

NUMERICAL SIMULATION OF THE SWELLING AND DESWELLING PROCESS OF POLYMER GEL

ISAMU RIKU AND KOJI MIMURA

Osaka Metropolitan University
1-1, Gakuen-cho, Naka-ku, Sakai City, Osaka 5998231, Japan
riku@omu.ac.jp

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Abstract. It is well known that the entropy elasticity of rubberlike materials and Brownian motion are described by formally analogous equations as both originated from thermal fluctuations. In rubberlike materials, the shear modulus is conventionally considered to be proportional to the absolute temperature and the proportionality factor is the number density of polymer chains for an affine polymer chains' network model. On the other hand, the self-diffusion coefficient of Brownian motion is described as the product of the mobility and the absolute temperature. However, for the polymer chains' network in a solvent, the interaction between the polymer chains and the solvent molecules occurs and the collective diffusion coefficient of the solvent molecules should be different to the self-diffusion coefficient of Brownian motion. Moreover, the shear modulus of the resultant polymer gel should be dependent on the swelling ratio due to the nonaffine movement of polymer chains. Therefore, to verify the analogy of the equations for the shear modulus of the nonaffine polymer chains' network model and the collective diffusion coefficient of the solvent molecules, in this study, the swelling and deswelling process of the polymer gel is investigated by the numerical simulations.

1 INTRODUCTION

Polymer gels contain a large number of the solvent molecules and can absorb additional solvent or lose solvent from the as-prepared state[1]. These processes are of course accompanied by volume changes in the polymer gel, i.e., swelling and deswelling. When a hydrogel is placed in an aqueous environment, such as in the living body, either swelling or contraction generally occurs to some extent, and there is a concomitant change in volume. Therefore, it is practically important to know to what extent swelling can occur and how the physical properties change with changes in volume change.

To account for the physical properties change due to swelling, in our former study[2], we investigated the development of the microstructure of polymer chains' network of the polymer gel based on a nonaffine polymer chains' network model[3], 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 due to deformation. It was found that the free

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

In this study, the nonaffine polymer chains' network model is employed to investigate the transient entangling structure's change together with the transient distribution of swelling ratio and that of stress of the polymer gel during swelling and deswelling process. With regard to the transient phenomenon of diffusion of the solvent molecules during swelling and deswelling process, in this study, Fick's laws of diffusion[4] is employed to investigate the transient distribution of the concentration of the solvent. Furthermore, the effect of the interaction between the polymer chains and the solvent molecules on the diffusion coefficient of the solvent molecules is discussed.

2 CONDITIONS OF EQUILIBRIUM

The basic idea of the derivation of the conditions of equilibrium for the dry polymer chains' network and the aqueous solution is from the work done by Hong et al.[5]. It is convenient to consider that, in the reference state, a block of dry network of polymer chains 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 the 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 polymer 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 polymer gel is a function of the concentration of the solvent:

$$J = 1 + vC. \quad (1)$$

That is, all molecules in a polymer gel are incompressible, and the volume of the polymer gel is the sum of the volume of the dry network and the volume of the pure solvent molecules, where v is the volume per solvent molecule. Eq. (1) determines the concentration of the solvent C , once the deformation gradient \mathbf{F} is known.

The Helmholtz free energy of the polymer gel in the current state, W , can be assumed to be separable into contributions from stretching the polymer chains' network and mixing the network and the solvent[6]:

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

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

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

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

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

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

3 FREE ENERGY FUNCTIONS

In the original Flory-Rehner model[6], specific functions are adopted for $W_{stretch}(\mathbf{F})$ and $W_{mix}(J)$. In this study, we employ the best known formulation[7] as:

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

where N is the number of polymer chains per unit volume, i.e. the density of crosslinks of 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:

$$\begin{aligned} \hat{W}(\mathbf{F}, \mu) &= \frac{1}{2} N k_B T (F_{ik} F_{ik} - 3 - 2 \log J) \\ &\quad - \frac{k_B T}{v} \left[(J - 1) \log \left(\frac{J}{J - 1} \right) + \frac{\chi}{J} \right] - \frac{\mu}{v} (J - 1). \end{aligned} \quad (6)$$

Usually, the affine movement of polymer chains is assumed and the value of N is fixed, and the affine model of the polymer gel is constructed. However, the observations on the double network polymer gel (DN gel) after the tensile test demonstrate that irreversible structural change takes place inside the DN gel, although their appearance is almost unchanged[8]. When the DN gel is in tensile, the 1st polymer chains' network is quite brittle and breaks into small pieces at small extensions. Subsequently, the 1st polymer chains' network fragments into small clusters and the clusters play a role of crosslinkers of the 2nd polymer chains' network. This irreversible structural change during the tension of the DN gel can be considered as one kind of the nonaffine movement of polymer chains, i.e. the density of crosslinks of polymer chains N vary from its initial value at the free swelling state, N_0 , to its current value which is depend on the deformation gradient of the network \mathbf{F} . In this study, the nonaffine model of the polymer gel is constructed and the value of N is proposed to vary inverse proportionally with the first invariant of right Cauchy-Green deformation tensor, I_1 :

$$\frac{N}{N_0} = \frac{1}{f} + \left(1 - \frac{1}{f}\right) \cdot \frac{3}{I_1}, \quad I_1 = F_{ik}F_{ik}, \quad (7)$$

where f is a scaling factor and can be specified based on the value of the density of chemical crosslinks and that of the physical crosslinks of polymer chains' network at the free swelling state.

4 STRESS-STRETCH RELATIONS

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

$$\begin{aligned} \frac{s_{ki}}{k_B T / v} = Nv(F_{ik} - H_{ik}) &+ \frac{1}{2}v(I_1 - 3 - 2\log J) \frac{\partial N}{\partial F_{ik}} \\ &+ \left[J \log \left(1 - \frac{1}{J}\right) + 1 + \frac{\chi}{J} - \frac{\mu}{k_B T} J \right] H_{ik}. \end{aligned} \quad (8)$$

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

Submerged in the solvent-containing environment but subject to no applied forces, the polymer gel attains a state of equilibrium, the free swelling state, characterized by an isotropic swelling ratio, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_0$. Based on Eq. (8), the relation between the principal stretch λ_0 and the chemical potential of the solvent molecules μ can be simplified as:

$$N_0 v \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_0^3} \right) + \log \left(1 - \frac{1}{\lambda_0^3} \right) + \frac{1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6} = \frac{\mu}{k_B T}. \quad (9)$$

5 DIFFUSION EQUATION

The diffusion of the solvent molecules during swelling and deswelling process of the polymer gel is assumed to obey Fick's laws[4]. Therefore, the concentration of the solvent C can be defined as a function that depends on location x and time t and the diffusion equation can be expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}. \quad (10)$$

where D is the diffusion coefficient of the solvent molecules.

6 COMPUTATIONAL MODEL

In this study, we have normalized the chemical potential of the solvent molecules μ by $k_B T$, and normalized the stress s by $k_B T / v$ as shown in Eq.(8). The Flory-Rehner free energy function introduces two dimensionless material parameters: Nv and χ . In the numerical results

below, we take the values $N_0v = 10^{-3}$ and $\chi = 0.1$. On the other hand, the parameter introduced in the nonaffine model of the polymer gel is specified as $f = 15$, which is same as the value presumed by our former study[9].

Computational simulations employ the three-dimensional finite element method for large deformation problems with the above-mentioned free energy functions. Fig.1 shows the computational model of a specimen of the polymer gel. The dimensions of the specimen in x , y and z direction is $w_0 = 1cm$, $t_0 = 1cm$ and $l_0 = 10cm$ respectively. The specimen is divided with 8-node linear brick, hybrid with constant pressure element(C3D8H). The symmetric boundary condition is applied to the planes: $x = 0$, $y = 0$ and $z = 0$.

During the swelling and deswelling process of the specimen of the polymer gel, the local concentration of the solvent develops with time and as a result, the shape of the specimen changes with time. However, the conditions of equilibrium given in Section 2 is for the equilibrium state of the polymer gel and the solvent after the swelling and deswelling process. To investigate the deformation of the specimen of the polymer gel during the swelling and deswelling process, in this study, diffusion analysis is at first performed based on Eq.(10) to give the distribution of the concentration of the solvent at any swelling and deswelling stage. And then, such derived distribution of the concentration of the solvent is imported as the initial condition for the mechanical analysis and the deformation behavior of the specimen is investigated based on Eq.(9).

7 RESULTS

Fig.2 shows the distribution of the concentration of the solvent at different swelling and deswelling stages. The value of 100% means that the number of the solvent molecules that diffuse into the local position has reached its maximum value and the value of 0% means that no solvent has diffused in the local position. At the time $t = 2s$, the high concentration region of the solvent appears at the left end of the specimen of the polymer gel and the gradient of the concentration of the solvent is quite high which promotes the diffusion of the solvent molecules to the right end of the specimen. At the time $t = 1000s$, the concentration of the solvent is almost 100% throught the whole specimen, i.e., a state at the end of the swelling and deswelling process.

Fig.3 shows the distribution of swelling ratio of the specimen of the polymer gel at different swelling and deswelling stages. By the way, the pink lines shows the original shape of the specimen before the swelling and deswelling process. At the time $t = 2s$, the high concentration of the solvent leads to a large swelling ratio of the specimen and a sharp variation of the outer shape of the left end of the specimen appears. At the time $t = 1000s$, the whole specimen swells and the sharp variation the outer shape of the left end of the specimen has been reduced.

Fig.4 shows the distribution of maximum principal stress in the specimen of the polymer gel at different swelling and deswelling stages. Even though the specimen is subject to no applied force, high stress region onsets at the left end of the specimen. Moreover, different to the distribution of the concentration of the solvent and that of swelling ratio shown above, maximum principal stress distributes much more locally. On the other hand, the value of principal stress at the time of $t = 1000s$ decrease to $1/20 \sim 1/100$ of the value of principal stress at the time

of $t = 2s$. This result suggests that the effect of localized stress on the diffusion of the solvent molecules is negligible at the later swelling and deswelling stages.

8 CONCLUSIONS

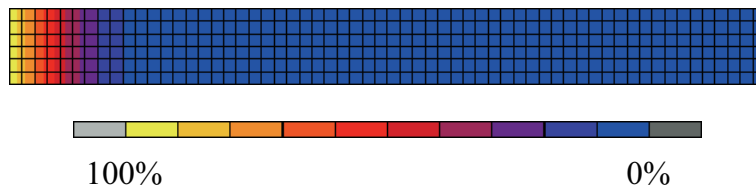
In this study, the diffusion analysis together with the mechanical analysis is performed to investigate the deformation behavior of the specimen of the polymer gel during swelling and deswelling process. The results show that a sharp variation of the outer shape and highly localized stress distribution appear at the early stages of the swelling and deswelling process. Therefore, it is necessary to define the collective diffusion coefficient of the solvent molecules, D , with the consideration of the localized stress distribution.

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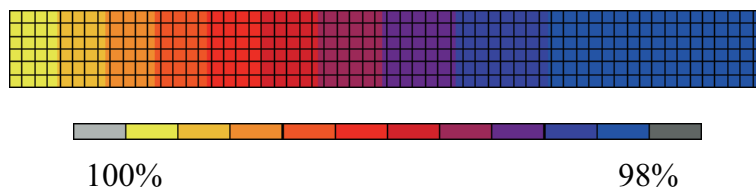
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Figure 1: Computational model



(a) $t = 2s$



(b) $t = 1000s$

Figure 2: Distribution of the concentration of the solvent

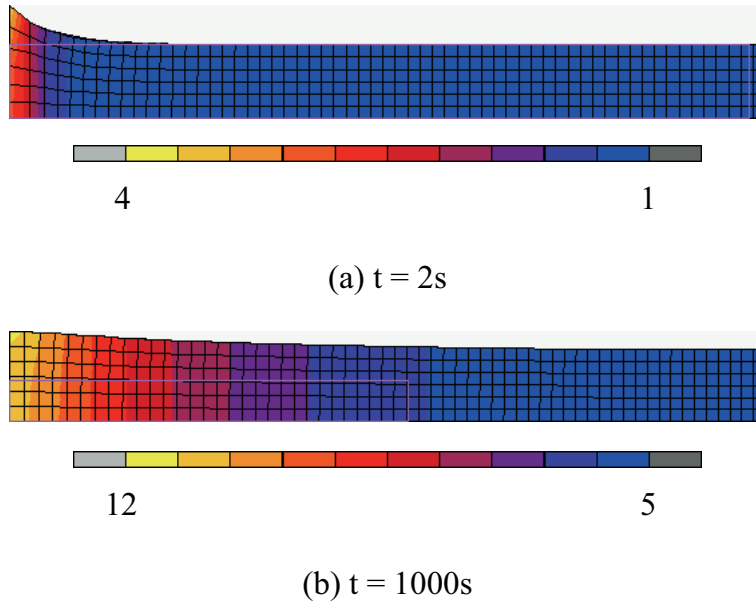


Figure 3: Distribution of swelling ratio

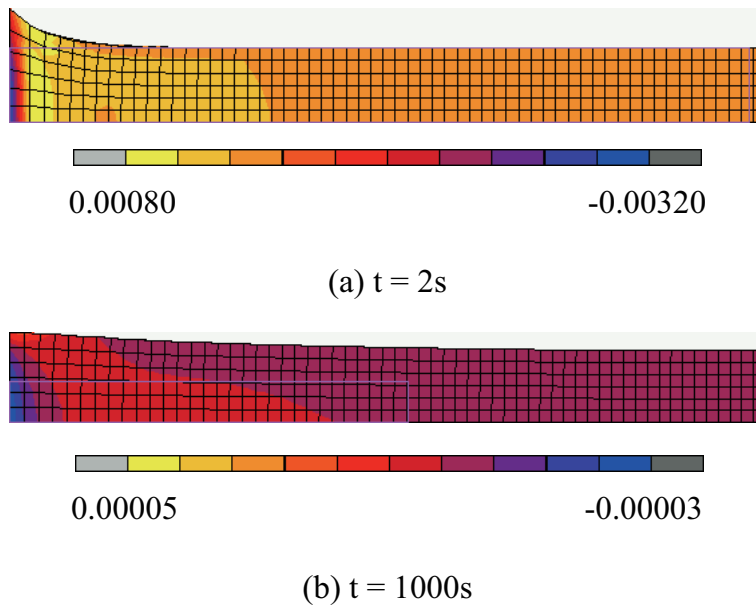


Figure 4: Distribution of maximum principal stress