

NUMERICAL SIMULATION OF NECK PROPAGATION IN DOUBLE NETWORK HYDROGEL

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Abstract. *In this study, we at first employ a nonaffine polymer chains network model to account for the irreversible structural change during the deformation of DN gels. And then, a finite element model of the DN gels under simple tension is constructed. On the other hand, neck propagation is one kind of localized instability and there will be a local transfer of strain energy from one part of the model to neighboring parts. To solve such unstable quasi-static problem, an automatic mechanism provided by Abaqus/Standard is employed. The simulation results show that the nonaffine polymer chains network model together with the stabilization algorithm for localized transformation of strain energy can be employed to reproduce the phenomenon of neck propagation in DN gels very well.*

1 INTRODUCTION

Double network (DN) gel is synthesized from monomers in the presence of a cross-linker via a two-step network formation: the first step is forming a tightly cross-linked network gel of polyelectrolyte. Then, the first gel is immersed in an aqueous solution of a second monomer with a low ratio of cross-linking agent and carrying out a second polymerization in the first network. Owing to the polyelectrolyte nature, the first polyelectrolyte gel highly swells in the second monomer solution. As a result, the first gel network is highly extended in the final product and the amount of the second network in the final gel is in large excess to that of the first network[1].

The DN hydrogels have drawn much attention as an innovative material having both high water content and high mechanical strength and toughness. The phenomenon such as yielding and neck propagation can be observed in some tough DN gels. For example, on tensile tests of DN gels that made from relatively sparse first networks, narrow zones appear in the sample and grow up with further stretching. During the neck propagation, a plateau region appears in the loading curve. The plateau value of the tensile stress hardly depends on the stretching rate. After the neck propagation, the gel becomes fairly soft, showing an elastic modulus *ca.* 1/10 of the virgin sample, and sustains large elongation, up to an elongation strain of around 20. The observations on the softened gels after the tensile test demonstrate that irreversible structural change takes place inside the gels, although their appearance is almost unchanged.

To account for such irreversible structural change in the DN gel, in one of our former studies[2], we investigated the development of the microstructure of polymer chains network of the gel based on a non-affine 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 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. More-

over, 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. Therefore, in this study, a nonaffine polymer chains network model of the DN gel is constructed and its possibility for the reproduction of the phenomenon of neck propagation is discussed.

With regard to the phenomenon of neck propagation, it is one kind of localized instability and there will be a local transfer of strain energy from one part of the model to neighboring parts. In another of our former studies[4], even though the possibility of the reproduction of such instability phenomenon is shown when the nonaffine polymer chains network model is employed with the finite element method, the computation diverges at certain deformation stage, where a very large deformation of the molecular chains occurs. Therefore, in this study, an automatic mechanism provided by Abaqus/Standard is employed for stabilizing such unstable quasi-static problem. With this automatic mechanism, a volume-proportional damping can be added to the constructed model automatically and the applied damping factors can vary spatially and with time to account for changes over the course of a step, where the damping factor is controlled by the convergence history and the ratio of the energy dissipated by viscous damping to the total strain energy.

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 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 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 \mathbf{F} is known.

The Helmholtz free energy of the 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 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 ideal 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 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:

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

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:

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

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. However, the observations on the DN gel after the tensile test demonstrate that irreversible structural change takes place inside the gel, although their appearance is almost unchanged[1]. 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 the polymer chains, i.e. the density of crosslinks of the polymer chains N vary from its initial value, 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 DN 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 :

$$\frac{N}{N_0} = \frac{1}{f} + \left(1 - \frac{1}{f} \right) \cdot \frac{I_{10}}{I_1}, \quad I_1 = F_{ik}F_{ik}, \quad (7)$$

where f is the ratio of the density of crosslinks of the 1st network to that of the 2nd network in its free swelling state and I_{10} is the deformation gradient of the network in its free swelling state.

4 STRESS-STRETCH RELATIONS

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

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

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 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 $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$.

4.1 Free Swelling State

Submerged in the solvent-containing environment but subject to no applied forces, the 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:

$$N_0v \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_0^3} \right) + \log \left(1 - \frac{1}{\lambda_0^3} \right) + \frac{1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6} = \frac{\mu}{k_B T}. \quad (9)$$

4.2 Simple Tension State

A unit cube of the 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. (8) gives

$$\begin{aligned} & Nv \left(\lambda_2 - \frac{1}{\lambda_2} \right) - 3N_0\lambda_0^2 \left(1 - \frac{1}{f} \right) [\lambda_1^2 + 2\lambda_2^2 - 3 - 2\log(\lambda_1\lambda_2^2)] \frac{\lambda_2}{(\lambda_1^2 + 2\lambda_2^2)^2} \\ & + \left[\lambda_1\lambda_2^2 \log \left(1 - \frac{1}{\lambda_1\lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{k_B T} \lambda_1\lambda_2^2 \right] \frac{1}{\lambda_2} = 0. \end{aligned} \quad (10)$$

Eq.(10) determine the transverse stretch λ_2 for a given longitudinal stretch λ_1 . Eq. (8) also relates the longitudinal stress s_1 to the stretches λ_1 and λ_2 as:

$$\begin{aligned} \frac{s_1}{k_B T/v} &= Nv \left(\lambda_1 - \frac{1}{\lambda_1} \right) - 3N_0\lambda_0^2 \left(1 - \frac{1}{f} \right) [\lambda_1^2 + 2\lambda_2^2 - 3 - 2\log(\lambda_1\lambda_2^2)] \frac{\lambda_1}{(\lambda_1^2 + 2\lambda_2^2)^2} \\ &+ \left[\lambda_1\lambda_2^2 \log \left(1 - \frac{1}{\lambda_1\lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{k_B T} \lambda_1\lambda_2^2 \right] \frac{1}{\lambda_1} = 0. \end{aligned} \quad (11)$$

5 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 DN gel is specified as $f = 15$, which is same as the value presumed by our former study[4]. The value of another parameter I_{10} can be calculated based on Eq.(9) and is specified as $I_{10} = 3\lambda_0^2 = 6.75$ when the value of the normalized chemical potential $\mu/k_B T$ is taken as -0.046 .

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 in its free swelling state. The dimensions of the specimen in x , y and z direction is $w_0 = 50mm$, $l_0 = 50mm$ and $t_0 = 10mm$ respectively. To initiate the necking at the bottom of the specimen, an initial geometrical imperfection of the dimension in x direction is added as $\Delta w_0 = -0.1\cos(\pi y/2l_0)$. 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 $z = 0$. A uniform tension is applied to the plane $y_0 = l_0$ under a shear-free condition.

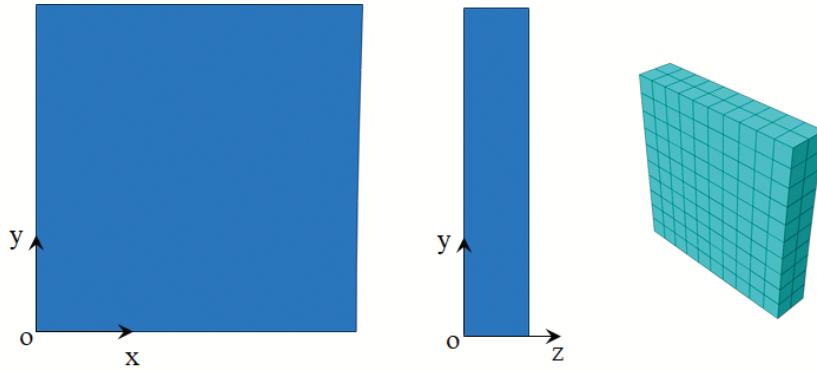


Figure 1: Computational model.

As the phenomenon of neck propagation is one kind of localized instability and there will be a local transfer of strain energy from one part of the model to neighboring parts, in this study, an automatic mechanism provided by Abaqus/Standard is employed for stabilizing such unstable quasi-static problem. With this automatic mechanism, a volume-proportional damping is added to the constructed model and the applied damping factors vary spatially and with time to account for changes over the course of a step. Moreover, the damping factor is determined in such a way that the dissipated energy for a given increment is a small fraction of the extrapolated strain energy and the value of such fraction is specified as 2×10^{-7} . Furthermore, to guarantee the determined value of the damping factor is optimal, it is controlled by the convergence history and the ratio of the energy dissipated by viscous damping to the total strain energy, where the value of such ratio is specified as 0.01.

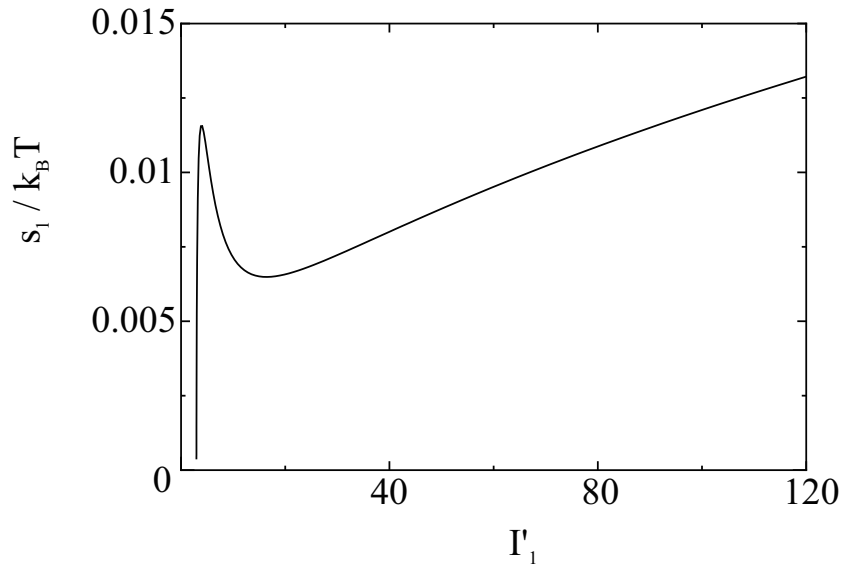


Figure 2: Simple tensile response of the homogeneous DN gel.

6 RESULTS

When an DN 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 the free swelling state of the gel as a updated reference state such that the polymer chains 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. Fig.2 shows the simple tensile response of the homogeneous DN gel with the consideration of the nonaffine movement of polymer chains. This result is derived from a calculation, which is performed based on Eq.(11). A remarkable material softening and a subsequent material hardening is observed. The material softening is due to the breakage of the 1st polymer chains network, whereas the subsequent material hardening is due to the orientational effect of the 2nd polymer chains network.

Fig.3 and Fig.4 shows the nominal stress-strain relation and the corresponding configurations of the nonuniform DN gel under simple tension, respectively. To compare with the experimental results[1], the nominal stress s is expressed with the dimension of MPa, meanwhile the value of $k_B T/v$ has been specified as 4×10^7 Pa. The nominal strain is expressed by u/l_0 , where u is the displacement of the plane $y_0 = l_0$. At the deformation stage (b), stress concentration occurs at the bottom of the specimen due to the initial geometrical imperfection. At the deformation stage (c), the necking onsets from the bottom of the specimen, which leads to a dramatic drop of the nominal stress. At the deformation stage (d), the neck propagates from the bottom to the top of the specimen and the nominal stress is almost constant with a little variation in a limit region. At the deformation stage (e), the neck propagation finishes and the specimen shows a uniform configuration. From then on, the nominal stress increases again due to the orientation hardening of the polymer chains of the 2nd network. By the way, the nominal stress-strain relation together with the configurations shown in Fig.3 and Fig.4 have reproduced the experimental results[1] very well.

7 CONCLUSIONS

In this study, the nonaffine polymer chains network model of the DN gel is proposed, in which the density of crosslinks of the polymer chains varies inverse proportionally with the first invariant of right Cauchy-Green deformation tensor. Employing with this model, a finite element model of a nonuniform DN gels under simple tension is constructed together with an automatic mechanism provided by Abaqus/Standard. The simulation results show that the nonaffine polymer chains network model together with the stabilization algorithm for localized transformation of strain energy can be employed to reproduce the phenomenon of neck propagation in DN gels very well.

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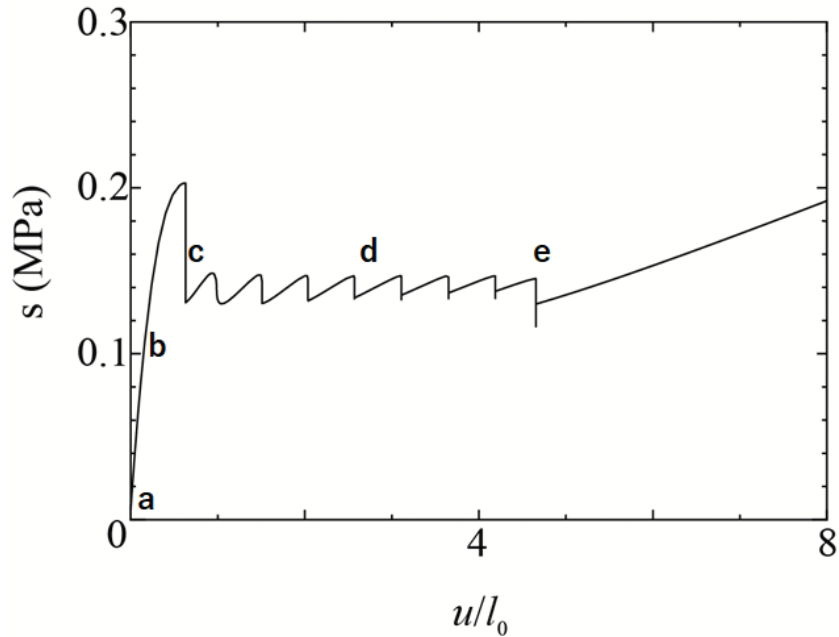


Figure 3: Simple tensile response of the nonuniform DN gel.

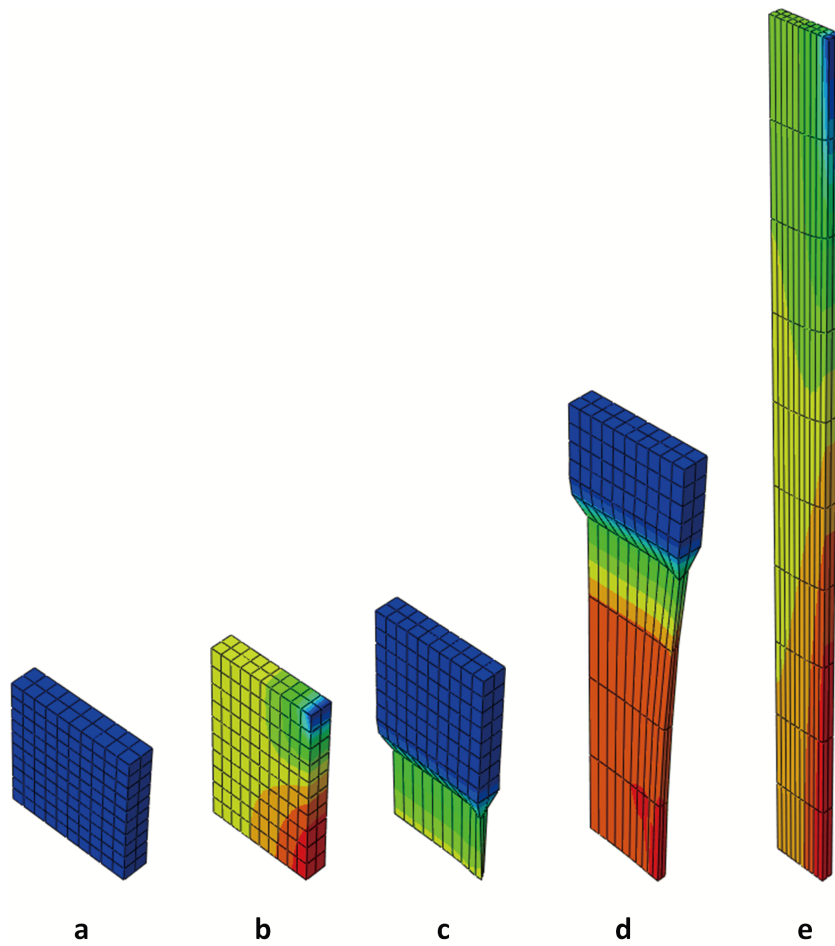


Figure 4: Configurations of the nonuniform DN gel during the neck propagation.