

Mechanical and swelling behaviour of well characterized polybutadiene networks

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This paper is dedicated to the late Prof. Paul J. Flory who made lasting contributions to polymer physics

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Endlinking of hydroxyl-terminated polybutadiene with the appropriate isocyanate has been used to prepare well characterized networks. Two networks have been studied with molecular weights of the prepolymers being 6100 and 2400 g/mole by g.p.c. Cylindrical specimens were prepared and the derivatives of the stored energy function with respect to the stretch invariants were determined by torque and normal force measurements in torsion. From these data the Valanis–Landel stored energy function derivatives $w'(\lambda)$ were determined for both networks. The stored energy function for the junction constraint model of Flory, which is a special form of the Valanis–Landel function, has been fitted to that determined from the experiments. The contributions, ΔA_{ph} and ΔA_c , to the stored energy function from the phantom network and from the junction constraints respectively do not agree with predictions from the topologies of the networks. In spite of this the form of $w'(\lambda)$ for the junction constraint model gives an excellent 'curve fit' to the data. Comparison is also made with equilibrium swelling.

(Keywords: junction constraint model; networks; polybutadiene; rubber elasticity; stored energy function; swelling)

INTRODUCTION

There has been considerable renewed interest in rubber elasticity theory recently, due to the success of the junction constraint model of Flory^{1–6}. In this paper we carry out mechanical and swelling measurements on well characterized polybutadiene networks and compare the results with the junction constraint model in a new way. To do this we use the concept from continuum mechanics of the Valanis–Landel⁷ (V–L) strain energy density function, i.e. a function in the principal stretches which can be represented as a separable sum of one function evaluated at each of the three principal stretches. We further derive the V–L function for the junction constraint model of Flory, and compare it with the experimental data.

There are two salient results from our work: (1) while the Flory model fits the data extremely well, the parameters related to the network topology are not in particularly good agreement with those calculated from the chemistry involved in making the networks and (2) the assumption that the elastic free energy of deformation is equal to the free energy of mixing at swelling equilibrium can be supported only if one includes a non-zero logarithmic term in the Valanis–Landel strain energy function.

In the following sections we describe how one determines the derivatives of the stored energy density function with respect to the stretch invariants for the rubber networks and how the Valanis–Landel function

relates to the invariant form of the strain energy density function. We also derive the V–L function relevant to the Flory junction constraint model. Then we describe our experimental procedures and compare our results with the junction constraint model.

THEORETICAL CONSIDERATIONS

Torsion of a cylinder

In this section we are concerned with determining the strain energy density function derivatives $\partial W/\partial I_1 = W_1$ and $\partial W/\partial I_2 = W_2$ for an incompressible elastic material from experiments in which a cylinder is subjected to a twist while the length is held constant. Here $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and $I_2 = 1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2$ are the invariants of the deformation tensor, the λ 's are the principal stretches and $W(I_1, I_2)$ is the strain energy density function for the material. The deformation geometry is given in *Figure 1*. Then the torque, T , and the normal thrust, N , applied to the ends of the cylinder are given by⁸:

$$T = 4\pi\psi \int_0^R (W_1 + W_2)r^3 dr \quad (1)$$

$$N = -2\pi\psi^2 \int_0^R (W_1 + 2W_2)r^3 dr \quad (2)$$

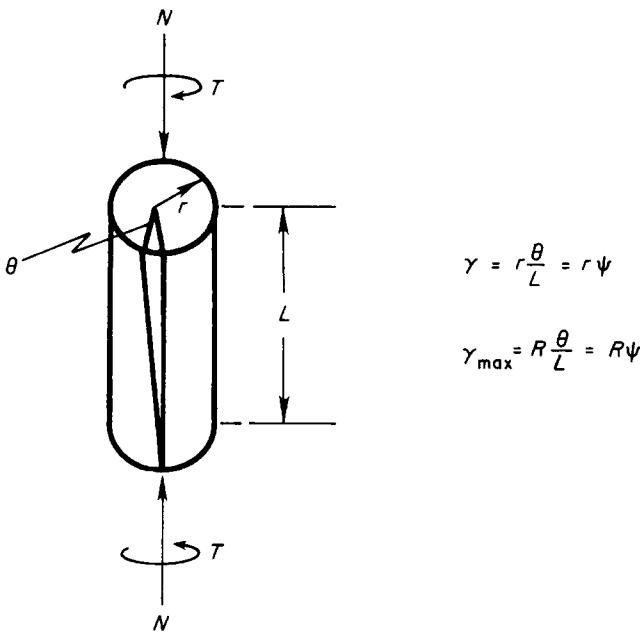


Figure 1 Geometry for a cylinder subjected to a torsional deformation

where ψ is the angle of twist per unit length and R is the radius of the cylinder.

Penn and Kearsley⁹ have shown that W_1 and W_2 can be obtained from torque and normal force measurements at different twists:

$$W_1 + W_2 = \frac{1}{4\pi\psi R^4} \left[3T + \psi \frac{dT}{d\psi} \right] \quad (3)$$

$$W_1 + 2W_2 = \frac{-1}{\pi\psi^2 R^4} \left[N + \psi^2 \frac{dN}{d(\psi^2)} \right] \quad (4)$$

Equations (3) and (4) can be solved simultaneously for W_1 and W_2 .

The Valanis-Landel strain energy function

Valanis and Landel (V-L)⁷ have introduced a constitutive equation for incompressible rubbers based upon the hypothesis that the strain energy density function can be represented as a separable function in the principal stretches, λ_1 , λ_2 and λ_3 , rather than in terms of the invariants of the stretch tensor, I_1 and I_2 , i.e.

$$W(I_1, I_2) = \hat{w}(\lambda_1, \lambda_2, \lambda_3) \\ = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) + \alpha \ln(\lambda_1 \lambda_2 \lambda_3) \quad (5)$$

where α is an arbitrary constant, and the principal stress differences are then represented as:

$$\sigma_{ii} - \sigma_{jj} = \lambda_i w'(\lambda_i) - \lambda_j w'(\lambda_j) \quad (6)$$

where $w'(\lambda_i) = \partial w / \partial \lambda_i$.

Rivlin and Sawyers¹⁰ have discussed the general relationships between $W(I_1, I_2)$ and $w(\lambda)$ and Kearsley and Zapas¹¹ have solved for the relationship between $w'(\lambda)$ and W_1 and W_2 in several deformations. In torsion the relationship is:

$$w'(\lambda) - \frac{w'(1)}{\lambda} = \frac{2}{\lambda} (\lambda^2 - 1) \left(W_1 + \frac{1}{\lambda} W_2 \right) \quad (7)$$

where $w'(\lambda) - w'(1)/\lambda$ is evaluated for values of $\lambda > 1$ from the torsional data with:

$$\lambda_{\max} = \frac{1}{2} [(\psi^2 R^2 + 4)^{1/2} + \psi R] \quad (8)$$

and for values of $\lambda < 1$ with:

$$\lambda_{\min} = \frac{1}{2} [(\psi^2 R^2 + 4)^{1/2} - \psi R] \quad (9)$$

and the range of values for which $w'(\lambda) - w'(1)/\lambda$ is evaluated is $\lambda_{\min} \leq \lambda \leq \lambda_{\max}$. Due to experimental difficulties such as elastic buckling, one cannot carry out experiments to the same equivalent stretch ratios in torsion as in extension or in compression (equibiaxial extension). However, the above equations permit a simple, accurate method of determining the V-L function for rubber over a reasonable range of λ .

Flory's junction constraint model

In his junction constraint model of rubber elasticity Flory¹⁻⁶ derives a Valanis-Landel⁷ form of strain energy function from molecular considerations. In Flory's model $\hat{w}(\lambda_1, \lambda_2, \lambda_3)$ is given as:

$$\hat{w}(\lambda_1, \lambda_2, \lambda_3) = \Delta A_{el} = \Delta A_{ph} + \Delta A_c \quad (10)$$

where ΔA_{el} is the total stored elastic energy of the network, ΔA_{ph} is the phantom network contribution to the stored energy and ΔA_c is the stored energy due to constraints on the fluctuations of the network junctions. The terms ΔA_{ph} and ΔA_c are given as:

$$\Delta A_{ph} = \frac{\xi k T}{2} \left[\sum_{i=1}^3 (\lambda_i^2 - 1) \right] \quad (11)$$

$$\Delta A_c = \frac{\mu k T}{2} \sum_{i=1}^3 \{ (1 + g_i) B_i - \ln[(B_i + 1)(g_i B_i + 1)] \} \quad (12)$$

where ξ is the cycle rank of the network, μ is the number of junctions, k is the Boltzmann constant and T is the absolute temperature. The B_i and g_i are given as:

$$B_i = (\lambda_i - 1) [1 + \lambda_i - \zeta \lambda_i^2] (1 + g_i)^{-2} \quad (13)$$

$$g_i = \lambda_i^2 [\kappa^{-1} + \zeta (\lambda_i - 1)] \quad (14)$$

ζ is a parameter defining the amount by which the probability function for junction displacement departs from the affine and κ measures the severity of the junction constraints due to neighbouring chains.

From the above it is clear that ΔA_{el} is of the Valanis-Landel form (i.e. separable in the λ_i 's) with $a=0$ and we can determine the V-L function for the junction constraint model simply by taking $\partial \Delta A_{el} / \partial \lambda_i$:

$$\frac{\partial \Delta A_{el}}{\partial \lambda} = w'(\lambda) = \xi k T \lambda + \frac{\mu k T}{2} \left\{ \dot{B}(1 + g) + \dot{g} B \right. \\ \left. - \frac{\dot{B}}{(B + 1)} - \frac{(g \dot{B} + B \dot{g})}{g B + 1} \right\} \\ = \xi k T \lambda + \frac{\mu k T}{2} \hat{F}(\lambda) = PH\lambda + AC[\hat{F}(\lambda)] \quad (15)$$

where we have dropped the subscript i for simplicity, we

introduce $\hat{F}(\lambda)$ for the term in $\{ \}$, we introduce $PH = \zeta kT$ and $AC = \mu kT/2$ as parameter names and where

$$\dot{B} = \partial B / \partial \lambda = \frac{2\lambda(1 + \zeta) - 3\zeta\lambda^2}{(1 + g)^2} - \frac{2(\lambda - 1)[1 + \lambda - \zeta\lambda^2]\dot{g}}{(1 + g)^3} \quad (16)$$

$$\dot{g} = 2\lambda(\kappa^{-1} - \zeta) + 3\zeta\lambda^2 \quad (17)$$

In order to compare the Flory model with the experimentally determined V-L function (see equation (7)) we note that when $\lambda = 1$

$$\hat{F}(\lambda) = 0 \quad (18)$$

$$\left. \frac{\partial \Delta A_{el}}{\partial \lambda} \right|_{\lambda=1} = w'(1) = \zeta kT = PH \quad (19)$$

then combining equations (19), (18) and (15) we have

$$w'(\lambda) - \frac{w'(1)}{\lambda} = \zeta kT \left(\lambda - \frac{1}{\lambda} \right) + \frac{\mu kT}{2} \hat{F}(\lambda) = PH(\lambda - 1/\lambda) + AC[\hat{F}(\lambda)] \quad (20)$$

where the values for $w'(\lambda) - w'(1)/\lambda$ are determined from the experimental torque and normal force data using equations (3), (4) and (7)–(9).

The junction constraint model of Flory¹ does not make any *a priori* predictions about the parameters κ and ζ , although for networks of a given functionality ϕ , κ is predicted to vary as the square root of the molecular weight between crosslinks¹³. In this work we use κ and ζ as fitting parameters.

Swelling

The equilibrium swelling behaviour of the networks can be analysed in the context of both the Valanis-Landel function and the junction constraint model of Flory^{1-6,13-15}. In both cases it is assumed that there are two contributions to the chemical potential of the diluent in a swollen network; one due to mixing and the other due to the elastic response of the network. Expressed as the difference from the chemical potential, μ_1^0 , of the pure solvent this can be expressed as:

$$(\mu_1 - \mu_1^0) = (\mu_1 - \mu_1^0)_{mix} + (\mu_1 - \mu_1^0)_{el} \quad (21)$$

where

$$(\mu_1 - \mu_1^0)_{mix} = RT[\ln(1 - v_2) + v_2 + \chi v_2^2] \quad (22)$$

$$(\mu_1 - \mu_1^0)_{el} = \frac{\bar{V}_1}{3V^{2/3}V_0^{1/3}} \sum_{i=1}^3 \hat{w}'_i(\lambda_1, \lambda_2, \lambda_3) \quad (23)$$

where R is the gas constant, v_2 is the volume fraction of polymer in the swollen network, χ is the Flory-Huggins interaction parameter, \bar{V}_1 is the molar volume of the solvent, V_0 is the volume of the unswollen rubber (reference volume), V is the total volume, and $\hat{w}'_i(\lambda_1, \lambda_2, \lambda_3)$ is the V-L function or $\partial A_{el} / \partial \lambda_i$ for the Flory model defined above (see equation (15) and preceding discussion).

In a swelling equilibrium, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$, $V = \lambda^3 V_0$ and

the left hand side of equation (21) is zero. Then we can write:

$$RT[\ln(1 - v_2) + v_2 + \chi v_2^2] + \frac{\bar{V}_1}{\lambda^2 V_0} \hat{w}'(\lambda_1, \lambda_2, \lambda_3) = 0 \quad (24)$$

Equation (24) will be used in discussing the relationship between the results from mechanical testing which are used to find $w'(\lambda)$ and the swelling results.

EXPERIMENTAL PROCEDURES

Network synthesis and characterization

Endlinked polybutadiene networks were prepared using a procedure developed by Rubio¹⁶. The crosslinking agent, triphenylmethane 4,4',4''-triisocyanate, was isolated from Desmondur R (Mobay Chemical Co)* by precipitation of some components with n-pentane followed by solvent stripping and two vacuum distillations to give a pale yellow waxy solid. The hydroxyl-terminated rubbers, Telegen HT-2000 and HT-5000 (General Tire Co.)* were dried *in vacuo* at 120°C for 24 h.

The molecular weights of the liquid rubber prepolymers were determined by size exclusion chromatography in 2-butanone. Peak elution volumes were converted to molecular weights using measured intrinsic viscosities and a 'universal' calibration curve¹⁷ constructed from data on monodisperse polystyrene standards (Pressure Chemical Co)*. Average hydroxyl functionalities were calculated from the g.p.c. molecular weight and the hydroxyl content, which was determined by titration according to ASTM-D 2849.

The crosslinking procedure was as follows: approximately 2 g of the triisocyanate were transferred to a weighed vial in a glove bag. The stoichiometric amount of rubber was weighed into a beaker and placed in the glove bag along with a mechanical stirrer. The triisocyanate was dissolved in several millilitres of tetrahydrofuran and 0.001% dibutyltin dilaurate and added to the stirred rubber. After 15 min stirring the viscosity of the mixture had increased noticeably and the solution was poured into cylindrical Teflon (Dupont)* moulds. Curing was completed in an oven swept with dry nitrogen in which the temperature was gradually raised to 110°C and held for 24 h. After preparation the samples were stored at -20°C and protected from light.

The amount of crosslinker added had been adjusted to correspond to the prepolymer number-average molecular weights, which turned out to be low, presumably due to the presence of small nonfunctional molecules. Therefore, both networks as formed contained excess of unreacted isocyanate groups. Moisture can react with these groups to form amines and/or urea linkages, and in fact after the mechanical testing, no residual isocyanate could be detected by infra-red spectroscopy. Each urea linkage formed would decrease the number of crosslink nodes by one. Thus, in a network with an isocyanate:hydroxyl ratio r , a fraction $r-1$ of the isocyanate groups could potentially enter into post curing reactions, raising the

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

number-average crosslink functionality from $3/r$ to a maximum of $f_n = 6/(3-r)$.

Sol fractions, determined by repeated extraction with benzene, were 0.020 for the network prepared from the lower molecular weight polybutadiene and 0.028 for that prepared from the higher molecular weight polybutadiene.

The equilibrium swelling was determined at 22°C in benzene using the method of weight and volume additivity given that $\rho_{\text{rubber}} = 0.928 \text{ g cm}^{-3}$ and $\rho_{\text{benzene}} = 0.879 \text{ g cm}^{-3}$. In Table 1 the characteristics of the prepolymers and crosslinked networks are given. Also given are the values of χ , the Flory-Huggins interaction parameters, for the polybutadiene-benzene system for each network based on the concentration of rubber, v_2 , in each swollen network using the χ values reported by Jessup¹⁸.

Mechanical testing

The cylindrical samples were machined to final dimensions ($\sim 1.25 \times 1.25 \text{ cm}$ cylinders) by adhesively bonding to a lathe fixture and removing material using a high speed grinding wheel. Fixturing was developed¹⁹ so that the specimens could be machined in the lathe and bonded to fixtures which were suitable for mounting in the testing machine. The procedure ensured that the specimen ends would be flat and perpendicular to the cylinder sides. In addition it provided a ready method of centering the specimens in the testing fixtures. A cyanoacrylate adhesive was used for bonding the samples to fixtures.

The torsional tests were carried out using a Rheometrics Mechanical Spectrometer (RMS)*. Single step torsional deformation histories were applied to the samples and the torque and normal force responses were recorded continuously with time. The tests were performed by deforming the samples to a given twist ψ_1 for 2 min and returned to zero deformation for a minimum of 4 min during which time the torque and normal force relaxed back to zero. A deformation of $-\psi_2$ ($\psi_2 \geq \psi_1$) was then applied for 2 min and the sample

again returned to zero for 4 min. This procedure was followed until the maximum deformation (or failure) was obtained. The samples showed very little time dependence in their responses ($d \log T / d \log t < 0.02$ and $d \log N / d \log t < 0.02$) and in fact the small amount of drift of the test machine became important at times greater than 200 s. All data are therefore reported only from 1 min isochrones.

The angles of twist applied to the samples ranged from 0.013 rad to 1.17 rad. The sample deformations corresponding to these twists varied with the exact sample geometry. The range of deformations was from approximately $\gamma = \psi R = 0.006$ to $\gamma = \psi R = 0.51$. (This corresponds to $I_1 = I_2 = 3.000036$ to $I_1 = I_2 = 3.2601$.) All tests were performed at $23.5 \pm 1^\circ \text{C}$.

RESULTS AND DISCUSSION

In Figures 2 and 3 reduced torque and reduced normal force vs. deformation, ψR , are plotted for polybutadiene samples PB-L3 and PB-H3. Sample PB-L3 shows a linear dependence of torque on deformation to deformations of approximately 0.15. Similarly the normal force varies as $(\psi R)^2$ to deformations of approximately 0.25. Sample PB-H3 shows similar dependences to values of $\psi R = 0.36$, the last deformation attained prior to sample failure. Interestingly, the sample PB-L3 failed at a larger deformation ($\psi R \approx 0.50$) than did sample PB-H3, which had a higher molecular weight between crosslinks.

The data of Figures 2 and 3 were used to determine W_1 and W_2 for both samples as functions of deformation from equations (3) and (4). The values are tabulated in Table 2. Interestingly, for the sample having the highest molecular weight between crosslinks, i.e. PB-H3, both W_1 and W_2 are constants, independent of deformation. However, for PB-L3, W_1 and W_2 decrease with increasing deformation above $\psi R \approx 0.15$.

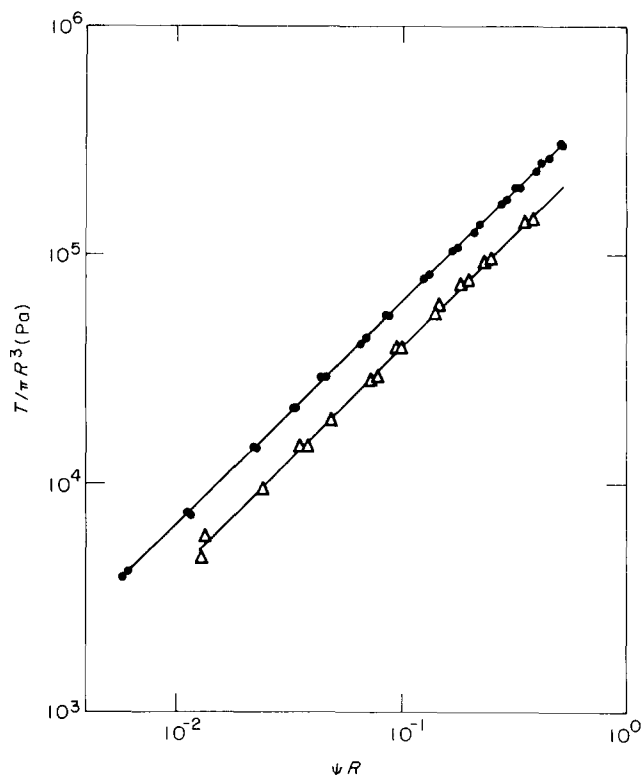


Figure 2 Torque (as $T/\pi R^3$) vs. ψR for polybutadiene networks (●) PB-L3, (△) PB-H3

Table 1 Prepolymer and network characteristics for polybutadiene rubbers

	PB-H3	PB-L3
Prepolymer		
M^a	6.1×10^3	2.4×10^3
Functionality ^b	2.1	1.9
Cis:trans:vinyl ^c	31:41:27	20:38:42
Network		
Equilibrium swelling in benzene, V/V_0^d	3.82 ± 0.12	3.09 ± 0.22
Sol fraction ^e	0.028	0.020
Maximum number-average crosslink functionality ^f	4.05	3.61
χ^g	0.283	0.290
Approximate M_c from swelling ^h	1850	1124

^a By g.p.c.; see text

^b Molecular weight/equivalent weight

^c From infra-red spectroscopy

^d Assuming volume and weight additivity

^e By benzene extraction

^f See text

^g $\chi = 0.27 + 0.06 v_2$ (ref. 18)

^h $M_c = \frac{[v_2^{1/3} - (1 - 1/\phi)]\rho \bar{V}_1}{-\ln(1 - v_2) + v_2 + \chi v_2^2}$

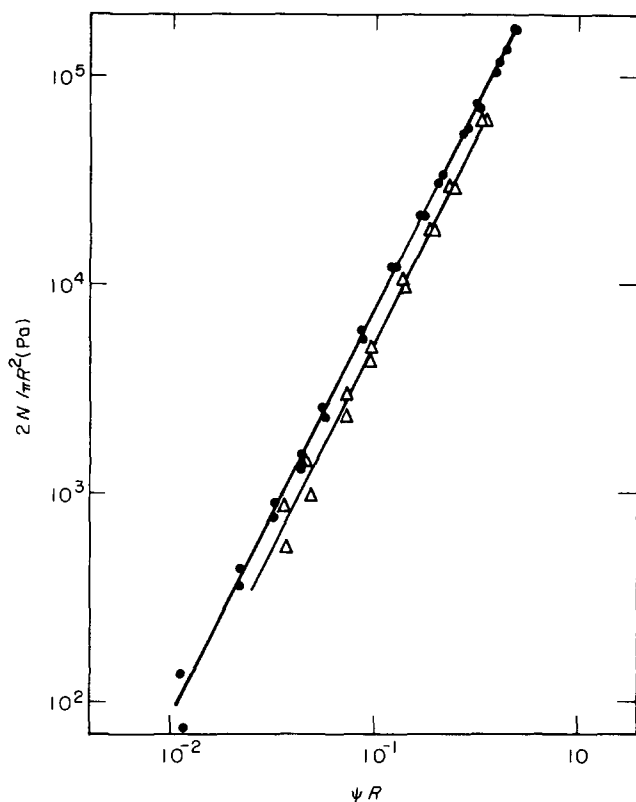


Figure 3 Normal force (as $2N/\pi R^2$) vs. ψR for polybutadiene networks (●) PB-L3, (△) PB-H3

Table 2 Values of the derivatives of the strain energy density function, $W_1 = \partial W/\partial I_1$ and $W_2 = \partial W/\partial I_2$ for model polybutadiene networks

Sample	ψR	W_1 (kPa)	W_2 (kPa)	$G/2 = W_1 + W_2$ (kPa)
PB-L3	0.01	540	112	652
	0.02	540	112	652
	0.04	540	112	652
	0.06	540	112	652
	0.08	538	113	651
	0.10	535	115	650
	0.15	524	116	640
	0.20	517	117	634
	0.30	505	103	608
	0.40	500	91	591
0.50	494	80	574	
PB-H3	0.0129	277	125	402
	to 0.355	277	125	402

Before passing on to the next section, we note several things about the data of Table 2. First, as we have found previously¹⁹ with a peroxide crosslinked natural rubber, the shear modulus $(W_1 + W_2) = G/2$ increases with increasing crosslinking, W_1 increases with increasing crosslinking but W_2 is relatively insensitive to degree of crosslinking. Furthermore, we find that W_2 does not become negative even at very small deformations, contrary to some results reported previously for natural rubber^{11,20,22} and butyl rubber²³.

Determination of $w'(\lambda)$

From equations (7), (8) and (9) and the data of Table 2 it is possible to obtain values of $w'(\lambda) - w'(1)/\lambda$ for both model networks at different values of λ_{max} and λ_{min} . These values are tabulated in Table 3.

Comparison of the junction constraint model with the experimental results

In Figures 4 and 5 $w'(\lambda) - w'(1)/\lambda$ for the PB-H3 and PB-L3 networks as determined from torque and normal force measurements are depicted. The points represent the experimental data and the lines represent non-linear least squares fits^{24,25} to equation (20) allowing all parameters to be fitting parameters. As can be seen the values for $PH = \xi kT/V_0$ and $AC = \mu kT/2V_0$ are not in very good agreement with values expected from the network chemistry (see Table 4, fitting procedure (1)). Furthermore, the values of κ and ζ are not very 'physical' in that Flory expects values of $\kappa \sim 10$ and $\zeta \sim 0.05$ (see refs. 4 and 5).

Due to the versatility of equation (20), non-ideality of the networks, and the potential for reinforcement of the elastomer and urethane-urea blocks, we carried out the statistical analysis in several other ways. In what we call fitting procedure (2) we set PH and AC to the values assumed from the network chemistry as given in Table 2 and allowed κ and ζ to be the fitting parameters. Although the fits to the data were reasonable, for both networks κ is negative and ζ was surprisingly large.

For fitting procedure (3), we set $AC = 0.488 PH$ for PB-L3 and $AC = 0.621 PH$ for PB-H3. (This assumes ideal networks but with functionalities corresponding to the maximum values calculated as described in the Experimental section.) Thus there were three fitting parameters PH , κ and ζ . In these instances we obtained good curve fits (see Figures 6 and 7). As can be seen in Table 4, the parameters obtained for the PB-L3 network using procedure (3) are similar to those obtained using fitting procedure (2), i.e. κ is negative, $\zeta \sim 0.2$ and the values for PH and AC are within 5% of the theoretical values based on the network chemistry. On the other hand, the values of PH and AC for the PB-H3 network are approximately 3.5 times those calculated from the network chemistry. Also the value of $\zeta = 0.380$ is quite high compared with the sort of value expected by Flory^{4,5} (i.e. $\zeta = 0.05$). κ on the other hand is somewhat reasonable at 2.81.

We further fit the data constraining either PH or AC to their theoretical values (procedures (4) and (5)). The results are summarized in Table 5. As can be seen for the PB-H3 network, when PH is constrained AC becomes very large and when AC is constrained PH becomes very large although the actual curve fits are not greatly affected (the residual sum of squares does not change greatly). The parameters obtained for the PB-L3 network are similar to those obtained using fitting procedures (2) and (3) where again PH and AC are in reasonable agreement with the values obtained based on the network chemistry.

For comparison, we also applied equation (20) to data for a peroxide crosslinked natural rubber of Penn and Kearsley⁹. Figure 8 shows the result for a general curve fit. In Table 6 the fitting parameters are given. Without an exact knowledge of the topology of the network the values of PH and AC are difficult to comment upon, although the relative values of PH and AC result in an effective perfect network functionality of $\phi = 3.3$. For this network, ζ is reasonable while κ is somewhat smaller than expected.

Swelling

There are two ways of treating the swelling data. First, we merely take the Flory junction constraint model for the strain energy density function and compare the free

Table 3 Values of $w'(\lambda) - w'(1)/\lambda$ for polybutadiene networks

Sample	ψR	λ_{\max}	λ_{\min}	$w'(\lambda_{\max}) - \frac{w'(1)}{\lambda_{\max}}$ (kPa)	$w'(\lambda_{\min}) - \frac{w'(1)}{\lambda_{\min}}$
PB-L3	0.0025 ^a	1.00125	0.99875	3.26	-3.27
	0.005 ^a	1.0025	0.9950	6.52	-6.54
	0.01 ^a	1.005	0.9950	13.0	-13.1
	0.02	1.010	0.990	26.0	-26.2
	0.04	1.020	0.980	51.8	-52.5
	0.06	1.030	0.970	77.5	-79.1
	0.08	1.041	0.961	102.8	-105.7
	0.10	1.051	0.951	127.8	-132.4
	0.15	1.078	0.928	187.2	-197.6
	0.20	1.105	0.905	245.1	-263.9
	0.30	1.161	0.861	348.8	-386.3
	0.40	1.220	0.820	448.9	-508.3
	0.50	1.281	0.781	542.8	-625.2
PB-H3	0.01 ^a	1.005	0.995	8.02	-8.07
	0.02	1.010	0.990	16.0	-16.2
	0.03	1.015	0.985	23.9	-24.3
	0.04	1.020	0.980	31.8	-32.6
	0.06	1.030	0.970	47.4	-49.2
	0.08	1.041	0.961	62.8	-66.0
	0.10	1.051	0.951	78.0	-83.0
	0.125	1.064	0.939	96.8	-104.7
	0.150	1.078	0.928	115.4	-126.7
	0.20	1.105	0.905	151.8	-171.8
	0.25	1.133	0.883	187.2	-218.7
	0.30	1.161	0.861	221.8	-267.3
	0.35	1.190	0.840	255.7	-317.8

^aCalculated assuming that W_1 and W_2 have the same values as at $\psi R = 0.02$

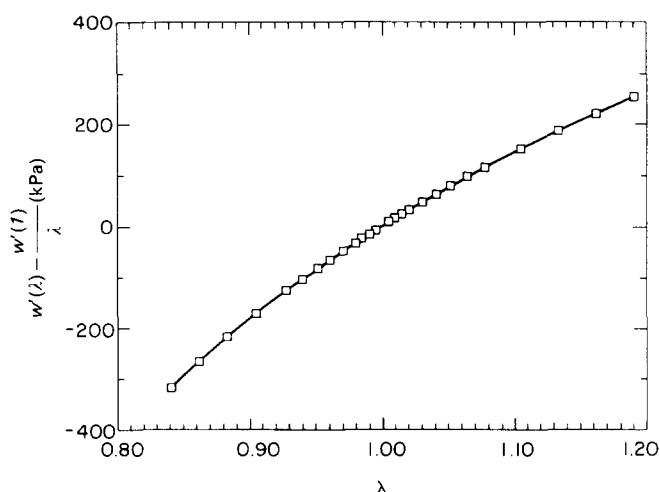


Figure 4 $w'(\lambda) - w'(1)/\lambda$ vs. λ for polybutadiene network PB-H3. (\square), experimental data; (—), general curve fit to equation (20)

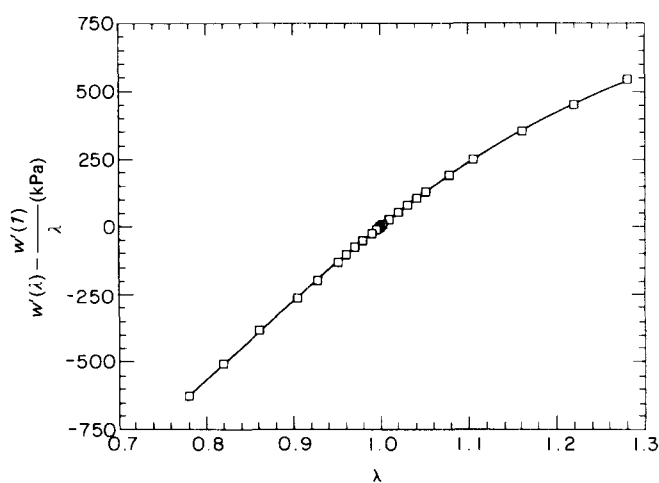


Figure 5 $w'(\lambda) - w'(1)$ vs. λ for polybutadiene network PB-L3. (\square), experimental data; (—), general curve fit to equation (20)

energy of mixing with the elastic free energy at swelling equilibrium. Then equation (24) becomes:

$$-RT[\ln(1 - v_2) + v_2 + \chi v_2^2] = \frac{\bar{V}_1}{\lambda^2} [PH\lambda + AC(\hat{F}(\lambda))] \quad (25)$$

In Table 6 we present a comparison of the left and right hand sides of equation (25) for values of $w'(\lambda)$ obtained using values of κ , ζ , PH and AC from fitting procedures (1) through (5). If the free energy of mixing and the elastic energy of the swollen network are separable they should be equal in magnitude. As can be seen in Table 6, this is not

the case. Although some of this error may be due to uncertainties in the extrapolation of $w'(\lambda)$, and in the χ parameter, the large differences are not readily accounted for and may be attributed either to (1) the lack of validity of the assumption that the free energies are simply additive or (2) the need for an explicit logarithmic term in the volume to describe the strain energy density function, as discussed below.

In the junction constraint model the effect of volume change of the swollen rubber on the strain energy density function is accounted for implicitly in the junction constraint term of equations (10) and (12). This can be seen

Table 4 Values for $PH = \zeta kT/V_0$, $AC = \mu kT/2V_0$, κ and ξ for junction constraint model determined from non-linear least square analysis for polybutadiene networks

Parameter	PH-H3	Theoretical	PB-L3	Theoretical
General curve fit (1)				
κ	1.84 ± 1.11	—	0.333 ± 1.76	—
ξ	0.056 ± 1.51	—	0.405 ± 50.2	—
PH (kPa)	533 ± 1013	190	855 ± 32000	424
AC (kPa)	628 ± 1013	92.8	$3037 \pm 1.7 \times 10^5$	264
Residual standard deviation	0.047	—	9.69	—
Constrained fit (2)				
κ	-2.81 ± 0.026	—	-6.37 ± 0.070	—
ξ	0.499 ± 0.0098	—	0.215 ± 0.004	—
PH (kPa)	190	190	424	424
AC (kPa)	92.8	92.8	264	264
Residual standard deviation	6.86	—	3.99	—
Constrained fit (3)				
κ	2.81 ± 0.037	—	-7.32 ± 0.907	—
ξ	0.380 ± 0.012	—	0.195 ± 0.017	—
PH (kPa)	662 ± 2.68	190	444.7 ± 16.4	424
AC (kPa)	323.2	92.8	287.4	264
Residual standard deviation	0.139	—	3.93	—
Constrained fit (4)				
κ	3.26 ± 0.060	—	-7.52 ± 1.075	—
ξ	-0.105 ± 0.0026	—	0.191 ± 0.020	—
PH (kPa)	190	190	424	424
AC (kPa)	738 ± 8.25	92.8	286 ± 18.2	264
Residual standard deviation	0.121	—	3.93	—
Constrained fit (5)				
κ	$4.90 \times 10^6 \pm 2.53 \times 10^{11}$	—	-7.12 ± 0.700	—
ξ	0.799 ± 0.135	—	0.201 ± 0.012	—
PH (kPa)	736 ± 10.8	190	471 ± 37.4	424
AC (kPa)	92.8	92.8	264	264
Residual standard deviation	2.01	—	6.74	—

(1) $w'(\lambda) - \frac{w'(1)}{\lambda} = PH(\lambda - 1/\lambda) + AC \hat{F}(\lambda, \zeta, \kappa)$

(2) AC and PH were both fixed to their theoretical values based upon the network chemistry

(3) $w'(\lambda) - \frac{w'(1)}{\lambda} = PH(\lambda - 1/\lambda) + \beta PH \hat{F}(\lambda, \zeta, \kappa)$ where $\beta_{PB-H3} = 0.488$ and $\beta_{PB-L3} = 0.621$

(4) $w'(\lambda) - \frac{w'(1)}{\lambda} = PH(\lambda - 1/\lambda) + AC \hat{F}(\lambda, \zeta, \kappa)$ where PH was fixed to the theoretical value for the curve fit. $PH_{PB-H3} = 190$ kPa, $PH_{PB-L3} = 424$ kPa

(5) $w'(\lambda) - \frac{w'(1)}{\lambda} = PH(\lambda - 1/\lambda) + AC \hat{F}(\lambda, \zeta, \kappa)$ where AC is fixed to the theoretical value for the curve fit. $AC_{PB-H3} = 92.8$ kPa; $AC_{PB-L3} = 264$ kPa

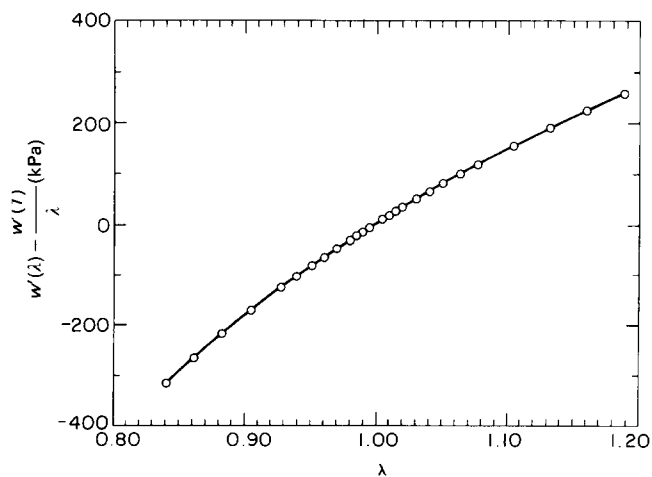


Figure 6 $w'(\lambda) - w'(1)/\lambda$ vs. λ for polybutadiene network PB-H3. (○), experimental data; (—), curve fit to equation (20) with $AC = 0.488 PH$

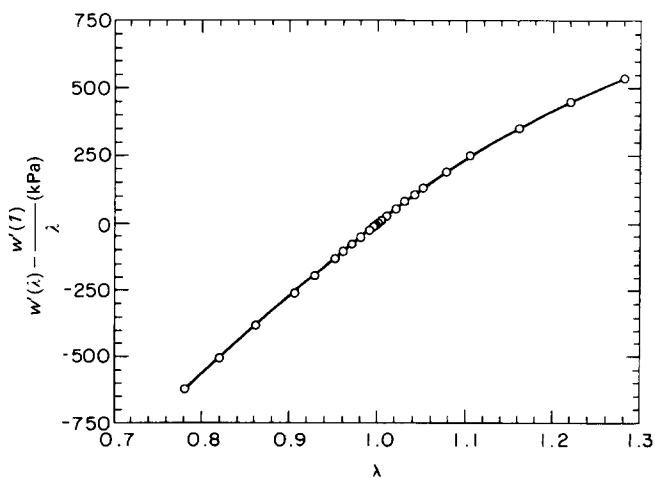


Figure 7 $w'(\lambda) - w'(1)/\lambda$ vs. λ for polybutadiene network PB-L3. (○), experimental data; (—), curve fit to equation (20) with $AC = 0.621 PH$

in the case in which $1/\kappa=0$ and $\zeta=0$ (the limit of affine deformations)^{26,27} where equation (10) becomes

$$\Delta A_{\text{affine}} = \Delta A_{\text{el}} = \frac{1}{2}\xi kT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + \frac{1}{2}\mu kT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) - \mu kT \ln \lambda_1 \lambda_2 \lambda_3 \quad (26)$$

where we note that the last term in equation (26) is a volume term which does not affect the mechanical properties at constant volume. Additionally, we note that the swelling analysis presented above is then dependent upon the specific form of the Flory junction constraint model which results in a special form (based on a molecular model) of the Valanis–Landel strain energy density function.

For the general V–L function, a swelling analysis would include the specific volume term $\alpha \ln \lambda_1 \lambda_2 \lambda_3$ in equation (5). Then, the swelling equation (24) would not change, but the parameter α appears because*:

$$\hat{w}'(\lambda_1 \lambda_2 \lambda_3) = w(\lambda) + \alpha/\lambda \quad (27)$$

Then equation (24) becomes:

$$-RT[\ln(1-v_2) + v_2 + \chi v_2^2] = \bar{V}_1/\lambda^2(w'(\lambda) + \alpha/\lambda) \quad (28)$$

Table 5 Values for PH , AC , κ and ζ for the junction constraint model for a peroxide crosslinked natural rubber sample^a determined from a general curve fit

Parameter	Value
κ	2.16 ± 3.26
ζ	0.0055 ± 1.05
PH (kPa)	310 ± 466
AC (kPa)	244 ± 289
Residual standard deviation	16.2

^aData from refs. 9 and 11

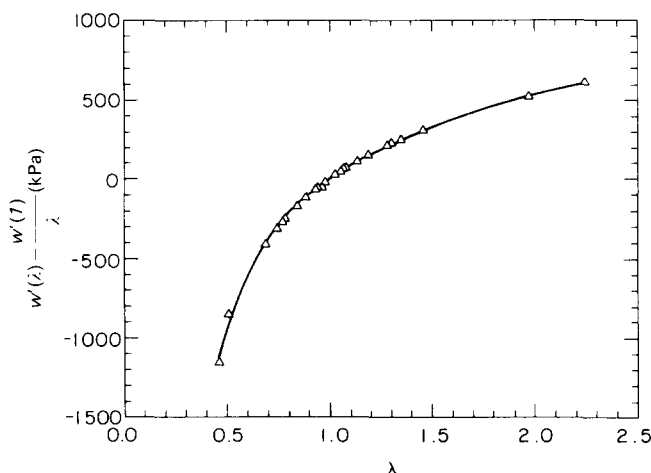


Figure 8 $w'(\lambda) - w'(1)/\lambda$ vs. λ for a peroxide crosslinked natural rubber. (Δ), experimental data (ref. 9); (—), general curve fit to equation (20)

*The $\alpha \ln(\lambda_1 \lambda_2 \lambda_3)$ term in the Valanis–Landel strain energy density function (equation (5)) is often a source of confusion in the literature when comparing V–L functions. α is an arbitrary constant which allows one to set $w'(1)=0$ without loss of generality when dealing with the mechanical properties of incompressible materials^{7,11}. A similar term appears in the strain energy density function for certain molecular theories^{12,15,26,27,28} although as noted in the text it appears only implicitly in Flory’s junction constraint model. The term can be important in dealing with swelling behaviour.

Table 6 Comparison of the free energy of mixing and elastic free energy at swelling equilibrium for polybutadiene networks swollen in benzene

Sample	Fitting procedure ^a	$(\mu - \mu_1^0)_{\text{mixing}}^b$ (J/mole)	$(\mu - \mu_1^0)_{\text{elastic}}^c$ (J/mole)	α^d (kPa)
PB-L3	(1)	-92.0	59.6	1125
	(2)	-92.0	38.1	1871
	(3)	-92.0	39.8	1812
	(4)	-92.0	39.0	1840
	(5)	-92.0	40.6	1785
PB-H3	(1)	-55.5	34.4	906
	(2)	-55.5	7.5	2062
	(3)	-55.5	38.2	743
	(4)	-55.5	27.6	1198
	(5)	-55.0	41.8	588

^a See Table 4 and text

^b $(\mu - \mu_1^0)_{\text{mixing}} = RT[\ln(1-v_2) + v_2 + \chi v_2^2]$

^c $(\mu - \mu_1^0)_{\text{elastic}} = \frac{\bar{V}_1}{\lambda^2} [PH\lambda + AC\hat{F}(\lambda)]$

^d α is the coefficient of the logarithmic term in equation (5)

If we now consider the previously determined Flory function as simply a fitting function to our data then equation (28) can be rewritten as:

$$-RT[\ln(1-v_2) + v_2 + \chi v_2^2] = \bar{V}_1/\lambda^2(PH\lambda + AC\hat{F}(\lambda) + \alpha/\lambda) \quad (29)$$

and the value of α required to fit the swelling data can be obtained from the curve fits for the Flory ‘fitting function’ and the calculated values of the left hand side of equation (29). The values of α for each of the five fitting procedures are presented in Table 6. As can be seen, independently of the fitting procedure these values are positive and greater than the magnitudes of either PH or AC obtained from the mechanical testing. We also note that they are greater than either $\partial W/\partial I_1$ or $\partial W/\partial I_2$.

In summarizing the swelling results it can be stated that the assumption that the free energy of mixing and the elastic free energy of the network at swelling equilibrium is not supported when the mechanical and swelling data are analysed within the context of the Flory junction constraint model. If however, the general Valanis–Landel function (with an explicit volume term in the strain energy function) is considered, the mechanical and swelling data presented here are consistent with the assumption of additivity of the free energies. The volume contribution to the elastic free energy is found to be significant.

Finally we note that in the Flory^{1-6,13,14} model, the form of the strain energy density function ΔA_{el} does not change upon swelling while in some other molecular theories^{15,28} this is not the case. The importance of this observation is not known at this time.

SUMMARY

Torque and normal force data from torsional experiments have been used to determine the derivatives of the strain energy density function for well characterized polybutadiene networks. These data were transformed to obtain the Valanis–Landel function $w'(\lambda)$ for the networks and were then curve fitted to the V–L function for the Flory junction constraint model for rubber elasticity. The results show that the model can be made to fit the data quite well. The values of $\xi kT/V_0$ and $\mu kT/2V_0$ for the network with the highest molecular weight

between crosslinks, determined from the curve fitting procedures, do not agree particularly well with the values calculated from the chemistry of the network. On the other hand the values of $\xi kT/V_0$ and $\mu kT/V_0$ for the network having the lowest molecular weight between crosslinks agreed reasonably well with the values calculated from the network chemistry. However, for both networks the values of κ and ζ required to fit the data were generally not very close to those expected for these parameters by Flory.

Swelling data were used to compare the free energy of mixing with the elastic free energy of the swollen chain. The results suggest that (1) the elastic energy of the chain in the junction constraint is not the same as the free energy of mixing and (2) a significant contribution to the elastic energy of the network results from the volume change.

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