Constitutive equations in finite elasticity of swollen elastomers

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**Abstract**

Constitutive equations are formulated for the mechanical behavior of rubber-like materials subjected to swelling under an arbitrary deformation with finite strains. Based on the Flory theory of polymer networks with constrained junctions, a novel expression is derived for free energy density of a swollen elastomer. This expression is applied to study the effect of strain rate on the elastic response of hydrogels under tension and compression.

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**1. Introduction**

This paper deals with constitutive modeling and numerical simulation of the elastic response of rubber-like materials subjected to swelling. We focus on the semi-dilute regime of swelling when degree of swelling and diffusion is the main mechanism of solvent transport.

Analysis of swelling of elastomers under loading has a long history that goes back to the seminal paper by Flory and Rehner (1943). Recent attention to this problem is explained by growing interest to mechanical and physical properties of hydrogels that demonstrate potential for a wide range of applications including biomedical devices, drug delivery carriers, scaffolds for tissue engineering, filters and membranes for selective diffusion, sensors for on-line process monitoring, soft actuators, and smart optical systems (Stuart et al., 2010; Deligkaris et al., 2010; Messing and Schmidt, 2011; Buenger et al., 2012).

The effects of mechanical loading on the kinetics of swelling of hydrogels have been investigated in a number of experimental studies, see Urayama and Takigawa (2012) for a brief review. Constitutive models for elastomers subjected to swelling have recently been developed by Dolbow et al. (2004), Hong et al. (2008), Hong et al. (2009), Doi (2009), Duda et al. (2010), Chester and Anand (2010), Chester and Anand (2011), Baek and Pence (2011), Yan and Jin (2012), Cai and Suo (2012), Bouklas and Huang (2012) and Lucantonio et al. (2013), to mention a few.

In the present study, we adopt a conventional approach and treat a rubber-like material as an elastic medium (a permanent network of chains). The latter does not exclude, however, that its mechanical behavior demonstrates viscoelastic and viscoplastic properties. Due to diffusion of fluid inside (outside) an elastomer immersed into a solvent and subjected to tension (compression), its response becomes time-dependent (which is observed in relaxation and creep tests (Choi et al., 2007; Kalyanam et al., 2009; Zhang et al., 2010; Lou et al., 2012), and rate-dependent (which is confirmed by experimental data in tensile tests with various strain rates (Konda et al., 2011)). For a discussion of constitutive models that accounts for viscoelasticity of swollen elastomers explicitly (for example, by allowing chains in the polymer network to rearrange), we refer to Hui and Long (2012) and Chester (2012).

Although constitutive equations for the mechanical behavior of elastomers subjected to swelling have been rigidly established, they reveal modest agreement with experimental data. For example, for the neo–Hookean model, large deviations between theoretical predictions and observations in uniaxial tensile tests were reported by Johnson and Mark (1972), de Candia (1972), Fontaine et al. (1989a), and Fontaine et al. (1989b), to mention a few. The latter may be explained by the fact that conventional expressions for strain energy density of a polymer network (that describe correctly stress–strain diagrams under volume preserving deformations) fail to predict the elastic response of rubber-like materials suffering finite volume changes.

The objective of this work is twofold: (i) to develop a novel expression for the strain energy density of a polymer network that accounts for its volumetric deformation induced by swelling, and...
(ii) to demonstrate applicability of this relation for prediction of rate-dependent phenomena in swollen elastomers.

The exposition is organized as follows. Constitutive equations for the mechanical response of rubber-like materials subjected to swelling under an arbitrary three-dimensional deformation with finite strains are discussed in Section 2, where it is shown that conventional models grounded on the separability principle (Section 2.4) describe poorly observations on dry and totally swollen elastomers. A new form of strain energy density is developed in Section 3 based on the Flory concept of polymer networks with constrained junctions (Flory, 1977). An advantage of the proposed expression is that it is relatively simple for theoretical analysis, involves two adjustable parameters only, and allows changes in elastic moduli induced by swelling to be described quantitatively. The influence of strain rate on solvent uptake and stress–strain diagrams of swollen elastomers subjected to uniaxial tension (compression) is analyzed numerically in Section 4. Concluding remarks are formulated in Section 5.

2. Constitutive equations for an elastomer subjected to swelling

An elastomer immersed in a solvent bath is treated as a two-phase continuum composed of a polymer network and solvent molecules diffusing through the network and inducing its swelling. Denote by \( \mathbf{F} \) deformation gradient for transition from the reference configuration of the elastomer (in its dry undeformed state) into the actual configuration. Both polymer network and solvent are presumed to be incompressible, which means that

\[
\det \mathbf{F} = 1 + \nu \kappa, \quad (1)
\]

where \( \kappa \) stands for number of solvent molecules per unit volume of an elastomer in its reference configuration, and \( \nu \) denotes volume of a solvent molecule. Although we use the term “molecule”, clustering of solvent molecules (Du et al., 2012) is not excluded, which means that a “molecule” means here a cluster of molecules that diffuse jointly through an elastomer, and \( \nu \) stands for its characteristic volume (which exceeds strongly volume of a solvent molecule). The incompressibility assumption (1) for solid and fluid phases of a swollen elastomer represents the conventional standpoint. Constitutive models grounded on other hypotheses were proposed by Dolbow et al. (2004) and Cai and Suo (2012).

2.1. Kinematic relations

Kinematic relations are derived following the approach suggested by Chester and Anand (2010). Macro-deformation of an elastomer subjected to swelling is treated as a superposition of two processes: (i) an increase in specific volume (swelling) due to solvent transport, and (ii) volume-preserving deformation of a polymer network. This leads to the multiplicative decomposition of the deformation gradient for macro-deformation

\[
\mathbf{F} = \mathbf{F}_n \cdot \mathbf{F}_s, \quad (2)
\]

where the dot stands for inner product (in the component form, \( F_{ij} = F_{n,im}F_{s, mj} \), where summation over \( m \) is presumed). The deformation gradient

\[
\mathbf{F}_n = k_n \mathbf{I}, \quad (3)
\]

where \( \mathbf{I} \) is the unit tensor, and

\[
k_n = (1 + \nu \kappa c)^{1/3}, \quad (4)
\]

describes swelling of the network, and the deformation gradient \( \mathbf{F}_s \) with

\[
\det \mathbf{F}_n = 1 \quad (5)
\]

characterizes isochoric deformation of the polymer network. Differentiation of Eq. (2) with respect to time \( t \) implies that

\[
\dot{\mathbf{F}} = \dot{\mathbf{F}}_n k_n + \dot{\mathbf{F}}_s k_n, \quad (6)
\]

It follows from Eqs. (2), (3), (6) that

\[
\mathbf{L} = \mathbf{L}_n + \dot{k}_n \mathbf{I}, \quad (7)
\]

where

\[
\mathbf{L} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1}, \quad \mathbf{L}_n = \dot{\mathbf{F}}_n \cdot \mathbf{F}_n^{-1} \quad (8)
\]

denote velocity gradients. Insertion of Eq. (4) into (7) results in

\[
\mathbf{L}_n = \mathbf{L}_n - \frac{\nu \kappa c}{3(1 + \nu \kappa c)} \mathbf{I}, \quad \mathbf{D} = \mathbf{D}_n = \frac{\nu \kappa c}{3(1 + \nu \kappa c)} \mathbf{I}. \quad (9)
\]

where

\[
\mathbf{D} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^T), \quad \mathbf{D}_n = \frac{1}{2} (\mathbf{L}_n + \mathbf{L}_n^T)
\]

stand for the rate-of-strain tensors.

Denote by \( \mathbf{B}_n \) and \( \mathbf{C}_n \) the Cauchy–Green tensors for deformation of the polymer network

\[
\mathbf{B}_n = \mathbf{F}_n \cdot \mathbf{F}_s^{-1}, \quad \mathbf{C}_n = \mathbf{F}_n^{-1} \cdot \mathbf{F}_n, \quad (10)
\]

where \( \top \) stands for transpose. Differentiating Eq. (10) with respect to time and using Eq. (8), we find that

\[
\frac{d}{dt} \mathbf{B}_n = \mathbf{L}_n \cdot \mathbf{B}_n + \mathbf{B}_n \cdot \mathbf{L}_n^T, \quad \frac{d}{dt} \mathbf{B}_n^{-1} = -\mathbf{B}_n^{-1} \cdot \mathbf{L}_n - \mathbf{L}_n^T \cdot \mathbf{B}_n^{-1}. \quad (11)
\]

The first two principal invariants \( J_{1n} \) and \( J_{2n} \) of the Cauchy–Green tensors are given by

\[
J_{1n} = \mathbf{B}_n : \mathbf{I}, \quad J_{2n} = \mathbf{B}_n^{-1} : \mathbf{I}. \quad (12)
\]

where the colon stands for convolution. Their third principal invariant \( J_{3n} \) equals unity.

It follows from Eqs. (11) and (12) that

\[
\dot{J}_{1n} = 2 \mathbf{B}_n : \mathbf{D}_n, \quad \dot{J}_{2n} = -2 (\mathbf{B}_n^{-1})^T : \mathbf{D}_n. \quad (13)
\]

where the prime stands for the deviatoric component of a tensor, and we use the fact that \( \mathbf{D}_n \) is a traceless tensor.

2.2. Diffusion of solvent

The surface element \( \mathbf{N} \cdot \mathbf{dA} \) with unit normal \( \mathbf{N} \) in the actual configuration is connected with the surface element \( \mathbf{N} \cdot \mathbf{da}_t \) with unit normal \( \mathbf{N} \), in the reference configuration by the equation

\[
\mathbf{N} \cdot \mathbf{dA} = (1 + \nu \kappa c) \mathbf{F}^{-T} \cdot \mathbf{N} \cdot \mathbf{da}_t = (1 + \nu \kappa c) \mathbf{N} \cdot \mathbf{F}^{-T} \cdot \mathbf{da}_t. \quad (14)
\]

Let \( \mathbf{j} \) and \( \mathbf{j}_s \) denote solvent flux vectors in the actual and reference configurations, respectively (number of solvent molecules moving through the unit area per unit time). Keeping in mind that

\[
\mathbf{N} \cdot \mathbf{j} \cdot \mathbf{dA} = \mathbf{N} \cdot \mathbf{j}_s \cdot \mathbf{da}_t, \quad (15)
\]

we find from Eq. (14) that

\[
\dot{\mathbf{j}} = (1 + \nu \kappa c) \mathbf{F}^{-T} \cdot \dot{\mathbf{j}}. \quad (16)
\]

Denote by \( \tilde{\mu} \) chemical potential per molecule of solvent. The chain rule for differentiation implies that

\[
V_t \tilde{\mu} = V \tilde{\mu} \mathbf{F} = \mathbf{F}^{-T} \cdot V \tilde{\mu}. \quad (17)
\]

We adopt the standard equation for solvent diffusion in the actual configuration

\[
\mathbf{j} = \frac{D c}{k_BT} \nabla \tilde{\mu}, \quad (18)
\]
where $T$ is the absolute temperature, $k_b$ is Boltzmann’s constant, $D$ stands for diffusivity, and

$$c = \frac{D c_r}{1 + v c_r}$$

(19)
denotes concentration of solvent in the actual configuration. Insertion of Eqs. (17)–(19) into Eq. (16) results in

$$j_i = \frac{-D c_r}{k_B T} F^{-1} \cdot V_i \tilde{\mu} \cdot F^{-1}.$$  

(20)
The mass conservation law for solvent flow reads

$$\dot{c}_i = -V_i \cdot j_i.$$ 

(21)
Combination of Eqs. (20) and (21) results in the nonlinear equation for diffusion of solvent

$$\dot{c}_i = \frac{D}{k_B T} V_i \cdot \left( c_i F^{-1} \cdot V_i \tilde{\mu} \cdot F^{-1} \right).$$

(22)

### 2.3. Stress–strain relations

Denote by $\mathbf{T}$, the first Piola–Kirchhoff tensor and by $\mathbf{T}$ the Cauchy stress tensor. It follows from the equality

$$\mathbf{N}_i \cdot \mathbf{T} \, d \mathbf{A}_n = \mathbf{N}_i \cdot d \mathbf{A}_n$$

(23)
and Eq. (14) that

$$\mathbf{T}_i = (1 + v c_i) F^{-1} \cdot \mathbf{T}.$$ 

(24)
The kinetic equation for free energy imbalance reads (Chester and Anand, 2010)

$$\dot{\psi}_i - \mathbf{T}_i : \dot{\mathbf{F}} - \tilde{\mu} \dot{c}_i + j_i \cdot V_i \tilde{\mu} \leq 0,$$ 

(25)
where $\psi_i$ stands for the specific free energy per unit volume in the reference configuration. The quantity $\psi_i$ is presumed to be a function of the first two principal invariants of the Cauchy–Green tensors and concentration of solvent

$$\psi_i = \psi_i(j_{1n} - j_{2n}, c_i).$$

(26)
Bearing in mind that

$$\mathbf{T}_i : \dot{\mathbf{F}} = (1 + v c_i) \mathbf{T}_i : \mathbf{D}_n = \frac{1}{3} v c_i \text{tr}(\mathbf{T}),$$

(27)
where $\text{tr}$ denotes the first principal invariant of a tensor, we rewrite Eq. (25) in the form

$$\dot{\psi}_i - (1 + v c_i) \mathbf{T}_i : \mathbf{D}_n - \tilde{\mu} \dot{c}_i + j_i \cdot V_i \tilde{\mu} \leq 0,$$ 

(28)
where

$$\tilde{\mu} = \mu + \frac{1}{3} v \text{tr}(\mathbf{T}).$$

(29)
It follows from Eq. (13) and the chain rule of differentiation that the derivative of function (26) is given by

$$\dot{\psi}_i = 2(\psi_i, \mathbf{B}_n - \psi_i, \mathbf{B}_n^{-1}) : \mathbf{D}_n + \psi_{i,3} \dot{c}_i,$$

(30)
where $\psi_{i,m}$ denotes derivative of $\psi_i$ with respect to its $m$th argument. Substitution of Eqs. (20) and (30) into Eq. (28) results in

$$\left[ 2(\psi_i, \mathbf{B}_n - \psi_i, \mathbf{B}_n^{-1}) - (1 + v c_i) \mathbf{T} \right] : \mathbf{D}_n + (\psi_{i,3} - \tilde{\mu}) \dot{c}_i - \frac{D c_r}{k_B T} (F^{-1} \cdot V_i \tilde{\mu}) \cdot (F^{-1} \cdot V_i \tilde{\mu}) \leq 0.$$ 

(31)
Inequality (31) is satisfied for an arbitrary deformation, provided that the Cauchy stress tensor reads

$$\mathbf{T} = -P I + \frac{2}{1 + v c_i} (\psi_i, \mathbf{B}_n - \psi_i, \mathbf{B}_n^{-1}) \dot{c}_i,$$ 

(32)
where $P$ stands for an unknown pressure, and

$$\tilde{\mu} = \psi_{i,3}.$$ 

This equality together with Eqs. (29) and (32) implies that

$$\tilde{\mu} = P v + \psi_{i,3}.$$ 

(33)
Given a specific free energy $\psi_i$, in the form (26), Eqs. (32) and (33) provide stress–strain relations for an elastomer subjected to swelling with finite deformations.

### 2.4. Free energy density

To close the constitutive equations, an expression should be introduced for the specific free energy $\psi_i$. The free energy density of a swollen elastomer is conventionally presumed to be equal to the sum of the specific free energy of a polymer network and the energy of mixing of solvent molecules with long (the number of monomers in each molecule is large compared with unity) polymer chains

$$\psi_i = \psi_{net} + \psi_{mix}.$$ 

(34)
With reference to the Flory–Huggins theory of mixing, the latter term is presented in the form (Hong et al., 2008; Hong et al., 2009)

$$\psi_{mix} = k_B T \left( c_i \ln \frac{v c_i}{1 + v c_i} + \frac{c_i}{1 + v c_i} \right).$$ 

(35)
where $\gamma$ denotes the Flory–Huggins parameter.

Although we utilize Eq. (35) in this study, it should be mentioned that this equation does not ensure an acceptable agreement with observations on hydrogels (Durning and Morman, 1993; Lou et al., 2012; Cai and Suo, 2012). The simplest way to improve this agreement is to multiply the right-hand side of Eq. (35) by a dimensionless coefficient (Lou et al., 2012). We choose a similar approach and treat volume of a solvent cluster $v$ as a parameter to be found by matching experimental data. More sophisticated refinements of Eq. (35) are grounded on replacement of this equation with its nonlinear analog (Durning and Morman, 1993) and introduction of terms proportional to the square of concentration gradient (Zhou et al., 2010). Conventional expressions for $\psi_{net}$ are based on the separability principle which presume the strain energy density of a polymer network to be presented as the sum of two components

$$\psi_{net} = w_1 + w_3,$$

where $w_1$ is a function of the first two invariants of the Cauchy–Green tensors, while $w_3$ depends on their third invariant $J_3$ only.

Choosing either the principal invariants $J_1, J_2$ (Hong et al., 2008; Hong et al., 2009; Chester and Anand, 2010; Baek and Pence, 2011), or the reduced principal invariants (Dolbow et al., 2004)

$$\tilde{J}_1 = \frac{J_1}{J_3}, \quad \tilde{J}_2 = \frac{J_2}{J_3}, \quad \tilde{J}_3 = k_B^6,$$

(36)
the Cauchy–Green tensor as arguments of $w_1$, and using Eq. (4) and the equalities

$$J_1 = k_B^6 J_{1n}, \quad J_2 = k_B^6 J_{2n}, \quad J_3 = k_B^6,$$

(37)
we arrive at the formulas

$$\psi_i = w_1 \left( 1 + v c_i \right)^\tilde{J}_{1n} \left( 1 + v c_i \right)^\tilde{J}_{2n} + w_3 \left( 1 + v c_i \right)^2$$

$$+ k_B T \left( c_i \ln \frac{v c_i}{1 + v c_i} + \frac{c_i}{1 + v c_i} \right).$$

(38)
and

\[ \psi_t = w_1(j_{1n}J_{2n}) + w_3(1 + \nu c_t)^2 \]
\[ + k_BT \left( c_t \ln \frac{\nu c_t}{1 + \nu c_t} + \frac{\nu c_t}{1 + \nu c_t} \right). \quad (39) \]

2.5. Comparison with observations of swollen elastomers

It follows from Eqs. (32) and (33) that constitutive equations for an elastomer with free energy density (38) read

\[ T = -\Pi + \frac{2}{1 + \nu c_t} \left[ w_{11}B_n - w_{12}(1 + \nu c_t)^2B_n^{-1} \right], \]

\[ \mu = k_BT \left[ \ln \frac{\nu c_t}{1 + \nu c_t} + \frac{1}{1 + \nu c_t} + \frac{\nu}{(1 + \nu c_t)} \right] + P + \frac{2}{3(1 + \nu c_t)} \]
\[ \times \left[ w_{11}(1 + \nu c_t)^2j_{1n} + 2w_{12}(1 + \nu c_t)^2j_{2n} + 3w_{11}(1 + \nu c_t)^2 \right]. \quad (40) \]

and those for an elastomer with free energy density (39) are given by

\[ T = -\Pi + \frac{2}{1 + \nu c_t} \left[ w_{11}B_n - w_{12}B_n^{-1} \right], \]

\[ \mu = k_BT \left[ \ln \frac{\nu c_t}{1 + \nu c_t} + \frac{1}{1 + \nu c_t} + \frac{\nu}{(1 + \nu c_t)} \right] + P + 2 \nu w_{11}(1 + \nu c_t). \quad (41) \]

To examine applicability of Eqs. (40) and (41) for the analysis of experimental data, we consider uniaxial tension–compression of an elastomer in its dry \((c_t = 0)\) and totally swollen \((\nu c_t = Q_0)\) states, where \(Q_0\) stands for the ultimate degree of swelling. In these limiting cases, chemical potential \(\mu\) is independent of time and spatial coordinates, which implies that \(c_t\) can be treated as a constant.

Under uniaxial tension–compression, tensor \(F_n\) reads

\[ F_n = k \varepsilon \otimes \varepsilon_t + kT \left( \varepsilon_e \otimes \varepsilon_e + \varepsilon_r \otimes \varepsilon_r \right), \quad (42) \]

where \(k\) denotes elongation ratio, \(e_m (m = 1, 2, 3)\) are unit vectors of a Cartesian coordinate frame in the reference (swollen and undeformed) state, and \(\otimes\) stands for tensor product. Inserting Eq. (42) into Eq. (40), and taking into account that the Cauchy stress tensor is given by

\[ T = \sigma k \varepsilon \otimes \varepsilon_t, \quad (43) \]

where \(\sigma\) denotes engineering tensile stress, we arrive at the formula

\[ \sigma = \frac{2}{1 + \nu c_t} \left[ w_{11} + w_{12} \frac{1}{k} (1 + \nu c_t)^2 \right] \left( k - \frac{1}{k^2} \right). \quad (44) \]

Denote by \(\sigma_{\text{dry}}(k)\) and \(\sigma_{\text{swollen}}(k)\) stress–strain dependencies for uniaxial tension of an elastomer in its dry and swollen states. For a neo–Hookean material with

\[ w_1 = \frac{C}{2}(J_1 - 3), \quad (45) \]

where the constant coefficient \(C\) denotes shear modulus, Eq. (44) implies that

\[ |\sigma_{\text{swollen}}(k)| \geq \frac{1}{1 + Q_0^2} \left| \sigma_{\text{dry}}(k) \right|. \quad (46) \]

where we introduce absolute values to account for both tension and compression. When the function \(w_1\) adopts the general expression

\[ w_1 = \sum_{m,n=0}^\infty c_{mn}(J_1 - 3)^m(J_2 - 3)^n \]

with non-negative coefficients \(c_{mn}\), Eq. (46) is replaced with the inequality

\[ |\sigma_{\text{swollen}}(k)| \geq \frac{1}{1 + Q_0^2} \left| \sigma_{\text{dry}}(k) \right|. \quad (47) \]

An important shortcoming of Eqs. (46) and (47) is that they predict observations in uniaxial tensile and compressive tests on swollen elastomers rather poorly. For the neo–Hookean material, this was demonstrated, for example, by Johnson and Mark (1972), de Candia (1972), Fontaine et al. (1989a), and Fontaine et al. (1989b). Moreover, Eq. (46) implies that the elastic modulus of a swollen elastomer decreases being proportional to \((1 + Q_0)^{-\frac{1}{2}}\), while observations reveal a scaling exponent that is noticeably higher than \(\frac{1}{2}\) (Durning and Morrow, 1993; Hedden et al., 2000; Kong et al., 2002).

Repeating the same transformations for Eq. (41), we arrive at the formula

\[ \sigma = \frac{2}{1 + \nu c_t} \left[ w_{11} + w_{12} \frac{1}{k} (1 + \nu c_t)^2 \right] \left( k - \frac{1}{k^2} \right). \quad (48) \]

For an analog of the neo–Hookean material with

\[ w_1 = \frac{1}{2} \mu J_1 - 3, \]

Eq. (48) implies that

\[ |\sigma_{\text{swollen}}(k)| = \frac{1}{1 + Q_0} \left| \sigma_{\text{dry}}(k) \right|. \quad (49) \]

To demonstrate that Eqs. (46) and (49) do not provide an acceptable agreement with observations, we refer to experimental data in uniaxial compressive tests on chloroprene (CR) and nitrile butadiene (NBR) rubbers reinforced with 25wt.% of carbon black (Chai et al., 2013). Experimental data on dry and swollen (immersed into a bath with a palm biodiesel for 30 days) elastomers in compressive tests with cross–head speed 0.1 mm/s are depicted in Figs. 1A and 1B together with predictions of the response of swollen specimens by means of Eqs. (46) and (49) (with \(Q_0 = 1.04\) for CR and \(Q_0 = 0.22\) for NBR).

As another set of experimental data, we consider observations on vulcanized butadiene rubber (BR) under uniaxial tension with strain rate \(\dot{\varepsilon} = 2 \cdot 10^{-3} \text{ s}^{-1}\) (Bitoh et al., 2010). Stress–strain curves for dry and fully swollen [in bis (2-ethylhexyl) adipate] elastomers are presented in Fig. 2 together with predictions of the response of swollen specimens by means of Eqs. (46) and (49) (with \(Q_0 = 1.94\)).
Finally, we analyze experimental data on poly (N-isopropylacrylamide) (NIPAm) hydrogel reinforced with 8wt.% of Laponite nanoclay (Wang et al., 2012). The nanocomposite hydrogels are prepared by free radical polymerization of NIPAm in Laponite suspensions. Stress–strain curves for as-prepared and swollen (immersed into water for 1 week) nanocomposite (NC) hydrogels in uniaxial tensile (strain rate \( \dot{\varepsilon} = 2 \cdot 10^{-2} \text{ s}^{-1} \)) and compressive tests are plotted in Figs. 3 and 4 together with predictions of the response of swollen specimens by means of Eqs. (46) and (49) (\( \ast \)).

Figs. 1–4 serve as unambiguous evidence that the constitutive equations based on Eq. (38) predict poorly observations on swollen elastomers and are inapplicable for fitting experimental data. Although stress–strain relations grounded on Eq. (39) ensure better approximation of observations (Fig. 4), these equations cannot be recommended for the analysis of swelling because Eq. (41) implies that chemical potential \( \mu \) depends on volumetric deformation only (through pressure \( P \)). The latter means that shear deformation of a specimen subjected to swelling does not affect its ultimate solvent uptake \( Q_0 \), which contradicts observations (Zanina and Budtova, 2002; Vervoort and Budtova, 2003; Zeo et al., 2005). With reference to these conclusions, it seems reasonable to treat the separability hypothesis with caution and to presume the strain energy density to depend on all three principal invariants of the Cauchy–Green tensor.

3. A network of flexible chains with constrained junctions

To develop a constitutive model for an elastomer with a non-separable strain energy density, we adopt the approach suggested by Flory (1977). According to it, an elastomer is treated as a combination of two interpenetrating networks of flexible chains with strain energy density

\[
\psi_{\text{net}} = W_1 + W_2;
\]

where \( W_m \) denotes strain energy density of the mth network. The first network involves \( N_1 \) chains (per unit volume in the reference configuration) that are connected to the network by means of entanglements, and these junctions move affinely with the network (deformation gradient for the motion of junction coincides with that for macro-deformation). Strain energy density of the first network is described by the conventional equation

\[
W_1 = \frac{1}{2} N_1 k_B T [f_1 - 3 - \ln f_1].
\]

The other network involves \( N_2 \) chains (per unit volume in the reference configuration) that are connected to non-affine junctions whose motion is constrained by surrounding chains. The strain energy density of the second network is given by

\[
W_2 = \frac{1}{2} N_2 k_B T (F + H),
\]

where \( F \) and \( H \) are functions of eigenvalues \( \Lambda_1, \Lambda_2, \Lambda_3 \) of the Cauchy–Green tensor \( C \) and some parameter \( \kappa > 0 \) that characterizes severity of the entanglement constraints. These functions read (Flory, 1977; Flory and Erman, 1982)

\[
F = \sum_{m=1}^{3} [b_m - \ln(1 + b_m)], \quad H = \sum_{m=1}^{3} [d_m - \ln(1 + d_m)],
\]

where

\[
\begin{align*}
  b_m &= \kappa^2 \frac{\Lambda_m - 1}{(\Lambda_m + \kappa)^2}, \\
  d_m &= \kappa \Lambda_m \frac{\Lambda_m - 1}{(\Lambda_m + \kappa)^2}.
\end{align*}
\]
3.1. Constitutive equations

To develop stress–strain relations for an elastomer subjected to swelling, we, first, replace the eigenvalues $\lambda_m$ in Eqs. (53) and (54) with principal invariants $J_m$. Omitting straightforward calculations, we arrive at the formulas

$$ F = F_1 - F_2, \quad H = H_1 - H_2, \quad \text{(55)} $$

where the quantities

$$ F_1 = \sum_{m=1}^{2} b_m, \quad F_2 = \sum_{m=1}^{2} \ln(1 + b_m), $$

$$ H_1 = \sum_{m=1}^{3} d_m, \quad H_2 = \sum_{m=1}^{3} \ln(1 + d_m) $$

are determined by the formulas

$$ F_1 = \frac{\kappa^2}{(\kappa^3 + J_1 \kappa^2 + J_2 \kappa + J_3)} \left[ (J_1 - 3) \kappa^2 + 4(J_2 - J_1) \kappa^3 + (J_1 - 2J_2 + J_3) \kappa^2 \right] $$

$$ + (J_2 - 2J_1 + 9J_3) \kappa^4 + 2(2J_1 - J_2 - 3J_3) \kappa^5 $$

$$ + (J_2 - 2J_1 - 9J_3) \kappa^2 + 4J_1(J_2 - J_1) \kappa + J_3(J_1 - J_2), $$

$$ F_2 = \ln \left[ \left( \frac{J_1^2 + J_2 - J_3}{J_1^2 + J_2^2 + J_3} \right)^2 \right] \left[ \frac{J_1^2 + J_2 + J_3}{J_1^2 + J_2^2 + J_3} \right] $$

$$ H_1 = \frac{1}{(\kappa^3 + J_1 \kappa^2 + J_2 \kappa + J_3)} \left[ (J_1 - 2J_2 - J_3) \kappa^3 + 2(J_2 - J_2 - J_3) \kappa^4 \right] $$

$$ + (2J_2 - J_1 - 9J_3) \kappa^2 + 4J_1(J_2 - J_1) \kappa + J_3(J_1 - J_2), $$

$$ H_2 = \ln \left[ \left( \frac{J_1^2 + J_2 + J_3}{J_1^2 + J_2^2 + J_3} \right)^2 \right] \left[ \frac{J_1^2 + J_2 - J_3}{J_1^2 + J_2^2 + J_3} \right] $$

$$ + (J_1^2 + J_2 + J_3) \kappa^2 + 2(J_1^2 - J_2 - 3J_3) \kappa^4 $$

$$ + (J_1^2 + J_2 - J_3) \kappa^2 + (J_1^2 + J_2 + J_3) \kappa + J_3^2. \quad \text{(56)} $$

Although Eqs. (55) and (56) are not overly complicated, it seems reasonable to simplify them for treatment. Following Drozdov and Christiansen (2006), we presume the parameter $\kappa$ to be small, $\kappa \ll 1$, while concentration of constrained junctions $N_2$ to be large compared with $N_1$ in such a way that $\kappa^2 N_2$ has the same order of magnitude as $N_1$. Expanding $F_1$ and $F_2$ into series in $\kappa$ and neglecting terms beyond the third order of smallness, we find that

$$ F_1 = F_2 = \kappa^2 J_3 \left( 2J_1 + J_2 - \frac{J_2^2}{J_3} \right), $$

which implies that

$$ F = 0 $$

with the required level of accuracy. Expanding $H_1$ and $H_2$ into series in $\kappa$ and disregarding terms beyond the second order of smallness, we obtain

$$ H_1 = \kappa \left( 3 - \frac{J_2}{J_3} \right), $$

$$ H_2 = \kappa \left( 3 - \frac{J_2}{J_3} \right) + \kappa^2 \left( \frac{3}{2} - \frac{J_2}{J_3} \right). $$

It follows from these equalities and Eq. (55) that

$$ H = \kappa^2 \left( \frac{J_2}{J_3} - \frac{J_2}{J_3} + 3 \right). \quad \text{(58)} $$

Substituting Eqs. (57) and (58) into Eq. (52), and using Eqs. (50), (51), we arrive at the formula

$$ \psi_{nt} = \frac{1}{2} G_1 (J_1 - 3) - \ln J_3 + \frac{1}{2} G_2 \left[ \left( \frac{J_2}{J_3} \right)^2 - \frac{J_2}{J_3} + 3 \right], \quad \text{(59)} $$

where

$$ G_1 = N_1 k_B T, \quad G_2 = \frac{1}{2} k_B^2 N_2 k_B T. $$

It follows from Eqs. (4), (35), (34), (37), and (59) that

$$ \psi = \frac{1}{2} G_1 \left( \left( (1 + \nu c_1)^3 J_1 - 3 \right) - 2 \ln (1 + \nu c_1) \right) $$

$$ + \frac{1}{2} G_2 \left[ \left( \frac{J_2}{J_3} - \frac{2J_2}{J_3} \right) - \frac{2J_2}{J_3} + 3 \right] $$

$$ + k_B T c_1 \left( \frac{\nu c_1}{1 + \nu c_1} + \frac{\nu c_1}{1 + \nu c_1} \right). \quad \text{(60)} $$

Substitution of Eq. (60) into Eqs. (32) and (33) results in the stress–strain relation

$$ T = -P + \frac{1}{1 + \nu c_1} \left[ \left( G_1 (1 + \nu c_1)^3 - \frac{2G_2}{(1 + \nu c_1)^3} \right) B_0 \right] $$

$$ - \frac{2G_2}{(1 + \nu c_1)^3} \left( \frac{J_2}{J_3} - 1 \right), \quad \text{(61)} $$

and the formula for chemical potential

$$ \mu = k_B T \left[ \ln \frac{\nu c_1}{1 + \nu c_1} + \frac{1}{1 + \nu c_1} \right] + PV $$

$$ + \frac{G_1 v}{3(1 + \nu c_1)^3} \left( (1 + \nu c_1)^3 J_1 - 3 \right) $$

$$ - \frac{2G_2 v}{3(1 + \nu c_1)^3} \left( \frac{J_2}{J_3} - 1 \right). \quad \text{(62)} $$

An advantage of constitutive Eqs. (32), (61), and (62) is that they (i) are grounded on a transparent physical model, and (ii) involve only two adjustable mechanical parameters $G_1$, $G_2$.

3.2. Fitting of observations

To evaluate accuracy of fitting experimental data, we approximate the stress–strain curves depicted in Figs. 1–4. It follows from Eqs. (32), (42), (43), and (61) that under uniaxial tension–compression, the engineering stress $\sigma$ reads

$$ \sigma = \frac{1}{1 + \nu c_1} \left[ G_1 (1 + \nu c_1)^3 + \frac{2G_2}{k(1 + \nu c_1)^3} \left( \frac{k - k^2}{(1 + \nu c_1)^3} - 1 \right) \right] (k - k^2). \quad \text{(63)} $$

Each set of observations (stress–strain diagrams for dry ($c_1 = 0$) and swollen ($\nu c_1 = \nu c_0$) specimens) is approximated separately. The coefficients $G_1$ and $G_2$ in Eq. (63) are determined by the least-squares method. The experimental data and results of numerical simulation are reported in Figs. 5–9. The following conclusions are drawn: (i) Eq. (63) describes adequately the effect of solvent content on the mechanical response of elastomers under uniaxial deformation, (ii) accuracy of matching observations under tension exceeds that under compression (which may be ascribed to the fact that engineering stress $\sigma$ is chosen for presentation of the data instead of true stress), (iii) discrepancies between the observations and their fits by Eq. (63) are rather large. The latter may be attributed to insufficient accuracy of the neo–Hookean expression (51) to predict the strain energy density of real elastomers.
To examine the latter assumption, we follow the idea suggested by Gent (1996) and replace Eq. (60) with its phenomenological counterpart

$$\psi_t = \frac{1}{2} G_1 \left[ J \ln \left( \frac{1 + (1 + \nu c_t) \frac{J_{11} - 3}{J} - 2 \ln(1 + \nu c_t)}{J} \right) \right. $$

$$+ \frac{1}{2} G_2 \left[ \frac{J_{22} - 2 J_{12}}{(1 + \nu c_t)^3} - \frac{2 J_{21}}{(1 + \nu c_t)^3} + 3 \right]$$

$$\left. + k_B T \left( \frac{c_t \ln(1 + \nu c_t) + k_B T}{1 + \nu c_t} + \frac{G_1}{1 + \nu c_t} \right) \right], \quad (64)$$

where $J$ is an additional adjustable parameter. Repeating the above transformations, we arrive at the following expression for engineering stress:

$$\sigma = \frac{1}{1 + \nu c_t} \left[ \frac{G_1(1 + \nu c_t)^3}{J(1 + \nu c_t)^3(k^2 - 2k^{-1})} - 3 \right. $$

$$+ \frac{2G_2}{k(1 + \nu c_t)^3} \left( \frac{k + k^{-2}}{(1 + \nu c_t)^3 - 1} \right) \left( k - k^{-2} \right). \quad (65)$$

Adjustable parameters in Eq. (65) are determined by matching observations presented in Figs. 1–4. The parameter $J$ is found by the method of nonlinear regression, and the coefficients $G_1, G_2$ are calculated by the least-squares technique. Figs. 5–9B demonstrate good agreement between the experimental data and results of numerical simulation for all sets of observations. Two results are worth to be mentioning: (i) when two-parameter model (64) ensures good fit of experimental data, the best function parameters $G_1$ and $G_2$ in Eq. (64) are close to those in Eq. (65) (Fig. 8), which means that the model is stable, and (ii) parameters $G_1, G_2$ for NC hydrogel determined by matching observations under tension (Fig. 8) differ from those found by fitting experimental data under compression (Fig. 9). This may be explained by different conditions of manufacturing specimens for tensile and compressive experiments and different strain rates in mechanical tests.

Phenomenological extension (64) of Eq. (60) is introduced to demonstrate that accuracy of fitting observations can be improved noticeably by an increase in number of adjustable parameters without dramatic changes in the structure of Eq. (60). We do not treat Eq. (64) as the best variant of generalization for Eq. (60) because this relation is merely phenomenological. Instead of the Gent model, an anonymous reviewer of this work suggested to replace
the linear function of \( J_1 - 3 \) in the first square brackets in Eq. (59) with the inverse Langevin function following the approach proposed by Arruda and Boyce (1993), which seems more appropriate from the physical standpoint. Comparison of applicability of various variants of extension of Eq. (60) to the analysis of observations in biaxial tests will be performed in another study.

3.3. Comparison with other theories

Our aim now is to compare strain energy density for an elastomer subjected to swelling (59) with the corresponding expressions developed by other methods.

Erman and Flory (1982) and Erman and Monnerie (1989) extended the original approach (Flory, 1977) by replacing \( b_n \) in Eq. (53) with \( g_n b_n \), where \( g_n \) are some functions of the eigenvalues of the Cauchy–Green tensor. This replacement ensures good agreement with experimental data (Erman and Flory, 1982; Fontaine et al., 1989a; Fontaine et al., 1989b), but it leads to noticeable complication of the stress–strain relations (whose analytical treatment becomes difficult even for uniaxial tension) and an increase in number of adjustable parameters.

Yan and Jin (2012) treated a swollen elastomer as a network of flexible chains with slip-links (Edwards and Vilgis, 1986). Although the Edwards–Vilgis model does not belong to the class of models grounded on the separability principle, which means that, in general, it can describe the influence of solvent on stress–strain diagrams, its shortcomings are that (i) the constitutive equations involve four adjustable parameters, and (ii) the model is overly complicated for theoretical analysis.

Bastide et al. (1981), Bastide et al. (1984) and Durning and Morrow (1993) suggested to describe the effect of swelling on the mechanical response of an elastomer by treating it as a network of flexible chains whose number (per unit volume) changes with concentration of solvent. In other words, this means that coefficient \( C \) in Eq. (45) is presumed to evolve being proportional to \( (1 + \psi C) \psi \) with a constant exponent \( \beta \). This modification of the constitutive equations allows stress–strain curves under uniaxial tension of dry and swollen elastomers to be described quantitatively. However, applicability of this approach (with \( \beta \) treated as a material constant) to other regimens of deformation (equi-biaxial extension, shear, etc.) has not yet been examined.

Cai and Suo (2012) proposed to reject the incompressibility assumption (1), to find pressure \( P \) by matching observations under uniaxial tension, and to connect the obtained dependency with concentration of solvent by means of a phenomenological relation. This approach results in an adequate description of stress–strain diagrams, but does not allow (without introduction of additional hypotheses) to predict experimental data under an arbitrary three-dimensional deformation.

4. Mechanical response under rapid and slow deformation

When a totally swollen elastomer (with degree of swelling \( Q_0 \)) is immersed into the solvent and subjected to uniaxial tension–compression, its degree of swelling \( Q = \psi C \) increases under tension and decreases under compression. Observations reveal that changes in \( Q \) are time-dependent and they result in a strong dependence of stress–strain diagrams on strain rate. To simplify the analysis, we concentrate on two limiting regimes of stretching: (i) tension with a high strain rate \( k \), when the effect of mass exchange with the environment may be disregarded, and (ii) tension with a low strain rate when thermodynamic equilibrium is established at any elongation ratio \( k \).

Keeping in mind that under uniaxial tension

\[
P = -\frac{1}{3} \sigma k,
\]

we find from Eqs. (62) and (63) that

\[
\dot{\mu} = k_b T \left[ \ln \frac{\nu C}{1 + \nu C} + \frac{1}{1 + \nu C} - \frac{\chi}{(1 + \nu C)^2} \right] + \frac{\nu}{1 + \nu C} \left[ \frac{G_1}{K} + \frac{2G_2 k}{(1 + \nu C)^2} \right] \left[ (1 + \nu C)^3 - k \right]. \tag{66}
\]

The condition of thermodynamic equilibrium reads

\[
\dot{\mu} = \dot{\mu}^0, \tag{67}
\]

where \( \dot{\mu}^0 \) stands for chemical potential per molecule of solvent in the bath. Taking into account that the elastomer has been in its equilibrium state before its deformation starts, we write

\[
\mu^0 = \ln \frac{Q_0}{1 + Q_0} + \frac{1}{1 + Q_0} + \frac{\chi}{(1 + Q_0)^2} + \frac{1}{1 + Q_0} \left( g_1 + \frac{2g_2}{(1 + Q_0)^2} \right) \left( (1 + Q_0)^3 - 1 \right). \tag{68}
\]

where

\[
\mu^0 = \frac{\dot{\mu}^0}{k_b T}, \quad g_1 = \frac{G_1 v}{k_b T}, \quad g_2 = \frac{G_2 v}{k_b T}.
\]

Combination of Eqs. (66) and (67) results in the nonlinear equation for degree of swelling \( Q \)

\[
\ln \frac{Q}{1 + Q} + \frac{1}{1 + Q} + \frac{\chi}{(1 + Q)^2} + \frac{1}{1 + Q} \left( \frac{g_1 v}{k_b T} + \frac{2g_2 k}{(1 + Q)^2} \right) \left( (1 + Q)^3 - k \right) = \mu^0. \tag{70}
\]

We begin with the analysis of Eq. (68) for NC hydrogel at room temperature. The ratio

\[
\frac{g_2}{g_1} = 0.139 \tag{71}
\]
is taken from Fig. 8, whereas $g_1$, $\chi$, and $\mu^0$ are treated as parameters. Dependencies of ultimate degree of swelling $Q_0$ on chemical potential of solvent in the bath $\mu^0$ are depicted in Figs. 10A and 10B for “small” and “large” values of $g_1$ and the entire interval where the Flory–Huggins parameter $\chi$ changes from 0.5 (poor solvent) to −1.5 (very good solvent). Given $\mu^0$, Eq. (68) is solved numerically by the Newton–Rashon method with 100 iterations.

The following conclusions are drawn from Fig. 10: (i) the graphs depicted in Fig. 10A are similar to those reported by Hong et al. (2009) and Yan and Jin (2012), to mention a few; (ii) an increase in dimensionless parameter $g_1$ (that characterizes strength of the polymer network) results in substantial (by several times) decrease in ultimate degree of swelling and flattening of the curves $Q_0(\mu^0)$; (iii) given $g_1$, a reduction in $\chi$ (transition from poor to good solvent) induces noticeable growth of ultimate degree of swelling.

We proceed with the numerical analysis of Eq. (70) for $Q_0 = 1.94$, ratio (71), two values of the Flory–Huggins parameter ($\chi = −0.5$ and $\chi = −1.5$) for good solvents, and various $g_1$ ranging from 0.05 to 0.25 (according to Eq. (69), these values correspond to $\nu$ changing in the interval between 0.61 and 3.04 nm$^3$ at ambient temperature). Results of simulation are reported in Figs. 11A ($\chi = −0.5$) and 11B ($\chi = −1.5$) where $Q$ is plotted versus elongation ratio $k$.

Fig. 11 demonstrates that (i) for a fixed $k$, an increase in $g_1$ accelerates solvent uptake, and (ii) given $g_1$, elongation of a specimen causes $\nu$ to change (by several times) increase in degree of swelling $Q_0$, in accord with experimental data. Comparison of Figs. 11A and 11B leads to an unexpected conclusion that a decrease in $\chi$ (improvement of the solvent quality) causes a decay of $Q$. This result is explained by interaction of parameters $\mu^0$ and $\chi$: when $Q_0$ is fixed, for a relatively poor solvent ($\chi = −0.5$), $\mu^0$ is close to zero, which means that the effect of mechanical factors (the last term in the left-hand side of Eq. (70)) is substantial, while for a good solvent ($\chi = −1.5$), $\mu^0$ is negative and large, which implies that the influence of strain energy density of the polymer network becomes negligible.

It is worth noting that simulation was performed for the values of $\nu$ that strongly exceed volume of a water molecule $V_{\text{water}} = 1.09 \cdot 10^{-2}$ nm$^3$. Calculation of parameters $g_1$ and $g_2$ with $V_{\text{water}}$ results in $g_1 = 2.43 \cdot 10^{-5}$, $g_2 = 6.94 \cdot 10^{-6}$.

Analysis of Eq. (70) with these coefficients reveal practically no increase in $Q$ with $k$ in contrast with observations.

Finally, we compare two solutions of Eq. (63). The first corresponds to slow stretching

$$\varepsilon = \frac{1}{1 + Q} \left[ G_1(1 + Q)^3 + \frac{2G_2}{k(1 + Q)^3} \left( \frac{k + k^2}{(1 + Q)^3} - 1 \right) \right] (k - k^{-2}),$$

where $Q$ is determined from Eq. (70), while the other corresponds to rapid stretching with $Q = Q_0$. Results of numerical simulation are depicted in Fig. 12 (tension) and Fig. 13 (compression). These figures show that a decrease in strain rate (in our case, transition from rapid to slow deformation) induces a substantial decrease in $\sigma$ under tension and a noticeable growth of $|\sigma|$ under compression due to diffusion of solvent inside (outside) the hydrogel. This conclusion is in qualitative agreement with experimental data in tensile tests with various strain rates on poly (acrylamide) hydrogels (Konda et al., 2011).

![Fig. 10. Degree of swelling $Q$ versus chemical potential of solvent $\mu_0$. Symbols: results of numerical simulation with $\chi = 0$ ($\circ$), $\chi = 0.5$ ($\ast$), $\chi = −1.5$ ($\bullet$) for $g_1 = 0.05$ (A) and $g_1 = 0.25$ (B).](image)

![Fig. 11. Degree of swelling $Q$ versus elongation ratio $k$. Symbols: results of numerical simulation with various $\nu$ nm$^3$ ($\bigcirc - \nu = 0.61$, $\bigast - \nu = 1.22$, $\bigbullet - \nu = 1.82$, $\bigcirc - \nu = 2.43$, $\bigast - \nu = 3.04$) for $\chi = −0.5$ (A) and $\chi = −1.5$ (B).](image)

![Fig. 12. Tensile stress $\sigma$ versus elongation ratio $k$. Symbols: results of numerical simulation with $\chi = −0.5$ for rapid ($\bigcirc$) and slow tension with various $\nu$ nm$^3$ ($\bigast - \nu = 0.61$, $\bigbullet - \nu = 1.82$, $\bigcirc - \nu = 2.43$, $\bigast - \nu = 3.04$, $\bigbullet - \nu = 4.26$).](image)
5. Concluding remarks

Constitutive equations are developed for the mechanical response of elastomers subjected to swelling under an arbitrary three-dimensional deformation with finite strains.

Results of numerical simulation demonstrate that models with free energy density based on separability principle (38) fail to describe adequately stress–strain diagrams for dry and swollen specimens under uniaxial tension and compression. A novel expression, Eq. (60), is derived for the specific free energy with reference to the concept of networks of flexible chains with constrained junctions. An advantage of Eq. (60) is that it involves two adjustable parameters only and provides an acceptable approximation of experimental data.

The model is applied to evaluate the mechanical response of swollen elastomers under uniaxial tension–compression with high (no transport of solvent) and slow (at each elongation ratio, thermodynamic equilibrium is reached) strain rates. Results of numerical simulation show that changes in tensile stress driven by diffusion of solvent can be predicted correctly when volume of a solvent molecule \( v \) is treated as an adjustable parameter (it equals volume of a cluster involving 10 to 100 molecules).

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Fig. 13. Compressive stress \( \sigma \) versus compressive strain \( \epsilon \). Symbols: results of numerical simulation with \( \gamma = -0.5 \) for rapid (\( \times \)) and slow compression with various \( v \) nm\(^3\) (\( \bullet \) \( v = 0.61 \); \( \ast \) \( v = 1.82 \); \( \bigcirc \) \( v = 3.04 \); \( \ast \ast \) \( v = 4.26 \)).

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