \lambda$ is the derivative of the VL function. In addition, we note that often the VL function is expressed as:

$$w(\lambda) = w_1(\lambda) + a \ln \lambda \quad (8)$$

where the logarithmic term has created much discussion† in the literature, but is not needed in the analysis that will follow⁸. (See also Appendix.)

Kearsley and Zapas²⁹ have shown how to obtain $w'(\lambda) - w'(1)/\lambda$ from torsion and normal force measurements on cylinders of dry rubber. Here we simply write their result that:

$$w'(\lambda) - \frac{w'(1)}{\lambda} = \frac{2}{\lambda} (\lambda^2 - 1) \left(W_1 + \frac{1}{\lambda^2} W_2 \right) \quad (9)$$

where the W_i represent the derivatives of the strain energy density function with respect to the i th invariant of the deformation tensor. W_1 and W_2 can be obtained from the torque and normal force measurements at different angular deformations using the Penn and Kearsley³⁰ scaling law approach.

An important thing in the understanding of the behaviour of rubber is the behaviour near the undeformed state. We have argued previously^{8,19,20} that in the undistorted state the value of $w'(\lambda)_{\lambda=1}$ is equal to zero. When this is the case, the results of equation (9) can be used to obtain the VL function derivative $w'(\lambda)$, which appears in the terms for the elastic contribution to the chemical potential discussed in the previous section. The arguments supporting the contention that $w'(1) = 0$ are set forth in the Appendix.

Calculation of χ_c

In this analysis we assume that the Frenkel–Flory–Rehner hypothesis^{1,2} of separability of the mixing and elastic contributions to the free energy is correct, that the Flory–Huggins expression^{6,7} for the mixing contri-

bution to the chemical potential is valid (equation (2)) and that equations (3), (4) and (6)–(9) are valid descriptions of the network elasticity in both the dry and swollen states. Then the value of the Flory–Huggins interaction parameter for the crosslinked rubber from swelling experiments carried out in an excess of solvent can be calculated by equating equation (2) with equation (4) and solving for χ_c :

$$RT[\ln(1 - v_2) + v_2 + \chi_c v_2^2] = -V_1 w'(\lambda_s) / \lambda_s^2 \quad (10)$$

Then:

$$\chi_c = \{ -V_1 w'(\lambda_s) / RT \lambda_s^2 - [\ln(1 - v_2) + v_2] \} / v_2^2 \quad (11)$$

and the variables have been defined previously.

There are several important assumptions used in this analysis, which will be important in considering and interpreting our results. First, we have assumed that the Frenkel–Flory–Rehner (FFR) hypothesis^{1,2} is correct. Although this is often assumed, we are using it here in a way that makes no assumptions about the validity of any particular model of rubber elasticity. We do presume, as did FFR, that the strain energy of the system in the swollen state is described by the same function as that which is relevant to the dry state, with differences being accounted for by the network (macroscopic) deformation alone. This assumption has been supported by recent results obtained in this laboratory^{19,20}. We further use assumptions about the phenomenological form of the strain energy density function, i.e. that the Valanis–Landel¹⁴ function describes the dry state elastic properties of the network and that its first derivative at zero deformation is equal to zero. Finally, we have assumed that the Flory–Huggins expression^{6,7} is correct and is a reasonable representation of the mixing contribution to the chemical potential, but that the interaction parameter χ_c is crosslink-dependent. It is the crosslink dependence of χ_c that we wish to examine.

RESULTS

The results from the torque and normal force measurements as functions of the angle of twist (deformation) on the series of natural rubber samples discussed here have been reported previously²⁰. From the torque and normal force responses we were able to determine W_1 and W_2 from the Penn and Kearsley³⁰ equations and then use equation (9) to determine $w'(\lambda)$, keeping in mind that $w'(1) = 0$. Typical results* are presented in *Figure 1* as $w'(\lambda) - w'(1)/\lambda$ versus λ . These data were used for the calculation of the elastic contribution to the chemical potential and subsequently the value of χ_c from the swelling measurements.

The results of the swelling measurements are presented in *Table 2*, where the degree of swelling as $1/v_2$ of each sample in each of the solvents is presented.

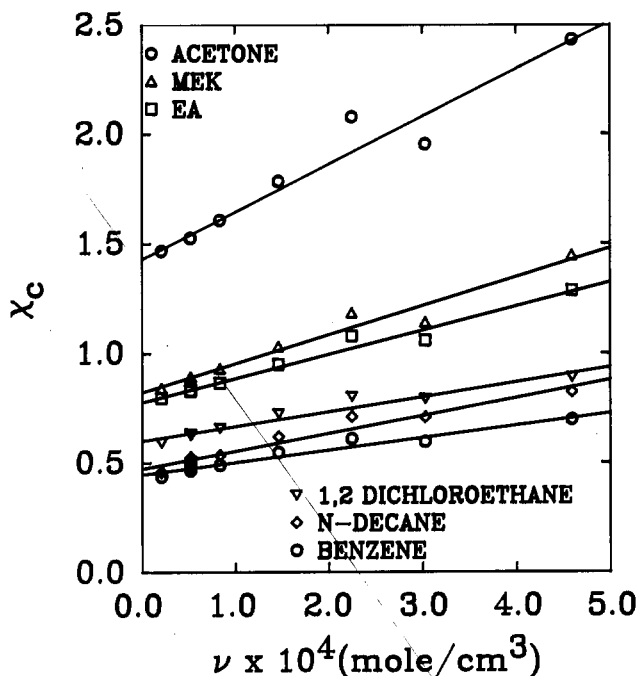
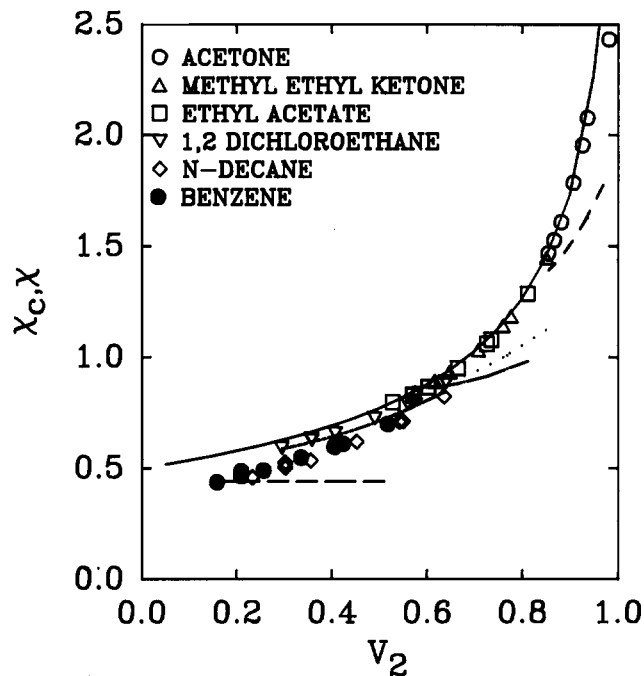
From our knowledge of $w'(\lambda)$ and the degree of swelling (swelling deformation = $\lambda_s = v_2^{-1/3}$) we were able to use

† The $a \ln(\lambda_1 \lambda_2 \lambda_3)$ term in the Valanis–Landel type strain energy density function is arbitrary and allows one to set $w'(1) = 0$ in equation (10) without loss of generality^{13,29,30}. On the other hand, in many molecular theories^{3–5,11} this term appears explicitly and it may or may not have important consequences depending on the specific model adopted. It is also interesting to note that the $\log \lambda$ term does not appear explicitly in the junction constraint model, but is present implicitly as it appears in one limiting case^{8,12}. (See also Appendix.)

* In instances in which the torsional data did not cover a sufficient range of deformations and the calculations of χ_c in the swollen state required extrapolation of the values of $w'(\lambda) - w'(1)/\lambda$, we used the Gaylord–Douglas³¹ model as empirically fitted to our data to carry out the extrapolations. The form of $w'(\lambda)$ in this case is $w'(\lambda) = A(\lambda - 1/\lambda) + B(1 - 1/\lambda)$. As seen by the curves of *Figure 1* the model fits the data very well. Furthermore, the extrapolations were not large, and we found little difference between the use of this equation and a simple graphical extrapolation by hand.

Table 2 Degree of swelling, $1/\nu_2$, for natural rubber crosslinked with dicumyl peroxide swollen to equilibrium in various solvents

Sample designation	Solvent (V_1 in $\text{cm}^3 \text{mol}^{-1}$)					
	Acetone (73.8)	MEK (89.8)	n-Decane (195.8)	Benzene (89.1)	Ethyl acetate (98.2)	1,2-Dichloroethane (80.1)
APHR1	1.172	1.739	4.303	6.317	1.898	3.402
APHR2	1.155	1.621	3.312	4.780	1.754	2.804
APHR3	1.134	1.543	2.814	3.908	1.661	2.460
APHR5	1.102	1.411	2.211	2.989	1.504	2.042
APHR7.5	1.092	1.290	1.818	2.364	1.360	1.755
APHR10	1.082	1.317	1.846	2.469	1.379	1.791
APHR15	1.063	1.174	1.571	1.935	1.233	1.567

**Figure 2** Dependence of χ_c on crosslink density ν for dicumylperoxide-crosslinked natural rubber swollen in different solvents, as indicated**Figure 3** Variation of χ_c and χ with volume fraction of rubber. Data points depict χ_c values in different solvents as indicated on graph. (—) is for limit of miscibility, calculated from equation (11) with the elastic term set to zero. The other curves correspond to χ values for uncrosslinked rubber reported in the literature and discussed in the text: (—) benzene; (—) 1,2-dichloroethane; (—) ethyl acetate; (·····) MEK; (----) acetone

equation (11) to calculate the value of χ_c for each rubber-solvent system. The values of χ_c were then plotted versus crosslink density as shown in Figure 2 and versus volume fraction of rubber as shown in Figure 3. There are two important features to be noted from these figures. First, from Figure 2, the values of χ_c increase linearly as the crosslink density increases. Secondly, from Figure 3, the value of χ_c is invariably greater than the value for the corresponding uncrosslinked rubber at the same volume fraction of rubber. These results are important and we discuss them in the following section.

DISCUSSION

Crosslink density dependence of χ_c in an excess of solvent

The results described above are for rubber crosslinked in the bulk state and subsequently swollen in an excess of solvent, i.e. at saturation. We make this distinction because there is a considerable body of literature dealing with the swelling activity parameter (so-called 'dilatational modulus'), which is obtained from measurements of the activities of the crosslinked and uncrosslinked rubber

made isopiastically, i.e. at constant vapour pressure. Although we see no obvious reason why such measurements should differ from those reported here, at this point we do make a distinction. The dilatational modulus measurements reported in the literature and their importance in the discussion of the dependence of the Flory-Huggins interaction parameter on crosslinking will be discussed in the next section. In this section we limit ourselves to a discussion of the results reported above.

Recalling Figure 2, where the dependence of the Flory-Huggins interaction parameter on the crosslink density is depicted, we performed a linear regression to equation (5) on the data for each solvent, i.e.:

$$\chi_c = \chi_0 + \alpha_1 \nu$$

The results of such an analysis are presented in Table 3. An interesting point to be made in examining the data presented in Table 3 is that the values of χ_0 for the good solvents approach the values for the uncrosslinked rubber

in the same solvents and at low concentrations†. Furthermore, χ_0 in the poor solvent systems is approximately equal to the value of χ for the uncrosslinked rubber in the same solvent at the volume fraction of rubber corresponding to the limit of miscibility of the polymer and solvent‡.

We also found that the data from the linear regression followed an equation of more 'universal' form (equation (6)):

$$(\chi_c - \chi_0)/\chi_0 = \alpha v$$

where, as shown in Table 3, we found that $\alpha = \alpha_1/\chi_0$ is nearly the same independent of the solvent type. In Figure 4 we depict the data in a reduced plot of $(\chi_c - \chi_0)/\chi_0$ versus v , which should collapse the data to a single line if equation (6) were strictly valid. Although the results are suggestive, the experimental uncertainty is great enough that further work needs to be done to determine how 'universal' this behaviour is.

An important possibility if equation (6) is valid was suggested by J. F. Douglas³⁵ of this laboratory, i.e. that there exists a normalization parameter which would make α in equation (6) dimensionless. A possibility that we suggested previously⁸ is that the normalization parameter is the critical crosslink density v^* , which is related to, for example, the gel point, and we wrote the

Table 3 Values^a of χ_0 , α_1 and α for crosslinked natural rubber in different solvents

Solvent	χ_0	α_1 (cm ³ mol ⁻¹)	α (cm ³ mol ⁻¹)
Acetone	1.43	2179	1524
MEK	0.823	1316	1600
Ethyl acetate	0.777	1096	1411
1,2-Dichloroethane	0.600	679	1131
n-Decane	0.472	819	1735
Benzene	0.445	569	1279

^a Values determined from least-squares fit of data to equation of the form $\chi_c = \chi_0 + \alpha\chi_0 v$ and then $(\chi_c - \chi_0)/\chi_0 = \alpha v$

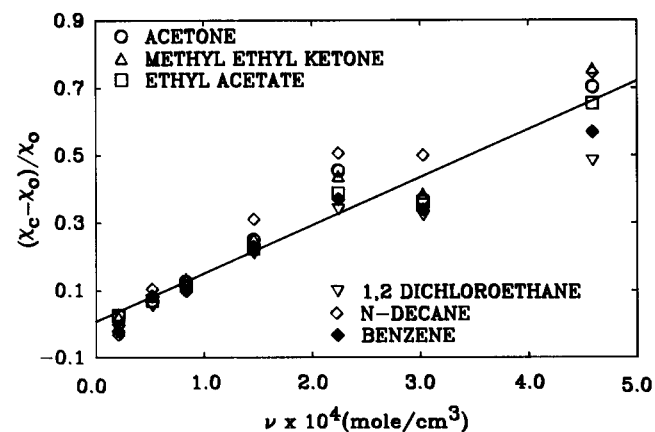


Figure 4 Reduced value of χ as $(\chi_c - \chi_0)/\chi_0$ vs. v for natural rubber networks swollen to equilibrium in different solvents, as indicated

† For acetone, ethyl acetate and MEK, we took values of χ for the uncrosslinked rubber from Booth *et al.*³². For the natural rubber-benzene system, χ has been reported to be independent of v_2 , and here we take the value of $\chi = 0.41$ reported by Gee³³. For the 1,2-dichloroethane system, we took the values reported by Huggins³⁴. We did not find any χ values for the n-decane-natural rubber system that were obtained using uncrosslinked rubber

following expression:

$$(\chi_c - \chi_0)/\chi_0 = \alpha_2 v/v^* \quad (12)$$

At this point this is merely speculative and we are currently performing experiments to explore this possibility‡. The important point of this section has been to present the evidence that the Flory-Huggins interaction parameter depends on crosslink density. In the next section we examine the evidence available which shows that χ_c is different in the crosslinked and uncrosslinked rubbers from considerations of the swelling activity parameter ('dilatational modulus').

Crosslink density dependence of χ_c at zero swelling: the swelling activity parameter§

There have been several experimental studies of the swelling activity parameter^{10,11,37,38}, all of which can be interpreted to show that the Flory-Huggins χ parameter is different in the crosslinked and uncrosslinked rubbers. Furthermore, the studies show that $\chi_c - \chi_u \sim 0.02$ at the limit of zero swelling, which is similar to the values obtained in this study for similar solvent quality and degree of crosslinking but in an excess of solvent.

The swelling activity parameter S is defined in terms of the activities of the polymer-solvent systems in the crosslinked and uncrosslinked states, a_c and a_u , respectively. S is written as follows^{4,11,12}:

$$S = \lambda_s \ln(a_c/a_u) \quad (13)$$

where we remind the reader that λ_s is the swelling deformation. The activities in the uncrosslinked and crosslinked rubbers are written as:

$$\ln(a_u) = [\ln(1 - v_2) + v_2 + \chi_u v_2^2] \quad (14)$$

$$\ln(a_c) = [\ln(1 - v_2) + v_2 + \chi_c v_2^2] + V_1 w'(\lambda_s)/RT \lambda_s^2 \quad (15)$$

where we recognize the Flory-Huggins expression^{6,7} for the mixing contribution to the activities of both crosslinked and uncrosslinked rubbers and the elastic term for the crosslinked rubber. In past analyses of swelling behaviour it has been assumed that $\chi_c = \chi_u$, in which case we find that S is simply a measure of the elastic term, i.e.:

$$S = V_1 w'(\lambda_s)/RT \lambda_s \quad (16)$$

If, however, one accepts the results presented in this paper, χ_c does not equal χ_u and we should write*:

$$S = (\chi_c - \chi_u) \lambda_s v_2^2 + V_1 w'(\lambda_s)/RT \lambda_s \quad (17)$$

From the prior arguments (see earlier footnote) that at zero (swelling) deformation ($\lambda_s = 1$) $w'(1) = 0$, if χ_c is equal to χ_u , then S is equal to zero at $\lambda_s = 1$. We know

‡ It is well known that the elastic modulus and degree of swelling of the network vary with the molecular weight M_p of the polymer prior to crosslinking³⁶. Furthermore, the number of crosslinks required to form a continuous network should change with M_p . Therefore, changing the molecular weight prior to crosslinking, but introducing a constant number of crosslinks should provide a test of equation (12)

§ What we refer to here as the swelling activity parameter has been called the 'swelling modulus' or the 'dilatational modulus' in the literature. Because it is a dimensionless thermodynamic parameter and is definitely not a modulus in the sense of being the second derivative of the free energy function, we find the terms dilatational or swelling modulus confusing and suggest using swelling activity parameter as an alternative, which is clearer. We use this term throughout the paper

* Richard J. Gaylord of the University of Illinois first pointed out to us in March 1988 that χ_c does not necessarily equal χ_u and equation (17) is the result³⁹

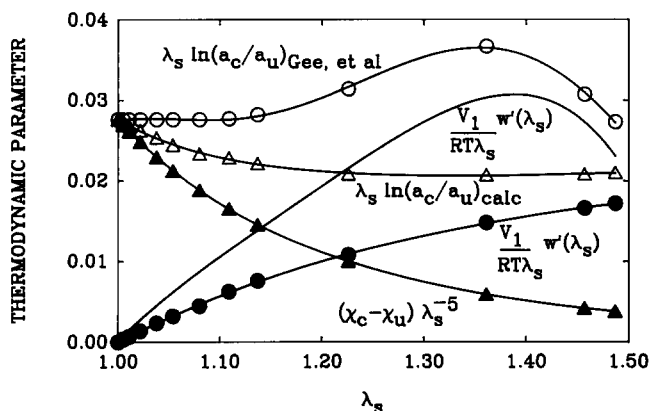


Figure 5 Thermodynamic parameters vs. swelling deformation (see text for discussion)

of no experimental study in which this is the case and, in fact, the data indicate quite dramatically that $\chi_c > \chi_u$. In Figure 5 we depict the data of Gee *et al.*¹¹ showing that S does not go through zero at $\lambda_s = 1$ (curve labelled $\lambda_s \ln(a_c/a_u)_{\text{Gee et al.}}$). We also show several other curves in this figure for comparison. The curve labelled $(\chi_c - \chi_u)\lambda_s^{-5}$ is the mixing contribution due to the difference between the Flory–Huggins interaction parameters in the cross-linked and uncrosslinked rubbers. There are two curves labelled $V_1 w'(\lambda_s)/RT\lambda_s$ which represent the elastic contribution to the swelling activity parameter calculated in two ways. The full curve with the full circles is the value of $V_1 w'(\lambda_s)/RT\lambda_s$ for the 5 phr dicumyl-peroxide-crosslinked rubber used in this study and calculated assuming that $w'(\lambda)$ for the swollen rubber is the same function as for the dry rubber. The full line without points gives the values of $V_1 w'(\lambda_s)/RT\lambda_s$ obtained by subtracting the mixing contribution $(\chi_c - \chi_u)\lambda_s^{-5}$ from the data of Gee *et al.* for $S = \lambda_s \ln(a_c/a_u)$. Obviously the two curves are significantly different—something that we discuss below. Finally, the curve labelled $\lambda_s \ln(a_c/a_u)_{\text{calc}}$ is the sum of the mixing contribution and the elastic contribution based on the assumption that the dry state and swollen state elasticities are the same. This is the prediction from equation (7).

A brief discussion of Figure 5 is important here. Because $\lambda_s \ln(a_c/a_u)_{\text{calc}}$ does not agree with the measured values of Gee *et al.*¹¹, it suggests that the information in equation (7) is inadequate to explain the behaviour of the swelling activity parameter. There are several possible explanations. The first is that the FFR additivity and separability hypothesis is incorrect and there is some sort of coupling between the mixing and elastic contributions to the free energy. Such coupling has been argued by Neuberger and Eichinger³⁷ based solely on measurements of the swelling activity parameter and assuming that $\chi_c = \chi_u$. However, we recently showed^{19,20} that the elastic contribution to the free energy function of the dry rubber is equal to that of the swollen rubber, which implies that such coupling occurs only in the sense that the free energy of mixing is altered by the network deformations—a possibility suggested by Deloche and Samulski⁴⁰. One other possibility arises and that is that the coefficient a of the logarithmic term in the free energy function is important and $w'(1) \neq 0$. However, the implication is that either $w'(1)$ or a varies with the solvent and/or the swelling deformation. This prospect is dis-

turbing, but experiments are currently under way to assess such a possibility.

As a penultimate comment, none of the prior works attempted to study systematically the crosslink dependence of χ_c as we did above. Furthermore, because the swelling activity parameter is not currently understood^{12,20,37,40}, it is unclear what the exact relationship is between the value of χ_c obtained from the value of S evaluated at $\lambda_s = 1$ and that obtained in our study in an excess of solvent. In any event, it is clear that under the present assumptions $\chi_c \neq \chi_u$ and the value of $\chi_c - \chi_u$ is of order 0.03 for good solvent systems at moderate crosslink densities. It increases as crosslink density increases or solvent quality becomes poorer.

Finally, we wish to comment that the crosslink dependence of χ was also observed in experiments by Gnanou *et al.*⁴¹ on end-linked poly(ethylene oxide) (PEO) networks swollen in water and dioxane. Gnanou *et al.* assumed a 'phantom' network model to calculate χ_c , but the 'phantom' modulus used in the calculation was that obtained by compression measurements on the swollen gel. Given these assumptions their data analysis needs to be viewed with caution, but does give some interesting results, as shown in Figure 6, where we plot their data as χ_c versus ν . A least-squares fit of their data to equation (5) (or (6)) results in values of α that are approximately the same for the two solvents ($\alpha = 1089$ for H₂O and 1150 cm³ mol⁻¹ for dioxane). Further, these values do not differ greatly from those which we report in this paper for the natural rubber system (Table 3). This is probably fortuitous given the vastly different nature of the procedures, network chemistries, etc., in the two studies, but merits further examination in the future. In the next section we examine the apparent linear crosslink density dependence of χ_c within the context of lattice model calculations of Freed and Pesci²³.

Comparison of results with the lattice model calculations of Freed and Pesci

Freed *et al.*^{21–25} have recently treated the problem of the crosslink dependence of χ by evaluating corrections to the Flory–Huggins approximation in a systematic expansion in a lattice model. As usual, this treatment has each lattice site occupied by a monomer or a solvent molecule in which there are van der Waals energies between non-bonded and nearest neighbours. Bond correlations are calculated in a cluster expansion of the mixing energy in inverse powers of the lattice coordination

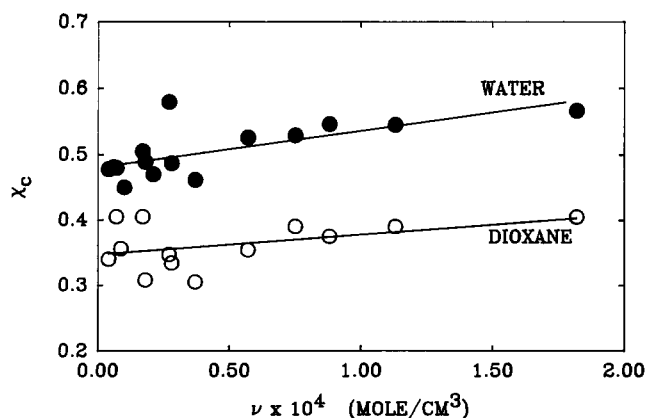


Figure 6 Variation of χ_c with crosslink density for PEO–water and PEO–dioxane systems (data from Gnanou *et al.*⁴¹)

number Z . The lattice coordination number is a measure of the 'range' of the interaction, with the mean-field theory corresponding to $Z \rightarrow \infty$. Freed *et al.*²¹⁻²⁵ have extended the calculations to the properties of linear and branched chains as well as of treating solvent molecules and monomers that have internal structure and, therefore, cover several lattice sites.

In the case of a tetrafunctional network swollen in a solvent made up of molecules having N_s flexible bonds and occupying $N_s + 1$ lattice sites, Freed and Pesci²³ find that the effective interaction parameter as defined through the chemical potential is given by:

$$(\chi_c - \chi_0)/\chi_0 = \{ (24/Z^2) + [16N_s/Z^3 \varepsilon \phi_p (N_s + 1)] + O(Z^{-4}) \} \phi_v \quad (18)$$

where $\phi_p = v_2$ is the volume fraction of polymer, ϕ_v is the volume fraction of crosslinks, $\varepsilon = (\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps})/kT$ is the dimensionless interaction parameter and the subscripts p and s refer to polymer and solvent respectively.

As noted by Freed and Pesci²³, there are difficulties in quantitative comparisons between equation (19) and the experimental results presented above because the parameters Z , ε , N_s and ϕ_v in the lattice model are not readily related to the actual experimental situation. Furthermore, we note immediately that equation (19) predicts a rubber volume fraction (ϕ_p) dependence of χ_c , which was not observed explicitly in our data. These points are dealt with below.

In order to estimate the values of Z , ε , N_s and ϕ_v that are relevant to the actual experimental situation, we first assume that $\varepsilon \approx Z^{-1}$, as did Freed and Pesci²³. The comparison of the lattice model crosslink volume fraction ϕ_v with the experimental crosslink density ν can be made by using reasonable estimates of how many lattice sites are taken per crosslink point. Freed and Pesci²³ assumed that each crosslink point was formed of two monomers and that the junction site is composed of $2y$ monomers. The molecular weight for isoprene is 58 so that the value of ϕ_v equals $116y\nu \text{ cm}^3 \text{ mol}^{-1}$.

We then carried out a least-squares analysis of our data to equation (19) for lattice coordination values of $Z = 4, 6$ and 8 and for the values of N_s corresponding to the number of flexible bonds estimated for each solvent based on its chemical structure. Table 4 shows that while the values of y obtained are not independent of solvent they are not unreasonable except perhaps for acetone and $Z = 8$. Since $2y$ is the number of monomers per crosslink junction, if $Z = 4$ for the tetrafunctional network the junction reaches two monomer units along each branch of the network. When $Z = 16$ then it reaches eight, which may be an overestimate. Of course, assigning physical meaning to the parameters of the Freed-Pesci²³ lattice model may be dangerous, although the data are well described by it and it allows an explanation of the apparent linear dependence of χ_c on the crosslink density (particularly when the degree of swelling is not extreme). Certainly further work is required to establish if other network or solvent parameters are important in the crosslink dependence of χ . A final point here is that the volume fraction dependence of χ_c in the Freed and Pesci²³ model does not greatly influence the results that we obtained, possibly because, for a given solvent, the range of volume fractions obtained upon swelling was not very large.

Table 4 Values of χ_0 and y determined from least-squares analysis of equation (19) for crosslink dependence of χ_c

Solvent	Fixed value of N_s^a	χ_0	y
$Z = 4$			
Acetone	2	1.44	8.4
MEK	3	0.81	4.8
Ethyl acetate	4	0.77	3.8
n-Decane	9	0.45	2.5
1,2-Dichloroethane	1	0.60	2.6
Benzene	0	0.45	3.2
$Z = 6$			
Acetone	2	1.44	16.4
MEK	3	0.81	9.1
Ethyl acetate	4	0.77	7.1
n-Decane	9	0.44	4.6
1,2-Dichloroethane	1	0.59	5.0
Benzene	0	0.45	7.3
$Z = 8$			
Acetone	2	1.44	29.2
MEK	3	0.81	16.1
Ethyl acetate	4	0.77	12.7
n-Decane	9	0.44	8.2
1,2-Dichloroethane	1	0.59	8.8
Benzene	0	0.45	12.9

^a C-C and C-O bonds in the chain backbone were counted as flexible. The benzene ring was taken as having no flexible bonds

SUMMARY

Mechanical and swelling measurements were carried out on a series of dicumyl-peroxide-crosslinked natural rubbers. By using the Valanis-Landel¹⁴ form of strain energy function we were able to obviate the use of any molecular model in the description of the elastic contribution to the free energy of the network. Then, assuming that the dry state properties and the swollen state properties are described by the same strain energy function, that the value of the first derivative of the strain energy function is zero at zero deformation and that the Flory-Huggins expression^{6,7} describes the thermodynamics of mixing, we were able to calculate an effective value of the Flory-Huggins interaction parameter for the crosslinked networks (χ_c). We found that the dependence of χ_c on crosslink density was well represented by a linear function, which could be written as $(\chi_c - \chi_0)/\chi_0 = \alpha\nu$, where we found that χ_0 was near the dilute-solution χ for the uncrosslinked rubber in good solvents or the χ value at the limit of miscibility for poor or non-solvents. The value of α was found to be almost independent of the solvent system studied. These results were compared with the recent lattice model calculations of Freed and Pesci²³. The results appear to be in qualitative agreement with the model.

We also considered other evidence in the literature that χ is a function of crosslink density. Gnanou *et al.*⁴¹ obtained data for χ_c on PEO networks using an approach that is somewhat like that used here. When we analysed the crosslink dependence of their χ_c values we found nearly the same behaviour as that observed for the natural rubber systems. In addition, reported evidence based on measurements of the swelling activity parameter is presented which supports the contention that χ_c differs from the χ value of the uncrosslinked rubber. Within the framework of our assumptions and knowing that the mechanical response in the dry and swollen systems is described by the same strain energy density function^{19,20},

we concluded that $\chi_c \neq \chi_u$ and that either the free energy of mixing is affected by network deformation or the logarithmic term in the elastic contribution to the free energy varies with solvent type. This latter speculation appears unsatisfactory.

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APPENDIX

The strain energy function near the undistorted state

Kearsley and Zapas²⁹ have discussed the behaviour of the Valanis-Landel¹⁴ form of strain energy density function near the undistorted state (configuration). They do not, however, consider the value of the first derivative explicitly, merely noting as did Valanis and Landel¹⁴ that $w'(1)$ can be set equal to zero without loss of generality. While this is adequate for the description of the mechanical properties, it becomes an assumption when dealing with the swelling of the rubber. Here we argue that $w'(1)=0$ for physical reasons consistent with the Frankel-Flory-Rehner hypothesis^{1,2}.

First we rewrite the VL function as was done in equation (3):

$$W(\lambda_1, \lambda_2, \lambda_3) = w(\lambda_1) + w(\lambda_2) + w(\lambda_3)$$

Because the FFR hypothesis implies that the strain energy density function is the same in the dry and swollen rubber, we argue that the function should be elastically stable for isotropic deformations as well as for volume-conserving ones.

The condition that W be at a (local) extremum in the function is that the total differential be equal to zero^{42,43}:

$$dW(\lambda_1, \lambda_2, \lambda_3) = w'(\lambda_1) d\lambda_1 + w'(\lambda_2) d\lambda_2 + w'(\lambda_3) d\lambda_3 = 0 \quad (\text{A.1})$$

where $w'(\lambda_i) = \partial w / \partial \lambda_i = dw(\lambda_i) / d\lambda_i$. In the undistorted configuration, $\lambda_1 = \lambda_2 = \lambda_3 = 1$ and it is obvious that $w'(1)=0$ is a solution to (A.1). It is not obvious that this is the only solution.

Another way of looking at the problem is to take equation (A.1) and divide each side by $d\lambda_i$, e.g. $d\lambda_1$. Then we find:

$$0 = dW/d\lambda_1 = w'(\lambda_1) + w'(\lambda_2) d\lambda_2/d\lambda_1 + w'(\lambda_3) d\lambda_3/d\lambda_1 \quad (\text{A.2})$$

and one arrives at three equations for each λ_i .

Obviously stability is maintained at zero deformation when $w'(1)=0$. However, for the volume-conserving deformation (i.e. for an incompressible material), $\lambda_1 \lambda_2 \lambda_3 = 1$, which makes the λ_i dependent. Then one can show using the method of Lagrange multipliers⁴³ that elastic stability is always maintained independent of the value of $w'(1)$. Thus, although $w'(1)=0$ is a sufficient

condition for stability, it is not necessary in the case of the incompressible material.

However, in swelling we do not have a volume-conserving deformation. Yet the FFR hypothesis implies that the elastic strain energy function relevant to both mechanical and swelling problems is the same. Therefore, we contend that one should consider the stability of the strain energy function for non-volume-conserving deformations. In particular, when $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_s$, for the isotropic (swelling) deformations, equation (A.2) becomes

$$0 = dW/d\lambda_s = 3w'(\lambda_s) \quad (\text{A.3})$$

and it is obvious that stability at $\lambda_s = 1$ requires $w'(1)=0$.

The consequences of this are quite important. In the determination of the Valanis-Landel¹⁴ function derivatives from the mechanical measurements we found that we could only determine $w'(\lambda) - w'(1)/\lambda$. When $w'(1)=0$ we find that we have actually determined $w'(\lambda)$. Also, this sheds some light on the $a \ln(\lambda_1 \lambda_2 \lambda_3)$ term which appears arbitrarily in the original Valanis-Landel¹⁴ paper and also appears in many molecular theories. Take the VL function in equation (3) and write $w(\lambda_i) = w_1(\lambda_i) + a \ln \lambda_i$. Upon differentiation with respect to λ_i we get $w'(\lambda_i) = w'_1(\lambda_i) + a/\lambda_i$. But at $\lambda_i = 1$ we have from the above that $w'(1)=0$. This implies that $w'_1(1) = -a$, which is necessary to calculate χ_c from equation (10).

The argument for equating $w'(1)=0$ is plausible, but needs to be tested independently. It may be testable by combined mechanical and scattering measurements on labelled dry networks, since the shear modulus is equal to twice the sum of the first and second derivatives of the strain energy density function and the scattering measurements at zero angle give the second derivative only. This suggests further experiments.

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