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Kinetics of swelling of cylindrical functionally graded temperature-responsive hydrogels

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ABSTRACT

Cylindrical hydrogels have a wide variety of applications in microfluidics; for example, they serve as micro-valves, micro-mixers, and micro-lenses. The main advantages of them can be mentioned as their autonomous functionality due to their responses to environmental stimuli and simple geometry. Furthermore, functionally graded hydrogels have recently found applications in hydrogel actuators. Therefore, in this work, the kinetics of swelling, shrinking, and force generation of cylindrical functionally graded temperature-responsive hydrogels are investigated. Kinetics of cylindrical structure is investigated analytically by developing a mathematical model based on available constitutive models of large deformation of hydrogels. The cross-link density of the hydrogel polymeric network varies along the radius of the cylinder linearly. In order to analyze the structure's behavior, the temperature is changed, and the response time of the structures with different distribution of cross-link density is investigated. In addition, to investigate the realistic actuators' performance, the cylindrical hydrogel is located inside a hollow cylinder, and the pressure of the hydrogel, which puts on the cylinder, is investigated. The results show that manipulation of cross-link density influences the response time of the cylindrical hydrogel; hence, it is a useful tool to manage the overall performance of cylindrical actuators.

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1. Introduction

Hydrogels are cross-linked hydrophilic polymers capable of absorbing surrounding water. Hydrogels are divided into responsive or non-responsive categories. In the case of the responsive hydrogels, they can absorb or lose water due to the change of some environmental stimuli such as temperature [1], pH [2, 3], salt concentration [4], light [5], etc. In recent years, hydrogels have found a multitude of applications. For example, they have applications in drug delivery systems [6], sensing and actuating devices [7-9], and microfluidics [10-13]. Hydrogels are used in microfluidic devices as sensors and actuators [11, 12, 14, 15]. A cylindrical shape micro-valve was a pioneer actuator introduced by Beebe et al. [12]. Afterward, Cylindrical hydrogels found application in micro-mixers [15] and micro-lenses [7]. The micro-mixer mentioned above comprises a cylindrical hydrogel placed inside an external spinning cylinder, which mixes fluids by spinning. When the hydrogel swells, it touches the exernal cylinder and stops it; therefore, the fluids would no longer mix. In this work, we investigate the swelling of micro-mixers made of temperature-responsive hydrogels due to the importance of temperature-sensitive smart actuators in general [16-19].

Mathematical models are essential for the optimal design of actuators, which can substantially reduce costs of experiments and numerical simulations. Moreover, analytical solutions can be performed as an appropriate tool to validate the numerical results [20]. To develop a mathematical model, using a constitutive model is necessary. Therefore, the modeling of hydrogels has attracted plenty of interest in recent years [1, 21-25]. A model considering fluid permeation and concurrent large deformation of non-responsive hydrogels was introduced by Hong et al. [22]. Later, Cai and Suo [1] proposed a model for temperature-responsive hydrogels. This model shows instability in the vicinity of phase transition temperature (PTT); this motivated Mazaheri et al. [24] to modify Cai and Suo's model. After introducing their model, they have examined it and showed that their model is in good agreement with experiments.

Analytical studies of hydrogels can be classified into equilibrium studies that consider the hydrogel in an equilibrium state and transient studies that consider the hydrogel's kinetics. Researchers have conducted many equilibrium studies on different hydrogel types [14, 26-29]. On the contrary, only a few works were conducted to examine the kinetics of hydrogels [30, 31]. Mazaheri et al. [14] have conducted an analytical and numerical study on temperature-sensitive micro-valve,

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considering only the equilibrium state of the hydrogel. They calculated the equilibrium radius of the cylinder at different temperatures and studied the effects of cross-link density. Arbabi et al. [26] analytically and numerically investigated a pH-responsive micro-valve and studied the effect of fluid pressure using the FSI method. Kinetics of swelling of a cylindrical non-responsive hydrogel containing a hard pillar was conducted by Cai et al. [30], and the effects of material parameters and geometry were studied. Also, Liu et al. [31] analytically and numerically investigated the kinetics of a cylindrical non-responsive hydrogel with a hard pillar using FEM.

Researchers have considered the synthesis of functionally graded (FG) hydrogels due to the possibility of reaching specific functionalities [32]. Such hydrogels are used in controlled drug delivery, tissue engineering [33], micro-valves [29], and hydrogel bilayers [34]. Therefore, the behavior of FG hydrogels has been the subject of many studies [28, 29, 34, 35]. Temperature-responsive cylindrical micro-valves were considered by Mazaheri and Ghasemkhani [28], and an analytical solution for the equilibrium state of them is performed, and the effect of the different distribution of cross-link density is investigated. Furthermore, Shojaeifard et al. [29] investigated the effect of temperature gradient inside the micro-valve made of FG hydrogel. Moreover, FSI investigation of the cylindrical FG pH-sensitive micro-valves was performed by Mazaheri et al. [35].

The swelling of hydrogels is a time-consuming process. Hence, having complete knowledge about the kinetics of swelling is essential for designing such actuators. In this work, an analytical solution for kinetics of swelling and shrinking of cylindrical FG temperature-responsive hydrogels is presented. Furthermore, the kinetics of force generation by a cylindrical structure, which is of major importance, is investigated. To this end, we have developed an analytical solution considering concurrent fluid permeation and large deformation of temperature-responsive hydrogels.

2. Summary of the model

To model the concurrent processes of absorbing water and deformation of the hydrogel, we must consider both fluid permeation into the network and force balance inside the hydrogel. Note that the heat transfer process inside the hydrogel is much faster than the diffusion process [25, 36]; hence the heat transfer is approximated as an instantaneous process [37].

The state that the hydrogel contains no solvent is considered as the reference state. Coordinate of an element at this state is denoted by $\mathbf{X}$. Note that Lagrangian formulation is used in this paper. Moreover, the deformed coordinate of the element and deformation gradient is denoted by $\mathbf{x}(\mathbf{X},t)$ and $\mathbf{F}(\mathbf{X},t)$, respectively.

The hydrogel is treated as a hyper-elastic material. The free energy density of the hydrogel is composed of two parts, the first part arises from the mixing of the solvent molecules and polymer chains, and the second arises from the stretching of the hydrogel network. The model of the hydrogel is based on the additive decomposition of the free energy density, which takes the form [38]:

$$W(\mathbf{F},C,T)=W_m(C,T)+W_s(\mathbf{F},T) \qquad (1)$$

where W_m , W_s , and $C(\mathbf{X},t)$ are the free energy density caused by mixing of the polymer chains and solvent molecules, the free energy density due to stretching of the network, and the number of water molecules in a unit of volume element in the reference state, respectively. The mixing part of the free energy density is based on the works of [39, 40] and takes the form [24]:

$$W_{mixing}=\frac{kT}{v}(J-1)\left[-\frac{1}{J}-\frac{1}{2(J)^2}-\frac{1}{3(J)^3}+\frac{\chi}{J}\right] \qquad (2)$$

where k , T , v , J and χ are Boltzmann constant, temperature, volume per molecule, determinant of the deformation gradient and interaction parameter, respectively. $\chi(J,T)$ is a dimensionless parameter depending on the temperature and polymer volume fraction, ϕ , which takes the form:

$$\begin{aligned}\chi(\phi,T)&=\chi_0+\phi\chi_1,\\ \chi_0&=A_0+B_0T,\\ \chi_1&=A_1+B_1T,\end{aligned} \qquad (3)$$

in which A_0 , B_0 , A_1 and B_1 are material parameters; for PNIPAM hydrogel, these parameters are reported by Afroze et al. [41] and shown in table 1.

Table 1. Material parameter of the PNIPAM hydrogel [41]

A_0	B_0	A_1	B_1
-12.947	0.04496 K^{-1}	17.92	-0.0569 K^{-1}

The Neo-Hookean model is employed for the free energy changes due to the stretching of the network [1]:

$$W_{stretch}=\frac{1}{2}NkT(I_1-3-2\ln J) \qquad (4)$$

where N and I_1 are the concentration of polymer chains and the first invariant of the right Cauchy–Green deformation gradient[2].

Under the most types of mechanical loads, the water molecules and polymer chains undergo configurational change without any volumetric change. Therefore, the volume of individual polymer chains and water molecules is assumed to remain constant. Thus, the change of volume of hydrogels initiates only from absorbing water. This condition is known as molecular incompressibility [1, 17, 19]. Namely,

$$J=1+vC \qquad (5)$$

By considering the condition of incompressibility, the principal true stresses of the hydrogel medium at any chemical

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[2] Note that the right Cauchy–Green deformation gradient is defined as $\mathbf{C}=\mathbf{F}^T\mathbf{F}$

potential of water molecules inside the hydrogel is obtained as [42]:

$$\sigma_i = \frac{\lambda_i}{J}\frac{\partial W}{\partial \lambda_i} - \frac{\mu(\mathbf{X},t)}{\nu} \tag{6}$$

in which σ_i and $\mu(\mathbf{X},t)$ are the true stresses at the principal direction of i and chemical potential of the solvent molecules inside the hydrogel. Chemical potential affects the network by adding a hydrostatic stress term to the stresses. When the system reaches the equilibrium state, the chemical potential throughout the hydrogel reaches the value of the chemical potential of the surrounding solvent, namely $\mu(\mathbf{X},\infty) = \mu_{sf}$, where μ_{sf} is the chemical potential of the surrounding solvent.

We consider a kinetic law that is proposed by Hong et al. [17]. The permeation of the solvent molecules inside the hydrogel is driven by the gradient of chemical potential inside the hydrogel. The kinetic law is of the following form:

$$j_K = -M_{KL}\frac{\partial \mu}{\partial X_L} \tag{7}$$

where M_{KL} and j_K are components of the mobility tensor and the vector of water flux inside the hydrogel. According to experiments [43], as hydrogels swell, the diffusivity changes, namely, it becomes greater in value. Therefore, different works have suggested taking the mobility tensor as $\frac{Dc}{kT}$, where c and D are true concentration of water molecules and diffusivity [22, 37, 44]. Hong, Zhao, Zhou, Suo [22] have considered the aformentioned expression and have derived the following form for the mobility tensor:

$$M_{LK} = \frac{D}{\nu kT}H_{iK}H_{iL}\left(J-1\right) \tag{8}$$

in which H_{iK} is the components of $\mathbf{F}^{-T}$.

To validate the model, a set of experiments available in the literature [45] is considered. The experiment is the kinetics of swelling of a thin PNIPAM hydrogel layer attached to a rigid sublayer. This is a one-dimensional swelling problem. We use the model to confront the problem and then compare the results with the experiments to check the model's validity.

The hydrogel film has occupied a domain { $0 \le X_1 \le H$, $0 \le X_2 \le L_1$, $0 \le X_3 \le L_2$ }, where X_i are Cartesian coordinates in the initial state. Thickness (H) of the hydrogel is small in comparison with its width (L_1) and length (L_2), so we consider the fluid permeation as a one-dimensional process and neglect the effects of diffusion at the edges of the film. The hydrogels were contained an amount of water at their initial state; it was due to the preparation method. In other words, the hydrogels were swollen to some degrees before fluid permeation occurred. Note that the hydrogels have not been equilibrated at preparation temperature. The stretches at this state are λ_0. Note that at the initial stage, the hydrogels were stress-free. Here, we consider this free swollen state as reference state and rewrite the free energy density [46] and the flux of solvent molecules as:

$$W' = \frac{W}{\lambda_0^3}, \tag{9}$$

$$j_i' = \frac{j_i}{\lambda_0^2}. \tag{10}$$

When the solvent molecules diffuse inside the hydrogel, the hydrogel deforms only in X_1 direction. Therefore, the stretch in X_2 and X_3 remain constant during the deformation. We decompose the deformation gradient into two parts, first, free swelling before attaching the hydrogels to the sublayer, and second, one-dimensional swelling. Stretches in principle direction are $\lambda_1 = \lambda_1'\lambda_0$ and $\lambda_2 = \lambda_3 = \lambda_0$, where $\lambda_1'(X_1,t)$ is:

$$\lambda_1' = \frac{\partial x_1}{\partial X_1} \tag{11}$$

Considering Eq. (10), the kinetic law, Eq. (8), is obtained as:

$$j' = -\frac{D(\lambda_1'\lambda_0^{\,3}-1)}{\nu kT\lambda_0^{\,4}\lambda_1'^2}\frac{\partial \mu}{\partial X_1} \tag{12}$$

Conservation of the water molecules requires that:

$$\frac{\partial C'}{\partial t} + \frac{\partial j_1'}{\partial X_1} = 0 \tag{13}$$

where C' is the number of water molecules in a unit of a volume element of reference state.

Stress at the top of the film is equal to the environment pressure, which is zero. Moreover, the mechanical equilibrium requires that:

$$\frac{\partial \sigma_1}{\partial X_1} = 0 \tag{14}$$

Therefore, σ_1 is equal to zero everywhere inside the hydrogel film. Hence, inserting σ_1 and stretches into Eq. (6) we obtain chemical potential. Finally, by adding Eq. (12) and the equation of chemical potential into Eq. (13) we derive a second-order PDE for λ_1' that should be solved using finite difference methods. Two boundaries and one initial condition are required to solve the PDE. On the surface of the hydrogel, where it is in contact with the fluid, the molecules of water in the hydrogel are in chemical equilibrium with those of in the fluid, so $\mu(H,t)$ equals to zero. Consequently, the surface of the hydrogel is in the equilibrium state, so we can find $\lambda_1'(H,t)$. Since the rigid sublayer is not permeable to water molecules, the flux of water vanishes at the substrate interface, namely, $\frac{\partial \mu(0,t)}{\partial X_1} = 0$. By considering the mechanical equilibrium, we change this condition to $\frac{\partial \lambda_1'(0,t)}{\partial X_1} = 0$. The initial condition is a pre-swollen condition with a pre-stretch λ_0 and $\lambda_1'(X_1,0) = 1$. After solving the PDE and obtaining the λ', by solving the simple ODE of Eq. (11) we can find the current position vector, $\mathbf{x}(\mathbf{X},t)$.

For two cases of experiments with differences in the initial height, the problem is solved, and the results are compared (figure 1). As shown, the result of the analytical solution and the experiments are in good agreement. By comparing the results, the coefficient of diffusion, $N\nu$, λ_0 and temperature are obtained as 1.3e-8 m^2/s (which is similar to the value reported by Ding, Toh, Hu, Liu, Ng [37] for PNIPAM hydrogels), 3.1e-3, 2.23 and 298 K, respectively.

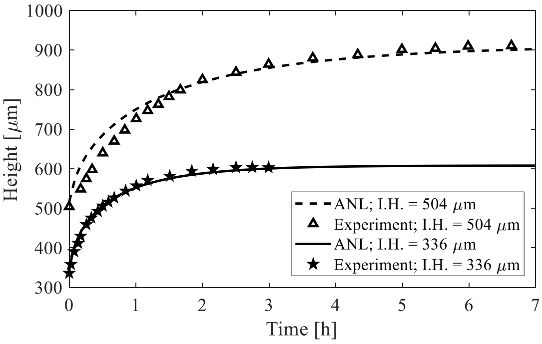

Figure 1. Results of the analytical solution next to the experiments presented by Yoon et al. [45] for one dimensional swelling with two initial height (IH).

3. Analytical Solution for the kinetics of FG hydrogels

The cross-link density of the hydrogel polymeric network varies along the radius of the cylinder as a linear function [29]:

$$N\nu(R) = N\nu_{in} + (N\nu_{out} - N\nu_{in})\left(\frac{R-A}{B-A}\right) \tag{15}$$

where A, B, $N\nu_{in}$, and $N\nu_{out}$ are the inner radius of the shell, the outer radius of the shell, cross-link density at the inner and outer radius of the hydrogel, respectively.

At the initial temperature, the hydrogel contains an amount of solvent and experiences a stress-free state because of the preparation method. Therefore, all initial stretches at this state are equal to λ_0. Note that due to the variation of the value of cross-link density, the value of λ_0 linearly differs at every radial point inside the hydrogel, which means λ_0 is a linear function [29].

We decompose the deformation gradient into two parts, first, initial swelling from the dry state to initial equilibrium state, and second, swelling after changing the temperature. Therefore, stretches in principle direction are $\lambda_i = \lambda_0 \lambda_i'$. Here, we consider the equilibrium state at the initial temperature as the reference state. Combining the Eqs. (1), (2) and (9) the free energy density can be rewritten as a function of principle stretches as follow:

$$\begin{aligned} W' = {} & \frac{NkT}{2\lambda_0^3}\left(\lambda_0^2 I_1' - 3 - 2\ln(\lambda_0^3 J')\right) + \frac{kT}{\nu\lambda_0^3}(\lambda_0^3 J' - 1)\times \\ & \left[-\frac{1}{\lambda_0^3 J'} - \frac{1}{2(\lambda_0^3 J')^2} - \frac{1}{3(\lambda_0^3 J')^3} + \frac{\chi_0}{\lambda_0^3 J'} + \frac{\chi_1}{(\lambda_0^3 J')^2}\right] \end{aligned} \tag{16}$$

Now, we consider the deformation of the network from the reference state. The deformation of the cylindrical hydrogel is axisymmetric, so at any time, the current radial position , r, is fully specified by the reference radial position, R. Moreover, the problem is a two-dimensional plane strain, because the axial deformation of the hydrogel shell in such actuators are confined. Therefore, the axial stretch obtained as:

$$\lambda_z' = 1. \tag{17}$$

Furthermore, the circumferential and radial stretches are obtained as [30]:

$$\lambda_\theta' = \frac{r}{R}, \tag{18}$$

$$\lambda_r' = \frac{\partial r}{\partial R}. \tag{19}$$

Using Eq. (6) and considering the free energy density function, true stresses inside the hydrogel are obtained.

Equation of the equilibrium in cylindrical coordinate and for an axisymmetric plane strain problem is [30]:

$$\frac{\partial(\lambda_\theta' \sigma_r)}{\partial R} + \frac{\lambda_\theta' \sigma_r - \lambda_r' \sigma_\theta}{R} = 0 \tag{20}$$

By adding stress and stretch terms Into Eq. (20) we end up with a second-order PDE. The PDE consists of two dependent variables and two independent variables, namely $r(R,t)$ and $\mu(R,t)$.

Using Eqs. (7), (8), (10) and considering the kinematics of the deformation, the flux of solvent molecules inside the hydrogel is derived as:

$$j' = -\frac{\left(\lambda_0^3 \lambda_r' \lambda_\theta' - 1\right) D}{kT \lambda_r'^2 \lambda_0^4} \frac{\partial \mu}{\partial R} \;. \tag{21}$$

Moreover, the conservation of mass in cylindrical coordinate requires that:

$$\frac{\partial C'}{\partial t} + \frac{\partial (Rj')}{R\partial R} = 0 \;. \tag{22}$$

By adding Eqs. (5), (19) and (21) into Eq. (22) another second-order PDE is obtained that is coupled with the other PDE obtained from Eq. (20) for the displacement field. Now, we have a system of two PDE that can be solved considering suitable initial and boundary conditions using finite difference methods.

To solve the above-mentioned PDEs, we have implemented finite difference methods by writing appropriate codes in MATLAB. Note that this numerical scheme was also implimented in [31] to solve governing equations of cylindrical non-responsive hydrogels. The only time related term is $\frac{\partial C'}{\partial t}$

in Eq. (22) which is discretized using the backward Euler difference. Now, using the values of $r(R,t)$ and $\mu(R,t)$ at the previous step, the system can be solved for the current time by using numerical packages, e.g., the function bvp5c.

The dimensionless parameters were analyzed by normalizing them. The normalized time, the normalized form of all of the stresses and pressures, and the normalized chemical potential are as $t^e = \dfrac{Dt}{H^2}$, $\sigma^e = \dfrac{\nu\sigma}{kT}$, and $\mu^e = \dfrac{\mu}{kT}$, respectively. Note that all normalized parameters are denoted by 'e' superscript.

4. Results and Discussion

Cylindrical hydrogels have been applied in various applications, including micro-mixer, micro-valves, micro-lens, etc. Here we consider a micro-mixer due to its simple boundary condition. The two-dimensional schematics of a micro-mixer is presented in Figure 2. The device has two inlets with two different fluids and one outlet. The external cylinder can spin. Moreover, the mixing of fluids can be caused by spinning the blades on the external cylinder. When the internal hydrogel swells, it touches the cylinder and stops the structure by exerting a force against it. In this case, the external cylinder is made of a porous material to let the water pass through. The basis of the micro-mixers' operation is in the force that these devices implemented to the external cylinder. Therefore, the force produced by the micro-mixers, which has a simple boundary condition, is investigated. Therefore, in this section, the swelling kinetics, shrinking kinetics, and force generation kinetics are investigated. Figure 3 illustrates the operation of the considered problems with their boundary condition.

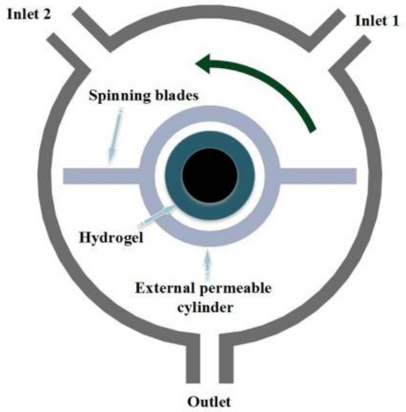

Figure 2. Two-dimensional schematics of the micro-mixer. The swelling of the hydrogel and touching the external cylinder builds up the force to stop the structure.

As mentioned before, the cross-link density is considered to be a linear function. Here, we have examined two cases, one an ascending type in which the cross-link density ascends from 0.02 at the inner radius to 0.04 at the outer radius. And the other is descending type, in which the cross-link density descends from 0.04 to 0.02. Also, for comparison, the results of the kinetics of homogeneous hydrogels are presented. The $N\nu$ parameter is considered to be 0.02, 0.04, and 0.029 for homogeneous ones. We chose homogenous hydrogel with $N\nu$ equal to 0.029 because the equilibrium swelling ratio of it approximately equals to FG ones; therefore, we can compare the results and examine the advantages of FG structures.

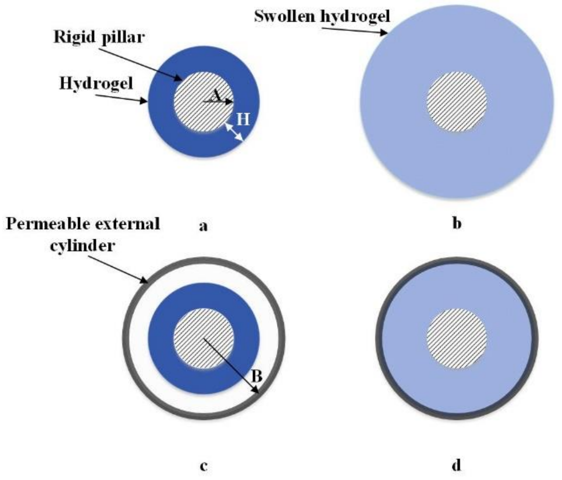

Figure 3. Schematics of the investigated problems. The hydrogel shell coated around a rigid pillar at a) initial and b) swollen state. The hydrogel rests on a rigid pillar and is placed inside a permeable cylinder at the c) initial state without contact and d) with contact with the cylinder.

4.1. swelling

First, the kinetics of swelling of the cylindrical hydrogel shell without the external cylinder is investigated. In this case, it is assumed that the initial temperature of the structure is equal to 309 K, and then the temperature is decreased to 300 K. Note that by lowering the temperature, the hydrogel tends to absorb more water and swell. The initial and boundary conditions are as follows. The hydrogel is coated around a rigid pillar; therefore, this layer maintains its initial position, namely $r(A,t) = A$. Furthermore, because the pillar is not permeable, the flux of solvent is zero at inner radius, which means the gradient of chemical potential is zero, namely $\dfrac{\partial\mu(A,t)}{\partial R} = 0$. There is no external force on the surface of the hydrogel; hence the radial stress on the surface is zero, $\sigma_r(A+H,t) = 0$. Water molecules at the surface of the hydrogel are in chemical equilibrium with the molecules in the surrounding solvent, means $\mu(A+H,t) = 0$. The hydrogel was prepared at 309 K and then attached to the pillar; therefore, the structure is stress-free at the initial time, i.e. $t = 0$.

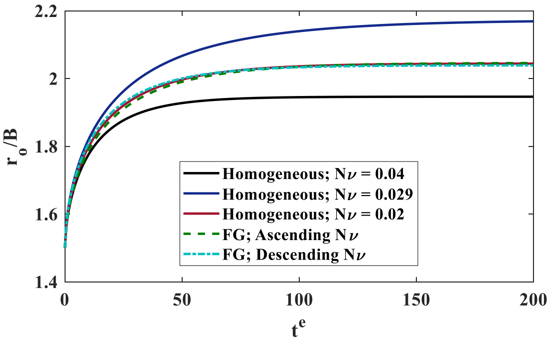

Figure 4. The evolution of the outer radius of the cylindrical hydrogel during the process of swelling.

The evolution of the hydrogel's outer radius during the swelling process is plotted in figure 4 for all five cases. As shown, for inhomogeneous hydrogels with smaller $N\nu$, the equilibrium radius is larger. Moreover, the equilibrium radius of FG hydrogels and the homogeneous one with $N\nu = 0.029$ are approximately equal.

In order to assess the process more precisely, a criterion for the response time of the system is introduced. The response time is equal to the time that 95% of the changes in the system happen. The system's response is determined as follows for swelling of a hydrogel shell on a rigid pillar:

$$\frac{r_{ot} - r_{oi}}{r_{of} - r_{oi}} = \frac{95}{100}, \tag{23}$$

where the footnotes i, f, and t indicate the initial, final, and current states, respectively. The response time for different hydrogels is presented in table 2. Considering hydrogels that the equilibrium radius of them are equal, the hydrogel with descending $N\nu$ equilibrates faster. Therefore, descending FG hydrogels has an advantage over other types of hydrogels, because swelling of hydrogels is a time-consuming process, and shortening the response time of actuators is important.

Table 2. Response time of swelling of the hydrogels with different cross-link density.

$N\nu =$ 0.04	$N\nu =$ 0.02	$N\nu =$ 0.029	$N\nu$ asc.	$N\nu$ desc.
37.80	98.72	59.08	64.22	53.21

4.2. Shrinking

In this section, the kinetics of shrinking of the swollen structure of the previous section is investigated. In this case, first, the temperature decreases from 309 K to 300 K, and the hydrogel is reached its equilibrium state, then the temperature rises from 300 K to 309 K; therefore, the hydrogel starts to shrink. The boundary conditions are the same as in the previous section, but the initial condition is different, and the new equilibrium state in which the hydrogel is not stress-free should be considered.

Table 3. Response time of shrinking of the hydrogels with different cross-link density.

$N\nu =$ 0.04	$N\nu =$ 0.02	$N\nu =$ 0.029	$N\nu$ asc.	$N\nu$ desc.
24.59	53.21	35.60	40.73	30.49

The evolution of the hydrogel's outer radius during the process of the shrinking is plotted in figure 5 for all five cases. Furthermore, the response time of them is calculated and shown in table 3. Like the swelling, the response time of the hydrogels with the equal equilibrium radius, the hydrogel with descending $N\nu$ equilibrates faster, which demonstrates the advantage of descending FG structure.

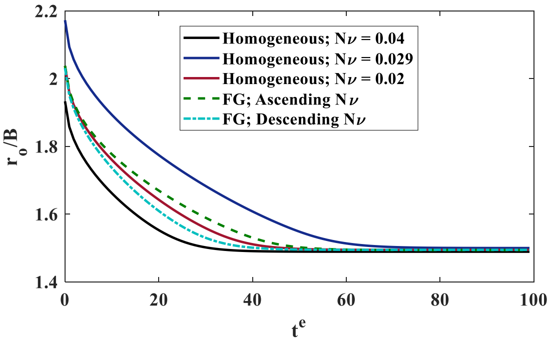

Figure 5. The evolution of the outer radius of the cylindrical hydrogel in shrinking.

4.3. Force generation

The performance of hydrogel micro-mixers depends on the force that these actuators put on the external cylinder. Therefore, in this section, we study the mechanism of force generation. In this actuator, the hydrogel fills the empty space with swelling and touches the external cylinder and creates contact pressure, p_c. In this regard, because of different boundary conditions, the problem is separated into two parts throughout the process: swelling until the moment of touch and swelling after that. In the first step, the problem is solved like a simple swelling problem. When the outer surface reaches the external cylinder, the second part of the solution process begins, and the new boundary condition is applied. The new boundary condition is that the external radius of the hydrogel remains constant and is equal to that of the external cylinder's radius, which is replaced by the free-surface boundary condition in the previous part. Here it is assumed that the temperature decreases from 309 to 300 K. Subsequently, the external cylinder radius is considered to be 1.8B to allow the hydrogel to touch it.

The obtained results of pressure exerted on the external cylinder are presented in Figure 6. As shown, the final pressure is larger for hydrogels with smaller $N\nu$. Moreover, the equilibrium pressure of FG hydrogels and the homogeneous one with $N\nu = 0.029$ are approximately equal. Therefore, we can compare the results of FG structures with this and examine the advantages of FG structures.

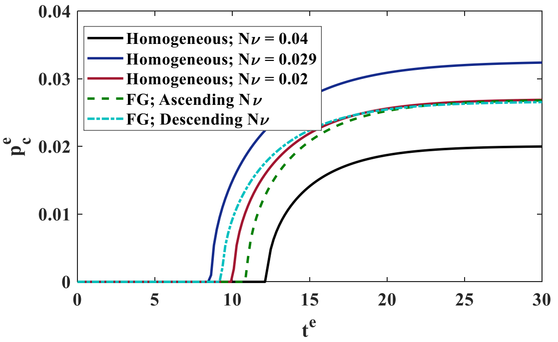

Figure 6. The evolution of force that the cylindrical hydrogel exerts on the external cylinder.

when the pressure exerted to the external cylinder is the subject of the study, the response time is defined as:

$$\frac{p_{ct}-p_{cf}}{p_{cf}}=\frac{95}{100}. \qquad (24)$$

In table 4, the time needed for hydrogel to touch the external cylinder, and the response time of the structure are presented. For the hydrogels with the approximately equal force generated, the time of touching the external cylinder and total response time for the hydrogel with descending $N\nu$ is shorter, which demonstrates the advantage of descending FG structure.

Table 4. Response time of force generation of the hydrogels with different cross-link density.

	Time to touch	*Time to reach 95% of final force*
$N\nu$ = 0.04	12.11	20.92
$N\nu$ = 0.02	8.62	20.08
$N\nu$ = 0.029	10.00	20.09
$N\nu$ asc.	10.83	20.83
$N\nu$ desc.	9.27	19.45

5. Conclusion

In this work, we investigated the kinetics of swelling, shrinking, and force generation of cylindrical FG temperature-responsive hydrogels. For this purpose, first, a summary of the constitutive model of large deformation of hydrogels was presented. Then, an analytical solution of the kinetics of cylindrical FG temperature-responsive hydrogels was performed. The result was a set of two coupled PDEs, one obtained from the hydrogel's deformation and the other from solvent permeation inside the hydrogel. Finally, the finite difference method was implemented by developing a MATLAB code to solve the obtained PDEs.

The cross-link density of the hydrogel shell changes along the radius of the cylinder with the linear trend. In order to study the behavior of the structure, the temperature was changed between 309 K and 300 K, and the kinetics of swelling and shrinking of the structure were studied. Also, to investigate the behavior of the micro-mixer actuators, the structure was placed inside a hollow permeable cylinder, and the pressure that this structure puts on the cylinder was investigated.

Different hydrogels with homogeneous cross-link and FG cross-link were considered, and results were compared. The comparison indicates that hydrogel with descending cross-link density from the inner radius to the outer radius of the cylinder has the fastest response to temperature changes. Therefore, descending FG hydrogels has an advantage over other types of hydrogels, because swelling of hydrogels is a time-consuming process, and shortening the response time of actuators is essential.

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