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Modeling programmable deformation of self-folding all-polymer structures with temperature-sensitive hydrogels

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Abstract

Combination of soft active hydrogels with hard passive polymers gives rise to all-polymer composites. The hydrogel is sensitive to external stimuli while the passive polymer is inert. Utilizing the different behaviors of two materials subject to environmental variation, for example temperature, results in self-folding soft machines. We report our efforts to model the programmable deformation of self-folding structures with temperature-sensitive hydrogels. The self-folding structures are realized either by constructing a bilayer structure or by incorporating hydrogels as hinges. The methodology and the results may aid the design, control and fabrication of 3D complex structures from 2D simple configurations through self-assembly.

(Some figures may appear in colour only in the online journal)

1. Introduction

A hybrid all-polymer inhomogeneous material system, formed either by a polymer bilayer or by insertion of several active hinges or junctions into a passive polymer film, may self-fold from 2D planar structures into 3D complex constructs when exposed to a simple homogeneous external stimulus [1–9]. This approach offers the possibility of quick, reversible and reproducible fabrication of 3D structures [10, 11]. These self-folding structures have diverse applications, ranging from drug delivery to controlled encapsulation, tissue scaffolds, adaptive optics, and energy storage [10–12]. See the excellent review by Ionov on self-folding all-polymer structures and the associated technologies developed recently [10, 11].

Hydrogel is a water-swollen soft active material, exhibiting marked volume change in response to a variety of external stimuli including pH, temperature, concentration, light, electric and magnetic fields, etc [13–16]. Combining active soft hydrogels with passive hard polymers results

in all-polymer composite systems that utilize the merits of both—soft active materials make the system smart and easy to deform, while hard passive materials offer the requisite stiffness and guarantee the integrity of the structure.

Among the family of stimulus-responsive hydrogels, the temperature-sensitive hydrogel poly(N-isopropylacrylamide) (PNIPAM) hydrogel has attracted intense attention due to its unique features such as simplicity of synthesis, ease of tunability and good integrability. Temperature-sensitive hydrogels have been chosen as an essential constituent to fabricate self-folding structures. Thermosensitive microcapsules, self-folding bilayers and soft microorigami are typical examples [2, 9, 11]. These thermoresponsive self-folding structures can be designed using the different thermal expansions of polymers, melting of polymers, shape memory effects or swelling/shrinking of PNIPAM [11]. Despite the various fabrication technologies explored and discussed in detail so far, modeling of the mechanism of self-folding and prediction of the process of self-folding, even at the qualitative level, are still absent.

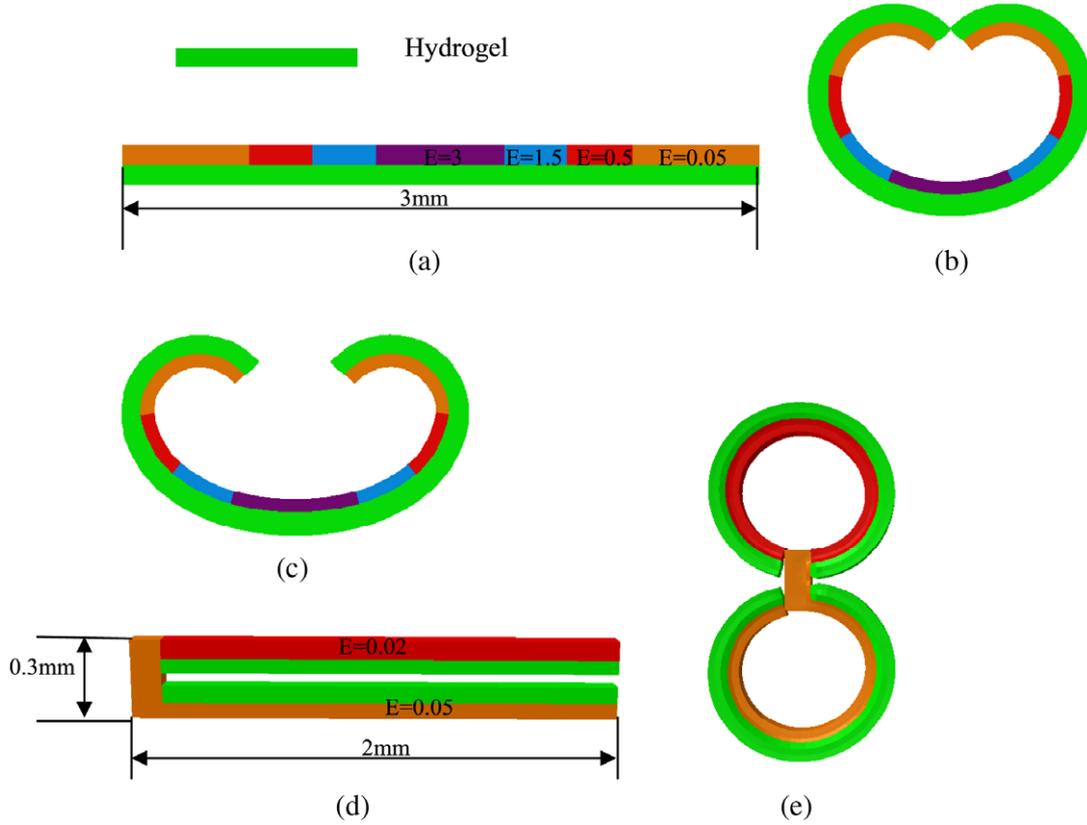


Figure 1. A slender self-folding bilayer beam consists of two materials: the passive polymer (with colors other than green) and the temperature-sensitive hydrogel (green). The material properties of the polymers are patterned; various colors representing various Young's moduli as marked by the normalized numbers. Upon decrease of temperature, the hydrogel swells while the passive polymer does not. The different behaviors of the two materials cause the bilayer beam to bend and self-fold. (a) Reference configurations of a straight bilayer beam; (b) and (c) final configurations of the straight beam without and with the gravity effect; (d) and (e) reference and final configurations of a parallel-beam structure.

As one of the possible pathways to realize self-folding all-polymer structures, we demonstrate the self-folding process actuated by the swelling/shrinking of PNIPAM hydrogel. This was implemented by coding the hydrogel material in the commercial software ABAQUS and modeling the swelling/shrinking deformation of the PNIPAM hydrogel in response to variation of temperature.

2. Methodology

A laminate, consisting of two layers of materials with different thermal expansion coefficients, would curl or self-fold upon ambient temperature variation. This is well understood in the literature. Timoshenko [17] was the first to study the bending of a uniformly heated bilayer strip with different expansion coefficients. Assuming only one directional bending of a bilayer strip, the curvature of the strip is given by [17]

$$\frac{1}{\rho} = \frac{6(\varepsilon_2 - \varepsilon_1)(1 + m)^2}{h(3(1 + m)^2 + (1 + mn)(m^2 + \frac{1}{mn}))}, \quad (1)$$

with ρ the radius of curvature, $h = a_1 + a_2$ the thickness of the bilayer, $m = a_1/a_2$ the ratio of the thicknesses of the two layers, $n = E_1/E_2$ the ratio of the Young's moduli of the two materials, and ε_1 and ε_2 the thermal expansion strains of the

two layers. If $\varepsilon_2 > \varepsilon_1$, the deflection of the strip would be convex down, and vice versa.

Although the swelling of hydrogel/polymer composite cannot be fully mimicked by the thermal expansion of a bilayer strip, the preceding Timoshenko formula does give us some hints for the design of self-folding structures. One of the key ideas behind the formula is that the final curvature depends on the ratio of moduli of the two materials. To obtain a self-folding configuration with desirable local curvatures, one way toward this goal is to have a tailor-made distribution of material stiffness. In our following examples, we learn this hint from the Timoshenko formula and pattern the inert polymer layer with various Young's moduli.

The core of our methodology is to model the programmable deformation of a temperature-sensitive PNIPAM hydrogel. We make recourse to commercial finite element software, ABAQUS, and program a user-defined UHYPER subroutine for the PNIPAM hydrogel. This is in line with other efforts to model equilibrium swelling or transient swelling of hydrogel using ABAQUS, see Hong [18], Zhang [19], Kang [20] and Qi [21].

Treating hydrogel as a hyperelastic material, and adopting the nonlinear field theory of coupled diffusion and

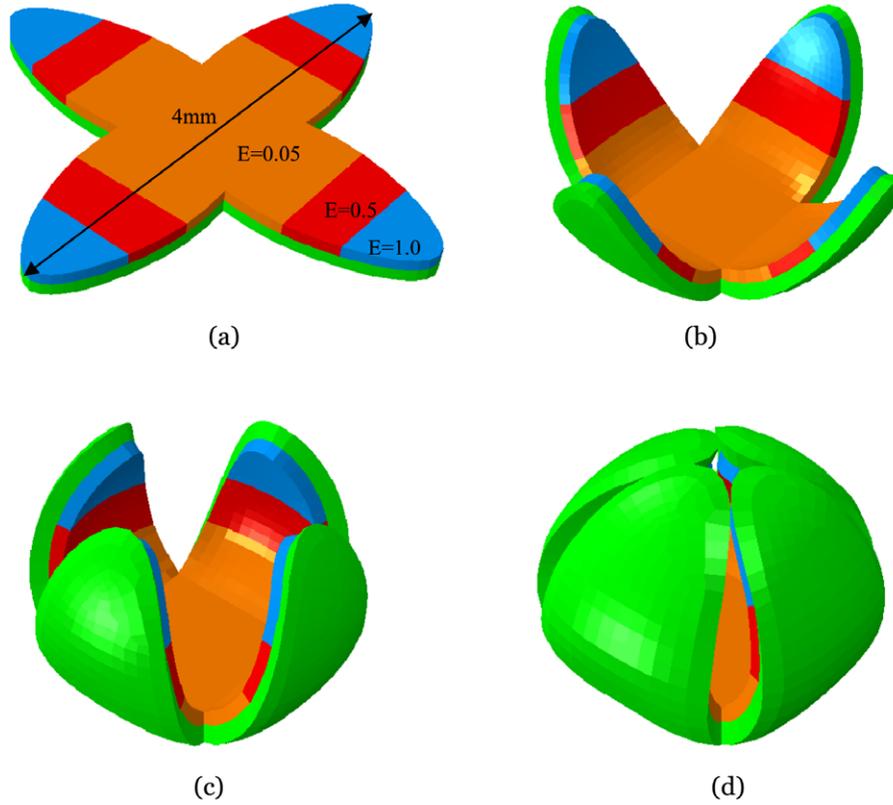


Figure 2. The self-folding history of a star-fish bilayer membrane. The upper polymer layer is patterned with various moduli. (a) Reference configuration with $T = 300$ K; (b) and (c) intermediate stages of self-folding with $T = 295$ K and $T = 290$ K respectively; (d) final configuration of the star-fish membrane at $T = 284$ K.

deformation [18, 22], the free energy of the hydrogel reads

$$W(I_1, I_3, \mu, T) = \frac{1}{2}Nk_B T(I_1 - 3 - 2 \log I_3) - \frac{k_B T}{v} \left[(I_3 - 1) \log \frac{I_3}{I_3 - 1} + \frac{\chi(T, I_3)}{I_3} \right] - \frac{\mu}{v}(I_3 - 1), \quad (2)$$

where $I_1 = F_{iK}F_{iK}$ and $I_3 = \det \mathbf{F}$ are the first and the third invariants of the deformation gradient tensor, \mathbf{F} , μ is the chemical potential, T is the temperature, N is the number of chains per polymer volume, v is the volume of a solvent molecule and k_B is the Boltzmann constant. Equation (2) has three parts: the elastic energy due to stretching of the network, the mixing energy of the polymer and the solvent and the work done by the chemical potential, μ . The incompressibility condition, $I_3 = 1 + Cv$, is implied and the last term in equation (2) is equal to μC , with C the nominal concentration. As the original version of the mixing energy is expressed in terms of concentration or volume fraction, the introduction of this simplification of incompressibility enables the rewriting of the mixing energy in terms of I_3 . This is helpful for the programming and this simplification holds for all the following derivations. Note that for the elastic part we actually adopt the classical neo-Hookean hyperelastic model and therefore only I_1 and I_3 appear; of course the methodology presented herein can be readily developed into other forms of hyperelastic models.

The Flory–Huggins interaction parameter, χ , measures the enthalpy of the mixing process and is expressed in terms of T and I_3 for a temperature-sensitive hydrogel,

$$\chi(T, I_3) = A_0 + B_0 T + (A_1 + B_1 T)/I_3. \quad (3)$$

The coefficients A_i and B_i are fitted to experiments on PNIPAM hydrogels and a lot of data have been accumulated in the literature [23].

With the free energy prescribed in equation (2), the derivatives of the free energy with respect to I_1 and I_3 are evaluated straightforwardly as

$$\frac{\partial W}{\partial I_1} = \frac{1}{2}Nk_B T, \quad (4)$$

$$\frac{\partial W}{\partial I_3} = -Nk_B T/I_3 - \frac{k_B T}{v} \left[\log \frac{I_3}{I_3 - 1} - \frac{1}{I_3} + \frac{I_3 (\partial \chi / \partial I_3) - \chi}{I_3^2} \right] - \frac{\mu}{v}. \quad (5)$$

The expression of stresses immediately follows and, for example, the first Piola–Kirchhoff stress, \mathbf{P} , is computed as

$$\mathbf{P} = \frac{\partial W_0(I_1, I_3)}{\partial \mathbf{F}} = \frac{\partial W_0(I_1, I_3)}{\partial I_1} \frac{\partial I_1}{\partial \mathbf{F}} + \frac{\partial W_0(I_1, I_3)}{\partial I_3} \frac{\partial I_3}{\partial \mathbf{F}}. \quad (6)$$

Other forms of stress tensors can also be obtained by using the stress relations. The ABAQUS UHYPER subroutine is chosen here because it is fairly simple and only equations (4) and (5) are needed. For other user-subroutines, the explicit

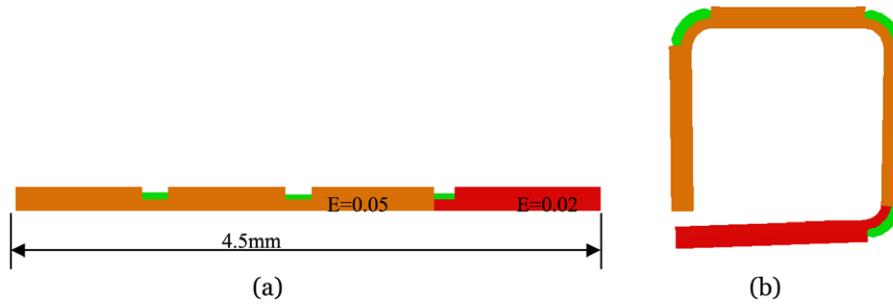


Figure 3. Self-folding of a polymer beam with three inserted active hydrogel hinges. One portion of the beam is clamped, as schematized by diagonal lines in (a). Decreasing the temperature induces swelling of the hydrogel hinges and eventually causes self-folding of the structure. A closed square is obtained by tuning the temperature, as shown in (b).

expressions of stresses and the tangent moduli are requisites for programming.

3. Results and discussion

In the following simulations, we normalize the stresses and the Young's modulus of materials by $k_B T/v$. The volume per solvent molecule is approximately $v = 10^{-28} \text{ m}^3$. At room temperature $k_B T/v$ is estimated as $4 \times 10^7 \text{ Pa}$. As an example, the shear modulus of the polymer network, $Nk_B T$, is normalized by $k_B T/v$ and a dimensionless parameter, $Nv = 0.01$, is set in the simulation for a typical hydrogel. The chemical potential in equation (5) is input as one of the material properties for this user-defined hyperelastic material. The parameters in equation (3) are fitted to experiments on PNIPAM hydrogel and are taken as [23] $A_0 = -12.947$, $B_0 = 0.0449 \text{ K}^{-1}$, $A_1 = 17.92$, $B_1 = -0.0569 \text{ K}^{-1}$. Before integration into the all-polymer structure, the hydrogel was assumed to be in a homogeneous free swelling state after synthesis. This state is characterized by an initial swelling ratio, λ_0 , equal for all three directions. Different synthesis conditions yield various initial swelling ratios and without loss of generality λ_0 is fixed to 1.5 in the calculation, which corresponds to an equilibrium chemical potential of $\mu = -0.0343$ for the material of the hydrogel. With these preparations and the developed UHYPER for temperature-sensitive hydrogel, we can design and model programmable deformations of all-polymer self-folding structures.

We start with a simple scenario: a temperature-sensitive PNIPAM hydrogel is glued with a passive polymer, say polycaprolactone, to form a bilayer and the bilayer will bend or fold when subject to a variation of temperature. Figure 1 shows the two simplest cases: a bilayer beam consists of an active hydrogel and a passive polymer material. In figure 1 and what follows, the green material is PNIPAM hydrogel and the materials with other colors are passive polymers. In response to a decrease of temperature, the temperature-sensitive hydrogel swells and expands in volume while the passive polymer layer is inert to this environmental variation. The difference in deformation causes self-folding of the bilayer beam. As we mentioned previously, the Timoshenko formula gives us hints on how to pattern the inert polymer layer with various material stiffnesses to retain the desirable local

curvatures. In all the figures presented here, the polymer materials are marked with different dimensionless Young's moduli and different colors. In experiments, synthesis of polymers with various stiffnesses is not an impossible task. Available strategies include varying the concentration of monomers and controlling the crosslink density [24].

If we place a stiffer polymer in the central region of the upper layer, say a polymer with nondimensional Young's modulus $E = 3$, but a softer polymer with $E = 0.05$ at the two ends, the original straight bilayer beam in figure 1(a) self-folds into a heart-shaped structure, as shown in figure 1(b). In this and the following simulation, we do not consider the gravity effect for the purpose of simplicity. However, it should be pointed out that the gravity force does affect the final configurations. To illustrate this point, we perform a simulation with the gravity force and the result is shown in figure 1(c) for comparison. For the two parallel bilayer beams connected and clamped at the left end in figure 1(d), the Young's modulus of the upper polymer layer was input as $E = 0.02$ while the bottom polymer layer was set as $E = 0.05$, and it would self-fold into an 8-shaped construct, as shown in figure 1(e). The simple idea of the bilayer structure can be developed further to design a self-folding star-fish membrane, and figure 2 demonstrates the self-folding history of the membrane as the temperature varies from $T = 300$ to 284 K . In this case we pattern the central region of the star-fish with a softer polymer with $E = 0.05$ while the tip regions with a stiffer polymer with $E = 1$.

An alternative to the bilayer structure to realize the self-folding is to integrate several hydrogel hinges into a polymer matrix. Figure 3 illustrates this concept by inserting three hydrogel hinges into a slender polymer beam. The three hydrogels are carefully patterned and serve as hinges to fold the beam. By tuning the temperature and clamping one portion of the beam, as indicated by figure 3(a), the beam will bend around these hinges and ultimately attain a closed square. We can also combine the concepts of bilayer and hinges to design a complex 3D origami through self-folding. Figure 4 demonstrates the self-folding of a 3D closed box from a planar structure. The initial configuration of the structure is a 2D planar structure patterned with a thin layer of hydrogel membrane and a hydrogel hinge, as depicted in figure 4(a) at $T = 300 \text{ K}$. Upon decrease of the temperature to $T = 290$ and 280 K and then to the final temperature $T = 273 \text{ K}$, we

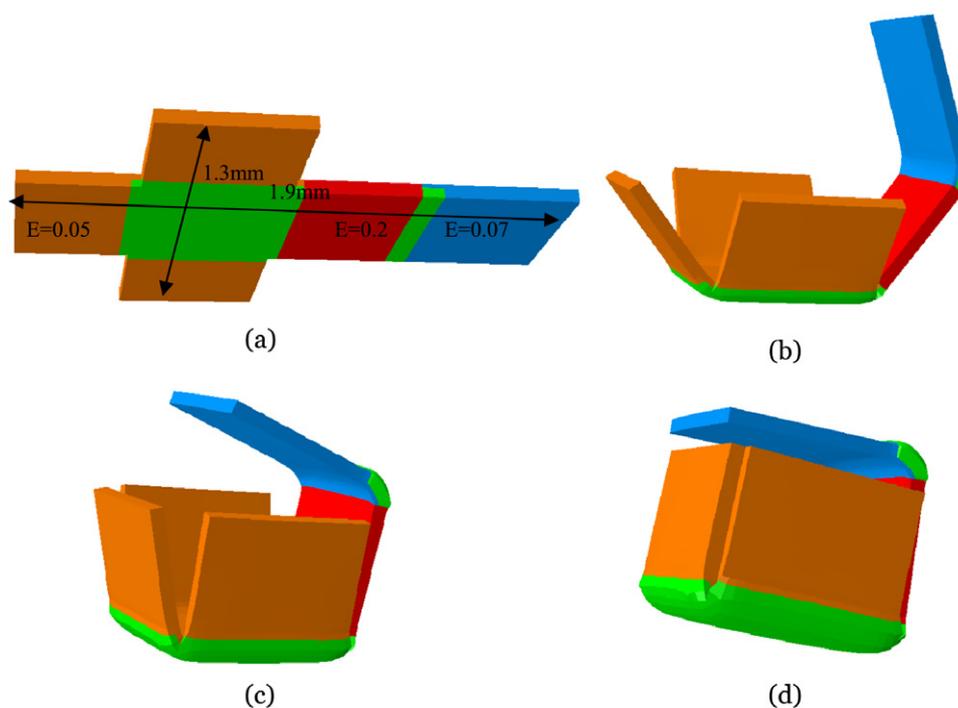


Figure 4. 3D origami obtained by self-folding a 2D planar structure into a 3D closed box. (a) Initial configuration of the 2D structure at $T = 300$ K with a polymer–hydrogel bilayer and a piece of hydrogel hinge; (b) and (c) intermediate stages of the self-folding process at $T = 290$ K and $T = 280$ K, respectively; (d) the final closed box corresponding to $T = 273$ K.

finally obtain the 3D closed box. The simulation model is motivated by the experiments reported in [9], and the results qualitatively reproduce the experimental demonstration in [9], where the self-folding is induced by the nonuniform thermal expansion of polystyrene due to the localized absorption of light. To model such a self-folding process, a total of 7604 3D C3D8H elements are used and multiple contacts are defined deliberately to perform the simulation. This proves the feasibility and powerfulness of our strategy.

4. Conclusion

In summary, we demonstrate a methodology for the design and simulation of all-polymer self-folding structures with temperature-sensitive hydrogels. We programmed a user-defined UHYPER subroutine for the PNIPAM hydrogel and integrated the code into a commercial FEM package. The self-folding structures can be realized either by a bilayer concept or by patterning hydrogels as hinges. We, therefore, can model any desired programmable deformation of self-folding structures.

Self-folding is also a ubiquitous phenomenon in Nature. *Oxalis rubra* is a flowering plant in which the flower opens at daytime but self-folds at night. The Venus Flytrap catches insects and arachnids by suddenly closing its trapping structures. Drying of leaves gives rise to curled 3D surfaces. The self-closing or self-folding deformations of these generalized structures are triggered by inhomogeneous growth or swelling. An understanding of the mechanism behind these self-folding deformations is not only crucial for the study of biological morphogenesis, but also opens a door

for fabricating 3D complex structures via self-folding of 2D structures. Our efforts pave the way for the understanding, control and development of 3D fabrication techniques through self-assembly.

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