Swelling in the Mechanically Loaded Polymer Networks

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Received April 23, 2009;
Revised Manuscript Received August 28, 2009

Abstract—Swelling of crosslinked polymers is treated as a set of correlated processes of diffusion of a solvent and deformation of a polymer matrix. A polymer and a solvent are assumed to be incompressible media. In this case, the chemical-potential gradient of a solvent, which is the driving force for diffusion, can be presented as divergence of the symmetric second-rank tensor or osmotic stress tensor. In contrast to the chemical potential, this tensor is a well-defined thermodynamic function of the state of the polymer–solvent system. Equations and boundary conditions for the description of swelling of polymer networks under different modes of mechanical loading are formulated in terms of the osmotic stress tensor. A general theory is illustrated for the description of the kinetics of swelling of a flat sample under the conditions of fixed uniaxial tensile drawing.

DOI: 10.1134/S0965545X10040139

INTRODUCTION

Swelling of crosslinked polymers in solvents plays an important role in many practical processes [1, 2], and in the physical chemistry of polymers, this process is used for the characterization of structure and characteristics of polymer networks [3, 4]. Many theoretical models have been elaborated for the description of the free swelling of materials; i.e., for the case when, in the course of the absorption of a solvent, the material is not subjected to external mechanical action [5–8]. However, in many real cases, absorption and diffusion of a solvent proceed under the parallel action of external mechanical loading. This factor can markedly change the diffusion-controlled kinetics of the transfer of a liquid, and the diffusion process can govern the deformational behavior of the material and its elastic response. The analysis of these phenomena is of evident interest from the standpoint of practical applications and for the development of new experimental methods for the characterization of the properties of polymer networks.

This study offers a general approach that makes it possible to formulate the mathematical models of nonequilibrium processes of swelling in polymer networks under the different modes of external mechanical loading. This approach is based on the theory of mechanodiffusion [9], which was earlier applied for the investigation of the diffusion regimes of free swelling and transport characteristics of network elastomers [10–13]. This theory describes the correlated processes of diffusion of a liquid and deformation in elastic mixtures, which consist of an elastic material and a liquid dissolved in this material. When these processes occur in network elastomers and in polymer gels, the polymer–solvent system can be modeled as an incompressible additive mixture. A polymer and a solvent are assumed to be incompressible media, and the volume of a solvent-swollen polymer is equal to the sum of volumes of the “dry” material and absorbed solvent.

In many cases, this approximation is well justified and widely used in the mechanics and physical chemistry of polymers. However, the formulation and solution of specific mechanodiffusion problems encounter certain difficulties because, in an incompressible mixture, hydrostatic pressure is not a thermodynamic function of the state of the system but the Lagrangian parameter, which takes into account the correlation between the volume deformation of the material and the concentration of the dissolved liquid. In this case, pressure is involved in the tensor of mechanical stresses and in the chemical potential of a solvent and, hence, in the expressions for the diffusion flow density of a solvent and in the equation of diffusion [9]. The initial problem is substantially simplified if hydrostatic pressure can be estimated from the solution of the equation of mechanical equilibrium and later can be excluded from the equation of diffusion. This procedure was applied for the solution of the problems describing the kinetics of free swelling of polymer networks [10–13].

This study shows that this procedure can be performed in its general form. As a result, the theory nat-
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The initial set of equations for the description of the mechanodiffusion processes (under isothermic conditions) in an incompressible mixture composed of an elastic material and a dissolved liquid (a solvent) is [9, 10]

\[ Dn_1/\partial t + n_1 \nabla \cdot v_2 = -\nabla \cdot j \]  
\[ Dn_2/\partial t + n_2 \nabla \cdot v_2 = 0 \]  
\[ \nabla \cdot T = 0 \]  
\[ j = -n_1 K \cdot \nabla \mu \]  
\[ T = F^T \cdot (\partial f/\partial F)_{n_1, n_2} - p E \]  
\[ \mu = (\partial f/\partial n_1)_{F, n_2} + V_1 \rho \]  
\[ f = f(F, n_1, n_2) \]  
\[ J = \phi_1^0/\phi_2 \]  
\[ \phi_1 = V_p n_1/(V_p n_1 + V_2 n_2), \quad \phi_2 = V_2 n_2/(V_p n_1 + V_2 n_2) \]  

Here, \( n_1 \) and \( n_2 \) are the molar densities (concentrations) of a solvent and an elastic matrix material, respectively; \( j = n_1 (v_1 - v_2) \) is the diffusion flow density of a liquid; \( v_1, v_2 \) are the rate fields of a liquid and an elastic matrix, respectively; \( D/\partial t = \partial/\partial t + v_2 \cdot \nabla \) is the material derivative with respect to time; \( T \) is the Cauchy stress tensor; \( \mu \) is the chemical potential of a solvent; \( p \) is the hydrostatic pressure; \( E \) is the unit tensor; \( K \) is the permeability coefficient of the matrix, which is the positive second-rank tensor and, in the general case, is dependent on the concentration of a solvent and on the strain of the material; \( \phi_1, \phi_2 \) are the molar volumes of a solvent and an elastic matrix material, respectively; \( \phi_1^0 \) is the volume fraction of the elastic matrix in the reference state (reference configuration); \( \phi_1, \phi_2 \) are the molar volumes of the solvent and the elastic matrix material; and \( J = \det F \) is the third invariant of strain gradient \( F \), which characterizes the volume (local) degree of swelling of the material with respect to the reference state.

Relationships (1) and (2) are the equations for the transfer of a solvent and for the balance of an elastic matrix material, respectively; Eq. (3) is the condition for the mechanical evolution of the mixture; and Eq. (4) is the physical equation for the diffusion flow density of a liquid. Cauchy stress tensor (5) and chemical potential of a solvent (6) are expressed through the free-energy density of the mixture, which is a function like (7).

Condition for incompressibility of the mixture (8) means that the single cause of changes in the volume of the material is the absorption of a solvent. Volume fractions of the mixture components are defined by Eqs. (9). However, for an incompressible additive mixture, \( V_p n_1 + V_2 n_2 = 1 \) and, hence,

\[ \phi_1 = V_p n_p, \quad \phi_2 = V_2 n_2 \]  

Nevertheless, in Eqs. (7)–(9), concentrations \( n_1 \) and \( n_2 \) of the mixture components should be treated as independent variables, while condition for incompressibility (8) should be the equation for the correlation between the stress tensor and the strain of the material. In stress-tensor expression (5) and chemical-potential expression (6), relationship (8) is taken into account by the method of Lagrangian factors [9, 14]. Here, the hydrostatic pressure is a Lagrangian factor; therefore, hydrostatic pressure is not a thermodynamic function of the state of the mixture.

The deformed state of an elastic mixture (at finite strains) is described as in the nonlinear theory of elasticity. Initially, a certain state of the mechanically unloaded material with a uniform distribution of a solvent is selected. This state is assumed to be undeformed and is referred to as the reference state. In this state, material (Lagrangian) system of coordinates \( (q^1, q^2, q^3) \) is introduced; this system is correlated with the elastic matrix. The space positions of the material particles of the elastic matrix in the reference state (reference configuration) is defined by the radius-vector \( r = r(q^1, q^2, q^3) \), while their position in the deformed (current) state is defined by the radius vector \( R = R(q^1, q^2, q^3), t) \). The reference and current configurations involve the coordinate bases \( r_i = \partial r/\partial q^i, R_i = \partial R/\partial q^i \), corresponding mutual bases \( r_i, R_i \) and \( r_i, R_i \) fitting relationship \( r_i = \delta_i^j, R_i = \delta_i^j \), and Hamiltonian operators

\[ \hat{\nabla} = \hat{R} \cdot \hat{r} = \hat{R}^T \cdot F, \quad \hat{C} = F \cdot F^T \]