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CONSTRUCTION OF MECHANICAL MODEL FOR SWELLING-DEFORMATION BEHAVIOR OF ELASTOMERIC GEL

I. RIKU and K. MIMURA

Department of Mechanical Engineering, Osaka Prefecture University
1-1, Gakuen-cho, Naka-ku, Sakai City, Osaka 599-8231, Japan

ABSTRACT

Elastomeric gels are soft-elastic materials consisting of a three-dimensional crosslinked polymer network and liquid filling the space between this network. To take advantage of the swelling-deformation behavior of elastomeric gel and explore its possibility for applications in engineering as a structural member, the construction of its mechanical model is indispensable. Therefore, in this study, two different nonaffine models are proposed for the elastomeric gel to account for the change of the entangling structure of polymer chains during the swelling-deformation process, in which the change of the number of polymer chains per unit volume N is depending on the first invariant of right Cauchy-Green tensor I_1 , or on the volume ratio of the gel J , separately. It is found that the dependency of the entangling structure of polymer chains on I_1 and that on J has quite different effect on the swelling-deformation responses of the gel. Moreover, such effects become remarkable in the solvent of its liquid phase compared with the solvent of its gas phase. Finally, the necessity and the availability of the proposed nonaffine models are discussed based on some experimental data of dry and swollen rubbers. It is also found that, by using weighting factors, the proposed models can reproduce the experimental data very well.

INTRODUCTION

The elastomeric gels, consisting of crosslinked polymer molecules and discrete solvent molecules, have a high permeability to small molecules and undergo reversible volume change by exuding or absorbing solvent in response to a wide range of stimuli, such as light, temperature, pH, ionic strength and chemical reactions. As a result, the gel has been developed for diverse applications and used as smart materials in sensors and actuators¹⁻³.

The elastomeric gels are synthesized by crosslinking polymer chains dissolved in a solvent. The developed three-dimensional crosslinked polymers eventually percolate the whole solution and change the system from a fluid sol to a solid gel^{4,5}. Because the polymer chains continually fluctuate in the solution, the crosslinking reaction tends to result in a complicated network with substantial defects, including dangling ends, loops, entanglements, and nonuniform crosslinker distribution⁶. To account for the effect of such defects on the mechanical behavior of gel, in our former study⁷, we investigated the development of the microstructure of polymer network of gel based on a nonaffine polymer chains network model^{8,9}, which was originally developed for the orientation hardening of amorphous polymers and may account for the change in the entanglement situation for the physical linkages during the deformation processes. It was found that the free swelling

process may lead to a larger change of the entangling structure of polymer chains compared with the simple tensional process. Moreover, the various combination of the effect of each process on the nonaffine movement of polymer chains may lead to such interesting mechanical response of the gel as yield.

On the other hand, the elastomeric gel can undergo large deformation of two modes in a solution. The first mode results from the fast process of short-range rearrangement of molecules, allowing the gel to change shape but not volume. The second mode results from the slow process of long-range migration of the solvent molecules, allowing the gel to change both shape and volume. Therefore, at the first mode, the gel deforms corresponding to the mechanical constraints only; at the second mode, the gel deforms corresponding to the mechanical constraints together with the chemical process. To characterize how mechanical constraint affects the amount of swelling and how chemical processes generate forces, Flory and Rehner proposed a statistical mechanical model¹⁰ for the network of polymer molecules and indicated that the swelling capacity of the gel is diminished by the application of an external stress. Recently, to compare theoretical prediction and experimental observations quantitatively, several nonlinear field theories have been developed¹¹⁻¹⁴. As we have discussed the first mode in our former study⁷, in this study, we continue to discuss the second mode, namely, the state of equilibrium achieved when a network has been in contact with a solvent for a long time. At first, the condition of equilibrium between the gel and the solution is derived based on the variational principle. And then, two different nonaffine models are proposed for the elastomeric gel to account for the change of the entangling structure of polymer chains during the swelling-deformation process, in which the change of the number of polymer chains per unit volume N is depending on the first invariant of right Cauchy-Green tensor I_1 , or on the volume ratio of the gel J , separately. Continuously, the corresponding stress-stretch relations of the gel are derived. And then, based on these derived equations, the effect of the movement of the polymer chains on the free swelling ratio and the swelling-deformation responses of the gel, such as tensional stress and volume ratio, under different chemical constraints is clarified. Finally, based on some experimental data of the swollen rubber, the necessity and the availability of the proposed nonaffine models is discussed.

CONDITIONS OF EQUILIBRIUM

The basic idea of the derivation of the conditions of equilibrium for the dry polymer and the solvent is from the work done by Ref. (12). It is convenient to consider that, in the reference state, a block of network of dry polymers is a

unit cube, and contains no solvent and subject to no applied forces. In the current state, the network is submerged in a solvent-containing environment, and the six faces of the block are subject to applied forces. When the network, the solvent, and the applied forces equilibrate, the network absorbs C number of solvent molecules, and deforms homogeneously into the shape of a parallelepiped. When the deformation gradient of the network is expressed by \mathbf{F} , the ratio of volume of the swollen gel to that of the dry network is determined as $J = \det \mathbf{F}$. As an idealization, it is assumed that the volume of the elastomeric gel is a function of the concentration of the solvent:

$$J = 1 + \nu C \quad (1)$$

That is, all molecules in a gel are incompressible, and the volume of the gel is the sum of the volume of the dry network and the volume of the pure solvent molecules, where ν is the volume per solvent molecule. Eq. (1) determines the concentration of solvent C , once the deformation gradient is known. Consequently, the nine components of the deformation gradient \mathbf{F} specify the state of the gel. Let W be the Helmholtz free energy of the gel in the current state. The Helmholtz free energy of the gel can be taken to be a function of the nine components of the deformation gradient \mathbf{F} , and is assumed to be separable into contributions from stretching the network and mixing the polymer and solvent¹⁰⁾:

$$W = W_{stretch}(\mathbf{F}) + W_{mix}(J) \quad (2)$$

The free energy due to the stretching of the network, $W_{stretch}(\mathbf{F})$, is a function of the deformation gradient, and depends on the density of crosslinks. The free energy due to the mixing of the polymer and the solvent, $W_{mix}(J)$, is a function of the concentration of the solvent in the gel, but is independent of the density of crosslinks. For the convenience of formulation, it is preferred to introduce another free energy function \widehat{W} by using a Legendre transformation:

$$\widehat{W} = W - \mu C \quad (3)$$

where μ is the chemical potential of the solvent molecules. Eq. (1), Eq. (2) and Eq. (3) form the bases for the model of ideal elastomeric gels. In equilibrium, the change of the Helmholtz free energy of the composite vanishes and one can obtain that

$$s_{ki} = \frac{\partial \widehat{W}(\mathbf{F}, \mu)}{\partial F_{ik}}, \quad C = -\frac{\partial \widehat{W}(\mathbf{F}, \mu)}{\partial \mu} \quad (4)$$

where s_{ki} is the nominal stress. Employing Eq. (4), the swelling-deformation responses of the gel under different mechanical and chemical constraints can be investigated directly.

FREE ENERGY FUNCTIONS

In the original Flory-Rehner model¹⁰⁾, specific functions are adopted for $W_{stretch}(\mathbf{F})$ and $W_{mix}(J)$. In this study, we employ the best known formulation as Ref. (15):

$$W(\mathbf{F}) = \frac{1}{2} N k_B T (F_{ik} F_{ik} - 3 - 2 \log J) - \frac{k_B T}{\nu} \left[\nu C \log \left(1 + \frac{1}{\nu C} \right) + \frac{\chi}{1 + \nu C} \right] \quad (5)$$

where N is the number of polymer chains per unit volume, i.e. the density of crosslinks of the polymer chains, k_B is Boltzmann constant, T is the absolute temperature and χ is a dimensionless measure of the enthalpy of mixing. A combination of Eq. (1), Eq. (3) and Eq. (5) gives the desired free energy function:

$$\widehat{W}(\mathbf{F}, \mu) = \frac{1}{2} N k_B T (F_{ik} F_{ik} - 3 - 2 \log J) - \frac{k_B T}{\nu} \left[(J - 1) \log \left(\frac{J}{J-1} \right) + \frac{\chi}{J} \right] - \frac{\mu}{\nu} (J - 1) \quad (6)$$

Usually, the affine movement of the polymer chains is assumed and the value of N is fixed, and the affine model of the gel is constructed. In this study, to account for the effect of the nonaffine movement of the polymer chains on the deformation behavior of the elastomeric gel, similar to our former study⁷⁾, we employ the simplest version of the nonaffine model⁸⁾ to accommodate the change of N . Here, two different development equations of N is proposed based on the first invariant of right Cauchy-Green tensor I_1 , or on the third invariant of right Cauchy-Green tensor I_3 , separately:

$$\frac{N}{N_0} = 1 - \frac{I_1 - 3}{I_1^{max}}, \quad I_1 = F_{ik} F_{ik} \quad (7)$$

$$\frac{N}{N_0} = 1 - \frac{I_3 - 1}{I_3^{max}}, \quad I_3 = J^2 \quad (8)$$

where N_0 is the number of polymer chains per unit volume of the gel in the reference state, I_1^{max} and I_3^{max} are the limit value of I_1 and I_3 , respectively.

STRESS-STRETCH RELATIONS

Inserting Eq. (6) into Eq. (4), we obtain that

$$\frac{s_{ki}}{k_B T / \nu} = N \nu (F_{ik} - H_{ik}) + \frac{1}{2} \nu (I_1 - 3 - 2 \log J) \frac{\partial N}{\partial F_{ik}} + \left[J \log \left(1 - \frac{1}{J} \right) + 1 + \frac{\chi}{J} - \frac{\mu}{k_B T} J \right] H_{ik} \quad (9)$$

Recall an algebraic identity, $\partial J / \partial F_{ik} = H_{ik} J$, where H_{ik} is the transpose of the inverse of the deformation gradient \mathbf{F} . For simplicity, we describe the deformation of the elastomeric gel in the coordinates of principal stretches. Let $\lambda_1, \lambda_2, \lambda_3$ be the principal stretches of the gel, so that $\mathbf{F} = \text{diag}(\lambda_1, \lambda_2, \lambda_3)$, $J = \lambda_1 \lambda_2 \lambda_3$ and $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$.

Free Swelling State

Submerged in the solvent-containing environment but subject to no applied forces, the elastomeric gel attains a state of equilibrium, the free swelling state, characterized by an isotropic swelling ratio, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda = J^{-1/3}$. Therefore, based on Eq. (9), the relation between the principal stretch λ and the chemical potential of the solvent molecules μ can be written as:

$$Nv \left(\frac{1}{\lambda} - \frac{1}{\lambda^3} \right) - \frac{3N_0v}{I_1^{max}} \lambda^2 (\lambda^2 - 1 - 2\log\lambda) + \log \left(1 - \frac{1}{\lambda^3} \right) + \frac{1}{\lambda^3} + \frac{\chi}{\lambda^6} = \frac{\mu}{k_B T} \quad (10)$$

when Eq. (7) is applied, or can be written as:

$$Nv \left(\frac{1}{\lambda} - \frac{1}{\lambda^3} \right) - \frac{3N_0v}{I_3^{max}} \lambda^3 (\lambda^2 - 1 - 2\log\lambda) + \log \left(1 - \frac{1}{\lambda^3} \right) + \frac{1}{\lambda^3} + \frac{\chi}{\lambda^6} = \frac{\mu}{k_B T} \quad (11)$$

when Eq. (8) is applied.

Simple Tension State

A unit cube of the elastomeric gel is equilibrated in a solvent of chemical potential μ , and is subject to a uniaxial stress s_1 along the longitudinal direction. The state of deformation can be characterized by the longitudinal stretch λ_1 and two transverse stretch $\lambda_2 = \lambda_3$. The stresses in the transverse directions vanish, so that Eq. (9) gives

$$Nv \left(\lambda_2 - \frac{1}{\lambda_2} \right) - \frac{N_0v}{I_1^{max}} \lambda_2 (\lambda_1^2 + 2\lambda_2^2 - 3 - 2\log\lambda_1\lambda_2^2) + \left[\lambda_1\lambda_2^2 \log \left(1 - \frac{1}{\lambda_1\lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{k_B T} \lambda_1\lambda_2^2 \right] \frac{1}{\lambda_2} = 0 \quad (12)$$

when Eq. (7) is applied, or gives

$$Nv \left(\lambda_2 - \frac{1}{\lambda_2} \right) - \frac{N_0v}{I_3^{max}} \lambda_1^2 \lambda_2^3 (\lambda_1^2 + 2\lambda_2^2 - 3 - 2\log\lambda_1\lambda_2^2) + \left[\lambda_1\lambda_2^2 \log \left(1 - \frac{1}{\lambda_1\lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{k_B T} \lambda_1\lambda_2^2 \right] \frac{1}{\lambda_2} = 0 \quad (13)$$

when Eq. (8) is applied. Eq. (12) and Eq. (13) determine the transverse stretch λ_2 for a given longitudinal stretch λ_1 . Eq. (9) also relates the longitudinal stress to the stretches as:

$$\frac{s_1}{k_B T/v} = Nv \left(\lambda_1 - \frac{1}{\lambda_1} \right) - \frac{N_0v}{I_1^{max}} \lambda_1 (\lambda_1^2 + 2\lambda_2^2 - 3 - 2\log\lambda_1\lambda_2^2) + \left[\lambda_1\lambda_2^2 \log \left(1 - \frac{1}{\lambda_1\lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{k_B T} \lambda_1\lambda_2^2 \right] \frac{1}{\lambda_1} \quad (14)$$

when Eq. (7) is applied, or as:

$$\frac{s_1}{k_B T/v} = Nv \left(\lambda_1 - \frac{1}{\lambda_1} \right) - \frac{N_0v}{I_3^{max}} \lambda_1 \lambda_2^4 (\lambda_1^2 + 2\lambda_2^2 - 3 - 2\log\lambda_1\lambda_2^2) + \left[\lambda_1\lambda_2^2 \log \left(1 - \frac{1}{\lambda_1\lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{k_B T} \lambda_1\lambda_2^2 \right] \frac{1}{\lambda_1} \quad (15)$$

when Eq. (8) is applied.

RESULTS

In this study, we have normalized the chemical potential μ by $k_B T$, and normalized the stress s_1 by $k_B T/v$ as shown

in Eq.(9). The Flory-Rehner free energy function introduces two dimensionless material parameters: Nv and χ . In the numerical results below, we take the values $Nv = 10^{-3}$ and $\chi = 0.1$. On the other hand, the values of the two parameters introduced in the nonaffine model are taken as $I_1^{max} = 50$ and $I_3^{max} = 4000$, which are corresponding to a virtual limit of the swelling ratio, $\lambda^{limit} = 4.0$, when an elastomeric gel is submerged in the solvent.

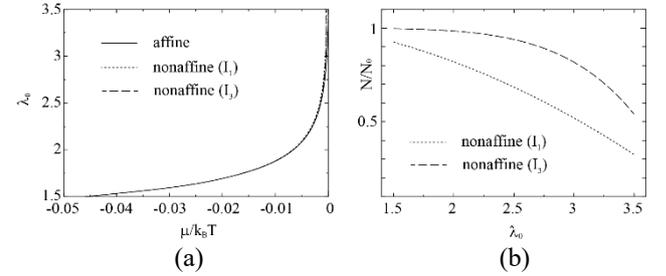


Fig. 1 Characteristics of the elastomeric gel in the free swelling state: (a) Isotropic swelling ratio-chemical potential relations; (b) Development of the number of polymer chains per unit volume.

Effect of Chemical Potential

In Figure 1(a), the isotropic swelling ratio of an elastomeric gel in the free swelling state λ_0 is plotted as a function of the chemical potential of the solvent μ . When the solvent is subject to a pressure p greater than its vapor pressure p_0 , the solvent is in its liquid phase, and the chemical potential of the solvent molecules is $\mu = (p - p_0)v$. When the solvent is subject to a pressure p less than its vapor pressure p_0 , the solvent in equilibrium becomes a gas, which we assume to be an ideal gas, so that the chemical potential of the solvent molecules is $\mu = k_B T \log(p/p_0)$. When the phase of the solvent changes from gas to liquid, i.e. the value of $\mu/k_B T$ increases from -0.05 to 0, the isotropic swelling ratio of the gel λ_0 increases at first linearly and then exponentially. With regard to the effect of the nonaffine movement of the polymer chains on the isotropic swelling ratio of the gel, no effect can be observed when the solvent is in its gas phase, i.e. the value of $\mu/k_B T$ is smaller than -0.01. However, when the solvent is close to its liquid phase, i.e. the value of $\mu/k_B T$ is larger than -0.01, the nonaffine movement of the polymer chains leads to a relatively early increase of the isotropic swelling ratio. Further details of the corresponding values of $\mu/k_B T$ for different value of λ_0 are shown in Table 1. Taking the virtual limit of the swelling ratio, $\lambda^{limit} = 4.0$, into consideration, in the subsequent discussion, the range of $\mu/k_B T$ is limited to -0.046~-0.0014, i.e. the corresponding value of λ_0 is limited to 1.5~2.5.

Table 1 Corresponding value of normalized chemical potential $\mu/k_B T$ for different isotropic swelling ratio λ_0 .

λ_0	$\mu/k_B T$		
	affine	Eq. (10)	Eq. (11)
1.5	-0.0460	-0.0460	-0.0460
2.0	-0.0066	-0.0067	-0.0066
2.5	-0.0014	-0.0016	-0.0015
3.5	0.00004	-0.0003	-0.0004

In Figure 1(b), the development of the number of polymer chains per unit volume N during the free swelling of the gel are shown. When the development of N is dependent on the first invariant of right Cauchy-Green tensor I_1 , i.e. based on Eq. (7), its value decreases almost linearly together with the increase of λ_0 . On the other hand, when such development is dependent on the third invariant of right Cauchy-Green tensor I_3 , i.e. based on Eq. (8), its value is almost constant at small isotropic swelling ratio, i.e. $\lambda_0 < 2.5$, and then decreases dramatically.

Swelling-Deformation Responses

When an elastomeric gel is subject to a uniaxial stress, and is in contact with a solvent of a given chemical potential, the state of equilibrium is assumed to achieve after a long time. For the calculation convenience, we choose a updated reference state such that the network, under no mechanical load, equilibrates with a solvent of chemical potential $\mu/k_B T$ and then the network is loaded under simple tension with the tensional stretch λ' , which is referred to the updated reference state. The swelling-deformation responses such as the number of polymer chains per unit volume, tensional stress and volume ratio of the gel in the current states are investigated.

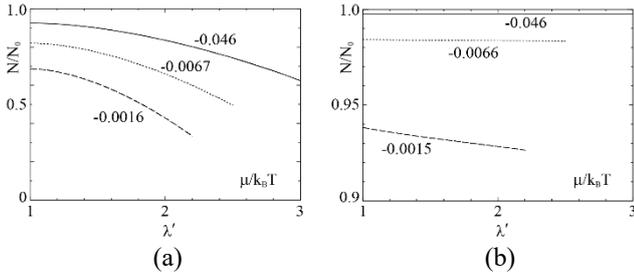


Fig. 2 Development of the number of polymer chains per unit volume of the elastomeric gel during simple tension in a solvent with different chemical potential: (a) based on Eq.(7); (b) based on Eq.(8).

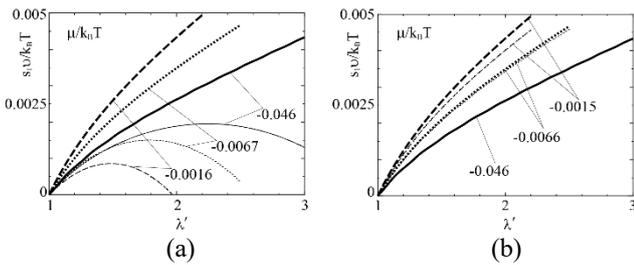


Fig. 3 Normalized tensional stress-tensional stretch relations of the elastomeric gel in a solvent with different chemical potential. (thick lines) affine model. (thin lines) nonaffine model: (a) based on Eq.(7); (b) based on Eq.(8).

In Figure 2, the development of the number of polymer chains per unit volume of the gel N is shown. When N is dependent on the first invariant of right Cauchy-Green tensor I_1 , i.e. based on Eq. (7), N decreases nonlinearly as shown in Figure 2(a). Especially, N decreases close to its half value at early deformation stage when the chemical potential of the solvent $\mu/k_B T$ increases. When N is dependent on the third invariant of right Cauchy-Green tensor I_3 , i.e. based on Eq.

(8), N decreases linearly, as shown in Figure 2(b), and no remarkable change can be found compared with its initial value.

In Figure 3, the effect of the nonaffine movement of the polymer chains on the tensional stress of the gel is shown, where the results of nonaffine model based on Eq. (7) and Eq. (8) are compared with the affine model in Figure 3(a) and Figure 3(b), separately. On the whole, the tensional stress of affine model is larger than that of nonaffine model, where quite different responses are given by the nonaffine model based on Eq. (7) and the difference is quite small when the nonaffine model based on Eq. (8) is employed. Moreover, from Eq. (9), it can be understood that the mechanical response of the gel is dependent on both the parameter of deformation λ' , and the parameter of material N . When N decreases, i.e. the density of crosslinks of the polymer chains decreases, the tensional stress-tensional stretch relation of nonaffine model deviates from that of affine model and the tensional stress decreases eventually, regardless of the continuous increase of λ' .

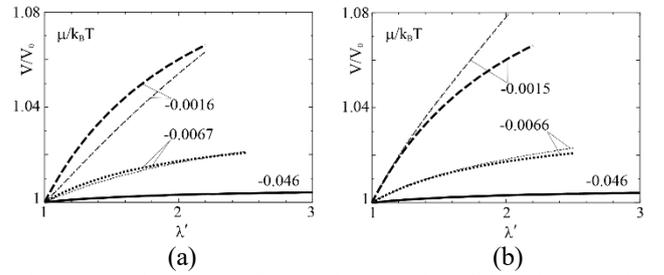


Fig. 4 Development of the volume ratio of the elastomeric gel during simple tension in a solvent with different chemical potential. (thick lines) affine model. (thin lines) nonaffine model: (a) based on Eq.(7); (b) based on Eq.(8).

In Figure 4, the effect of the nonaffine movement of the polymer chains on the volume ratio of the gel is shown, where the results of nonaffine model based on Eq. (7) and Eq. (8) are compared with the affine model in Figure 4(a) and Figure 4(b), separately. V and V_0 is the volume of the gel in the current state and in the updated reference state, respectively. On the whole, the volume ratio of the gel V/V_0 increases together with the tensional stretch λ' regardless of the affine or nonaffine movement of the polymer chains. The difference between the results of the affine model and that of the nonaffine model becomes remarkable when the chemical potential of the solvent $\mu/k_B T$ increase, where the results of the nonaffine model based on Eq. (7) is smaller than that of the affine model and the results of the nonaffine model based on Eq. (8) is larger than that of the affine model.

DISCUSSION

In this section, the necessity and the availability of the proposed nonaffine models above are to be discussed. Gee did his experimental work on the elastic behaviour of dry and swollen rubbers⁶. Because the swollen rubber can be considered as one kind of the elastomeric gel, Gee's experimental data are here employed to validate our theoretical model. Gee gave his experimental results in the form of

$$\frac{\rho_r R}{M_c} = Nk_B \quad (16)$$

where ρ_r is the density of the rubber, R is gas constant, and M_c is the mean molecular weight between adjacent junction points of the network. One of the Gee's experimental data, the dependence of Nk_B on the first invariant of right Cauchy-Green tensor I_1 of the dry nature rubber under simple tension, are shown in Figure 5. Because there is no volume change in this case, the experimental data can be employed to identify the value of I_1^{max} in Eq. (7). To do this, we at first linearize the experimental data to give a linear relation as

$$Nk_B = 21.435 - 1.9493I_1 \quad (17)$$

After inputting the value of $I_1 = 3$ to Eq. (17), we derive the value of N_0k_B , which is corresponding to the unstrained state of rubber. Continuously, we normalize the vertical axis of Figure 5 by N_0k_B and linearize the recalculated data with Eq. (7) as

$$\frac{N}{N_0} = 1 - \frac{I_1 - 3}{8} \quad (18)$$

As a result, the value of I_1^{max} for the nature rubber is equal to 8. With regard to the swollen rubber, Gee indicated that Nk_B tends to become more nearly constant as the rubber is progressively swollen, and becomes substantially constant for small extensions at sufficiently high degrees of swelling. For example, when the swelling ratio of the swollen rubber $J = 3$, the value of N/N_0 would be a constant one as 0.65 no matter with the degree of tensional deformation. Therefore, in this case, the value of N/N_0 can be considered as a function of the volume ratio of the swollen rubber J only and the value of I_3^{max} in Eq. (8) can be identified as 23. In other word, Eq. (8) can be rewritten as

$$\frac{N}{N_0} = 1 - \frac{I_3 - 1}{23} \quad (19)$$

Based on the above discussion, it can be understand that to reproduce the experimental data of the elastomeric gel, the dependence of the entangling structure of polymer chains on I_1 and on J should be investigated separately as shown in Eq. (7) and Eq. (8).

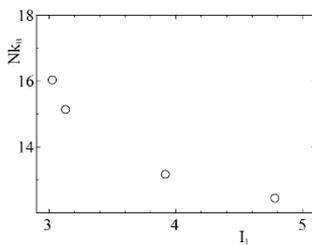


Fig. 5 Development of Nk_B of the dry nature rubber under simple tension.

Now, let's focus the discussion on the availability of the proposed nonaffine models, i.e. Eq. (18) and Eq. (19) to reproduce the experimental data of swollen rubber with different swelling ratio as given in Ref. (16). Gee at first

prepared the partial swollen rubber test pieces and then extended them without appreciable loss of liquid by evaporation. During the extension, the test pieces change their shape only and their volume remain constant, i.e. deform in the first mode as mentioned in INTRODUCTION. Therefore, we combine Eq. (18) and Eq. (19) in the form of

$$\frac{N}{N_0} = \alpha \left(1 - \frac{I_3 - 1}{23} \right) - \beta \frac{I_1 - 3}{8} \quad (20)$$

where α and β are weighting factors. The first term is corresponding to the variation of the entangling structure of the polymer chains during the partial swelling process of rubber test pieces and the second term is corresponding to such variation during the extension. Figure 6 shows the experimental data from Gee and the calculation results of Eq. (20). The corresponding values of α and β for different swelling ratio J of the swollen rubber are shown in Table 2. By using weighting factors, Eq. (20) can reproduce the experimental data very well. However, as the value of the weighting factor β decreases almost linearly together with the increase of the swelling ratio J , the value of the weighting factor α varies irregularly. It is maybe due to the linear formulation of Eq. (8), which is the simplest version of the nonaffine model⁽⁸⁾.

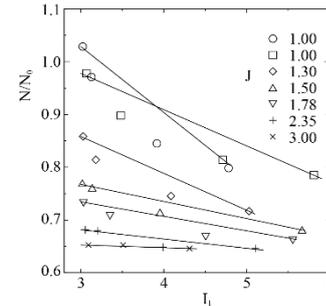


Fig. 6 Comparison of the experimental data (symbols) and theoretical calculation results (lines) of the swollen rubber under simple tension.

Table 2 Corresponding value of weighting factors α and β in Eq. (20) for different swelling ratio J of the swollen rubber.

J	α	β
1.00	1.02870	1.00
1.00	0.97782	0.56
1.30	0.88408	0.55
1.50	0.81219	0.26
1.78	0.81040	0.22
2.35	0.84878	0.14
3.00	1.00925	0.04

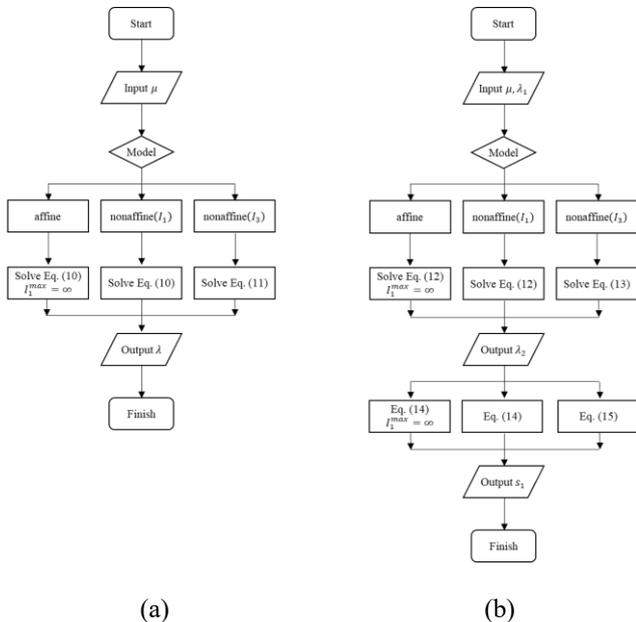
On the other hand, most calculation of this study is carried out for the elastomeric gel that changes both shape and volume, i.e. deforms in the second mode as mentioned in INTRODUCTION. To show the correctness of the calculated results, the corresponding experimental data is indispensable. Unfortunately, up to now, we have not found such experimental data. However, for diverse applications, the elastomeric gel is usually immersed in the solvent and deforms under various mechanical environment. The

verification of the correctness of our theoretical model can be left to the finite element simulation of a real system, which contains the elastomeric gel and the solvent. Such simulation work is in progress now and the corresponding results is hoped to be reported in the foreseeable future.

CONCLUSION

In this study, two different nonaffine models are proposed for the elastomeric gel to account for the change of the entangling structure of polymer chains during the swelling-deformation process, in which the change of the number of polymer chains per unit volume N is depending on the first invariant of right Cauchy-Green tensor I_1 , or on the volume ratio of the gel J , separately. The effect of such dependency on the free swelling ratio and the swelling-deformation responses of the gel under different chemical constraints is investigated. It is understood that the nonaffine movement of the polymer chains leads to a relatively early increase of the free swelling ratio. Moreover, the decrease of N leads to a early onset of the decrease of the tensional stress of the gel under simple tension when the chemical potential of the solvent increases, i.e. when the solvent is in its liquid phase. On the other hand, the volume ratio of the gel increases continuously during the swelling-deformation process regardless of the affine or nonaffine movement of the polymer chains. Furthermore, it is clarified that the proposed two different nonaffine models can be combined with weighting factors to reproduce the experimental data of swollen rubber.

NOMENCLATURE



Flow charts: (a) free swelling state; (b) simple tension state.

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