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Extended Stress-Diffusion Coupling Model for Swelling Dynamics of Polymer Gels

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ABSTRACT: We extend the stress-diffusion model presented by Yamaue and Doi (Yamaue, T.; Doi, M. *Phys. Rev. E* **2004**, *69*, 41402) by eliminating the solvent velocity but treating the polymer volume fraction as a field variable during swelling. We show two equivalent descriptions of conservation of polymer molecules and incorporate this law via an algebraic relation, simplifying the enforcement of boundary conditions and numerical implementation of the extended model. The extended stress-diffusion model was implemented by finite element method. The examples presented in this paper demonstrate the effectiveness and the versatility of the numerical method, indicating the potential and the capability of simulating more complicated dynamic problems.

1. INTRODUCTION

Polymer gel is a cross-linked, solvent-swollen composite structure. In response to a variety of external stimuli, gels swell or shrink and function as active materials, paving the way for soft machines or robots.[1−5] The sensitivity of gels, i.e., the dynamic response of gels to environmental changes, is an indispensable factor to be accounted for in the synthesis and design of gel devices. This has inspired tremendous efforts in past decades, both theoretical and experimental, to explore the swelling dynamics of polymer gels. The early works of gel swelling stem from Biot's formulation on consolidation of porous continuum[6,7] and were later developed further into the mixture theory or the biphasic or triphasic theory.[8] Tanaka et al., on the basis of the so-called collective diffusion concept, proposed the Tanaka−Hocker−Benedek (THB) model,[9] which was found to be capable of interpreting lots of experiments, particularly the free swelling of sphere gels.[10−12] The collective-diffusion concept was also adopted by other researchers, for example, de Genns.[13] Astarita et al. studied the coupled diffusion and morphological changes of polymers.[14] Berens and Hopfenberg explored the diffusion and relaxation in glassy polymers.[15] Recently, the intriguing physics behind gel swelling dynamics have triggered emerged research on the coupled diffusion and deformations; see refs 16−18 for reviews and recent developments.

Although the original version of the THB model was successful for predicting many gel swelling experiments, inconsistency or discrepancies with experiments remain in the gel literature, particularly for free swelling of nonspherical gels and constrained swelling of gels.[19] The inadequacy of the THB model stems from the use of a single, lumped shear modulus, with the fluid pressure not explicitly accounted for.[19,20] The shear modulus would minimize the nonisotropic deformations, making the transport phenomena during gel swelling more complex and hardly regarded as a pure diffusion process.[19] Not explicitly incorporating the fluid pressure and the coupling between the diffusion and fluid transport, on the other hand, renders the THB model incomplete and may give inconsistent

results for even simple experiments.[20] Doi and Onuki[21,22] first noticed the importance of fluid pressure and formulated a framework of the two-fluid model for dynamics of gels and polymer solutions. The model is based on a molecular picture of the network and solvent composite and treats both phases as fluids in nature.

Most of the experiments and the above-mentioned theories are mainly concerned with free swelling cases, and only simple shapes of gels, for instance, spherical, cylindrical, or disk-shaped, are measured and analyzed. Emerging applications of gels in laboratories and engineering devices are evolving to more complex structures utilizing the anisotropic, constrained swelling of gels. As one of the typical experiments, Suzuki and Hara[23] conducted the swelling and shrinking measurement of a thin gel membrane with top and bottom surfaces glued to rigid glasses. In this circumstance, the in-plane deformations of the gel membrane were constrained, letting the deformation be purely one-dimensional and only occurring in thickness. The most intriguing fact is that the thickness of the thin layer evolves exponentially and the characteristic time depends on the lengths of constrained surfaces rather than on the thickness,[23] a fact that in no way can be explained by the THB model. Yamaue and Doi,[24] therefore, presented the stress-diffusion model to analyze this experiment analytically, and later they further developed the model for swelling dynamics of cylindrical and disk-shaped gels.[25,26]

The analytical results of Yamaue−Doi's stress-diffusion model, nevertheless, are only valid for the particular experiment where a thin layer of gel is sandwiched between two rigid surfaces and the deformation is only one-dimensional; the deformations of any planes parallel to the two surfaces are uniform and independent of the in-plane coordinates. Furthermore, the original Yamaue−Doi's stress-diffusion model

and most of the above-mentioned models, for example, the THB model or Biot's mixture model, are limited to small deformations. The volume fraction of the polymer is assumed to be constant during the swelling, which holds true only for limited degrees of swelling. In this paper, we extend the stress-diffusion model to incorporate the variation of polymer volume fraction, enabling our model to simulate swelling dynamics of gels with large deformation and volume change. If polymer volume fraction is introduced as an independent variable, the conventional procedure of conservation of polymer molecules would encounter difficulties of enforcing boundary conditions. We show two equivalent ways of stating the conservation of polymers and implement it in an alternative way. Our formulations were implemented by using the commercial finite element software, COMSOL 3.5a, and expected to be used to model gels with arbitrary shapes and boundary conditions.

2. YAMAUE−DOI'S STRESS-DIFFUSION MODEL[24]

Assuming a material marker bound to the network occupies a position $\mathbf{r}$, the marker undertakes a displacement, $\mathbf{u}(\mathbf{r},t)$, due to swelling. The velocity of the polymer is $\mathbf{v}_p = d\mathbf{u}(\mathbf{r},t)/dt = \dot{\mathbf{u}}(\mathbf{r},t)$. The gel is treated as a mixture of two fluids, both having velocities and interacting via friction due to relative motion. Denoting the velocity of fluid as $\mathbf{v}_s(\mathbf{r},t)$ and the friction constant as ξ, the original Yamaue−Doi's stress-diffusion model can be stated as[24]

$$\xi(\mathbf{v}_s - \dot{\mathbf{u}}) = -(1 - \phi)\nabla p \tag{1}$$

$$\nabla \cdot (\boldsymbol{\sigma} - p\mathbf{I}) = \mathbf{0} \tag{2}$$

$$\nabla \cdot [(1 - \phi)\mathbf{v}_s + \phi\dot{\mathbf{u}}] = 0 \tag{3}$$

where $\boldsymbol{\sigma}$ is the elastic stress tensor, p is the pressure, and ϕ is the polymer volume fraction. The three equations are complete with three basic unknowns: polymer displacement, $\mathbf{u}$, solvent velocity, $\mathbf{v}_s$, and the pressure, p. Equation 1 expresses the momentum transport due to polymer−solvent relative motion; eq 2 represents the force balance of gel, treating the two phases as a whole; and eq 3 dictates that the divergence of the average velocity vanishes due to the incompressibility conditions. It should be pointed out that in Yamaue−Doi's stress-diffusion model, the polymer volume fraction, ϕ, is regarded as a constant during swelling, which is valid only for small deformation and limited degrees of swelling. Gels can swell with a very large swelling ratio, and polymer volume fraction in this case should be taken as a field variable, whose variation influences the osmotic pressure and ultimately the force balance in the gel. Taking ϕ as an independent field variable, the following conservation of polymer should be supplemented to eqs 1−3 to make the equations complete,

$$\frac{\partial\phi}{\partial t} + \nabla \cdot (\phi\dot{\mathbf{u}}) = 0 \tag{4}$$

3. TWO EQUIVALENT DESCRIPTIONS OF CONSERVATION OF POLYMER MOLECULES

Standard in form and easy to interpret the physical meaning, however, it is difficult to impose boundary conditions to eq 4.[24] The boundary conditions associated with eq 4 are, in general, expressed in terms of chemical potentials of solvent inside the gel and their correlations with that outside the gel, which are highly nonlinear equations of ϕ and can only be solved iteratively. We show here that the conservation of polymer
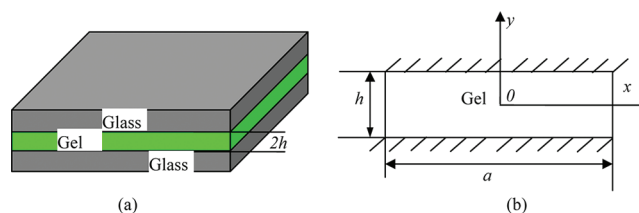

Figure 1. (a) Computational model for a thin-layer gel sandwiched between and clamped by two rigid glass plates. (b) Half of the gel is considered and modeled, and the problem is taken as a plane strain problem. The top and bottom surfaces of the gel are mechanically constrained and chemically clamped due to symmetry.
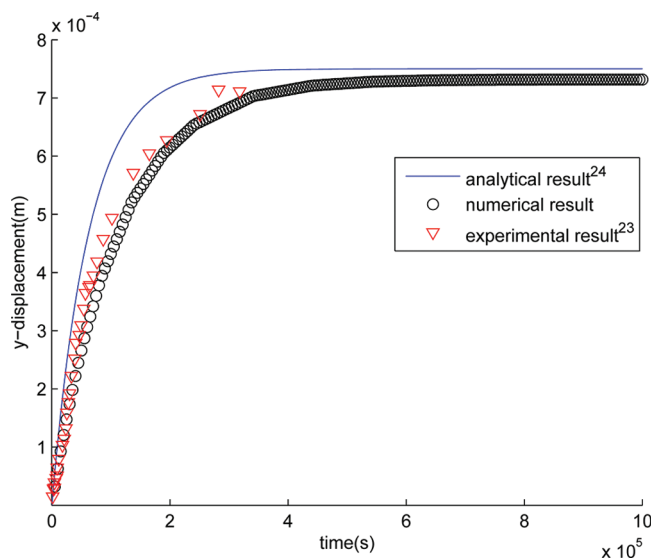

Figure 2. Comparison of the time history of y-displacements predicted by the extended stress-diffusion model, the analytical method given by Yamaue and Doi,[24] and the experimental result given by Suzuki and Hara.[23]

molecules can be enforced equivalently by an alternative way. Denoting the initial polymer volume fraction in the relaxed state as ϕ_0, the conservation of polymer molecules dictates that the current value of ϕ relates to ϕ_0 via

$$\frac{\phi_0}{\phi} = J = \det \mathbf{F} \tag{5}$$

in which J is the determinant of deformation gradient, $\mathbf{F}$. Taking material derivatives of both hands of eq 5 with respect to time gives

$$\frac{DJ}{Dt} + \frac{J}{\phi}\frac{D\phi}{Dt} = 0 \tag{6}$$

Plugging $DJ/Dt = J\nabla \cdot \dot{\mathbf{u}}$ into eq 6 and invoking the standard definition of material time derivative, $(D())/(Dt) = (\partial())/(\partial t) + \dot{\mathbf{u}} \cdot \nabla()$, eq 6 exactly reduces to eq 4. We, therefore, point out that eq 5 is another equivalent description of conservation of polymers and can be used instead of eq 4 in the simulation.

4. EXTENDED STRESS-DIFFUSION MODEL

If one solves eq 1 to eq 3 and eq 4 or equivalent eq 5 simultaneously, there are totally four independent variables and associated equations. We can simplify this process if we are only concerned with gel deformation and gel velocity and polymer
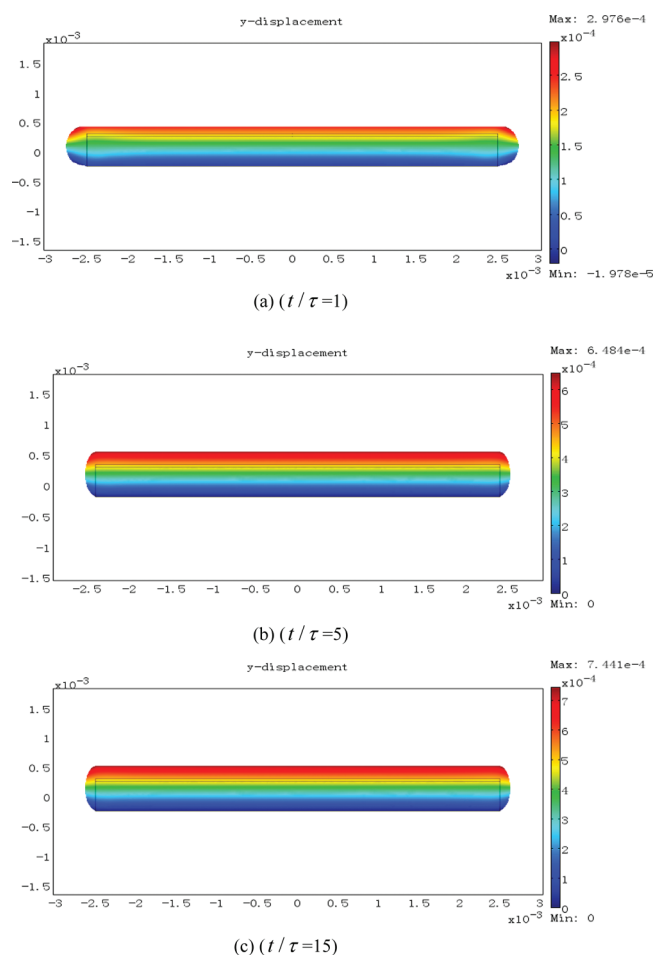
(a) ($t/\tau = 1$)

(b) ($t/\tau = 5$)

(c) ($t/\tau = 15$)

Figure 3. Deformed shape and the *y*-displacements of a gel clamped with a glass on the top surface.

volume fraction. This indicates that we can eliminate solvent velocity, $\mathbf{v}_s$, and leave it undetermined and reduce the number of unknowns to three. Multiplying eq 1 by $((1 - \phi)/\xi)$ and taking divergence yield

$$\nabla \cdot ((1 - \phi)\mathbf{v}_s) - \nabla \cdot ((1 - \phi)\dot{\mathbf{u}}) = -\nabla \cdot \left(\frac{(1 - \phi)^2}{\xi} \nabla p \right)$$

(7)

Subtracting eq 7 from eq 3 gives

$$\nabla \cdot \dot{\mathbf{u}} = \nabla \cdot \left(\frac{(1 - \phi)^2}{\xi} \nabla p \right)$$

(8)

Thus we finally obtained eq 2, eq 5, and eq 8 for three independent variables: polymer displacement, $\mathbf{u}$, fluid pressure, p, and polymer volume fraction, ϕ. Equation 5 is an algebraic relationship, such that no boundary conditions are needed. The boundary conditions of the model can thus be divided into two groups: chemical boundary conditions associated with p that can be prescribed as in ref 24 and mechanical boundary conditions associated with $\mathbf{u}$ imposed either as displacement or stress boundary conditions. Physical interpretation and enforcement of boundary conditions for this extended model are straightforward and readily implemented. The extended stress-diffusion model was implemented in the framework of finite
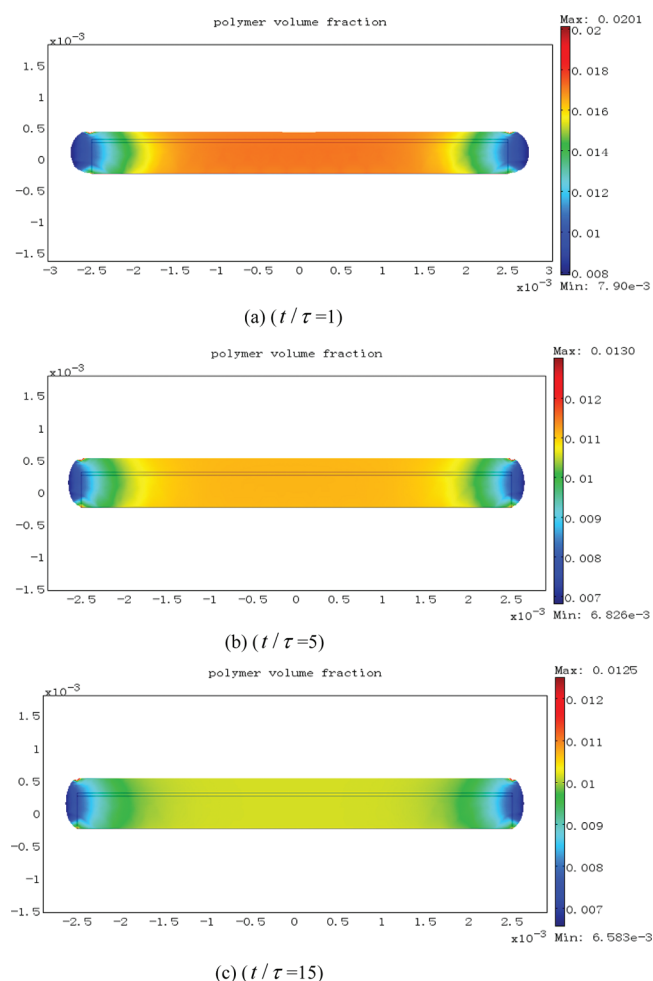

(a) ($t/\tau = 1$)

(b) ($t/\tau = 5$)

(c) ($t/\tau = 15$)

Figure 4. Variation of polymer volume fraction of a gel clamped with a glass on the top surface.

element method and in a multiphysics software, COMSOL 3.5a.

5. NUMERICAL EXAMPLES

Figure 1 depicts the thin-plate gel used in the experiment[23] and the analysis model in ref 24. We use it here to demonstrate the extended stress-diffusion coupling model. The total height of the gel is $2h$, but only half of the gel is considered and modeled. The bottom surface of the gel is therefore chemically clamped and mechanically constrained due to symmetry. The first example considered herein is the thin-plate gel with the top surface clamped by a rigid glass. We modeled the gel swelling dynamics as a plane strain problem.

The inside and outside of the gel were prescribed with different pressure, and the difference of pressure drives the swelling of the gel. The displacements of the two directions of the top and bottom surfaces were constrained, and zero-flux boundary conditions were imposed on these two surfaces. On the left and right side surfaces of the gel, the pressure inside the gel was set to equal that of the solution, and stress-free boundary conditions were enforced. This implies the assumption of local chemical equilibrium on the two side surfaces of the gel. With these physics-specific boundary conditions and proper initial conditions, we can solve eqs 2, 5, and 8 simultaneously by the finite element method.
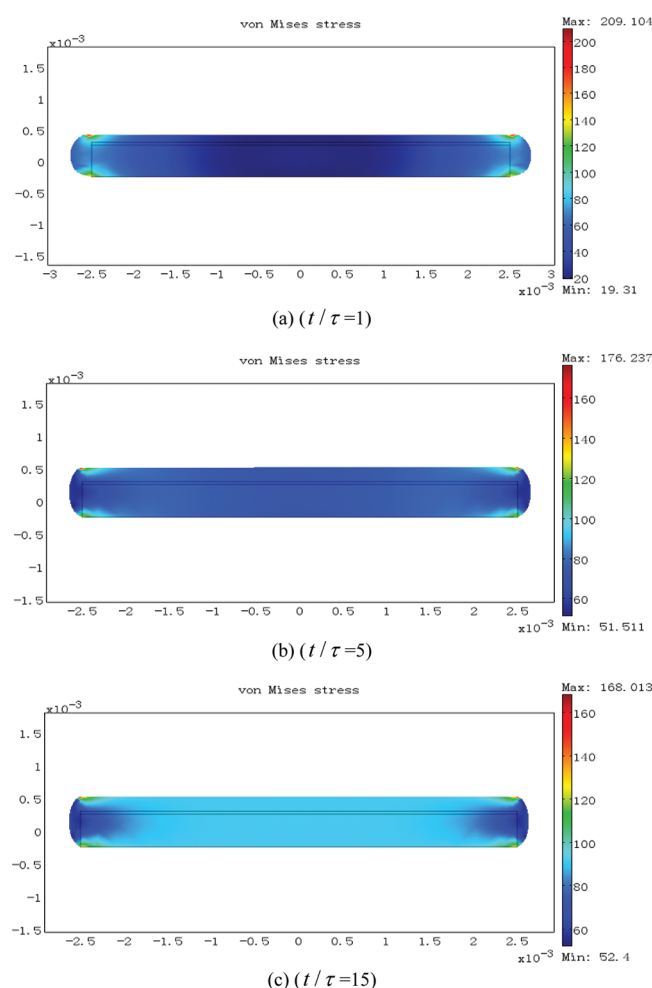
(a) (t/τ =1)

(b) (t/τ =5)

(c) (t/τ =15)

Figure 5. Distribution of von Mises stress of a gel clamped with a glass on the top surface.

(a) (t/τ =1)

(b) (t/τ =10)

(c) (t/τ =40)

Figure 6. Deformed shape and the y-displacements of a gel with a compliant but impermeable top surface.

For the first example, we model and discretize both the hydrogel and the glass glued on the top surface of the gel. The parameters used in the simulation are adopted from the literature of hydrogel experiments and summarized as follows: the pressure outside the gel is fixed as p_{out} = 105 Pa, the initial value of polymer volume fraction is ϕ = 0.025, the shear modulus of the gel is G = 22 Pa, the bulk modulus of the gel is K = 40.67 Pa, and the friction coefficient between water and polymer is ζ = 3.5$10^{12}$ (N·s)/m^4.[9−12] The friction coefficient should be in principle a function of volume fraction, and scaled as ϕ^2 in the semidilute solution.[27,28] For a very dilute solution, i.e., a high swollen hydrogel considered in this paper, it is reasonable to assume a constant friction coefficient. The model presented herein, however, can definitely be developed to handle the cases with a variable friction coefficient. The dimensions of gel sample are 5 mm × 8 mm × 0.5 mm. The glass is a model as an isotropic material with a pretty large Young's modulus as compared to gel.

Since the extended stress-diffusion model can predict the time history of displacements, pressure inside the gel, and the polymer volume fraction, it is interesting to compare the kinetic history of y-displacements predicted by the numerical method and the analytical method given by Yamaue and Doi[24] and compare these with the experimental restults of Suzuki and Hara.[23] This comparison is plotted in Figure 2. Note that the numerical result and the analytical result agree well in the sense
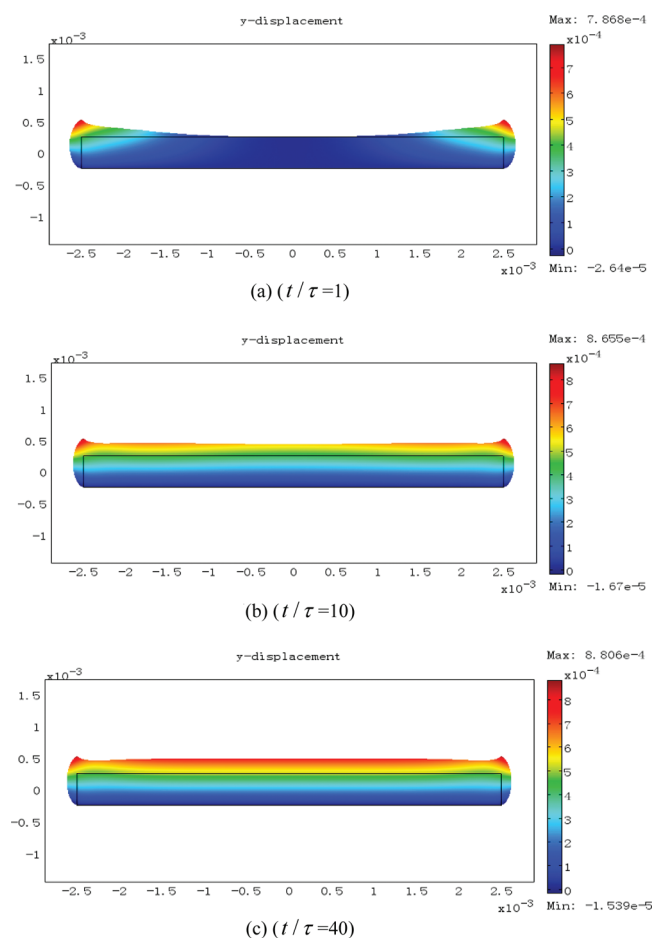
of the order of magnitude of relaxation time, τ, approximately 10^5 s for both methods, and coinciding with experiment. Both methods predicts similar variation trends; however, there exists a minor difference regarding either the specific value of transient or steady y-displacements. The analytical result is a little bit larger than the numerical result, and the latter is consistent better with experimental result than the former. This minor discrepancy between the numerical and the analytical results is understood as follows: The same pressure difference between the inside and the outside of the gel induces same swelling ratio and the same volume change of the gel. The analytical scheme assumes only a one-dimensional deformation along the y-direction, ignoring the deformation in the x-direction. The deformation of the area far from the sided boundaries is nearly one-dimensional due to the constraint of top and bottom surfaces, while the area near the side boundaries is in a two-dimensional deformation state. The numerical method here, however, carried out a full two-dimensional calculation, taking both x and y deformations into account. From eq 5 one knows that for the same given swelling ratio, ϕ_0/ϕ, ignoring the x-direction deformation would overestimate the displacement in the y-direction. Omitting the edge effects of the analytical approach gives a relatively large value of y-displacement as compared to two-diimensional (2D) finite element simulation.

To probe the deformed shape and, particularly, the deformation contour of displacements in the y-direction, we show in Figure 3 the swollen shape of the gel and the contour of y-displacements at various dimensionless time steps. In Figure 3

(a) $(t/\tau = 1)$

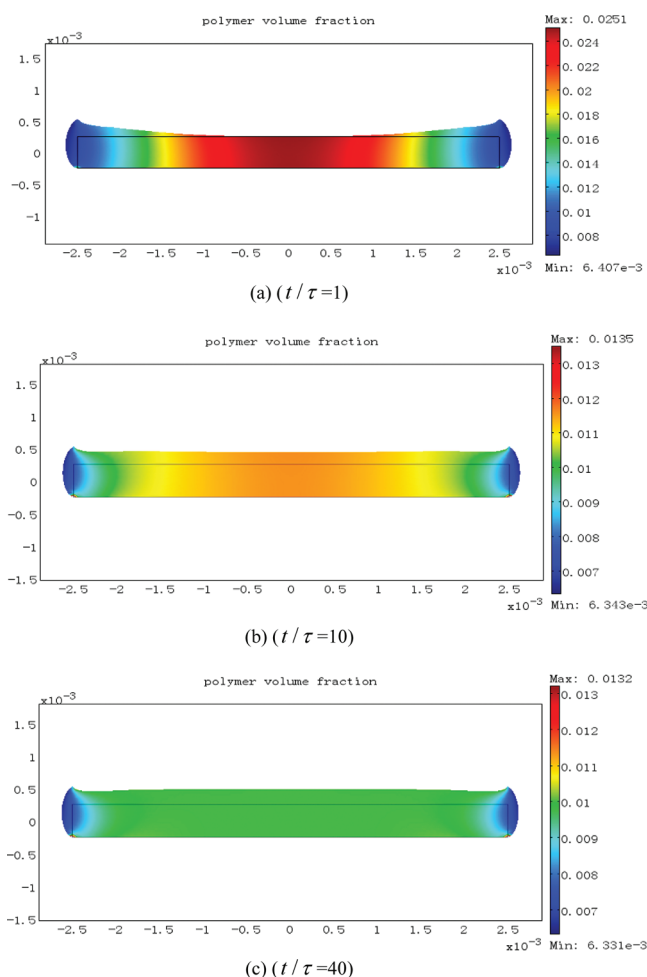
(b) $(t/\tau = 10)$

(c) $(t/\tau = 40)$

Figure 7. Polymer volume fraction of a gel with a compliant but impermeable top surface.

and the figures that follow it, the solid black line in these figures represents the original state of the gel and the rigid glasses glued to it. The physical time, t, is normalized by the analytical relaxation time,[24] τ, and parts a–c of Figure 3 correspond to $t/\tau = 1$, $t/\tau = 5$, and $t/\tau = 15$, respectively. We note from Figure 3 that, due to the constraint of rigid glass covered on the top surface of the gel, the y-displacements of any layer parallel to the bottom surface are uniform except near the left and right edges of the gel. Since the thickness of the gel is small compared to its planar dimensions, the nonuniform displacements near the edges of the gel can be ignored and the y-displacement of any point in the gel is assumed to be a function of the y-coordinate only, an assumption adopted in the analytical model of Yamaue and Doi.[24] As explained previously, ignoring the edge 2D deformation effects would produce a little bit higher value of y-displacement.

Figure 4 shows the distribution contour of polymer volume fraction at various time steps. The polymer volume fraction varies from the initial value of 0.025, to nearly 0.015 at $t/\tau = 1$, then approaches its steady value of 0.01 after $t/\tau > 5$. It is obvious that pretty large variation of ϕ is possible during the swelling/shrinking process, and it is more reasonable to deal with it as a field variable. The numerical method can evaluate the stress distribution of gel readily during the swelling process; we found that the effective stress of the gel does not change much during the swelling process, and the results are shown in Figure 5 for the first example.

To further demonstrate the versatility and the effectiveness of the method, we modeled the second example with the same conditions and parameters as the first example but the rigid glass constraint was removed. This means that the boundary conditions on the bottom surface remain unchanged while the top surface is coated with a very thin and compliant layer which is impermeable to water. The water can only migrate from the outside into the inside of the gel from the side boundaries of the gel, following the same diffusion path as in the first example. In this case, the y-displacements of any layer parallel to the bottom surface are no longer uniform, implying that the assumption used in the analytical approach, the y-displacement is only a function of y, does not hold and renders the analytical approach invalid. The numerical model presented herein, nevertheless, does not limit itself to such limitations. Figure 6 plots the deformed shape and the y-displacements, Figure 7 shows the distribution of polymer volume fraction of the gel at different time steps, and Figure 8 plots the distribution of
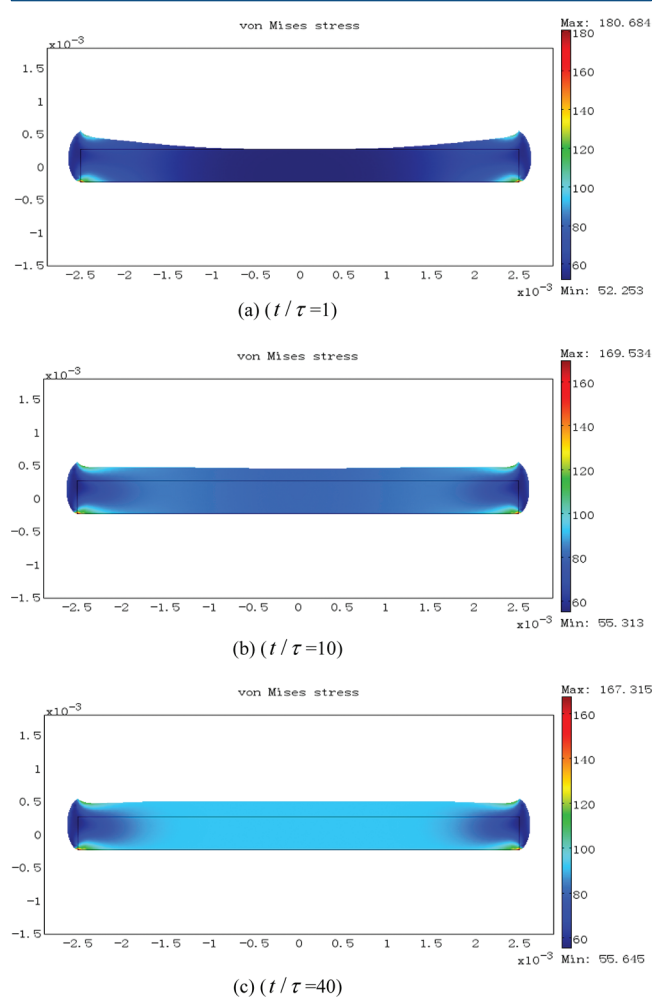

(a) $(t/\tau = 1)$

(b) $(t/\tau = 10)$

(c) $(t/\tau = 40)$

Figure 8. Distribution of von Mises stress of a gel with a compliant but impermeable top surface.

stresses. The nonuniform deformation of the gel and variation of the polymer volume fraction are obvious in this case, and our methodology can successfully capture these phenomena without difficulties. We also note that removal of the top surface constraint would affect the swelling kinetic process, in the sense that the relaxation time in this case is longer than the first example. This is reasonable since the external constraint will

reduce the degree of swelling and decrease the characteristic relaxation time scale, a useful rule for the design and fabrication of hydrogel devices when fast response is desirable.[2]

6. CONCLUDING REMARKS

The unique feature of polymer gel is its swelling/shrinking deformation in response to diverse stimuli. Synthesis and fabrication of novel gels with programmable control of swelling or shrinking is crucial to gel applications and as yet ongoing efforts. Modeling and understanding the mechanism behind gel swelling dynamics, although remaining a hot topic for several decades, is far from being fully understood. This paper describes our efforts on an extended stress-diffusion model for swelling dynamics of gels. We reformulate the standard stress-diffusion model by eliminating the solvent velocity as a basic variable. We demonstrate the equivalence of two descriptions of conservation of polymer molecules and incorporate this as an algebraic relation. The model is straightforward for enforcing boundary conditions and readily realized by finite element method. The model circumvents the limitations of the standard stress-diffusion model and can model the swelling process with large variation of polymer concentration. We also demonstrate the versatility and powerfulness of the model to simulate gel swelling dynamics with complex geometries and boundary conditions.

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Notes

The authors declare no competing financial interest.

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