Simulation of the Transient Behavior of Gels Based on an Analogy Between Diffusion and Heat Transfer

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The transient behaviors of the swelling and deswelling of gels involve concurrent mechanical deformation and solvent diffusion and exhibit a fascinating phenomenon. In this paper, a simple numerical tool is developed by using an analogy between diffusion and heat transfer when large deformation presents for gels. Using this analogy, a finite element method is developed in the framework of a commercial finite element package ABAQUS via two material-specific user subroutines to describe the mechanical and mass diffusion behaviors of gels. The present method is not limited to any specific materials; therefore, this method can be extended to other materials that featured with coupled deformation and diffusion. This method is expected to be able to serve as a useful numerical tool to study related materials and problems due to its simplicity.
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A gel is formed as the solvent aggregated in a crosslinked polymeric network. When the solvent diffuses in and out of the polymeric network, gel swells and shrinks, respectively, which endows gels the capability of large and reversible deformation as well as the dual attributes of a solid and a liquid. Gels have been extensively used in nature and in engineering for a variety of applications, such as drug delivery [1,2], tissue engineering [3,4], food processing [5], and oilfield management [6,7]. There are some efforts to formulate theories for the coupled mass diffusion and deformation in gels [8–11], and specifically large deformation has been rigorously considered [12]. Numerical approaches have been developed correspondingly for gels. Some are based on the phase field method [13], and some are based on the finite element methods [14–19]. Many efforts on the finite elements methods are based on commercial package ABAQUS via its user-defined subroutines. For example, a user-defined hyperelastic material was developed to model the equilibrium state of gels [17], and a user-defined element was used to treat the fields of diffusion and deformation concurrently as independent field variables for transient problems [19].

This paper develops an alternative method to study the transient behavior of gels by an analogy between mass diffusion and heat transfer with a rigorous consideration of large deformation. The analogy between these two transport phenomena has been utilized dated back to Prussin in the 1960s [20], though it was for small deformation. In this paper, this analogy is implemented via several user defined material subroutines in ABAQUS. Due to the fact that this implementation does not involve any development of new elements to couple mass diffusion and deformation in finite element methods, it is expected that this approach can be more straightforwardly utilized. As the following discussion is not specifically tied to any of the aforementioned theories, the methodology can be applied to the general field theories to couple mass diffusion and deformation when large deformation presents.

The mass diffusion in a large deformation framework was described [12] using the nominal variables and is summarized here using the true variables in order to compare with heat transfer. In large deformation, deformation gradient $\mathbf{F} = \partial \mathbf{x}(\mathbf{X},t)/\partial \mathbf{X}$ is used to map between the reference state (with coordinate $\mathbf{X}$) and the current state (with coordinate $\mathbf{x}(\mathbf{X},t)$). The conservation of mass can be expressed by nominal variables $(\partial C/\partial t) + (\partial J_K/\partial X_K) = 0$, where t is the time, C is the nominal solvent concentration, and $\mathbf{J}$ is the nominal flux. An equivalent way to express the flux is through the true flux j_i, $j_i n_i da = J_K N_K dA$, where $n_i da$ is the element of area in the current state deformed from its counterpart $N_K dA$ in the reference state. Using the conservation of mass in an integration form, i.e., $(d/dt) \int_V C dV + \int_A J_K N_K dA = 0$ and the divergence theorem, its differential form can be expressed by true flux, $(1/\det(\mathbf{F}))(\partial C/\partial t) + (\partial j_i/\partial x_i) = 0$. The nominal concentration C relates to the deformation via the condition of incompressibility [12], i.e., $1 + vC = \det(\mathbf{F})$, and the true concentration of solvent is related to the nominal concentration via $\det(\mathbf{F})$, i.e., $c \det(\mathbf{F}) = C$. The true flux j_i is given by the gradient of the chemical potential [21], $j_i = -cD(\partial \mu/\partial x_i)$, where D is the diffusivity, and μ is the normalized chemical potential (by $kT = 4 \times 10^{-21} J$, the temperature in the unit of energy) of the solvent inside the gel.

Thus the conservation of mass can be expressed as

$$\frac{1}{\det(\mathbf{F})} \frac{\partial [\det(\mathbf{F}) - 1]}{\partial t} + \frac{\partial \left\{ -\dfrac{[\det(\mathbf{F}) - 1]D}{\det(\mathbf{F})} \dfrac{\partial \mu}{\partial x_i} \right\}}{\partial x_i} = 0 \quad (1)$$

This equation is similar to the conservation of heat in heat transfer,

$$\rho \frac{\partial U}{\partial t} + \frac{\partial f_i}{\partial x_i} = 0 \quad (2)$$

where ρ is the density, U is the internal heat energy, and f_i is the true heat flux.

By comparing Eq. (1) for mass diffusion and Eq. (2) for heat transfer, an analogy can be made for large deformation: mass diffusion is analogous to heat transfer by the following equivalence:

$$\rho = \frac{1}{\det(\mathbf{F})}$$
$$U = \det(\mathbf{F}) - 1 \quad (3)$$
$$f_i = -\frac{[\det(\mathbf{F}) - 1]D}{\det(\mathbf{F})} \frac{\partial \mu}{\partial x_i}$$

This particular heat transfer behavior can be modeled in ABAQUS via its user-defined heat transfer subroutine UMATHT, in which the internal heat energy U and the heat flux f_i are to be defined based on Eq. (3). The normalized chemical potential μ is analogous to the temperature T. In addition, the gradients f_i with respect to temperature T and temperature gradient $\partial T/\partial x_i$ (or equivalently chemical potential μ and its gradient $\partial \mu/\partial x_i$) are also needed as these terms will contribute to the stiffness matrix of this user-defined heat transfer problem. Specifically, one needs to define $\partial f_i/\partial \mu = 0$ and $\partial f_i/\partial (\partial \mu/\partial x_j) = -([\det(\mathbf{F}) - 1]D/\det(\mathbf{F})\delta_{ij})$. The mechanical constitutive relation of gels is implemented in ABAQUS via its user-defined hyperelastic material UHYPER [17] by prescribing the free energy density. One choice of the free energy density is the Flory–Huggins model [22,23], where the normalized nominal free energy density $\hat{W}(\mathbf{F})$ is given by [12]

$$\hat{W}(\mathbf{F}) = \frac{W(\mathbf{F})}{\frac{k_B T}{v}} = \frac{1}{2}Nv[F_{iK}F_{iK} - 3 - 2\log(\det \mathbf{F})]$$

$$- \left[(\det \mathbf{F} - 1)\log\left(\frac{\det \mathbf{F}}{\det \mathbf{F} - 1}\right) + \frac{\chi}{\det \mathbf{F}}\right]$$

$$- \mu(\det \mathbf{F} - 1) \qquad (4)$$

Here, two dimensionless parameters are involved, namely, Nv for shear modulus of the dry polymer and χ for enthalpy of mixing. Here $v = 10^{-28}m^3$ is a representative value of the volume per solvent molecule. Thus the shear modulus of the dry polymer NkT is related to the normalized shear modulus by $NkT = 4 \times 10^7 Nv(Pa)$. The nominal chemical potential μ in Eq. (4) is a parameter instead of field variable as $\mathbf{F}$.

Thus, the transient analysis of the gels with coupled mass diffusion and large deformation is realized through coupled heat transfer and deformation by defining specific heat transfer behavior (UMATHT) and mechanical constitutive relations (UHYPER). Since this implementation does not involve element development (e.g., user-defined element [19]), it can be more straightforwardly utilized. It should be emphasized here that this problem is nonlinear, though the diffusion part is linear. Iterations are conducted to reach convergent results.

There is a distinct feature of the gel simulation: the deformation is extremely sensitive to chemical potential. A slight variation of chemical potential leads to significant deformation especially for short-time behavior once a dry polymer (with $\mu = -\infty$) contacts with a solvent (with $\mu = 0$). The deformation on the other way affects chemical potential. Therefore, the iteration between deformation and diffusion fluctuates severely for short-time behavior, and this fluctuation oftentimes results in divergent results, which makes this problem numerically difficult. Here we should emphasize that this severe fluctuation is not necessarily physical but a result of numerical iteration. In order to mitigate this fluctuation, a damping-like method is introduced, i.e., the term $\partial f_i/\partial (\partial \mu/\partial x_j)$ is multiplied by a scaling factor $\alpha(>1)$. The scaling factor contributes to the stiffness matrix but not the residual vector (e.g., f_i and $(1/\rho)(\partial U/\partial t)$) of this nonlinear problem. Since the convergence of nonlinear problems is governed by the residual vector, this scaling factor and the resulted approximated stiffness matrix do not affect the accuracy of the results. In fact, this method of changing stiffness in a nonlinear problem has been applied in many different scenarios. One example is that the modified Newton's method uses an approximated stiffness matrix to save computational cost. Another example is that in ABAQUS' coupled thermal stress analysis, the off diagonal components of the stiffness matrix are ignored without affecting the accuracy of the solution [24]. A similar scenario can also be found in coupled poromechanics problems, where various types of stabilization techniques are introduced [25] and the stabilization factor is influenced by time step and element size [26] as well.

The method of using scaling factor α is verified by studying a free swelling of a cubic gel as illustrated in Fig. 1(a), in which a dry cubic gel is set to contact with solvent from its outside surfaces and thus swells without constraints. Due to symmetry, 1/8 of this cube with size $L \times L \times L$ is used in the modeling. Equation (4) is used to describe the mechanical constitutive relation of the gel with $Nv = 0.001$ and $\chi = 0.2$. Figure 1(b) compares the normalized displacement w/L in the z-direction for three points (A, B, and C) versus normalized time Dt/L^2 for two cases where the scaling factor $\alpha = 1$ (i.e., accurate $\partial f_i/\partial (\partial \mu/\partial x_j)$ is used) and $\alpha = 100$. It is clearly found that the results for $\alpha = 1$ and $\alpha = 100$ overlap. It is also noticed that by using the scaling factor $\alpha = 100$, the swelling behavior at short time where the chemical potential changes more dramatically can be captured. For the times that both $\alpha = 1$ and $\alpha = 100$ can reach, the results are identical. However, $\alpha = 100$ can capture much shorter swelling time than $\alpha = 1$. This example verifies the viability of the scaling method. The shorter time that is achieved by using the scaling factor method is very important for the transient analysis of gel. It needs to be mentioned here that the scaling factor slows down the speed of convergence as the stiffness matrix is not accurate, which is similar to the case of the modified Newton's method versus Newton's method.

The current method is benchmarked by studying a one-dimensional confined swelling problem. Figure 2(a) illustrates a
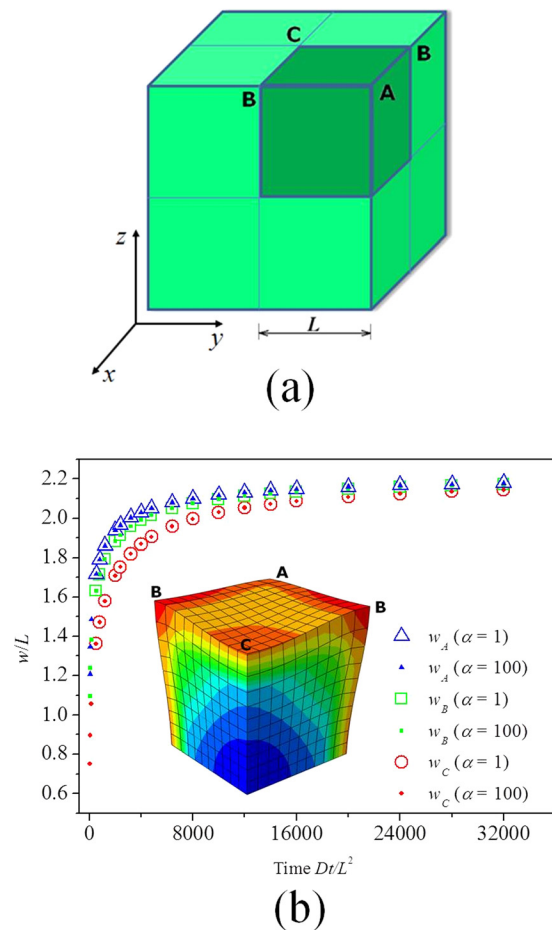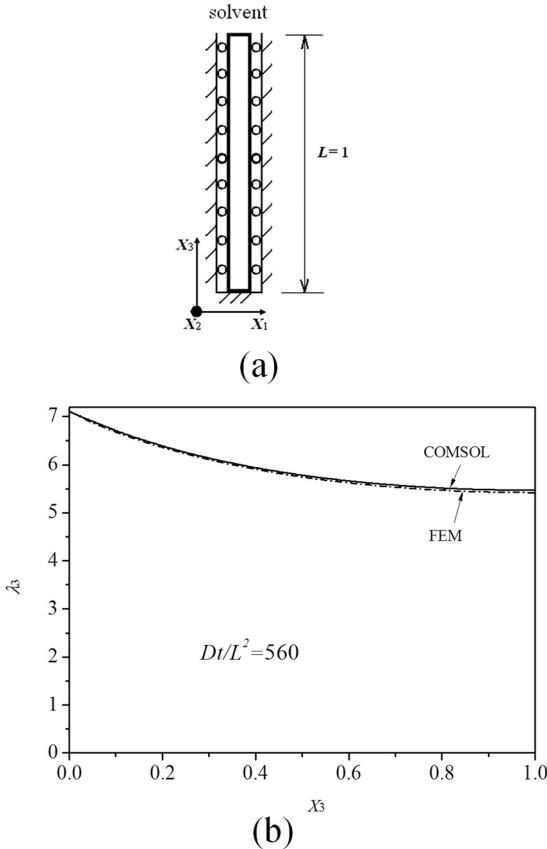

(a)

(b)

Fig. 1 (*a*) Schematic of a cubic gel swelling under no constraint. Three points *A*, *B*, and *C* are marked. (*b*) Normalized vertical displacements *w/L* of three characteristic points (*A*, *B*, and *C*) versus normalized time *Dt/L²* for both scaling factors $\alpha = 1$ and $\alpha = 100$. The inset shows the max principal strain contour at *Dt/L² = 160*.

Fig. 2 (*a*) Schematic of a gel bar swelling in X_3 direction. (*b*) Stretch in X_3 direction λ_3 as a function of X_3 when $Dt/L^2 = 560$ using both COMSOL and the present method.

gel bar with a unit length that only swells in the X_3 direction but not in the X_1 and X_2 directions, which has nonvanishing stretching λ_3 in the X_3-direction. The evolution of $\lambda_3(X_3, t)$ as a function of X_3 and time t is to be solved. As solvent diffuses in the gel, the chemical potential μ also evolves with X_3 and time t as determined by minimizing the free energy density $\tilde{W}(\mathbf{F})$ from Eq. (4). Substituting $\mu(X_3, t)$ into Eq. (1), an evolution equation for $\lambda_3(X_3, t)$ is achieved,

$$\frac{\partial \lambda_3}{\partial t} = D \frac{\partial}{\partial X_3} \left\{ \frac{\lambda_3 - 1}{\lambda_3^2} \left[\frac{1}{\lambda_3^2(\lambda_3 - 1)} - \frac{2\chi}{\lambda_3^3} + Nv \left(1 + \frac{1}{\lambda_3^2} \right) \right] \frac{\partial \lambda_3}{\partial X_3} \right\} \tag{5}$$

This equation is solved by using COMSOL Multiphysics 4.2 as the benchmark for the present finite element method. One thousand three-dimensional coupled displacement-temperature brick elements (C3D8T) are used. The material parameters are the following: $Nv = 0.001$ and $\chi = 0.2$. Figure 2(*b*) plots $\lambda_3(X_3)$ as a function of X_3 for $Dt/L^2 = 560$. It is found that the results from the present method and COMSOL agree very well, which verifies the accuracy of the present method.

In the following, we study two transient problems using the present finite element method. The first problem is the gel indentation. Recently, indentation experiments have been used to characterize gels and soft materials [27–30]. The migration of solvent in and out of the network of gels endows the gel viscoelastic behavior. The creep (i.e., indentation with a constant force) and relaxation phenomena (i.e., indentation with a fixed depth) are observed. Specifically for a relaxation indentation experiment, the gel is suddenly indented by a fixed indentation depth. At short-time limit ($t = 0$) (i.e., right after the gel is indented by a fixed depth), the solvent has no time to migrate out of the gel, and
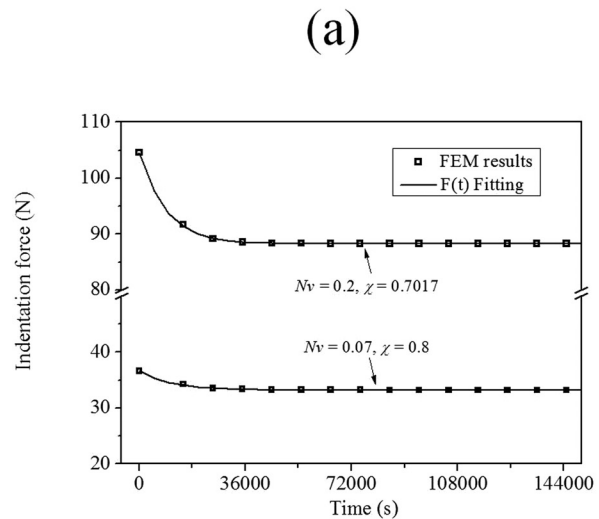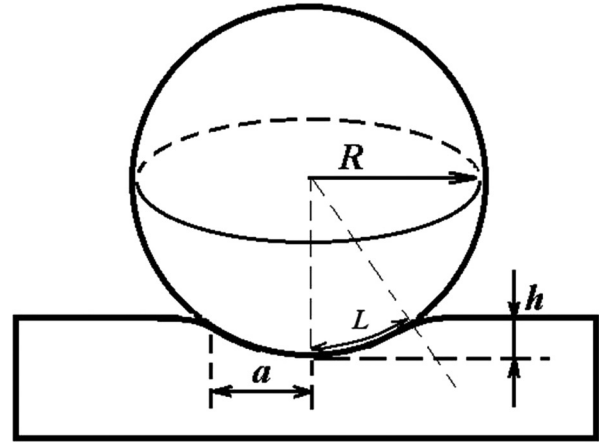
Fig. 3 (*a*) Schematic of gel indentation. (*b*) Evolution of indentation force $F(t)$ with time t for two gels with different material parameters. The fitting curve based on $F(t) = F(0) + [F(\infty) - F(0)][1 - \exp(-\frac{t}{\tau_{\text{ind}}})]$ is also given.

the gel behaves as an incompressible material. The indentation force is denoted by $F(0)$. As the solvent migrates out of the gel network, the gel becomes a compressible material, and thus the applied indentation force gradually relaxes and reaches another steady state $F(\infty)$ at the long-time limit. $F(0)$ and $F(\infty)$ are related to two material properties of gels, namely shear modulus and Poisson's ratio, for given indentation geometries [31–33]. The evolution of $F(t)$ provides a way to determine the diffusivity of a solvent. In simulation, obtaining $F(0)$ and $F(\infty)$ is a static problem. We recently have studied the large deformation effect on this regard [33]. It becomes a transient problem to determine $F(t)$, which is the focus of this example.

The present finite element method is used to simulate the relaxation experiment. A rigid spherical indenter with radius $R = 3\,\text{mm}$ indents $h = 1\,\text{mm}$ on a fully swollen gel modeled by 12,395 C3D8T elements (Fig. 3(*a*)). Two sets of material parameters are used, namely, $Nv = 0.2$, $\chi = 0.7$, and $Nv = 0.07$, $\chi = 0.8$, with both providing an equilibrium swelling ratio $\lambda_{eq} = 1.2$ (by minimizing the free energy density $W(\mathbf{F})$, Eq. (4)). Diffusivity of solvent is taken as $D = 8 \times 10^{-4}\,\text{mm}^2/\text{s}$. Figure 3(*b*) shows the evolution of indentation force $F(t)$ with time. The indentation force decays as expected. As a first approximation, the evolution

of $F(t)$ can be expressed by $F(t) = F(0) + [F(\infty) - F(0)]$ $[1 - \exp(-(t/\tau_{ind}))]$ and is also shown in Fig. 3(b), where τ_{ind} is the relaxation time of the gel under indentation. This relaxation time is found to be approximately 10,000 s for these two gels. As discussed before, this relaxation is due to the diffusion of the solvent inside the gel. Upon indentation, the solvent inside the gel diffuses out of the gel to reach the equilibrium with the external solvent. The characteristic diffusion length is the contour length L (Fig. 3(a)). In this simulation, the characteristic diffusion time is given by $\tau_{diff} = (L^2/D) = 8,000$ s, which is on the same order of τ_{ind}. When the history of $F(t)$ is obtained from experiments, the simulation can be used to determine the diffusivity.

The second example is related to a recent application of gels in the oilfield industry, primarily for zonal isolation. The gel, or as they are more often named swellable elastomers, are used for zonal isolation. A string of self-reactive swellable elastomer is placed inside a set of complex tube assemblies. Either water-reactive or oil-reactive swellable elastomer are available depending on the chemical composition of the elastomer. In the following, we study a water-reactive elastomer where the elastomer is swellable when exposed to water but not oil so that it remains at the dry state and allows the oil to freely flow. When the water presents, which is undesirable since it is very costly to separate oil and water, the elastomer swells to block the oil flow. In this application, the transient behavior is very important as it determines the history of pressure $p(t)$ built on the pipeline as the elastomer swells. Figure 4(a) illustrates our model where the elastomer surrounding a rigid core is inside a pipe with modulus $E = 200$ GPa and Poisson's ratio $\nu = 0.25$. In the following simulation, the radii of the gel and pipe are 90 mm and 100 mm, respectively. Figure 4(b) shows two contour plots of $p(t)$ as elastomer swells. The material parameters used in Fig. 4(b) are $Nv = 0.1$, $\chi = 0.4253$, and $D = 8 \times 10^{-4} \text{mm}^2/\text{s}$. It is found that the maximum pressure $p(t)$ applied on the pipe is on the same order of the shear modulus NkT (= 4 MPa) of the elastomer, which is unique for soft matters with large swelling ratios. To study the effect of material parameters on the history of pressure $p(t)$, Fig. 4(c) plots the average $p(t)$ on the pipe versus t for different material parameters. It is found that the pressure $p(t)$ increases with the shear modulus (or equivalently, the normalized shear modulus Nv) of the elastomer in an approximate linear fashion for the same equilibrium swelling ratio. The approximated linear fashion can be understood from the dimensional analysis that the shear modulus is the only dimension towards the pressure $p(t)$. For the same shear modulus, the elastomer with a larger equilibrium swelling ratio provides higher stress than that with a smaller equilibrium swelling ratio. Overall, it is found that the pressure $p(t)$ mainly depends on the shear modulus of the elastomer but not the equilibrium swelling ratio. Therefore, this result suggests choosing an elastomer with a larger modulus and also a smaller χ to reach a larger equilibrium swelling ratio. It should be noticed here that the working environment in the oilfield is much harsher (such as very high pressure) so that the example shown here only attempts to show the basic physics.

In summary, this paper establishes an analogy between diffusion and heat transfer when large deformation presents for gels. Using this analogy, a finite element method is developed in the framework of a commercial finite element package ABAQUS via two material-specific user subroutines to describe the mechanical and mass diffusion behaviors of gels. This method is then used to study two transient problems of gels, namely indentation and swellable elastomers. Since this method does not involve any element development, but limits on the material level, many built-in capabilities in ABAQUS can be straightforwardly used, such as, the contact problem that has been used in the indentation and swellable elastomer problems. More importantly, the discussion in this paper is not limited to any specific materials; therefore, this method can be extended to other materials that featured with coupled deformation and diffusion, such as, visco-elastic material coupled with diffusion. It is hoped that this method is able to serve as a useful numerical tool to study related materials and problems due to its simplicity.

(a)

$t = 167$ hours $t = 5222$ hours

(b)

(c)
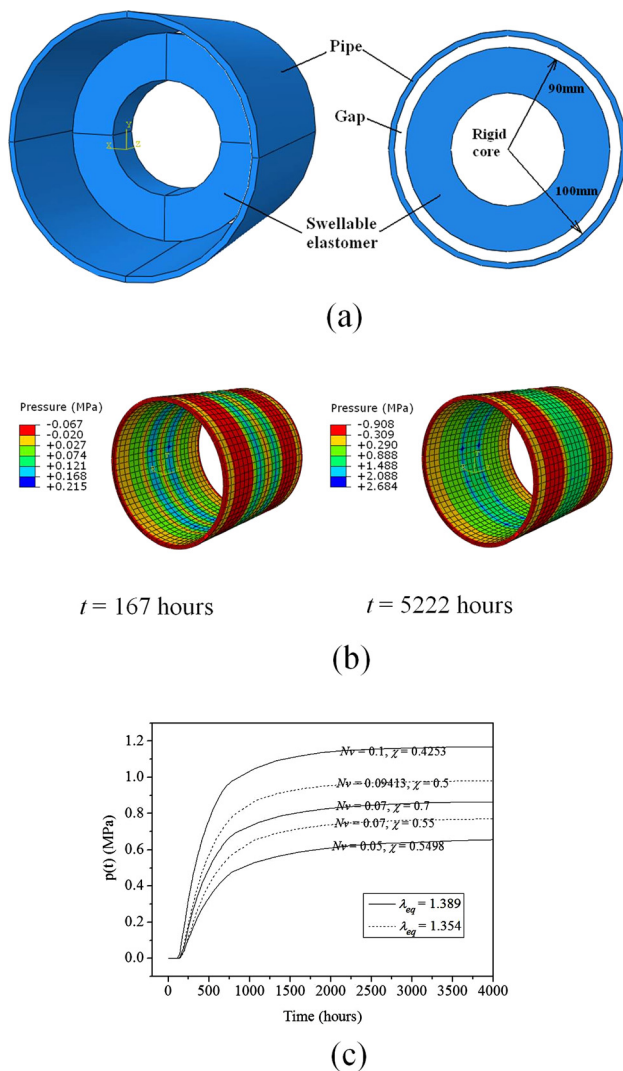
Fig. 4 **(a)** Schematic of a swellable elastomer inside a pipe. **(b)** The contour plots of pipe pressure $p(t)$ at different times. **(c)** Evolution of average pipe pressure $p(t)$ with time t for different elastomers.

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