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Non-Gaussian Model for Rubber Elasticity: (II) Comparison with Experiment Data for Unswollen and Swollen Rubbers

Yoshio Hoei

S&S Japan Company Ltd., 6-1-18, Hamazoe-dori, Nagata-ku, Kobe, Hyogo 653-0024, Japan

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Summary

From the non-Gaussian model that has very recently been developed in the paper (I), new stress-strain equations have been derived. They have been examined in comparison with mechanical data taken from the literature for unswollen and swollen rubbers. It is found that the model can well explain the literature data.

Introduction

In the first paper [1] two free energy terms for rubber elasticity have been derived in terms of finite chain extensibility and entanglement constraints. These terms involve the extent of suppression of junction fluctuation represented by the well-known empirical factor h [1,2] and a power law [1,3] characterized by the exponent γ that describes the strain-dependence of spatial constraints. In this work, the total free energy is applied to get stress–strain equations for dry and swollen rubber networks. The resulting equations are compared with experimental data taken from the literature for both uniaxial and biaxial deformation. Molecular information on their network-states can be provided by the two parameters.

Network Free Energy

The total network free energy per unit network volume that consists of the two free energy terms is expressed by [1]:

$$\Delta\tilde{F}_{EL,total}/RT = -\tilde{\nu}N_c \ln\left\{\frac{1-(3/2)(1/N_c)[(1-h\tilde{\mu}/\tilde{\nu})(1/3)\sum_i \lambda_i^2 + (h\tilde{\mu}/\tilde{\nu})]}{1-(3/2)(1/N_c)}\right\}$$
$$+(\tilde{\nu}-h\tilde{\mu})N_c(b^2/\langle D_0{}^2\rangle)(1/3)\,(\sum_i \lambda_i{}^{2\gamma}-3) \qquad \mathbf{(1)}$$

where R is the gas constant, $\tilde{\nu}$ is the total number of chains between adjacent crosslinks in unit network volume, $\tilde{\mu}$ is the total number of crosslinks in unit network volume, at which the number of chains f is jointed together, N_c is the number of segments per chain, b is the segment length, h is the junction suppression parameter between zero and unity, D_0 is the tube diameter in the natural network state, γ is the tube-deformation related parameter between zero and unity, λ_i is the principal deformation ratio in the i-direction. The firs term of eq. 1 is the elastic energy that has been derived from Teramoto's chain distribution function describing the effect of finite chain extensibility [1,4]. This term reduces to the classical form $(1/2)(v - h\mu)$ $(\sum\lambda_i^2 - 3)$ if expanding its logarithmic term with respect to $1/N_c$ on the assumption that N_c is very large and taking only the first term. The second term is the confinement energy calculated on the assumption that v tubes of diameter D_0 containing v equivalent chains in the tubes are deformed under the power law of exponent γ [1].

Stress–Strain Equations

First of all, the "reference volume" during the network formation is assumed to be equivalent to the volume before the application of stress. Also the network is assumed to be incompressible, so that the volume before and after the application of the stress are the same. S-S expressions for two experimental situations, uniaxial extension (or compression) and biaxial extension can be derived via the following standard thermodynamic relation for an isothermally deformed material [5, 6]

$$\sigma_i = p\prod_{k\neq j\neq i}\lambda_k\lambda_j + (\partial\Delta\widetilde{F}/\partial\lambda_i)_{T,\lambda_k,\lambda_j} \tag{2}$$

Here, p is the internal pressure, and σ_i and λ_i are the stress per unit initial area and deformation ratio along the i th-coordinate direction, respectively. Therefore, if substituting eq.1 into eq.2 and eliminating the p term of eq. 2 under the given conditions $\sigma_2 = \sigma_3 = 0$, $\lambda_2 = \lambda_3$, and $\lambda_1\lambda_2\lambda_3 = 1$, then the first case of uniaxial extension or compression can be given by

$$\sigma_1 = (\tilde{\nu} - h\tilde{\mu})RT(\lambda_1 - \lambda_1^{-2})/\Gamma_{uni} + (\tilde{\nu} - h\tilde{\mu})N_cRT(b^2/\langle D_0{}^2\rangle)(2\gamma/3)(\lambda_1^{2\gamma-1} - \lambda_1^{-\gamma-1}) \tag{3}$$

with

$$\Gamma_{uni} \equiv 1 - (3/2)(1/N_c)\left[(1 - h\tilde{\mu}/\tilde{\nu})(1/3)(\lambda_1^2 + 2\lambda_1^{-1}) + (h\tilde{\mu}/\tilde{\nu})\right] \tag{4}$$

For the second case of unequalbiaxial deformation, we can calculate in a similar way to the above case under the given conditions, $\sigma_1 \neq 0$, $\sigma_2 \neq 0$ and $\sigma_3 = 0$ and $\lambda_1\lambda_2\lambda_3 = 1$ and give the following equations

$$\begin{aligned}\sigma_1 = {} & (\tilde{\nu} - h\tilde{\mu})RT(\lambda_1 - \lambda_1{}^{-3}\lambda_2{}^{-2})/\Gamma_{bia} \\ & + (\tilde{\nu} - h\tilde{\mu})N_cRT(b^2/\langle D_0{}^2\rangle)(2\gamma/3)(\lambda_1^{2\gamma-1} - \lambda_1^{-2\gamma-1}\lambda_2{}^{-2\gamma})\end{aligned} \tag{5}$$

and

$$\begin{aligned}\sigma_2 = {} & (\tilde{\nu} - h\tilde{\mu})RT(\lambda_2 - \lambda_2^{-3}\lambda_1^{-2})/\Gamma_{bia} \\ & + (\tilde{\nu} - h\tilde{\mu})N_cRT(b^2/\langle D_0{}^2\rangle)(2\gamma/3)(\lambda_2^{2\gamma-1} - \lambda_2^{-2\gamma-1}\lambda_1^{-2\gamma})\end{aligned} \tag{6}$$

with

$$\Gamma_{bia} \equiv 1 - (3/2)(1/N_c)\left[(1 - h\tilde{\mu}/\tilde{\nu})(1/3)(\lambda_1^2 + \lambda_2^2 + \lambda_1^{-2}\lambda_2^{-2}) + (h\tilde{\mu}/\tilde{\nu})\right] \tag{7}$$

Furthermore, the small-strain (equilibrium) modulus G_0 can be obtained by using Young's modulus expression ($\partial\sigma/\partial\lambda\,|_{\varepsilon\to 0}^{\lambda=1+\varepsilon}$)

$$G_o = (\tilde{\nu} - h\tilde{\mu})RT/[1-(3/2)(1/N_c)] + (\tilde{\nu} - h\tilde{\mu})N_c RT(b^2/\langle D_0{}^2\rangle)(2\gamma^2/3) \qquad \textbf{(8)}$$

The first and second terms of eq. 3 express elastic contributions of chemical junctions (G_c) and trapped entanglements (G_e) to the network modulus G_0, respectively. That is, they are given by

$$G_c = (\tilde{\nu} - h\tilde{\mu})RT/[1-(3/2)(1/N_c)] \qquad \textbf{(9)}$$

and

$$G_e = (\tilde{\nu} - h\tilde{\mu})N_c RT(b^2/\langle D_0{}^2\rangle)(2\gamma^2/3) \qquad \textbf{(10)}$$

If N_c is large, the first terms (i.e., elastic term) in all the above equations of σ vs. λ reduce to the classical expressions (the case of $h = 0$ or 1) since the denominators 4 and 7 approach unity. For a network of smaller N_c (or larger crosslink density), the denominator becomes more effective. Since the present network consists of Teramoto chains [1,4] that do not have stipulations related to the Gaussian statistics, its application to non-Gaussian behaviors of highly crosslinked networks will also be possible. As for the second terms of the S-S equations, they are the additional stress terms due to fluctuations of a network chain within the tube (i.e., a change in "lateral wiggling" as the chain is deformed) [7]. Particularly, the form of the G_e equation (eq. 10) agrees with that of the Kaliske-Heinrich tube model [8], which is a result of deformation dependence of tube diameter. Furthermore the tube deformation parameter γ involved in the second terms of the S-S equations and the G_e equation (eq. 10) for the network can be described more specifically: namely, if $\gamma = 0$, then the network has no contribution of entanglement constraints to the mechanical properties. Thus, the second terms in S-S equations vanish and the G_e equation becomes zero. Also, if $\gamma = 1$, then the network has the maximum contribution of entanglement constraints to the mechanical properties.

Lastly, an S-S equation for simple elongation is derived which can be applied to a swollen rubber via the following thermodynamic relation [9,10]

$$\sigma = (1/A_\mathrm{d})(\partial\Delta F_{EL,SWELL}/\partial L)_{T,V,N\mathrm{o}} = (1/A_\mathrm{d}L_{id})(\partial\Delta F_{EL,SWELL}/\partial\lambda)_{T,\varphi} = (\partial\Delta\tilde{F}_{EL,SWELL}/\partial\lambda)_{T,\varphi}$$

where $\Delta F_{EL,SWELL}$ is the network free energy for a swollen rubber, A_d is the sectional area of the undeformed, dry rubber sample, $L_{id} = L/\lambda$ is the length of undeformed (isotropic) sample in the state of volume ($A_\mathrm{d}L_{id} = V_d$). Since $\Delta\tilde{F}_{EL,SWELL}$ can be given by considering $\lambda_1 = \lambda$, $\lambda_2 = \lambda_3 = (\varphi\lambda)^{-1/2}$ in eq. 1, the result becomes

$$\sigma_1 = (\tilde{\nu} - h\tilde{\mu})RT\,[(\lambda - \varphi^{-1}\lambda^{-2})/\Gamma^{\varphi}_{1,\lambda}$$
$$+ (M_\mathrm{c}/m_\mathrm{s})(\mathrm{b}^2/<D_0{}^2>)(2\gamma/3)(\lambda^{2\gamma-1} - \varphi^{-\gamma}\lambda^{-\gamma-1})] \qquad \textbf{(11)}$$

with

$$\Gamma^{\varphi}_{1,\lambda} \equiv 1 - (3/2)(m_\mathrm{s}/M_\mathrm{c})[(1 - h\tilde{\mu}/\tilde{\nu})(1/3)(\lambda^2 + 2\varphi^{-1}\lambda^{-1}) + h\tilde{\mu}/\tilde{\nu}] \qquad \textbf{(12)}$$

where $N_c = M_c/m_\mathrm{s}$ and M_c and m_s are the network and segment molecular weights, respectively. Needless to say, at $\varphi = 1$ eq. 11 becomes equal to eq. 3. Also, since the "reduced stress" $[\sigma^*]$ that is a measure of the modulus of the swollen rubber [6] can be given by $[\sigma^*] = \sigma/(\lambda - \varphi^{-1}\lambda^{-2})$ using eq. 11, one can analyze S-S data in the Mooney-Rivlin (MR) representation of $[\sigma^*]$ vs. $1/\lambda$ [5,6].

Results and Discussion

First, as a test of the model, we have fit eqs. 5 and 6 to experimental data taken from the report of Urayama et al.(UKK) [11] on well-characterized end-linked PDMS networks. They have provided full network structure information: $M_c = 8.25\times10^4$ g/mol; $\tilde{\nu} = 3.22$ mol/m^3; $\tilde{\mu} = 2.04$ mol/m^3; $f = 3.16$; $G_0 = 6.49\times10^4$ Pa. In Figures 1A and 1B are show their multiaxial deformation isotherms. The solid lines are the best fits of eqs. 5 and 6, respectively, depicted by setting $h = 0$ (this is reasoned later) and assigning values of γ as $\gamma = 0.74$ and 0.76. The other basic parameter values were assigned: $D_0 \approx 35$ Å for uncrosslinked PDMS [12], $b = 11.4$ Å (a repeating unit size = ca. 1.9 Å [13]; the number of repeating units per segment = 6), and $m_s = 445$ g/mol. It should be noted that the repeating unit size corresponds to a half spacing between the neighboring methyl groups in the trans conformation that is most probably taken in the real system [13]. UKK concluded that the fitting situation of the Edwards-Vilgis (EV) model [14] was much more successful than those for the other models that they tested. The best fits of the EV model to the data gave $h \approx 0$ (representing the junction-affine network). This result is consistent to the fact that the theoretical modulus ratio (G_e/G_c) estimated by the EV model was as low as 7.0. This value is very close to the minimum in the admissible range $6.7 \leq G_e/G_c \leq 20$ for the end-linked PDMS [11], where the minimum and maximum correspond to the extreme cases for $h = 0$ and 1, respectively [11]. Therefore, we have also adopted $h = 0$. Under the condition of $h = 0$, the calculated modulus ratios were found to be $G_e/G_c = 7.1$ and 7.5 for the theoretical (solid) lines of Figures 1A and 1B, respectively. Also, these two ratios are both accompanied by the calculated value for the small-strain modulus $G_0 = G_c + G_e =$ *ca.* 0.7 MPa. Thus these results are comparable to those estimated by UKK using the EV model. The difference between the calculated equilibrium modulus and UKK's experimental value ($G_0 = 0.649$ MPa) is not big in that the percentage deviation between them is less than *ca.*11 %. From the above results, our model as well as the EV model shows quantitatively that the end-linked PDMS under consideration is obviously an entanglement-dominated system so that both the two models may be said to have almost the same ability.

In addition, using UKK's uniaxial extension and compression data [11]for the same PDMS samples as in the above unequalbiaxial case, we have compared the data to eq. 3. This is shown in Fig. 2. The solid line in the figure represents the best-fit curve for $h = 0$ and $\gamma = 0.72$ and the other basic parameter conditions are the same as in the unequalbiaxial case. The γ value is only slightly different from the unequalbiaxial case. This confirms that the present model can show satisfactory agreement of experiment and theory also in the uniaxial case.

Next, we have fit eq. 11 to the Flory and Tatara (FT) data [9] for uniaxial extension for swollen (randomly crosslinked) PDMS samples including the unswollen sample (designated Sample C) [9]. First, as a basic parameter, the network molecular weight M_c of the sample C was estimated as follows: in the FT work, the so called C_1 term that corresponds to that of the Mooney- Rivlin equation [i.e., $\sigma = C_1(\lambda - \lambda^{-2}) + C_2(1 - \lambda^{-3})$] was determined for sample C as $C_1 = 0.107$ MPa. Therefore this C_1 value may be regarded as either the corresponding factor for the affine (Gaussian) network model

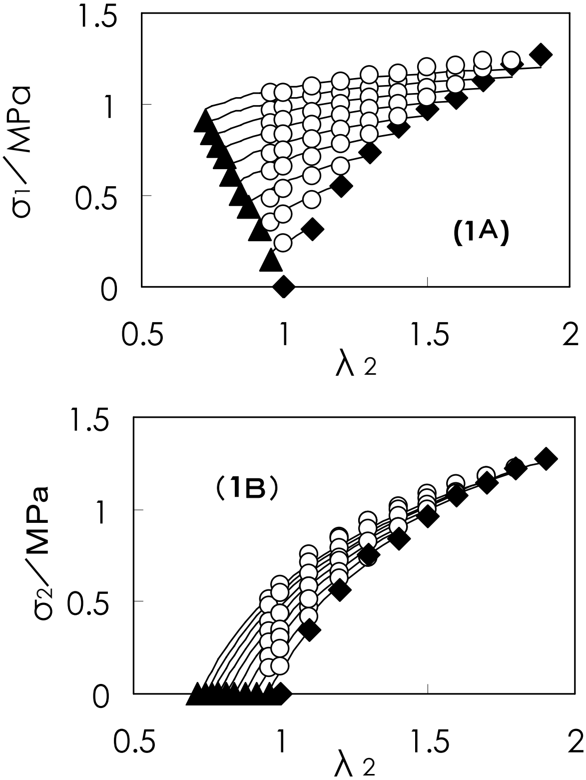

Figure 1. Comparison of the theoretical curves of σ $_i$ vs. λ_2 (at same λ_1; λ_1=1, 1.1, 1.2,…, 1.9), calculated using eqs. 5 and 6, with experimental data for end-linked PDMS. Points are data from Urayama et al. [11] and lines are model calculations.

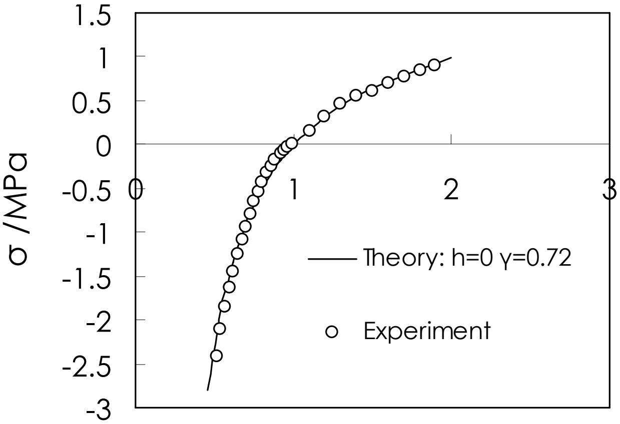

Figure 2. Compression of the theoretical curve of σ vs. λ, calculated using eq. 3 to uniaxial extension-compression data for end-linked PDMS. Points are data from Urayama et al. [11] and the line is model calculation.

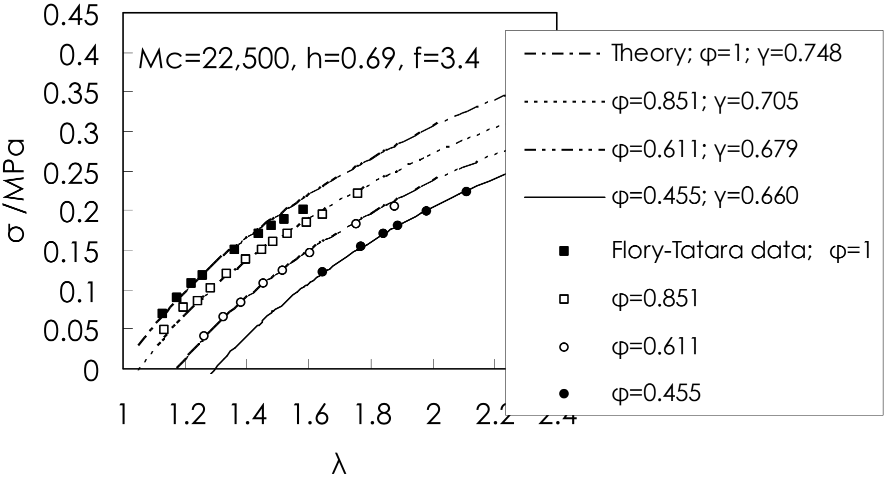

Figure 3. Comparison of the theoretical curves of σ_1 vs. λ, calculated using eq. 11, with experimental data for randomly crosslinked PDMS. Points are data from Flory and Tatara [9] for different volume fractions of rubber φ, and lines are model calculations.

(i.e., $\tilde{\nu} RT \approx dRT/M_c$ where d is polymer density) or that for the phantom network model (i.e., $\tilde{\nu} RT/2 \approx dRT/2M_c$) [6]. Therefore, two extreme values for M_c were obtained as $M_c = 22{,}500$ from the former relation and as $M_c = 11{,}250$ from the latter. We thus considered the two cases of M_c for the present work. Values of the other related parameters, $\tilde{\mu}$, h, $b^2/\langle D_o^2\rangle$ and m_s, were assigned: namely, for the h, $b^2/\langle D_o^2\rangle$ and m_s, we took the same values as earlier employed for end-linked PDMS network. As to the $\tilde{\mu}$, since the model assumes a perfect network, its value can be calculated via the network-topological relation $\tilde{\mu} = 2\tilde{\nu}/f$ [1,6]. As a value of f for the PDMS, we have used $f = ca.\ 3.4$ that is the middle value of $f = 3.2$—3.6 taken from the literature data [15]. We also took $h = 0.69$ from the same literature where it was determined together with the f value range for the same type PDMS. Employing all the known parameter values, we first depicted theoretical curves of σ vs. λ adjusting values of γ so as to fit eq. 11 to the reproduced F-T data points for the unswollen and swollen samples and found the best-fit curves for the samples. In Fig. 3 are shown typical plots of σ vs. λ for the case of $M_c = 22{,}500$. In the figure the F-T data points for the samples at $\varphi = 1$, $\varphi = 0.851$, $\varphi = 0.611$, and $\varphi = 0.455$ are indicated by black squares, white squares, white circles, and black circles, respectively, and the corresponding best-fitted theoretical curves are represented by dash-dot, dotted, dash-double dot, and solid lines, respectively. In this case, the best-fitted values of γ were respectively determined to be 0.748, 0.705, 0.679, and 0.660, as described in the Appendix. In Fig. 4 we show the corresponding situations in the MR representation of $[\sigma^*]$ vs. $1/\lambda$, calculated using eq. 11 under the same parameter conditions as in the above case of σ vs. λ.

Obviously the MR representation is found to be more sensitive [16], but the deviations of theory from experiment are very small within ca.±7 % (see the Appendix) so that the fits are very good. Also, the above results of γ show that it will decrease an increase in dilution. This supports the assumption of Allen et al [17] that the number of entanglements contributable to stress is reduced in the presence of solvent, which is present in addition to the fixed chemical junctions.

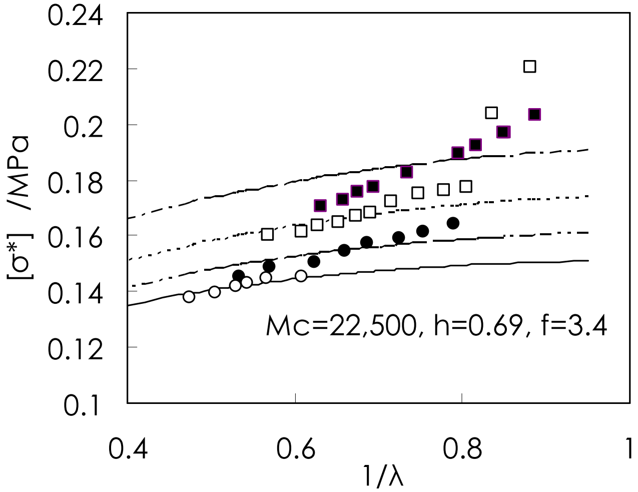

Figure 4. Comparison of the theoretical curves of [σ^*] vs. 1/λ with experimental data for randomly crosslinked PDMS. Points are data from Flory and Tatara [9] for different volume fractions of rubber φ, and lines are model calculations.

From the analytical results presented here, we conclude that the present model will be useful in order to describe network molecular situations for unswollen and swollen rubbers.

Appendix. Rating of deviation of theory from experiment

The best-fitted γ-values for σ vs. λ data were determined when the deviation of theory from experiment became approximately minimum by using the relation $[(\sigma_{obs} - \sigma_{calc})/\sigma_{obs}] \times 100\ \%$ where σ_{obs} and σ_{calc} are experimental and theoretical σ-values at the same value of λ, respectively. The determined results are shown in Table 1. Also the parentheses attached for the φ = 0.851 network mean excluding the two data points in the small region of λ. This exclusion is because only the two depart remarkably from the theoretical curve (indicated by a dotted line), as seen in Fig. 4, and seem to be very difficult to be observed in the considerably small region of λ.

Table 1. Best-fitted γ-value and deviations for randomly crosslinked PDMS[1)]

Sample C	M_c = 11,250 case		M_c = 22,500 case	
φ = 1	0.494	±7.4 %	0.748	±6.6 %
φ = 0.851	0.420	(±4.6 %)	0.705	(±3.0 %)
φ = 0.611	0.318	±5.7 %	0.679	±3.3 %
φ = 0.455	0.115	±3.3 %	0.660	±1.1 %

[1)] Calculated for h = 0.69 and f = 3.4 taken from the Flory-Tatara data.

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