

# Study on the change of entangling structure of molecular chains during the tensional and swelling process of elastomeric gel

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## Abstract

A nonaffine model is proposed for elastomeric gel to account for the change of the entangling structure of molecular chains during the tensional and swelling process, in which the change in the number of polymer chains per unit volume,  $N$ , is depending on the first invariant of right Cauchy-Green tensor,  $I_1$ , and on the volume of the gel,  $J$ , separately. It is found that the free swelling process may lead to a larger change of the entangling structure of molecular chains rather than the tensional process does. Moreover, the various combination of the effect of each process on the nonaffine movement of molecular chains may lead to different interesting mechanical responses of the gel, such as yield.

**Keywords:** Entangling structure, Elastomeric gel, Computational model, Tensional and swelling process

## Introduction

The elastomeric gel, consisting of cross-linked 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 actuators [1-3].

To characterize how mechanical constraint affects the amount of swelling, and how chemical processes generate forces, several nonlinear field theories have been developed [4-7]. Flory and Rehner proposed a statistical mechanical model for the network of polymer molecules and indicated that the swelling capacity of the gel is diminished by the application of an external stress [8]. Recently, Cai et al. [9] employed an alternative approach, in which a set of equations of state is developed based on two assumptions: the amount of the solvent in the gel varies when the gel changes volume, but remains constant when the gel changes shape; the Helmholtz free energy of the gel is separable into the contributions of stretching the network and mixing the polymer and the solvent. However, in these studies, the computational models are just phenomenological ones and the change of entangling structure of molecular chains during the swelling process has not been accounted for explicitly.

Therefore, in this study, we focus on the discussion of the mechanical behavior of elastomeric gel based on a nonaffine molecular chain network model (nonaffine model) [10], 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. After formulating the dependence of the number of polymer chains per unit volume on the first invariant of right Cauchy-Green tensor and the swelling ratio of the elastomeric gel, a computational model is proposed and employed to investigate the mechanical response of the gel during constrained swelling process.

## Conditions of Equilibrium

The derivation of the conditions of equilibrium for the dry polymer and the solvent has been done by Cai et al. [9]. 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 and that of the dry network is determined as  $J = \det \mathbf{F}$ . Subject to applied forces, the gel changes shape readily, but the volumes of individual polymer chains or solvent molecules remain nearly unchanged. As an idealization, it is assumed that the volume of the gel is a function of the concentration of the solvent:

$$J = f(C) \quad (1)$$

That is, the amount of the solvent in the gel varies when the gel changes volume, but remains constant when the gel changes shape.

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 solvent [8]:

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

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. Eq. (1) and Eq. (2) form the basis 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

$$\sigma_{ij} = F_{jk} \frac{\partial W_{stretch}(\mathbf{F})}{J \partial F_{ik}} - \Pi(J) \delta_{ij}, \quad (3)$$

where  $\sigma_{ij}$  is the true stress, which is defined by imagining a small cube cut from the parallelepiped,  $\delta_{ij}$  is the Kronecker delta and  $\Pi(J)$  is the osmotic pressure due to mixing the network and the solvent.

## Free Energy Functions

In the original Flory-Rehner model [8], specific functions are adopted for  $W_{stretch}(\mathbf{F})$  and  $W_{mix}(J)$ . The free energy associated with stretching the network is given by the Gaussian-chain model [8]:

$$W_{stretch}(\mathbf{F}) = \frac{1}{2} N k_B T (F_{ik} F_{ik} - 3 - 2 \log J), \quad (4)$$

where  $N$  is the number of polymer chains per unit volume,  $k_B$  is Boltzmann constant and  $T$  is the temperature. It is obviously that the variation of the effect of the swelling ratio,  $J$ , on the elastic modulus of the gel has been considered. However, this model is just a

phenomenological one and the change of entangling structure of molecular chains during the swelling process of gel has not been accounted for explicitly.

Therefore, in this study, based on the molecular chain network theory [11], the microstructure of the gel is assumed to consist of long molecular chains which are randomly distributed in space. A single chain, which consists of several segments containing monomers, is defined by two linkages which are assumed to be chemically or physically entangled points of molecular chains. The physical links are corresponding to the pseudo entanglement points and may change depending on deformation. On the other hand, chemical links are permanent and preserve the entanglement situation. The physical links may suffer breakdown during the thermodynamic process [12]. The decrease in the number of entangled points due to deformation causes an decrease in the number of polymer chains per unit volume,  $N$ , an enhanced extensibility, and a reduction in the stiffness of the material, i.e., softening. To account for the effect of the nonaffine movement of the polymer chain on the deformation behavior of the gel, we employ the simplest version of the nonaffine model [10] to accommodate the change in the number of polymer chains per unit volume,  $N$ , depending on the first invariant of right Cauchy-Green tensor,  $I_1$ , and on the volume of the gel,  $J$ , separately as

$$\frac{N}{N_0} = 1 - \alpha \left[ 1 - \left( \frac{I_1 - I_1^{\max}}{3 - I_1^{\max}} \right)^{m_1} \right], \quad (5)$$

$$\frac{N}{N_0} = 1 - \beta \left[ 1 - \left( \frac{J - J^{\max}}{1 - J^{\max}} \right)^{m_2} \right], \quad (6)$$

where  $N_0$  is the number of polymer chains per unit volume of the gel in the reference state,  $\alpha$ ,  $\beta$ ,  $m_1$ ,  $m_2$  are the parameters for identification,  $I_1^{\max}$  and  $J^{\max}$  are the limit value of  $I_1$  and  $J$ , separately.

As chemomechanical interactions are material-specific and can be very complex, in this study, we just consider some special cases, in which the discussion of the effect of nonaffine movement of the polymer chains can be done without any assumption of the function  $W_{mix}(J)$ .

### Stress-Stretch Relations

Inserting Eq. (4) into Eq. (3), we obtain that

$$\sigma_{ij} = \frac{Nk_B T}{J} (F_{jk} F_{ik} - \delta_{ij}) - \Pi(J) \delta_{ij}. \quad (7)$$

In relating the model to experiments, we describe the deformation of the 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  $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ . Rewrite Eq. (7) in terms of the principal stretches and principal stresses:

$$\sigma_i = \frac{Nk_B T}{J} (\lambda_i^2 - 1) - \Pi(J). \quad (8)$$

### Reference State

Consider the elastomeric gel is in the reference state, i.e. a block of network of dry polymers, where the swelling ratio  $J$  is always equal to unit. When the dry block is subject to a uniaxial tensile force, the relation between the stretch  $\lambda$  and the stress  $\sigma_T$  on the tensile direction can be rewritten based on Eq. (8) as:

$$\sigma_T = Nk_B T(\lambda - \lambda^{-2}), \quad (9)$$

which can also be used to define the shear modulus of the gel in the reference state,  $G_0 = N_0 k_B T$ .

### *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,  $\lambda_1 = \lambda_2 = \lambda_3 = \lambda = J^{-1/3}$ . When a gel in the free swelling state is subject to a uniaxial tensile force, in a short time the solvent in the gel has no time to redistribute, so that the concentration of the solvent in the gel remains fixed, and the gel behaves like an incompressible material. Therefore, the relation between the additional stretch  $\tilde{\lambda}$ , which is defined referred to the free swelling state, and the stress  $\sigma_T$  on the tensile direction can be rewritten based on Eq. (8) as:

$$\sigma_T = J^{-1/3} Nk_B T(\tilde{\lambda} - \tilde{\lambda}^{-2}), \quad (10)$$

which can also be used to define the shear modulus of the gel in the free swelling state,  $G = J^{-1/3} Nk_B T$ .

### *Constrained Swelling State*

Submerged in the solvent-containing environment but subject to constrained displacement at one direction,  $\lambda_3 = 1$ , the elastomeric gel attains a state of equilibrium, the constrained swelling state, characterized by an bidirectional swelling ratio,  $\lambda_1 = \lambda_2 = \lambda = J^{-1/2}$ . The relation between the swelling ratio  $\lambda$  and the stress  $\sigma_T$  on the constrain direction can be rewritten based on Eq. (8) as:

$$\sigma_T = Nk_B T(\lambda^2 - 1). \quad (11)$$

## **Results**

In Fig. 1(b), the theoretical predictions are compared with experimental data [13] for the elastomeric gel under uniaxial tensile. Even though the affine model can reproduce the experimental result at the initial deformation stage very well, the overestimation of the stress increases greatly at the large deformation stage. Therefore, we suppose that the number of polymer chains per unit volume of the gel,  $N$ , in Eq. (9) changes together with the uniaxial deformation according to Eq. (5), in which the value of parameters has been identified as:  $\alpha = 0.21$ ,  $I_1^{\max} = 27.2$ . It is obviously that the proposed nonaffine model can reproduce the experimental data successfully. On the other hand, from Fig. 1(a), it can be understood that the dramatic change of the entangling structure of molecular chains during the uniaxial tensile process of gel may occur mostly at the early deformation stage, not the later deformation stage.

In Fig. 2(b), the theoretical predictions are compared with experimental data [14] for the elastomeric gel under different swelling ratios. Here, we suppose that the number of polymer chains per unit volume of the gel,  $N$ , in Eq. (10) changes together with the swelling ratio according to Eq. (6), in which the value of parameters has been identified as:  $\beta = 0.8$ ,  $J^{\max} = 27.3$ . Quite similar to that shown in Fig. 1(b), it is obviously that the proposed nonaffine model can reproduce the experimental data successfully. However, compared with the minimum value of  $N/N_0$  shown in Fig. 1(a), that value shown in Fig. 2(a) decreases remarkably, which means that the free swelling process may lead to a larger change of the entangling structure of molecular chains rather than the tensional process does.

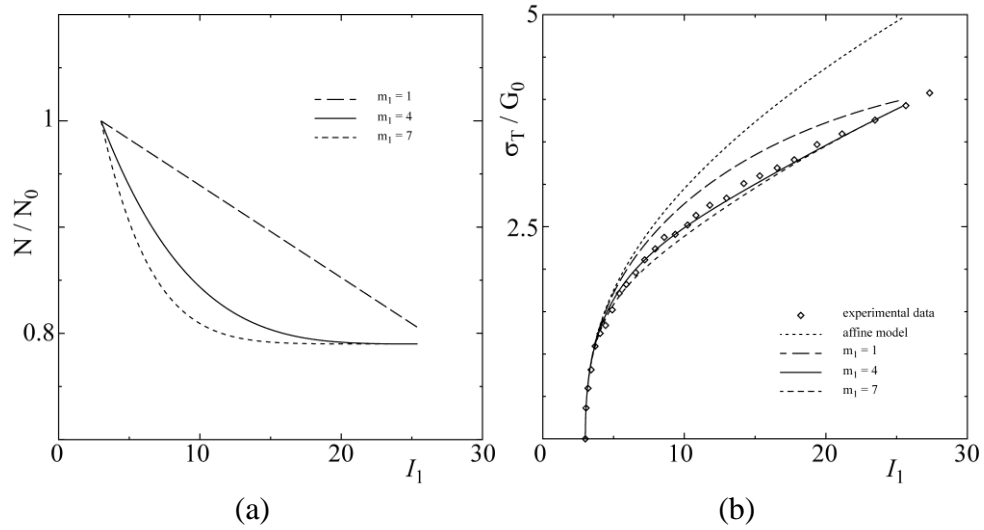
In Fig. 3, the theoretical prediction of the mechanical resistances of the elastomeric gel during the constrained swelling process. As the tensional process and the swelling process occur simultaneously in this case, we estimate the effect of each process on the change of the entangling structure of molecular chains with the weighted parameters,  $A$  and  $B$ , separately. When the value of  $A$  increases, the mechanical resistance of the gel increases and gets close to that predicted by affine model. Interestingly, when the value of  $B$  is equal to unit, the stress-stretch relation of the gel shows a yield region, which is left to our future study.

## Conclusions

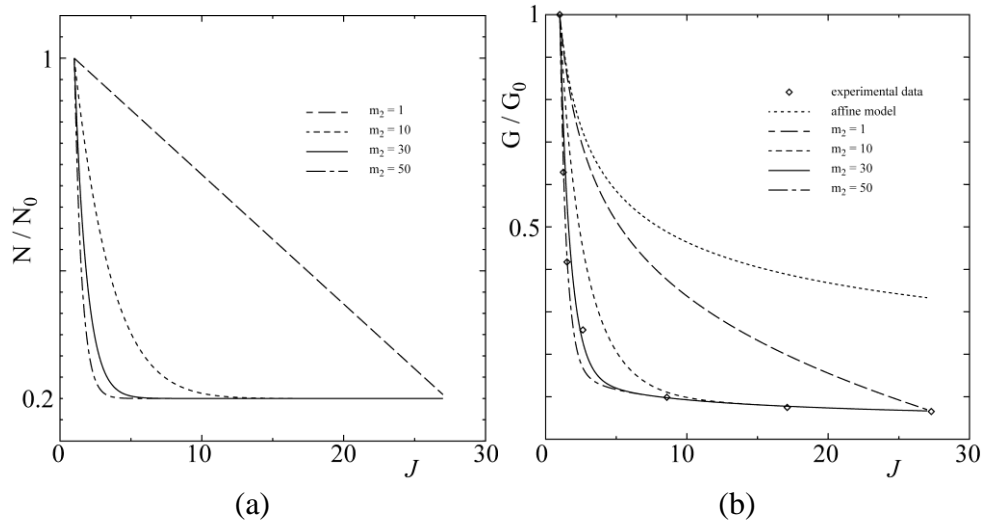
In this study, a nonaffine model is proposed for elastomeric gel to account for the change of the entangling structure of molecular chains during the tensional and swelling process. It is found that the free swelling process may lead to a larger change of the entangling structure of molecular chains rather than the tensional process does. Moreover, the various combination of the effect of each process on the nonaffine movement of molecular chains may lead to different interesting mechanical responses of the gel, such as yield.

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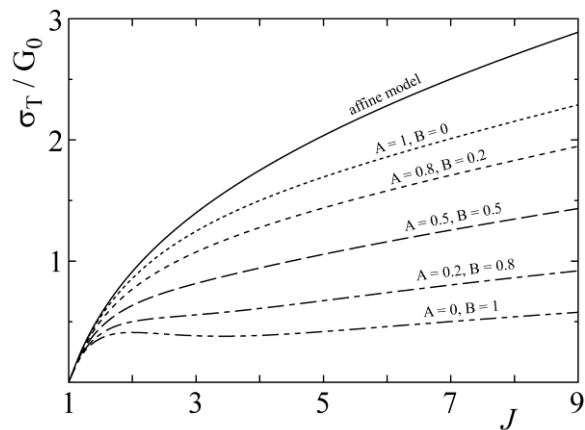
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**Figure 1. Characteristics of the gel in the reference state**  
**(a) variations of the entangling structure; (b) uniaxial tensile responses**



**Figure 2. Characteristics of the gel in the free swelling state**  
**(a) variations of the entangling structure; (b) variations of shear modulus**



**Figure 3. Mechanical resistances of the gel during the constrained swelling process**