Finite Bending of Bilayer pH-Responsive Hydrogels: a Novel Analytic Method and Finite Element Analysis

Nasser Arbabi¹, Mostafa Baghani^{*1}, Jalal Abdolahi¹, Hashem Mazaheri² and Mahmoud Mousavi Mashhadi¹

¹School of Mechanical Engineering, College of Engineering, University of Tehran, Tehran, Iran.

²Faculty of engineering, Department of Mechanical Engineering, Bu-Ali Sina University, Hamedan, Iran.

*Corresponding Author Email: baghani@ut.ac.ir

Abstract

Recently bilayer smart hydrogel beams are widely used in various applications such as sensors, actuators, self-folding structures and switches. Developing a strong tool for designing these bilayer smart hydrogel beams is necessary. In this article, we developed an analytical method to solve the swelling induced bending of bilayer beams made of a pH-sensitive layer attached to an inert elastomer layer. A total deformation gradient tensor, without assuming any intermediary virtual state, is defined to map the initial configuration to the deformed state. An exponential function with four constants is employed to describe the deformation of the pH-sensitive gel layer. The proposed method leads to a system of equations with six unknowns that can be simply solved via numerical techniques. As a case study, this method is implemented to solve the swelling induced bending of several bilayer beams with various parameters. The outcomes of the analytical solution are in excellent agreement with the finite element method results, thus confirming the strength of the presented method.

Keywords: pH-sensitive hydrogel, finite bending, bilayers, Analytical solution, Finite element.

1 Introduction

Hydrogels are three-dimensional networks made of lightly cross-linked polymer chains, which are capable of imbibing vast amount of water. Based on the structure and composition of the polymer chains, the swelling ratio of hydrogel networks might be affected by various external stimuli such as pH [1-8], temperature [9-16], light [17, 18], mechanical loads [19] and electrical fields [20-22]. Smart hydrogels have been found to be a suitable material for a wide range of biomedical [23, 24], drug delivery [5, 23], sensor and actuator [22, 25, 26], soft robotic [14, 27, 28] and tissue engineering [28-30] applications.

Making use of hydrogels in the above-mentioned applications requires a suitable constitutive model for design steps and related sub-steps such as simulation and inverse problems. Thus, swelling behavior of hydrogels has been investigated within the framework of various theories. Most of the swelling theories are based on thermodynamic equilibrium employing the additive decomposition of the Helmholtz free energy density which is originated by a pioneering work of Flory [31] in 1942. Thereafter, some theories were developed to contain coupling behavior of these materials due to environmental stimuli (Hong, Zhao [32] (2008) , Marcombe, Cai [1] (2010), Cai and Suo [11] (2011), Chester and Anand [13] (2011), Drozdov, deClaville Christiansen [2] (2016), Lucantonio, Nardinocchi [33] (2013)). Especially, Marcombe, Cai [1] in 2010 developed a model to capture the behavior of pH-sensitive hydrogels. In this model, the Helmholtz free energy density includes four separate energies, each describing specific mechanical or chemical energy. This theory is found to be reliable and is employed by many researchers for simulation of homogeneous and inhomogeneous swelling behavior of hydrogels in various applications [8, 34].

A bilayer beam made of materials with different characteristics is one of the classical sensor and actuator design concepts. A familiar example is the bimetal strip thermometers, which were first analyzed by Timoshenko [35]. The idea of the bi-strip sensor has developed over decades into advanced

biocompatible and largely deformable polymeric sensors and actuators. Kwon, Choi [36], in 2009 used an electrically sensitive hydrogel bilayer as a micro switch for flow control of a micro-channel. Kwon, Jeong [37], in 2011 implemented a bilayer hydrogel beam to design a microfluidic valveless micro-pump that operates via an electric field. Their micro-pump had low energy consumption and showed high durability in the long term, which are the result of using the hydrogel bi-strip beam actuator. Guo, Li [15], in 2013 modeled self-folding structures that employed bilayer hinges as folding actuators. The hinges were made of a temperature sensitive hydrogel layer attached to an inert elastomeric layer, which bends by ambient temperature changes.

Swelling-induced bending of bilayers made of smart hydrogels has attracted a great deal of interest in recent years. The bilayer hydrogel beams mostly are made of a sensitive layer attached to a neutral one. Inert elastomers mostly are treated as incompressible rubbers. Roccabianca, Gei [38], in 2010 solved plane strain bending of multilayered thick plates made of incompressible rubbers. The analysis revealed the possibility of the existence of several neutral axes for specified geometries. Their method was verified by comparing to the experimental tests and approved to be accurate for the analysis of incompressible rubbers. Lucantonio, Nardinocchi [39], in 2014 used analytical, semi-analytical and numerical approaches to solving the swelling induced deformation of neutral hydrogel bilayers. Morimoto and Ashida [16], in 2015 proposed an analytical solution to the swelling induced plane strain bending of bilayers made of temperature sensitive hydrogels. In their method, they used a decomposition of the deformation into a virtual one-dimensional swelling state, and then an incompressible bending. They compared the results with a linear model of elastic bi-strips for validation. However, the linear model is inaccurate to detect the nonlinearities arose from the large deformation of hydrogels swelling. Thus, their validation method was not appropriate and their results are unreliable. Nardinocchi and Puntel [40], in 2016 proposed a method to solve finite bending of layered neutral gels based on the basic assumption of a multiplicative decomposition of the deformation gradient tensor.

They also compared outcomes of their method with numerical results in the literature. Drozdov and Christiansen [41] (2016) solved the swelling-induced bending of bilayer neutral gel beams with a slight difference in layers characteristics. They modeled water absorption employing the theory of constrained swelling in finite strains, while the bending is considered as a small perturbation of the equilibrium in the swollen state. Abdolahi, Baghani [42] (2016) proposed a method for solving finite bending of temperature sensitive hydrogel bilayers. Their results conform well to FEM outcomes.

In this work, based on the swelling theory proposed by Marcombe, Cai [1], we propose a new analytical method for solving swelling bending of bilayer beams made of a pH-sensitive hydrogel layer attached to a neutral elastomeric one. In this regard, the bilayer is introduced in the Cartesian coordinate system at the initial state. We defined a total deformation gradient tensor, without the fundamental assumption of considering any virtual intermediate state, which maps the initial states to the deformed configuration in the polar coordinates. An exponential function is employed to describe the radial deformation of the swelling layer. The method leads to a system of six algebraic equations with six unknowns that are solved applying numerical methods. Then, the proposed method results are verified with the finite element results, to validate the proposed analytical model.

The article is organized as follow: first, in section 2 we define the problem and describe the geometry. This section is divided into two separate parts: In section 2.1, the deformation kinematics and related equations are presented. Then, the swelling theory is briefly discussed and the kinetic equations, including the stresses and the balance equation are fully explained in section 2.2. Later in this section, the parameters and the system of equations are introduced. Thereafter, a case study is undertaken to demonstrate the accuracy, strength and reliability of the proposed method in section 3. Finally, we present a summary and draw conclusions in section 4.

2 Plane Strain Finite Bending of Bilayer Hydrogel

As illustrated in Figure 1, we consider a beam made of two different layers: one layer ($n=1$) is made of incompressible elastomer and the other layer ($n=2$) is made of pH-sensitive hydrogel. Through the whole text, we use a superscription (n) to distinguish the parameters related to each of the layers. In the reference state (the initial configuration), the bilayer is in a stress-free state and has a rectangular shape (Figure 1a). When the bilayer is immersed in a solution with high pH, the smart hydrogel layer starts to swell in all directions; however, the sub-layer prevents the hydrogel from swelling in the longitudinal direction and causes the bilayer to bend (Figure 1b). In order to further simplification of the problem into 2D, the out of plane dimension is taken to be infinite and the bending of the bilayer is treated as a plane strain problem.

Figure 1: The schematics of the hydrogel bilayer geometry: a) the initial configuration and b) the deformed configuration.

2.1 Kinematics

Since the bilayer is initially straight, the initial configuration is defined within the Cartesian coordinate framework. Referred to Figure 1a, indicating the position of any point in reference state by

$\mathbf{X} = (X_1, X_2, X_3)$, we have:

$$\mathbf{X} = X_1 \mathbf{e}_1 + X_2 \mathbf{e}_2 + X_3 \mathbf{e}_3 \quad \text{with} \quad \begin{cases} X_1 \in [-L/2, L/2] \\ X_2 \in [0, H^{(1)}] \cup [H^{(1)}, H] \\ X_3 \in (-\infty, +\infty) \end{cases} \quad (1)$$

where $H = H^{(1)} + H^{(2)}$ is the initial thickness of the bilayer. In order to solve the swelling induced bending of the bilayer, we defined a deformation gradient tensor that maps the initial configuration at the reference pH to the current configuration in the desired pH-value. The end effects are neglected and it is assumed that the cross-section of the bilayer remains plane after the deformation. Consequently, the bilayer forms a semi-annular shape after bending. As depicted in Figure 1b, the current configuration is defined in the polar coordinates as:

$$\mathbf{x}^{(n)} = r^{(n)} \mathbf{e}_r + \theta \mathbf{e}_\theta + z \mathbf{e}_z \quad \text{with} \quad \begin{cases} r^{(1)} \in [r_1, r_2], r^{(2)} \in [r_2, r_3] \\ \theta \in [-\bar{\theta}, \bar{\theta}] \\ z \in (-\infty, +\infty) \end{cases} \quad (2)$$

where $\bar{\theta}$ is the bending semi-angle, and r_1, r_2, r_3 are the internal, the interfacial and the outer radii of the deformed bilayer, respectively.

The deformation in z direction is restricted, so the stretch in this direction is $\lambda_z = 1$. Since there is no variation of variables in the tangential direction, all stretches depend only on location vector $r^{(n)}(X_2)$, a function of X_2 that describes the radius of the element in the current state. The tangential direction in the current configuration is assumed as a linear function of X_1 . Therefore, every straight line with the initial length of L in the X_1 direction in the reference configuration would be an arc with the radius of

$r^{(n)}(X_2)$ and central angle of $2\bar{\theta}$ after deformation. Having these definitions in mind, the hoop stretch is $\lambda_\theta^{(n)} = 2\bar{\theta}r^{(n)}(X_2)/L$ for both layers. The radial stretch for the pH-sensitive layer is $\lambda_r^{(1)} = dr(X_2)/dX_2$ [38]. The radial stretch for the elastomeric layer can be found applying the incompressibility condition as below:

$$J^{(1)} = \lambda_r^{(1)}\lambda_\theta^{(1)}\lambda_z^{(1)} = 1 \rightarrow \lambda_r^{(1)} = \frac{L}{2\bar{\theta}r^{(1)}(X_2)} \quad (3)$$

in which $J^{(n)} = \det(\mathbf{F}^{(n)})$ is the third invariant of the deformation gradient tensor correspondent to each layer. The deformation gradient for the pH-sensitive and elastomeric layers become:

$$\mathbf{F}^{(1)}(X_2) = \frac{L}{2\bar{\theta}r^{(1)}(X_2)}\mathbf{e}_r \otimes \mathbf{e}_1 + \frac{2\bar{\theta}r^{(1)}(X_2)}{L}\mathbf{e}_\theta \otimes \mathbf{e}_2 + \mathbf{e}_z \otimes \mathbf{e}_3 \quad (4)$$

$$\mathbf{F}^{(2)}(X_2) = \frac{dr^{(2)}(X_2)}{dX_2}\mathbf{e}_r \otimes \mathbf{e}_1 + \frac{2\bar{\theta}r^{(2)}(X_2)}{L}\mathbf{e}_\theta \otimes \mathbf{e}_2 + \mathbf{e}_z \otimes \mathbf{e}_3. \quad (5)$$

$r^{(2)}(X_2)$ for the pH-sensitive layer should be determined through the kinetic equations, however, $r^{(1)}(X_2)$ can be found in terms of r_1 , using the incompressibility constraint for the elastomeric layer as below [38]:

$$r^{(1)}(X_2) = \sqrt{\frac{L}{\bar{\theta}}X_2 + r_1^2} \quad (6)$$

2.2 Distribution of Stresses in Both Layers

The swelling behavior of pH-sensitive hydrogels is well defined by a constitutive theory proposed by Marcombe, Cai [1]. In this theory, the swelling phenomenon is formulated by introducing the Helmholtz free energy density. The Helmholtz free energy density for pH-sensitive hydrogels includes different

contributions which are functions of deformation gradient ($\mathbf{F}$) and nominal concentration of counter-ions (C_+), hydrogen ions (H^+) and co-ion (C_-) as below :

$$W^{(2)}(\mathbf{F}^{(2)}, C_+, C_{H^+}, C_-) = W_{net}^{(2)}(\mathbf{F}^{(2)}) + W_{sol}(\mathbf{F}^{(2)}) + W_{ion}(\mathbf{F}^{(2)}, C_+, C_{H^+}, C_-) + W_{dis}(\mathbf{F}^{(2)}, C_+, C_{H^+}, C_-) \quad (7)$$

where $W_{net}^{(2)}$ is elastic energy, W_{sol} is solvent and network mixing energy, W_{ion} is ions mixing energy and W_{dis} is related to the dissociation of acidic groups. The incompressible elastomeric layer is treated as a hyperelastic material that can be modeled using a Helmholtz energy that includes only the elastic energy. The free energy density for the elastomer is just a function of the deformation gradient tensor as:

$$W^{(1)}(\mathbf{F}^{(1)}) = W_{net}^{(1)}(\mathbf{F}^{(1)}) \quad (8)$$

The Neo-Hookean model is used for defining the elastic energy of both the pH-sensitive and the elastomer layers. An additional term is added to the elastic energy of the elastomer to account for the incompressibility constraint.

$$W_{net}^{(1)}(\mathbf{F}^{(1)}) = \frac{1}{2} NkT [I_1^{(1)} - 3 - 2 \log(J^{(1)})] + \pi (\log(J^{(1)}))^2 \quad (9)$$

$$W_{net}^{(2)}(\mathbf{F}^{(2)}) = \frac{1}{2} NkT [I_1^{(2)} - 3 - 2 \log(J^{(2)})] \quad (10)$$

where N is the number of polymer chains divided by the volume of the dry network, k is the Boltzmann constant and T is the absolute temperature. The term NkT is the elastic modulus of the layers [1] and it is assumed to be equal for both layers. $I_1^{(n)}$ is the first invariant of the right Cauchy-Green deformation tensor. The term π , in the elastic energy of the elastomer layer, is a Lagrange multiplier accounts for the hydrostatic pressure, and is defined via applying boundary conditions.

The free energy of mixing the network and the solvent is taken to be:

$$W_{sol}(\mathbf{F}^{(2)}) = \frac{kT}{\nu_s} \left[\left(J^{(2)} - 1 \right) \log \left(1 - \frac{1}{J^{(2)}} \right) - \frac{\chi}{J^{(2)}} \right] \quad (11)$$

where ν_s is the volume of a single molecule of the solvent and χ is a dimensionless parameter representing the enthalpy of mixing.

The mixing energy of the mobile ions is:

$$W_{ion}(\mathbf{F}^{(2)}, C_+, C_{H^+}, C_-) = kT \left[C_{H^+} \left(\log \frac{C_{H^+}}{c_{H^+}^{ref} J^{(2)}} - 1 \right) + C_+ \left(\log \frac{C_+}{c_+^{ref} J^{(2)}} - 1 \right) + C_- \left(\log \frac{C_-}{c_-^{ref} J^{(2)}} - 1 \right) \right] \quad (12)$$

where $c_{H^+}^{ref}$, c_+^{ref} , c_-^{ref} are reference values for the concentration of the hydrogen ions, the counter-ions and the co-ions, respectively.

The free energy change due to the acidic dissociation is:

$$W_{dis}(\mathbf{F}^{(2)}, C_+, C_{H^+}, C_-) = kT \left[C_{A^-} \log \left(\frac{C_{A^-}}{C_{A^-} + C_{AH}} \right) + C_{AH} \log \left(\frac{C_{AH}}{C_{A^-} + C_{AH}} \right) \right] + \gamma C_{A^-} \quad (13)$$

where C_{AH} and C_{A^-} are the nominal concentration of associated acidic groups and of the fixed charges, respectively. γ is the enthalpic energy release of an acidic group dissociation. The electroneutrality assumption states that $C_{H^+} + C_+ = C_{A^-} + C_-$ and $C_{AH} + C_{A^-} = f / \nu$ where f is the number of acidic groups on a chain divided by the total number of monomers on that chain and ν is the volume of a single monomer molecule and is taken to be equal to ν_s .

The free energy density is related to the Cauchy principal stresses by $\sigma_i = (\lambda_i^{(n)} / J^{(n)}) (\partial W / \partial \lambda_i^{(n)})$. So the principal Cauchy stresses for the elastomer become:

$$\sigma_i^{(1)} = NkT ((\lambda_i^{(1)})^2 - 1) + 2\pi \log(J^{(2)}) \quad (14)$$

Using the free energy density of the pH-sensitive hydrogel, the principal stresses for the pH-sensitive layer become [1]:

$$\sigma_i^{(2)} = kT \left[\frac{N}{J} \left((\lambda_i^{(2)})^2 - 1 \right) - (c_{H^+} + c_+ + c_- - \bar{c}_{H^+} - \bar{c}_+ - \bar{c}_-) + \frac{1}{\nu_s} \left(\log \left(1 - \frac{1}{J^{(2)}} \right) + \frac{1}{J^{(2)}} + \frac{\chi}{(J^{(2)})^2} \right) \right] \quad (15)$$

where c_α are the concentration of α species in the current configuration ($C_\alpha = c_\alpha J^{(2)}$) and $\bar{c}_\alpha$ are concentrations of the α species in the external solution.

The Donnan equations for ionic equilibrium relates the internal concentration of species to the external concentrations as:

$$c_+ / \bar{c}_+ = c_{H^+} / \bar{c}_{H^+} \quad (16)$$

$$c_- / \bar{c}_- = (c_{H^+} / \bar{c}_{H^+})^{-1} \quad (17)$$

The chemical dissociation equilibrium is:

$$\frac{c_{H^+} (c_{H^+} + c_+ + c_-)}{(f / \nu) (J^{(2)})^{-1} - (c_{H^+} + c_+ + c_-)} = N_A K_a \quad (18)$$

where N_A and K_a are Avogadro number and the constant of acidic dissociation, respectively. In light of the Donnan equations (Eq.(16) and Eq.(17)) along with Eq.(18) we can define the stresses in Eq.(15) as a function of deformation gradient and external concentrations of the hydrogen ions ($\bar{c}_{H^+}$) and the counter-ions ($\bar{c}_+$).

Substituting the radial and the hoop stretches of each layer from related deformation gradient (Eq.(4)) into Eq.(14) and Eq.(15), the radial and the hoop stresses for both layers are defined as functions of $r_1, \bar{\theta}$ and $r^{(n)}(X_2)$.

There is no variation with respect to the θ direction, therefore, the equilibrium equation in the cylindrical coordinates becomes:

$$\frac{\frac{\partial \sigma_r^{(n)}}{\partial X_2}}{\frac{\partial r^{(n)}(X_2)}{\partial X_2}} + \frac{\sigma_r^{(n)} - \sigma_\theta^{(n)}}{r^{(n)}(X_2)} = 0 \quad (19)$$

Substituting the hoop and radial stresses for each layer to the equilibrium equation (19) and integrating with respect to X_2 , we can obtain a radial stress that satisfies equilibrium equation. We name this stress the equilibrium stress $\bar{\sigma}_r$:

$$\bar{\sigma}_r^{(n)} = \int -\frac{\sigma_r^{(n)} - \sigma_\theta^{(n)}}{r^{(n)}(X_2)} \frac{dr^{(n)}(X_2)}{dX_2} dX_2 + \zeta^{(n)} \quad (20)$$

where $\zeta^{(n)}$ is the integration constant that can be found from boundary conditions for each layer.

For the elastomeric layer, $\zeta^{(1)}$ is determined via setting the $\bar{\sigma}_r^{(1)} = 0$ at the internal boundary, that is $X_2 = 0$. Substituting the fully defined equilibrium radial stress $\bar{\sigma}_r^{(1)}$ back into the equilibrium equation (19) the equilibrium hoop stress $\bar{\sigma}_\theta^{(1)}$ can be calculated. The equilibrium stresses for the incompressible elastomeric layer is equal to the actual stresses Eq.(14) [38]. Considering Eq.(6), the hoop and radial stresses of the elastomer are found as a function of r_1 , $\bar{\theta}$ and X_2 as below:

$$\sigma_r^{(1)} = -\frac{1}{8} \frac{NkT \left(-16r_1^4 \bar{\theta}^4 - 16LX_2 r_1^2 \bar{\theta}^3 + L^4 \right) X_2}{\bar{\theta}^2 L \left(r_1^2 \bar{\theta} + LX_2 \right) r_1^2} \quad (21)$$

$$\sigma_\theta^{(1)} = -\frac{1}{8} \frac{NkT \left(-32r_1^6 \bar{\theta}^5 - 80LX_2 r_1^4 \bar{\theta}^4 - 48L^2 X_2^2 r_1^2 \bar{\theta}^3 + 2L^4 r_1^2 \bar{\theta} + L^5 X_2 \right)}{\bar{\theta}^2 \left(r_1^2 \bar{\theta} + LX_2 \right) L^2 r_1^2} \quad (22)$$

For the pH-sensitive gel layer, we pursue the same method employed to the elastomer layer. However, we need to determine the functionality of $r^{(2)}(X_2)$ to use it inside the integration of the equilibrium equation (20). Meticulously examining different types of functions such as polynomials and exponential functions, we chose an exponential form with four unknown constants to form the $r^{(2)}(X_2)$:

$$r^{(2)}(X_2) = a \exp(bX_2) + c \exp(dX_2) \quad (23)$$

where a, b, c, d are constants to be determined. The exponential function has the advantages of being easily manipulated **with fewer constants**, which reduces the computational cost, and having infinite derivatives since second derivatives are necessary for this problem. **This is while the linear function could not predict the stress field successfully, because its derivatives do not have the sufficient flexibility (constant first derivatives and zero second derivatives) to calculate the stress field accurately, and in case of polynomials, in order to have flexible derivatives, the polynomial degree must be increased, which makes it computationally inefficient.** On the other hand, the exponential function with four constants is flexible enough to accurately capture the variation of variables.

Substituting the exponential function Eq.(23) into the radial and the hoop stresses, the equilibrium radial stress for the pH-sensitive layer $\bar{\sigma}_r^{(2)}$ is determined using Eq.(20). The integration constant $\zeta^{(2)}$ is calculated enforcing the zero radial stress condition in the outer radius ($\bar{\sigma}_r^{(2)} = 0$ at $X_2 = H_1 + H_2$). Similar to the elastomeric layer, the equilibrium hoop stress for the pH-sensitive layer is calculated through putting $\bar{\sigma}_r^{(2)}$ in equilibrium equation (19) and solving for $\bar{\sigma}_\theta^{(2)}$.

Up to this point we have six unknowns ($r_1, \bar{\theta}, a, b, c, d$) to be determined, so we need to seek for six equations to solve for these unknowns. The radial stress is zero at the outer boundary, Eq.(24). The radius of the two layers must be equal at the interface as the layers are fully attached at the interface, Eq.(25). The radial stress of the elastomeric layer is equal to the radial stress of the pH-sensitive layer, Eq.(26). The equilibrium hoop stress should be equal to the hoop stress determined through the free

energy ($\sigma_{\theta}^{(2)} = \bar{\sigma}_{\theta}^{(2)}$), however, since it is difficult to have this equilibrium on every point, we used a weak form (that is Eq.(27)). The whole bilayer bends in response to internal forces and there is no external load acting on it, consequently, the force and the moment caused by the hoop stresses at any cross-section of the bilayer must be zero. A weak form of the force and the moment equilibrium equations are Eq.(28) and Eq.(29). All stated equations are presented collectively as follow:

$$\sigma_r^{(2)} = 0 \text{ at } X_2 = H \quad (24)$$

$$r^{(1)}(X_2) = r^{(2)}(X_2) \text{ at } X_2 = H^{(1)} \quad (25)$$

$$\sigma_r^{(1)} = \sigma_r^{(2)} \text{ at } X_2 = H^{(1)} \quad (26)$$

$$\int_{H^{(1)}}^H \sigma_{\theta}^{(2)} \frac{dr^{(2)}(X_2)}{dX_2} dX_2 = \int_{H^{(1)}}^H \bar{\sigma}_{\theta}^{(2)} \frac{dr^{(2)}(X_2)}{dX_2} dX_2 \quad (27)$$

$$\int_0^{H^{(1)}} \sigma_{\theta}^{(1)} \frac{dr^{(1)}(X_2)}{dX_2} dX_2 + \int_{H^{(1)}}^H \sigma_{\theta}^{(2)} \frac{dr^{(2)}(X_2)}{dX_2} dX_2 = 0 \quad (28)$$

$$\int_0^{H^{(1)}} r^{(1)}(X_2) \sigma_{\theta}^{(1)} \frac{dr^{(1)}(X_2)}{dX_2} dX_2 + \int_{H^{(1)}}^H r^{(2)}(X_2) \sigma_{\theta}^{(2)} \frac{dr^{(2)}(X_2)}{dX_2} dX_2 = 0 \quad (29)$$

Solving the system of equations employing numerical methods, all six unknowns are fully defined.

3 Results and Discussion

In this section, we set up some problems that demonstrate the applicability and robustness of the presented method. We consider a bilayer with the thickness and the length of $H = 0.01 \text{ m}$ and $L = .04 \text{ m}$, respectively. The material parameters used for the pH-sensitive layer are borrowed from Marcombe, Cai [1]. These parameters are: $\nu = 10^{-28} \text{ m}^3$, $\chi = 0.1$, $K_a = 10^{-4.3}$, $kT = 4 \times 10^{-21} \text{ J}$, $f = 0.05$ and $\bar{c}_+ = 0.001 \text{ M}$. Both layers have the same thickness ($H^{(1)}=H^{(2)}=H/2$), except for the case that the

thickness ratio of the layers are investigated. The elastic modulus (NkT) is assumed to be equal for both layers throughout all the studies. The reference pH value is taken to be $pH = 2$.

In order to model the behavior of the bilayer gel numerically, the swelling model proposed by Marcombe, Cai [1] is implemented as a UHYPER subroutine to the ABAQUS, a well-known commercial finite element software. The UHYPER subroutine is commonly used for defining large deformations of hyperelastic materials, and only requires the strain energy density function (in this case the Helmholtz free energy density) and its derivatives with respect to the strain invariants and J to be defined. Once the UHYPER is defined, it can be used to simulate any kind of structural analysis including 3D, plane strain, and plane stress models. The swelling state of the hydrogel can be determined by minimization of the free energy density. In fact, ABAQUS uses the UHYPER code to find the configuration of the hydrogel structure in which the free energy density becomes minimum, regarding the specified pH value.

Since the end effects are neglected in our analytical approach, the ends of the bilayer modeled in ABAQUS are confined so that they remain plane while the whole bilayer undergoes large deformations and swelling. The FEM model conforms the plane strain condition, similar to our assumption in the analytical method. The analytical results, obtained using the method presented in this article, are compared to outcomes of Finite Element Method (FEM) to validate the capability of the proposed method.

Figure 2: The comparison of FEM and analytical solutions of $r^{(n)}(X_2)$ at pH=5, 6 and 8 for $N_v=0.001$.

Figure 2 depicts $r^{(n)}(X_2)$ calculated from both the analytical (ANL) solution and the FEM for pH=5, 6 and 8. As stems from FEM solutions, $r^{(n)}(X_2)$ functionality is nearly to linear form for both layers, however, the linear function is incapable of detecting stresses which must be obtained from the function derivatives. Additionally, the linear function does not provide adequate parameters for the system of six equations mentioned earlier. Thus, for solving the analytical governing equations, the exponential function is suggested for $r^{(2)}(X_2)$. Besides, the constants that are calculated from the system of equations, proved to be powerful enough to capture the location vector as well as the radial and the hoop stresses accurately. As illustrated in Figure 3, the presented analytical method showed perfect conformity to the FEM results both for the displacement and the stress fields. This confirms the high reliability of the presented method.

Figure 3: The analytical and the FEM a) the normalized radial stress and b) the normalized hoop stress distributions at pH=5, 6 and 8. The Stresses are normalized by kT/v .

As one may observe from Figure 3, increasing the pH value, the stresses increase due to large swelling of the hydrogel layer. The swelling itself and the resulting deformation, both contribute to the increasing stresses field in the layers. Figure 4 distinctively compares the radial and the hoop stress contours calculated utilizing the proposed analytical method and the FEM at pH=8 in which the swelling ratio and the displacements are large. In order to make the results comparable, the beam ends are constrained to remain plane through the deformation in FEM. The stress contours and the deformed shape of the bilayer that are computed by either method are in a very good agreement for this large displacement condition.

Figure 4: The radial and the hoop stress distributions on the deformed bilayer at pH=8 for $N_v=0.001$

a) FEM radial stress, b) ANL radial stress, c) FEM hoop stress and d) ANL hoop stress.

The stiffness of the layers has a significant influence on the bilayer bending curvature ($\kappa = 1/r^{(n)}(X_2)$) as well as the stresses. With the increasing of N_v , that is a normalized stiffness by the constant kT/v , the number of cross-links increases and the gel becomes stiffer. The higher the stiffness of the layers is, the less the bilayer bends. Figure 5 demonstrates the curvature and the bending semi-angle of the bilayers with different stiffness during the swelling. Below pH=3 the radius of the beam goes to infinity and the problem encounters numerical difficulties. For this reason, the curvature and the bending semi-angle are calculated above pH=3. Increasing the pH value, the curvature of the bilayer increases, and the bilayer shape resembles the tubular shape. Soft bilayers bend more than the stiff ones as a result of high swelling ratio and less resistance to the deformation.

Figure 5: a) swelling curvature normalized by initial length (L) and b) corresponding bending semi-angle for the bilayer with $N_v=0.001$, 0.005 and 0.02 at $\text{pH}=8$.

Figure 6 depicts the radial and the hoop stress distribution in bilayers with different stiffnesses at their maximum bending state, that is $\text{pH}=8$. The trends are the same for different material stiffnesses despite the difference in the magnitude of the stresses. The stiffer ($N_v=0.02$) bilayer has an extreme magnitude of the hoop and the radial stresses in comparison to the softer ones. A highly cross-linked network resists to deformation as a result of high stiffness. Consequently, the stresses inside the stiff gels are higher than those of soft gels under even fewer deformations. The radial stress is zero at the inner and the outer boundaries, as it is constrained by the boundary conditions. The radial stress of the elastomeric layer is also equal to that of the pH-sensitive layer at the interface. The hoop stress is tensional in elastomeric layer side of the interface and becomes compressive at the pH-sensitive layer side.

The hoop stress is zero at approximately $X_1/H=0.2$ and 0.9 for the studied bilayers with different materials (see Figure 6(b)). These points are considered as the neutral axes of the bilayer. The bilayer that is assumed for this study, contains two neutral axes, each one on every layer, which their locations

are fixed for the materials with different Nv 's. The number and location of the neutral axes might be influenced by the geometry or the difference between the stiffness of the layers.

Figure 6: a) radial stress and b) hoop stress distributions normalized by kT/v for $Nv=0.001, 0.005$ and 0.02 at $pH=8$.

In order to investigate the influence of the geometry on the final shape of the bilayer, the curvature and the bending semi-angle are calculated for various ratios of the layers thickness. As demonstrated in Figure 7, the curvature and the bending semi-angle decreases with the increasing of the stiffness. This means that the softer bilayers bend more in comparison to those with higher Nv . The curvature and bending semi-angle of the bilayer also increases and then decreases with increasing the layers thickness ratio. So to reach the maximum curvature, the thickness ratio of the layers can be optimized employing the presented method with much less effort compared to the FEM, since the FEM models need modification and re-meshing for any modification in the geometry.

Figure 7: a) curvature normalized by the bilayer initial length (L) and b) corresponding bending semi-angle vs. normalized layers thickness ratio for $N_v=0.001, 0.005$ and 0.02 at $\text{pH}=8$.

4 Summary and Conclusion

In this article, we developed an analytical method to solve pH-responsive bending of bilayer hydrogel. One layer is made of pH-sensitive hydrogel and the other is taken to be an inert elastomer. The elastomer layer is considered as an incompressible rubber. An exponential function containing four constants is taken to define the constrained swelling behavior of the pH-sensitive layer. This function is found to be flexible enough to capture both the deformation and the stresses accurately. The method was led to a system of equations with six unknowns that are solved using a numerical method.

The results presented in this paper were intended to show the flexibility and the robustness of the proposed analytical approach. The radial and the hoop stresses demonstrated to be increasing by increasing the pH value. The perfect agreement of the analytical and the FEM results confirms the accuracy of the proposed method. We also showed that depending on the geometry and the material parameters, multiple neutral axes might be encountered. It is also revealed that the maximum curvature of the bilayer beams depends on thickness ratio of the layers and might not occur with the equal thickness of the layers. The analytical method presented in this paper could provide the basis for

accurate analysis and design of the sensors and actuators in various applications such as pH sensors, self-folding structures and drug delivery systems.

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References

- [1] Marcombe R, Cai S, Hong W, Zhao X, Lapusta Y, Suo Z. A theory of constrained swelling of a pH-sensitive hydrogel. *Soft Matter*. 2010;6(4):784.
- [2] Drozdov AD, deClaville Christiansen J, Sanporean C-G. Inhomogeneous swelling of pH-responsive gels. *Int J Solids Struct*. 2016.
- [3] Drozdov AD, DeClaville Christiansen J. Modeling the effects of pH and ionic strength on swelling of anionic polyelectrolyte gels. *Modell Simul Mater Sci Eng*. 2015;23(5).
- [4] Drozdov AD, Declaville Christiansen J. Swelling of pH-sensitive hydrogels. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*. 2015;91(2).
- [5] Li H, Go G, Ko SY, Park JO, Park S. Magnetic actuated pH-responsive hydrogel-based soft micro-robot for targeted drug delivery. *Smart Materials and Structures*. 2016;25(2).
- [6] Li P, Kim NH, Siddaramaiah, Lee JH. Swelling behavior of polyacrylamide/laponite clay nanocomposite hydrogels: pH-sensitive property. *Composites Part B: Engineering*. 2009;40(4):275-83.
- [7] Wang W, Wang J, Kang Y, Wang A. Synthesis, swelling and responsive properties of a new composite hydrogel based on hydroxyethyl cellulose and medicinal stone. *Composites Part B: Engineering*. 2011;42(4):809-18.
- [8] Mazaheri H, Baghani M, Naghdabadi R, Sohrabpour S. Coupling behavior of the pH/temperature sensitive hydrogels for the inhomogeneous and homogeneous swelling. *Smart Mater Struct*. 2016;25(8):085034.
- [9] Mazaheri H, Baghani M, Naghdabadi R, Sohrabpour S. Inhomogeneous swelling behavior of temperature sensitive PNIPAM hydrogels in micro-valves: Analytical and numerical study. *Smart Materials and Structures*. 2015;24(4).
- [10] Mazaheri H, Baghani M, Naghdabadi R. Inhomogeneous and homogeneous swelling behavior of temperature-sensitive poly-(N-isopropylacrylamide) hydrogels. *J Intel Mat Syst Str*. 2015;1045389X15571381.
- [11] Cai S, Suo Z. Mechanics and chemical thermodynamics of phase transition in temperature-sensitive hydrogels. *J Mech Ph Solids*. 2011;59(11):2259-78.
- [12] Go G, Choi H, Jeong S, Ko SY, Park JO, Park S. Selective microrobot control using a thermally responsive microclasper for microparticle manipulation. *Smart Materials and Structures*. 2016;25(3).
- [13] Chester SA, Anand L. A thermo-mechanically coupled theory for fluid permeation in elastomeric materials: Application to thermally responsive gels. *J Mech Ph Solids*. 2011;59(10):1978-2006.
- [14] Yoon C, Xiao R, Park J, Cha J, Nguyen TD, Gracias DH. Functional stimuli responsive hydrogel devices by self-folding. *Smart Materials and Structures*. 2014;23(9).
- [15] Guo W, Li M, Zhou J. Modeling programmable deformation of self-folding all-polymer structures with temperature-sensitive hydrogels. *Smart Materials and Structures*. 2013;22(11).
- [16] Morimoto T, Ashida F. Temperature-responsive bending of a bilayer gel. *International Journal of Solids and Structures*. 2015;56:20-8.
- [17] Katz JS, Burdick JA. Light-Responsive Biomaterials: Development and Applications. *Macromol Biosci*. 2010;10(4):339-48.
- [18] Ahn S-k, Kasi RM, Kim S-C, Sharma N, Zhou Y. Stimuli-responsive polymer gels. *Soft Matter*. 2008;4(6):1151-7.
- [19] Doi M. Gel Dynamics. *Journal of the Physical Society of Japan*. 2009;78(5):052001.
- [20] Attaran A, Brummund J, Wallmersperger T. Modeling and simulation of the bending behavior of electrically-stimulated cantilevered hydrogels. *Smart Materials and Structures*. 2015;24(3).
- [21] Elshaer SE, Moussa WA. Comparative study of chemo-electro-mechanical transport models for an electrically stimulated hydrogel. *Smart Materials and Structures*. 2014;23(7).

- [22] Jabbari E, Tavakoli J, Sarvestani AS. Swelling characteristics of acrylic acid polyelectrolyte hydrogel in a dc electric field. *Smart Materials and Structures*. 2007;16(5):1614-20.
- [23] Cho IS, Cho MO, Li Z, Nurunnabi M, Park SY, Kang SW, et al. Synthesis and characterization of a new photo-crosslinkable glycol chitosan thermogel for biomedical applications. *Carbohydrate Polymers*. 2016;144:59-67.
- [24] Pollini M, Paladini F, Sannino A, Maffezzoli A. Development of hybrid cotton/hydrogel yarns with improved absorption properties for biomedical applications. *Materials Science and Engineering C*. 2016;63:563-9.
- [25] Ionov L. Biomimetic hydrogel-based actuating systems. *Advanced Functional Materials*. 2013;23(36):4555-70.
- [26] Nasser Arbabi, Mostafa Baghani, Jalal Abdolahi, Hashem Mazaheri, Mahmoud Mousavi Mashhadi. Study on pH-sensitive Hydrogel Micro-valves: a Fluid Structure Interaction (FSI) Approach. Under revision at: *Intelligent Material Systems and Structures*. 2016.
- [27] Migliorini L, Santaniello T, Yan Y, Lenardi C, Milani P. Low-voltage electrically driven homeostatic hydrogel-based actuators for underwater soft robotics. *Sensors and Actuators, B: Chemical*. 2016;228:758-66.
- [28] Zhao X, Lang Q, Yildirim L, Lin ZY, Cui W, Annabi N, et al. Photocrosslinkable Gelatin Hydrogel for Epidermal Tissue Engineering. *Advanced Healthcare Materials*. 2016;5(1):108-18.
- [29] Ahadian S, Banan Sadeghian R, Yaginuma S, Ramón-Azcón J, Nashimoto Y, Liang X, et al. Hydrogels containing metallic glass sub-micron wires for regulating skeletal muscle cell behaviour. *Biomaterials Science*. 2015;3(11):1449-58.
- [30] Eslami M, Vrana NE, Zorlutuna P, Sant S, Jung S, Masoumi N, et al. Fiber-reinforced hydrogel scaffolds for heart valve tissue engineering. *Journal of Biomaterials Applications*. 2014;29(3):399-410.
- [31] Flory PJ. Thermodynamics of High Polymer Solutions. *The Journal of Chemical Physics*. 1942;10(1):51-61.
- [32] Hong W, Zhao X, Zhou J, Suo Z. A theory of coupled diffusion and large deformation in polymeric gels. *Journal of the Mechanics and Physics of Solids*. 2008;56(5):1779-93.
- [33] Lucantonio A, Nardinocchi P, Teresi L. Transient analysis of swelling-induced large deformations in polymer gels. *Journal of the Mechanics and Physics of Solids*. 2013;61(1):205-18.
- [34] He T, Li M, Zhou J. Modeling deformation and contacts of pH sensitive hydrogels for microfluidic flow control. *Soft Matter*. 2012;8(11):3083.
- [35] Timoshenko S. Analysis of bi-metal thermostats. *JOSA*. 1925;11(3):233-55.
- [36] Kwon GH, Choi YY, Park JY, Woo DH, Lee KB, Kim JH, et al. Electrically-driven hydrogel actuators in microfluidic channels: fabrication, characterization, and biological application. *Lab on a chip*. 2010;10(12):1604-10.
- [37] Kwon GH, Jeong GS, Park JY, Moon JH, Lee SH. A low-energy-consumption electroactive valveless hydrogel micropump for long-term biomedical applications. *Lab on a chip*. 2011;11(17):2910-5.
- [38] Roccabianca S, Gei M, Bigoni D. Plane strain bifurcations of elastic layered structures subject to finite bending: theory versus experiments. *IMA Journal of Applied Mathematics*. 2010;75(4):525-48.
- [39] Lucantonio A, Nardinocchi P, Pezzulla M. Swelling-induced and controlled curving in layered gel beams. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences: The Royal Society*; 2014. p. 20140467.
- [40] Nardinocchi P, Puntel E. Finite bending solutions for layered gel beams. *Int J Solids Struct*. 2016.
- [41] Drozdov AD, Christiansen Jd. Swelling-induced bending of bilayer gel beams. *Composite Structures*. 2016;153:961-71.
- [42] Abdolahi J, Baghani M, Arbabi N, Mazaheri H. Analytical and numerical analysis of swelling-induced large bending of thermally-activated hydrogel bilayers. *Int J Solids Struct*. 2016;99:1-11.

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Figure 1: The schematics of the hydrogel bilayer geometry: a) the initial configuration and b) the deformed configuration.

Figure 2: The comparison of FEM and analytical solutions of $r^{(n)}(X_2)$ at pH=5, 6 and 8 for $N_v=0.001$.

Figure 3: The analytical and the FEM a) the normalized radial stress and b) the normalized hoop stress distributions at pH=5, 6 and 8. The Stresses are normalized by kT/v .

Figure 4: The radial and the hoop stress distributions on the deformed bilayer at pH=8 for $N_v=0.001$ a) FEM radial stress, b) ANL radial stress, c) FEM hoop stress and d) ANL hoop stress.

Figure 5: a) swelling curvature normalized by initial length (L) and b) corresponding bending semi-angle for the bilayer with $N_v=0.001, 0.005$ and 0.02 at pH=8.

Figure 6: a) radial stress and b) hoop stress distributions normalized by kT/v for $N_v=0.001, 0.005$ and 0.02 at pH=8.

Figure 7: a) curvature normalized by the bilayer initial length (L) and b) corresponding bending semi-angle vs. normalized layers thickness ratio for $N_v=0.001, 0.005$ and 0.02 at pH=8.