



Ultimate swelling described by limiting chain extensibility of swollen elastomers

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ARTICLE INFO

Keywords:
Elastomers
Swelling
Hyperelasticity
Limiting chain extensibility
Gels

ABSTRACT

In this study, we study ultimate swelling characterized by limiting chain extensibility of swollen elastomers. Limiting chain extensibility is introduced into the Flory–Rehner theory using the Arruda–Boyce eight chain model and the Gent phenomenological model. The difference between these models is unified by defining a single scalar function. The inequality derived from this function allows for analysis to provide an ultimate value of swelling ratio. This ultimate value is not exceeded at equilibrium swelling regardless of the set of material constants. Under uniaxial loading at equilibrium swelling, deswelling can occur even in tension. Further, the very large swelling behavior of pH sensitive hydrogels is found to originate from the resistance generated by approaching the ultimate value of swelling ratio.

1. Introduction

Swelling of elastomers by solvents was first investigated for the combination of natural rubbers and organic liquids [1,2]. Recently, a number of polymeric gels represented by hydrogels are regarded as swollen elastomers [3,4]. The Flory–Rehner theory is used to describe the mechanical and swelling behavior of swollen elastomers [1,5]. The free energy function consists of the sum of two terms associated with polymer stretching and the mixing of polymer and solvent molecules, which are derived from the Gaussian network theory (i.e., a Neo–Hookean (NH) model) and the Flory–Huggins solution theory, respectively. The Flory–Rehner theory has been systematically implemented into the commercially available finite element software [6,7], thereby allowing researchers to analyze a variety of swelling-induced mechanical problems [4,6,8,9]. However, the NH model may be too simple to describe the nonlinear elasticity of elastomers undergoing large deformations.

When the NH model in the Flory–Rehner theory is replaced by a more sophisticated strain-energy function for rubber elasticity, it is natural to consider models that include the non-Gaussian chain effect, i.e., the effect of limiting chain extensibility. In non-Gaussian network theory [2,10], the limited extensibility of the single chain is expressed approximately using the inverse Langevin function with an additional material constant, n , i.e., the number of rigid links in the single chain. Arruda and Boyce [11] developed the 8-chain model (AB model), which is based on a cubic representative cell containing 8 chains along diagonal directions (cf. 3- and 4-chain models). In contrast, the well-known phenomenolog-

ical model by Gent [12] (G model) is a simple and accurate approximation of the AB model without the inverse Langevin function [13,14]. The G model has the additional material constant, J_m , instead of n used in the AB model. The AB and G models are appropriate to investigate the effect of limiting chain extensibility because the physical significance of the additional material constants, n and J_m , is clear.

Chester and Anand [15,16] and Li et al. [17] introduced the AB and G models to the Flory–Rehner theory, respectively, to investigate the effect of limiting chain extensibility. Chester and Anand [15,16] compared the transient swelling response of a constrained gel predicted by Gaussian and non-Gaussian network theories. Here, the constant related with n was fixed and was not parameterized. Li et al. [17] showed that by adjusting J_m in the G model, the discrepancy of osmotic pressure functions was removed for very large swelling ratios of two different pH sensitive hydrogels. In addition, although Boyce and Arruda [18] investigated the use of the AB model, the effect of the swelling ratio on the stress–stretch behavior under uniaxial tension and compression did not involve the use of the Flory–Rehner theory; i.e., the swelling ratio was fixed during uniaxial loading. Thus, the effect of limiting chain extensibility on the mechanical responses of swollen elastomers is not sufficiently clear at full length.

In addition to those models described above based on the Flory–Rehner approach, other modeling approaches may be found in the literature. One such approach is based on the classical work of Terzaghi [19] and Biot [20] which focused on poroelasticity for geomechanics. Others following the work of Truesdell [21], Bowen [22] and Shi et al. [23] are based on the theory of mixtures. Recent models using these

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approaches have found success in modeling the behavior of swollen elastomers [24,25]. Lastly, Bouklas and Huang [26] have demonstrated that a linear poroelasticity theory is consistent with the Flory–Rehner theory under the condition of small perturbations from a freely swollen state. However, in what follows we take the approach of extending the Flory–Rehner theory to account for limiting chain extensibility. It is worthwhile to elucidate the interaction between limiting chain extensibility and swelling in swollen elastomers undergoing finite deformations because a more comprehensive analysis may provide a deeper interpretation to the mechanical and swelling behavior of gels, such as pH sensitive hydrogels with very large swelling ratios.

In this study, ultimate swelling characterized by limiting chain extensibility of swollen elastomers is examined. Section 2 presents the fundamental relations derived from the Flory–Rehner theory. Limiting chain extensibility is introduced via the AB and G models. The difference between these models is unified by defining a single scalar function. Section 3 shows that an inequality is derived from the limit included in this scalar function, which is used for ultimate analysis in Sections 4 and 5. The ultimate analysis is performed under free swelling and uniaxial loading, respectively, which yields an ultimate value of the volume swelling ratio. This ultimate value is not exceeded at equilibrium swelling regardless of the set of material constants. Under uniaxial loading at equilibrium swelling, deswelling can occur even in tension. Further, in Section 6, the very large swelling behavior of pH sensitive hydrogels is found to result from the resistance generated by approaching the ultimate value of swelling. Finally, conclusions are presented in Section 7.

2. Fundamental relations

Flory and Rehner [5] assumed that to describe the mechanical and swelling behavior of elastomers, the free energy function is expressed as the sum of two terms associated with polymer stretching and the mixing of polymer and solvent molecules:

$$W = W_e(\lambda_i) + W_m(C), \tag{1}$$

where W_e is the elastic strain energy and W_m is the mixing energy. The use of the Gaussian network theory and the Flory–Huggins solution theory gives:

$$W_e = \frac{E_0}{6} (I_1 - 3 - a \log J), \quad \text{Neo–Hookean (NH) model}, \tag{2}$$

$$W_m = -\frac{kT}{v} \left\{ vC \log \left(1 + \frac{1}{vC} \right) + \frac{\chi}{1 + vC} \right\}, \tag{3}$$

where λ_i ($i = 1, 2, 3$) are the principal stretches so that the invariants are expressed as $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$, $I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2$ and $J = \lambda_1 \lambda_2 \lambda_3$, and C is the nominal concentration of solvent molecules.

In Eq. (2), E_0 is the reference Young’s modulus. For the NH model, E_0 is defined as the Young’s modulus of the undeformed, unswollen state (i.e., $\lambda_i = 1$). The logarithmic term $-a \log J$ originates from the entropy of deformation [1]. The value of a depends on the theory and can be taken as $a = 0, 1$ and 2 [1,2,7,27]. It is also possible to take a negative value to describe phenomenologically the experimental data [28]. This logarithmic term will be introduced into the AB and G models in the same manner. However, for simplicity, $a = 0$ is used as the representative value (see Appendix A). In Eq. (3), kT is the absolute temperature expressed as a thermal energy, v is the volume per solvent molecule, and χ is the Flory–Huggins interaction parameter that characterizes the enthalpy of mixing.

When the NH model is replaced by the AB or G models including the non-Gaussian chain effect, W_e for the AB model [11] is expressed as:

$$W_e = \frac{E_0}{6} \left\{ 2\sqrt{n}\beta\Lambda + 2n \log \left(\frac{\beta}{\sinh \beta} \right) - a \log J \right\}, \tag{4}$$

Arruda–Boyce (AB) model,

where n is the number of rigid links in the single chain related to limited extensibility, and

$$\Lambda = \sqrt{(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)/3} = \sqrt{I_1/3}, \tag{5}$$

$$\beta = L^{-1}(\Lambda/\sqrt{n}). \tag{6}$$

Here, $L^{-1}(x)$ is the inverse Langevin function defined as $x = \coth \beta - 1/\beta = L(\beta)$. In contrast, W_e for the G model [12] is expressed as:

$$W_e = \frac{E_0}{6} \left\{ -J_m \log \left(1 - \frac{I_1 - 3}{J_m} \right) - a \log J \right\}, \quad \text{Gent (G) model}, \tag{7}$$

where J_m is a material constant to describe the limiting chain extensibility. When Eqs. (4) and (7) take the limit as $n \rightarrow \infty$ and $J_m \rightarrow \infty$, respectively, the AB and G models reduce to the NH model [14].

In the AB model, the effect of limiting chain extensibility is described as a process where $L^{-1}(x)$ takes the limit as $x \rightarrow 1$, i.e., $\beta \rightarrow \infty$. Note that $L^{-1}(x)$ cannot be written in a closed form and this feature prevents further analytical analysis [29]. To avoid this problem simply, the Padé approximant can be used to approximate the inverse Langevin function [30], that is,

$$\beta = L^{-1}(x) \approx 3x \frac{35 - 12x^2}{35 - 33x^2}, \quad \text{Padé (P) approx.} \tag{8}$$

Eq. (8) is a simple form and is able to take the limit as $x \rightarrow (35/33)^{1/2} \approx 1.03$, leading to $\beta \rightarrow \infty$ (cf. a truncation of the Taylor series of $L^{-1}(x)$). Thus, the employment of Eq. (8) makes analytical manipulation easy using the AB model. In addition, the G model takes the limit as $I_1 \rightarrow 3 + J_m$ (see Eq. (7)). Although there are different approximations originating from the Padé approximant [14,29,30], the present study simply focuses on Eq. (8) as a standard case.

Assuming that the network of polymer and liquid solvent is incompressible, the volume of swollen elastomers is the sum of the volume of the dry network and that of the swelling solvent [2,6]. The volume swelling ratio of swollen elastomers is equal to J and is expressed as

$$J = 1 + vC. \tag{9}$$

When a Lagrange multiplier is used in Eq. (1) to impose the constraint of Eq. (9),

$$W = W_e(\lambda_i) + W_m(C) + \Pi(1 + vC - J), \tag{10}$$

where Π is the Lagrange multiplier, and is referred to as the osmotic pressure due to mixing in the present study [7,31,32].

Eq. (10) gives the nominal stress in each direction of the principal stretches ($i = 1, 2, 3$),

$$s_i = \frac{\partial W}{\partial \lambda_i} = \frac{E_0}{3} \left(\Omega \lambda_i - \frac{a}{2\lambda_i} \right) - \Pi \frac{J}{\lambda_i}, \tag{11}$$

where Ω is the scalar function that depends on the models (Eqs. (2), (4) and (7)), that is,

$$\Omega(I_1) = \begin{cases} 1, & \text{NH model} \\ \frac{\sqrt{n}\beta}{3\Lambda}, & \text{AB model} \\ \frac{35n-4I_1}{35n-11I_1}, & \text{AB model + P approx.} \\ \frac{J_m}{J_m - I_1 + 3}, & \text{G model} \end{cases} \tag{12}$$

The nominal stress of Eq. (11) is transformed into the true stress,

$$s_i = \frac{s_i \lambda_i}{J} = \frac{E_0}{3J} \left(\Omega \lambda_i^2 - \frac{a}{2} \right) - \Pi, \quad \text{no sum on } i. \tag{13}$$

Eqs. (11) and (13) imply that the difference between the models is unified via the single scalar function Ω . Next, when μ presents the chemical potential of the external solvent, Eqs. (3), (9) and (10) lead to

$$\mu = \frac{\partial W}{\partial C} = kT \left\{ \log \left(\frac{J-1}{J} \right) + \frac{1}{J} + \frac{\chi}{J^2} \right\} + \Pi v = 0. \tag{14}$$

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