Mechanics-Based Design of Stimuli-Responsive Hydrogel Structures and Devices

by

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Abstract

Stimuli-responsive hydrogels undergo large shape change in response to a wide variety of stimuli, such as temperature, biochemical molecule, pH, electric or magnetic field. Programmable shape changing devices made from stimuli-responsive hydrogels have potentially wide-ranging applications, including drug delivery, soft robotics, and biomedical devices. The current main challenges of advancing stimuli-responsive hydrogel devices into real-life applications lie in both the design and fabrication stage. From the design perspective, it is challenging to construct a multi-physics constitutive model to accurately describe the material behavior of hydrogels and execute finite element modeling to guide the design of stimuli-responsive hydrogel structures. Most models that have been developed in the research community are computational with qualitative experimental validation. Thus, simple strategies based on mechanics are needed to guide the design of these devices with complicated shape changes. From the fabrication perspective, traditional fabrication methods such as lithography can only make 2D planar structures, limiting the number of achievable device geometries. Advanced manufacturing is needed to achieve the device designs with
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more complicated functionalities. The objective of this work is to develop an efficient design framework for stimuli-responsive hydrogels. I aimed to advance the field of stimuli-responsive hydrogels in both the design and fabrication aspects. In this work, I have developed a design methodology that covers from constitutive modeling, finite element simulation, mechanics-based design rules, to experimental validation. This hybrid modeling design methodology provides an efficient design framework for stimuli responsive hydrogel structures and devices of functional importance.

In the first part of this work, I applied a chemo-mechanical constitutive model to describe the swelling and mechanical behavior of a novel DNA hydrogel (AAm-co-DNA). In order to estimate the elastic modulus of DNA hydrogel that cannot be measured by traditional experimental approach, I used finite element analysis to study the curving of bilayer beams composed of the DNA gel and a passive gel (polyacrylamide, pAAM), and compared the finite element simulations to the experiment result. To explore the design space, I further applied the finite element model to investigate the influence of bilayer geometric and material properties on the equilibrium curvature. I used the modified Stoney formula for the curving of film/substrate system to develop a simple design rule for predicting the equilibrium curvature of bilayer gel beams with different dimensions and material properties. In the second part of this work, I report the design, fabrication, and characterization of segmented 3D printed gel tubes composed of an active thermally responsive swelling gel (poly N-isopropylacrylamide, pNIPAM) and a passive thermally nonresponsive gel (pAAM). Using finite element
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simulations and experiments, I demonstrated a variety of primitive shape changes including uniaxial elongation, bending, buckling, and gripping based on different segment arrangements of two gels. The assembly of shape-changing primitives could be directly printed and used to achieve complicated tasks. In the final part of this work, I report on the unusual periodic buckling behavior of a 4D printed tubular structure, composed of alternating vertical strips of pNIPAM segments and pAAM segments. The tube design was inspired by the buckled surfaces observed in nature, such as on cacti and euphorbias. I found that the tubes show tunable periodic buckling modes in water at the room temperature, due to the development of compressive stresses in the soft swellable segments induced by the constraint of the stiff non-swellable segments. I developed finite element models to explore the design space and investigate the effects of geometric and material design parameters on the buckling mode. Modeling the swellable segments as the buckling of a bar on an elastic foundation, I derived a bucking parameter that combines the effects of geometry and material properties to predict the transition between different periodic buckling modes and constructed a phase diagram to guide the design of periodic buckling tubes for bioinspired functional gel structures.
ABSTRACT

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Dedication

This thesis is dedicated to my family, especially my mum, Qingling Kong, who brought me up by herself. I hope that I can make a better life for her.
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Chapter 1

Introduction

This chapter provides a brief overview for stimuli-responsive hydrogels. First, we introduce the interesting properties of stimuli-responsive hydrogel, and dive into a specific type of thermo-responsive poly N-isopropylacrylamide, and a novel poly acrylamide hydrogel crosslinked by DNA molecules. Then, we provide a brief summary of the design strategies and mechanics underlying the shape change of common thermo-responsive hydrogel structures. Particular attention is given to 4D printing, a new fabrication method that is recently developed to overcome the current limitations in lithography and facilitate more complicated shape change of thermo-responsive hydrogels. Next, previous modeling approaches of hydrogel structures are summarized. The introduction provides background information for the research in the following chapters. This chapter concludes with the objectives of this thesis.
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1.1 Thermo-responsive hydrogels

Stimuli-responsive materials, also known as soft active materials or smart materials, is a class of materials that deforms in response to a wide variety of external stimuli, including temperature, pH, salt, specific (bio)chemical signals, light, electric and magnetic field, and so on [16, 17]. Hydrogels have naturally emerged as an important stimuli-responsive material, because of their stimuli responsive large swelling ratio, the ease of combination with other types of materials, and the similarity in stiffness between hydrogels and biological tissues. In this thesis, we focused on one of the most commonly used stimuli-responsive hydrogels, thermo-responsive hydrogel, because temperature change is a commonly found environmental stimulus in nature and can be easily controlled in experimental settings.

Hydrogel is composed of a polymer network and its surrounding solvent. When placed in a solvent, the swelling behavior of the hydrogel is the consequence of competition between the hydrophilic and hydrophobic interactions among polymer molecules and solvent molecules. For thermo-responsive hydrogels, temperature change plays an important role in this competition and triggers a phase transition. During the phase transition, the polymer-solvent system transforms from a homogeneous phase to a bi-phasic state consisting of a polymer concentrated phase and a dilute phase. Two major types of thermo-responsive hydrogels are commonly used. When this transformation occurs above a critical temperature, it is categorized as lower criti-
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critical solution temperature (LCST) transition; when this transformation occurs below a critical temperature, it is referred as upper critical solution temperature (UCST) transition [18, 19]. We are particularly interested in thermo-responsive hydrogels with LCST.

Thermo-responsive hydrogels with LCST transforms from a hydrophilic to hydrophobic material when heated above the LCST and consequently deswells. The transformation is reversed by cooling to below the LCST allowing the material to swell. We used poly N-isopropylacrylamide (pNIPAM) as our thermo-responsive gel with LCST, and its chemical structure is shown in Fig. 1.1. pNIPAM undergoes a transition from a swollen state in aqueous media to a deswollen state at a temperature just below physiological temperatures (LCST is between 32°C and 36°C) [16, 20–22]. During the phase transition, the polymer chains undergo a change in conformation from an extended coil to a globular structure [23]. From a thermodynamics point of view, the Gibbs free energy of mixing the polymer molecules with solvent molecules $\Delta G = \Delta H - T\Delta S$ is dependent on the enthalpy of dissolution $\Delta H$, the entropy contribution $\Delta S$, and temperature $T$. When the system is at low temperature, $\Delta G$ is negative, signifying that the mixing of polymer and solvent is energetically favorable, and thus the hydrogel is in a swollen state. When the system is at high temperature, $\Delta G$ becomes positive, signifying that the mixing of polymer and solvent is no longer energetically favorable, and the hydrogel expels the solvent and resorts to a deswollen state. Such behavior is possible only if both $\Delta H$ and $\Delta S$ are negative. The negativity
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of the enthalpy of dissolution $\Delta H$ means that the bonding between polymer chain and solvent molecules is favorable, and the negativity of the entropy contribution $\Delta S$ means that entropy decreases with hydration. When the temperature increases, the contribution from the entropy term of the Gibbs free energy $T\Delta S$ becomes dominant, resulting in the change of $\Delta G$ from negative values to positive values, consequently phase separation and deswelling of the hydrogel occur. From the polymer chemical structure point of view, the macroscopic reaction of pNIPAM is the consequence of competition between the hydrophilic groups, which consist of the oxygen and nitrogen rich domains, and the hydrophobic groups, which consists of the isopropyl groups and the polymethylene backbones [24]. When the temperature is low, the hydrogen bonds formed between the hydrophilic groups and solvent molecules dominate, and thus the hydrogel swells. The hydrogen bonds start to break with the increasing temperature. When the temperature is above LCST, the hydrophobic interaction becomes dominant, resulting in the deswelling of the hydrogel. The LCST is strongly dependent on the polymer structure, and can be tuned by modifying the polymer backbones or side chains such as introducing more hydrophilic groups.

Programmable shape changing structures of thermo-responsive hydrogels have a wide range of applications, including drug delivery [25–31], soft robotics [32–37], and biomedical applications [4, 38, 39]. Here, two interesting example applications are demonstrated. Tang et al. [1] used pNIPAM-based substrates for cell sheet fabrication. When heated above LCST, the hydrophobic nature of pNIPAM favors cell
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Figure 1.1: Chemical structure of poly (N-isopropylacrylamide), pNIPAM.

attachment; and when the temperature is below LCST, the polymer surface becomes hydrophilic and the cells can be harvested in a confluent monolayer, as shown in Fig. 1.2. Garbern et al. [40] designed a hydrogel by copolymerizing pNIPAM with propylacrylic acid (PAA), and used it to protect the encapsulated drug from the harsh pH conditions in the stomach allowing drug release into the intestine. A more comprehensive overview of the promising applications are documented in [41, 42].

1.2 DNA-crosslinked hydrogels

Environmental stimuli such as temperature, light, electromagnetic stimuli, or pH are nonspecific, and can only be used to trigger reaction uniformly across a material. This lack of specificity also restricts the possibility of producing controllable outcomes in specific material domains. Biomolecules, such as DNA sequences, offer unprecedented tunability and specificity without the need of wired controls. The ability of each strands of DNA sequences to direct the swelling of a specific material domain would
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Figure 1.2: Schematic of deswelling (A) and swelling (B) of comb-type grafted pNIPAM gel and the swelling of comb-type grafted pNIPAM gel modified surface (C). Reprinted with permission [1]. Copyright 2010, Elsevier.
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greatly improve the complexity of shape changes and functionalities.

DNA-crosslinked poly-acrylamide hydrogels have been applied for biomolecular actuation in recent studies [43]. These gels utilize the DNA hybridization processes to direct the release of particles [44], or to melt, crosslink themselves [45–47]. The stiffness of these gels could be modulated through the incorporation of DNA strands to the crosslinks. Hybridization exchange can also induce size or shape changes of DNA-linked nanostructures [48], thin films [49], and colloidal crystals [50–52]. However, the DNA-crosslinked gels can only swell by 10-15\% during the exchange of DNA strands, which is insufficient to induce shape changes of macroscale gel architectures [53, 54]. Hence, the main focus in making DNA-triggered shape-changing hydrogels was to substantially increase the degree of swelling. Cangialosi et al. have developed a novel DNA-crosslinked poly-acrylamide hydrogel (DNA hydrogel) that overcame this limitation to achieve substantially larger shape change [2]. The degree of swelling of this gel was greatly increased by lengthening crosslinks successively using a DNA activation in which multiple DNA molecules are inserted into a duplex (Fig. 1.3). One hundred-fold volumetric hydrogel expansion was achieved by this new shape change mechanism. The advances in DNA hydrogels expanded the possibilities of building soft devices that respond to diverse biochemical inputs for medical applications.
1.3 Design strategies of stimuli-responsive hydrogel structures

Stimuli-responsive hydrogel typically undergoes isotropic volumetric expansion and contraction. To achieve more complicated shape change than isotropic swelling or deswelling, stimuli-responsive hydrogels have been combined with stiffer materials that restrict swelling in certain positions or directions, thus inducing anisotropic swelling and a swelling gradient. Another important advantage of combining stimuli-responsive hydrogel with other high modulus materials is to increase the overall stiffness of the structure. A significant limitation of these hydrogels is their low stiffness. For example, soft robotic tools of solely soft hydrogels are too floppy to securely grip objects and operate. The overall stiffness of the structure can be increased by a com-
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**Figure 1.4**: Schematic of the microfabrication lithography process for the soft-stiff hydrogel composite structure. Reprinted with permission [3]. Copyright 2017, Elsevier.

A composite design that combines soft swellable hydrogels with stiff nonswellable materials [55–57]. In this section, we provide a brief summary of the existing design strategies underlying shape changing of stimuli-responsive hydrogel structures.

Currently, most research in this field focus on the self-folding of two dimensional (2D) thin film structures to three dimensional (3D) geometries. The utilization of 2D thin-film geometry is popular because these structures can be fabricated by 2D lithography, a process that is low cost, high resolution and high throughput. In this fabrication process, photosensitive chemical photoresist is placed on the substrate in a thin-film geometry, and light is transferred through a photomask to create a geometric pattern on the photoresist (Fig. 1.4). Depending on the material pattern with mismatched swelling capabilities and mechanical properties, 2D thin film structures can change shape by rolling, twisting, expansion, buckling and wrinkling[6, 58–63].

One of the most commonly used design strategies is referred as "bilayer design" (Fig. 1.5A). The bilayer design is achieved by material layers with mismatched elastic
properties and actuation strain [64–66], or by the generation of crosslink gradients through the thickness of a film to produce swelling gradients [67, 68]. Numerous devices based on the bending of bilayer designs have been reported. Comprehensive reviews can be found in [61, 69]. Jamal et al. [70] demonstrated the bending of hydrogel bilayers into various 3D geometries including cylinders, spherical capsules, and helices, and the feasibility of bilayer hydrogels as cell-culture scaffolds. Yang et al. [71] fabricated bilayers that deformed into spherical capsules that could close tightly to encapsulate small molecules for controlled release. More complex shape changes have been achieved by localizing bilayer bending to specified hinge regions. For example, Yoon et al. [68] designed a cube, a pyramid, and a gripper by using bilayer hinges to fold rigid plates. Ionov et al. [72] took advantage of the position of hinges in hydrogel bilayers to produce 3D pyramids.

In-plane variations in swelling ratio of hydrogels also allows for programmable shape changes (Fig. 1.5B, C). The material with swelling ratio \( \Omega \) varying radially from high in the center to low on the edges yields a spherical cap, while the inverse pattern produces a saddle. Compared with bilayer designs, the shape changes of thin sheets with in-plane variations in swelling are largely unexplored. A few examples are discussed here. For example, Hayward et al. [5, 73] patterned responsive hydrogel thin films into two or more alternating stripes. These strips are composed of stiff nonswelling material and soft swelling material. The resulting shape change is a “bottleneck” shape (Fig. 1.6), where two cylinders are connected by a transitional
Figure 1.5: (a) A bilayer with a mismatch strain between the two materials undergoes bending, while (b, c) in-plane gradients in swelling can yield shapes with such as spherical cap and saddle. Reprinted with permission [4]. Copyright 2017, ACS.

The authors showed that the transition width and radius of curvature depend on the thickness and lateral dimensions of the strips. By tilting the axis of the junctions, helices can also be generated. Further, Kumacheva et al. [74] used 2D patterns of stiff stripes in a soft gel matrix to create short and long rolls, toroids, and twisted helices. In another study, structures composed of highly crosslinked dots of spatially varying size in a lightly crosslinked matrix were fabricated [6]. Depending on the pattern arrangement, the thin plate can transform into a spherical cap, a saddle, a nearly closed sphere shape, and an “egg carton” structure (Fig. 1.7).

Trilayer designs have recently been introduced to generate the self-folding of thin film structures to complicated 3D geometries. Hayward et al. [7, 75] used trilayers composed of a soft swelling poly (N-isopropylacrylamide-co-acrylamidobenzophenone)
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**Figure 1.6:** A gel film laterally divided into high- and low-swelling regions (left) results in a ‘bottleneck” shape (right). Reprinted with permission [5]. Copyright 2012, Royal Society of Chemistry.

**Figure 1.7:** Various 3D shapes are realized by axisymmetric and non-axisymmetric patterns of stiff dots in soft matrix. Reprinted with permission [6]. Copyright 2012, AAAS.
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Figure 1.8: A thermo-responsive flapping bird fabricated from hydrogel trilayers. Reprinted with permission [7]. Copyright 2015, Wiley-VCH.

(pNIPAM-BP) hydrogel layer sandwiched between two layers of rigid poly (p-methylstyrene-co-acrylamidobenzophenone) (PpMS-BP) hydrogel to yield complex origami structures. The direction, angle, and location of folds can be programmed by designing different patterns of stiff strips. Fig. 1.8 shows an origami flapping bird that can be reversibly folded and unfolded at varying temperature. Achieving high resolution self-folding structures with larger fold densities and smaller sizes using lithographic methods are still on-going efforts in the community.

1.4 4D printing

Traditional fabrication methods for programmable shape changing structures such as 2D lithography limits the number of achievable 3D geometries, limiting the application of these materials[2, 3, 57, 76–78]. Recent developments in 3D printing of stimuli-responsive materials allow for fabrication of 3D structures that can undergo more
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complicated shape changes. This is referred to as 4D printing with time as the additional dimension [8, 9, 79–90].

3D printing, also known as additive manufacturing, was invented in 1984 by Charles Hull [91] as a new process for material prototyping before mass production. The layer-by-layer fabrication method allows for manufacturing of 3D objects with arbitrary geometry and complexity. The concept of 4D printing was first introduced by Tibbits et al. in 2014 [8, 92]. Compared with conventional 3D printing of passive structures, multi-material printing was used to print a 3D object that can change shape with external stimuli over time. The authors printed linear structures of interchanging soft hydrophilic polymer and stiff nonswelling polymer to form a variety of hinges for folding, curling, twisting, linear expansion/shrinkage of printed structures (Fig. 1.9).

Combined with 3D printing, stimuli-responsive hydrogel structures with arbitrary geometries and complexity could be manufactured, and increased complexity in printed structures could potentially be implemented for accomplishing real-life tasks. However, the majority of existing 4D printed structures studied thus far are still restrained to folding of 2D shapes into 3D structures, which undermines the original intention of combining stimuli-responsive hydrogels with 3D printing. There are a number of reasons why most 4D printed structures remained as 2D thin film geometries. First, it is technically challenging to print tall 3D geometries with stimuli-responsive hydrogels. The low stiffness of hydrogels often leads to collapsing of structures during
Figure 1.9: (A) Rendered illustration of the linear stretching bar. It is an assembly of rigid disks with expanding materials in the middle. (B) Rendered illustration of the ring stretching structure. This is based on expansion of the ring shape into a bar. (C) Rendered illustration of the folding bar. This design is also composed of bars and disks. The disks in the center act as stoppers. Reprinted with permission [8]. Copyright 2014, Springer Nature.
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3D printing, and the low accuracy of printing (usually in the order of 0.1 mm) results in printing errors which accumulate in each layer of printing. Thus printing 3D tall structure is much more challenging than printing 2D planar structures. Furthermore, the design of true 3D-to-3D shape change is challenging. Compared with 2D thin film structures where the design strategies are usually bilayer, in-plane variation, and trilayer, the design patterns of different materials in the 3D space is unlimited.

Recent attempts in achieving simple shape changes using 4D printing have been described in [87, 90], and here we discuss only some of the most interesting recent examples in the field. One of the most cited works is the 4D printing of hydrogel bilayers containing stiff cellulose fibrils by Lewis et al. [9]. In this work, hydrogel inks containing stiff cellulose fibrils were developed, and these stiff fibrils were aligned along the printing direction to define the swelling and elastic anisotropies. By printing bilayer patterns with either a $90^\circ/0^\circ$ or $-45^\circ/45^\circ$ print paths, the printed 2D flat flowers can bend or twist when the initially flat forms swell in water (Fig. 1.10). In another approach, Qi et al. [10, 82–84] printed shape-memory polymers to create stimuli-responsive structures. These structures were fabricated in their intended (final) form. Then the structures were warmed to a temperature above the glass transition temperature ($T_g$), mechanically deformed to an intermediate shape, and cooled down below $T_g$ to lock the shape. Upon reheating the structure above $T_g$, the shape changes back to the originally printed form (Fig. 1.11). So far, only simple shape changes have been demonstrated.
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Figure 1.10: Simple flowers composed of (A) $90^\circ/0^\circ$ and (B) $-45^\circ/45^\circ$ bilayers oriented with respect to the long axis of each petal, with time-lapse sequences of the flowers during the swelling process (scale bars 5 mm, inset scale bars 2.5 mm). Reprinted with permission [9]. Copyright 2016, Springer Nature.

Figure 1.11: A 4D printed unfolded box composed of shape-memory polymers that folds back into its original conformation when immersed in warm water. Reprinted with permission [10]. Copyright 2015, Springer Nature.
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Recently, several studies of 3D-to-3D shape changes have been reported. Jin et al. [11] printed a pNIPAM-graphene oxide cylinder on top of a pNIPAM cylinder (Fig. 1.12) to create a microfluidic valve. Depending on temperature stimulus or near-infrared radiation, each section of the two cylinders can deswell and function as designed. Han et al. [12] developed a stereolithography method of printing pNIPAM hydrogel. The authors printed four bilayer beams on a substrate. Due to the different levels of light intensity used for curing pNIPAM, the bilayer beams exhibited two different swelling properties and can close as a gripper with increasing temperature (Fig. 1.13). Kokkinis et al. [13] developed a printing process where magnetized stiff platelets inside the inks can be controlled by applying magnetic fields when printing. As a result, two materials with different platelet orientation and mechanical properties can be printed, and the authors designed a cuboid with bilayer walls (Fig. 1.14). The experiments correspond well with finite element simulations, and the cuboid can function as a tube fastener. Though innovative, the shape changes in these printed structures remain elementary and did not make full use of the advantage of the printing of different materials in 3D spatial patterns. The design space of arranging multi materials with different properties in 3D to achieve complicated shape changes and functions is yet to be explored.
**Figure 1.12:** 4D printing of multistimuli-controlled microfluidic valves. Reprinted with permission [11]. Copyright 2018, ACS.

**Figure 1.13:** A gripper consisting of four beams was printed. The difference in the swelling ratio between the two regions caused the beams to bend towards the center at high temperature (scale bar: 500 μm). Reprinted with permission [12]. Copyright 2018, Springer Nature.
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Figure 1.14: (a) Finite element simulations and actual pictures of the cuboids. Scale bars, 10 mm. (b) Cuboid-mediated fastening of two tubes achieved through the shape change of the printed object. Scale bar, 20 mm. Reprinted with permission [13]. Copyright 2015, Springer Nature.

1.5 Modeling of hydrogel structures

Computational models of hydrogel systems can be used to predict the material behavior and structural response in the design stage. With the increasing interest of active gels in diverse fields, the demand for modeling of polymeric gels has substantially increased.

A simple way of simulating the swelling of a gel is by prescribing a volumetric strain, such as thermal expansion. However, this method is erroneous because it does not take into account the softening that occurs during the swelling of gel. During the swelling process simulated by thermal expansion, the elastic modulus of gel remains constant. However, in reality, when the gel swells at a given temperature, it absorbs
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more solvent and the polymer volume fraction of the gel decreases. As a result, the elastic modulus of the gel also decreases with the swelling [93]. Therefore, simulating the gel swelling by prescribing a volumetric strain cannot produce quantitative agreement, only qualitative agreement.

In 1943, Flory and Rehner [94] used statistical mechanics to develop a free-energy function to describe the material behavior of a polymeric gel. The function takes into account the entropy of stretching the network, the entropy of mixing the network polymers and the solvent molecules, and the enthalpy of mixing. This theoretical model captures the physical response of hydrogels and has been widely adapted by researchers since its introduction. Based on this theory, the final configurations of gel swelling under simple deformations with simple boundary conditions have been solved using analytical or semi-analytical methods. For example, Treloar [95] analyzed the swelling of vulcanized natural rubber in benzene and heptane under uniaxial tension, biaxial tension and uniaxial compression, by extending the Flory-Rebner statistical theory. Zhao et al. [96] used a nonlinear differential equation to analyze swelling of a gel in shell shape around a rigid spherical core. Treloar [97], Gandhi and Usman [98] used the Flory-Huggins theory to study swelling of a rubber cylinder that was bonded to a rigid cylindrical core. Gandhi et al. [99] solved a swollen cylinder under combined extension and torsion. Gandhi et al. [100] analyzed the flexure of a fluid-saturated cuboid due to a bending moment or inhomogeneous swelling.

In recent years, focus has been directed towards developing a more comprehensive
model for describing the response of gels by coupling the diffusion deformation theory. Liu and a few others have applied hydrogel model to study the instability in growth and swelling of biological structures and bioinspired gel structures [101]. Liu et al. [102] studied how deformation patterns of leaves and fruits in the growing and drying processes can be described via the instability theory of hydrogels. Amar and Goriely [103], and Li et al. [104] used an incremental deformation theory to study the growth of soft tissues and mucosa, respectively. Dervaux and Amar [105] simulated the growth and drying processes of a tumor by the volumetric expansion and shrinking of a hydrogel. The associated buckling phenomena were studied via energy minimizing approaches. Newell et al. [106], and Green et al. [107–109] explained the phyllotactic patterns of plants from a mechanics point of view in their series of work. They adopted the beam, plate and shell buckling theories to characterize and explain the patterns of plant organs. Mahadevan et al. [110–113] adopted a simple mathematical model and a combination of scaling concepts, stability analysis, and numerical simulations to study the mechanisms of various plant growth processes and deformations, such as snap-buckling instability, long leaf morphologies, and tendril coiling.

The past few years have also seen several publications related to the numerical implementation of hydrogel constitutive models for solving complicated boundary value problems for gels. For example, Hong et al. [114, 115] constructed a hydrogel constitutive theory based on a nonlinear field theory of swelling or deswelling. The scenario of a gel layer constrained in its plane and subjected to a force in the normal direction
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was studied. Chester et al. [93, 116, 117] developed a constitutive model to describe the combined effects of mechanical deformation, fluid permeation, and heat transfer of thermo-responsive gels. Numerical simulations for axisymmetric, plane strain, and three-dimensional geometries were demonstrated. However, it is still challenging to design stimuli-responsive hydrogel structures and devices with these modeling approaches. First, the implementation of constitutive model into finite element code and the execution of finite element analysis (FEA) require specific expertise and skills. It is not straightforward for most experimentalists from a non-mechanical background to incorporate these approaches for the design of stimuli-responsive devices. Simpler design strategies are needed to translate the knowledge obtained from mechanics and modeling to analytical rules that are easy to implement. Second, most work in the modeling of hydrogels are either purely computational without any experimental validations, or only in qualitative agreement with experiment results [115, 117]. The effect of the coupling between mechanics and swelling is important for hydrogels, because the swelling ratio of hydrogels is highly dependent on the local hydrostatic stress. Quantitative validation with experiments is essential for providing more realistic material models to study fundamental questions about how complex 3D biological morphogenesis is formed and guide the design of bioinspired functional gel structures of functional importance.

The uniqueness of this work lies in the effectiveness of the hybrid modeling design methodology. I first used FEA to explore the design space and then brought in
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theory to derive universal design parameters that can be used to analytically predict the shape changes with different moduli and dimensions. The design parameters consolidated results from FEA and theory, and provide an elegant and efficient way of predicting the structural response and optimizing the device design. The design rules eliminated the need of conducting detail FEA and can be easily implemented by experimentalists for designing devices. The other distinct component of this work was that the proposed structures were fabricated to experimentally validate the model and design rules. The model can quantitatively capture the various measurements of shape change (such as curvature, bending angle, buckling periodicity) of different designs under various environmental stimuli and mechanical loadings.

1.6 Objectives of this work

The aim of this work was to develop an efficient design framework for stimuli responsive hydrogels. I first developed finite element models to explore the shape change of structures with different patterns of active and passive hydrogels with different moduli. Once a pattern has been identified to produce the desired shape change, theoretical models were developed to provide a design parameter that combines the effects of geometry and material properties to tailor the shape change. The designs were fabricated and tested to validate the modeling predictions. To validate the 3D shape changing design, I developed a 4D printing platform capable of printing tall 3D devices with complicated geometries and segment arrangements. The developed
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methodology includes constitutive modeling, finite element simulation, mechanics-based design rules, and experimental verification. The unique contribution of this work was that the developed design parameters allow for efficient design of shape change with varying material moduli and geometry dimensions. The model and design rules were also quantitatively validated with experiments.

In Chapter 2, I developed a finite element model to study a novel DNA hydrogel [2]. Volumetric expansion occurs in DNA hydrogels by successive opening of DNA hairpin crosslinks by the complementary DNA molecules. One hundred-fold volumetric swelling was achieved and the swelling decreased the modulus of gel dramatically. The elastic modulus for the soft gel after volumetric expansion was experimentally unpractical to measure. To estimate the elastic modulus, swelling experiments and finite element simulations were conducted on bilayer beams composed of an active DNA hydrogel layer and a passive BIS-crosslinked polyacrylamide (BIS) hydrogel layer. I further applied the finite element model to investigate the individual effects of the bilayer parameters on the swollen bilayer curvature. I extended Stoney’s formula to model the DNA hydrogel bilayer structure and developed a design parameter for predicting the bilayer curvature given geometry and material properties.

In Chapter 3, I report the design, fabrication, and characterization of segmented 3D printed gel tubes composed of an active thermally responsive swelling gel pNIPAM and a passive thermally nonresponsive gel (polyacrylamide, pAAM). Using finite element simulations and experiments, I found that by arranging materials with different
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mechanical properties in various segment patterns, primitives with versatile shape changes including uniaxial elongation, radial expansion, bending, and gripping could be achieved. Further, the primitives could be combined to achieve a complicated task such as reaching to the bottom of the water tank and firmly grabbing an object. The model was able to quantitatively capture the shape change of each design at different temperatures. The studies present a powerful approach to achieve shape changes that are important to robotics and biomedical engineering by 4D printing.

In Chapter 4, I designed a 4D printed tubular structure composed of vertical soft swellable pNIPAM segments and stiff non-swellable pAAM segments, inspired by the buckled surfaces commonly observed in nature, such as on cacti and euphorbias. I found that mismatched swelling and elastic properties of materials lead to accordion-like periodic buckling of the tubes. To explore the design space of this periodic buckling behavior, I used a chemo-mechanically coupled constitutive model to describe the swellable hydrogel, and developed a finite element model to investigate the individual effects of the tube design parameters on the buckling modes. Modeling the swellable strips as a bar buckling on an elastic foundation, I developed a universal design parameter combining the effects of geometric and material properties to predict the periodic buckling mode.

Chapter 5 summarizes the key results and discussed the limitations of this work. The chapter ends with a discussion of future research directions.
Chapter 2

Modeling the shape changing behavior of DNA hydrogel bilayers

DNA hydrogel is a novel poly acrylamide hydrogel crosslinked by DNA molecules [2]. Successive opening of DNA hairpin crosslinkers by the inclusion of complementary DNA molecules allows the DNA hydrogels to undergo volumetric expansion. The developed DNA gel successfully achieved a 100-fold volumetric swelling, however, its modulus decreased dramatically, which became challenging to measure experimentally. We applied a chemo-mechanical constitutive model and finite element simulations to study the shape change of DNA hydrogel bilayer to estimate the elastic modulus of the DNA gel. Then, we conducted a parameter study using finite element analysis to explore the design space and to investigate the effects of the geometric and material parameters on the curvature of the swollen bilayer. We further extended
modified Stoney’s formula [118] to model the DNA hydrogel bilayer and formulated a
universal design parameter combining the effects of geometric and material properties
to predict the bilayer curvature.

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Yoon, Jiayu Liu, Qi Huang, Jingkai Guo, Thao D. Nguyen, David H. Gracias, Re-
becca Schulman, "DNA sequence-directed shape change of photopatterned hydrogels

2.1 Introduction

Stimuli such as temperature, light, electromagnetic stimuli, or pH have commonly
been used to direct shape change [4, 77, 119, 120]. The limitation of these stimuli is
that they are nonspecific and can not direct shape change of a structure in a specific
domain. The resulting global shape change of the entire structure limits the applica-
tion of these systems. Cangialosi et al. [2] invented a new hydrogel, where the poly-
acrylamide polymer network was crosslinked by DNA biomolecules (DNA hydrogel).
In the swelling process, DNA hairpin crosslinks are opened by the complementary
DNA molecules, and are lengthened by the successive insertion of additional DNA

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directed shape change of photopatterned hydrogels via high-degree swelling", Vol. 357, Issue 6356,
pp. 1126-1130, 2017[2].
molecules into the crosslinks. One hundred-fold volumetric swelling was achieved and the swelling decreased the modulus of gel dramatically. They have also developed a photolithography process to pattern DNA hydrogels into precisely defined architectures. DNA hydrogel served as the active material, and another hydrogel composed of poly-acrylamide polymer network crosslinked by N,N’-methylenebisacrylamide (BIS), which does not respond to DNA molecules, was developed to serve as the passive material (BIS hydrogel). The following chapter describes the mechanical characterization and modeling of DNA hydrogels materials and bilayers to estimate the elastic modulus, and guide the design of hydrogel bilayers with different geometry and material properties.

2.2 Methods

2.2.1 Swelling experiments of DNA/BIS bilayers

Bilayer beams composed of an active DNA gel layer and a passive BIS gel layer were fabricated using the photolithography process described in detail in [2]. After photopatterning, the bilayer beams were put into a DNA-free buffer solution (1 M NaCl). Subsequently corresponding DNA biomolecules were added to the buffer to induce swelling of the DNA gel. We found that although the beams curled only slightly in DNA-free buffer because of different rates of solvent uptake by DNA and BIS gels, they curled much more tightly when subsequently exposed to their corresponding
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

DNA molecules (Fig. 2.1). The volumetric swelling ratios of the BIS and DNA gel domains within the bilayer beams were measured using a Nikon AZ100 multi-zoom epifluorescence microscope and Zeiss Axio Observer Yokogawa CSU-X1 spinning disc confocal microscope. The sizes of the DNA and BIS domains of the 12 bilayer beams were characterized. We measured the contour lengths, widths and thicknesses of the BIS and DNA layers of all the bilayers before and after adding DNA hairpins and averaged the values. The dimensions in the hydrated state before adding DNA hairpins were \( l = 4.925 \text{ mm} \) in contour length and \( w = 0.528 \text{ mm} \) in width. The thicknesses of the DNA and BIS layers were \( t_{\text{DNA}} = 60.6 \mu\text{m} \) and \( t_{\text{BIS}} = 71.6 \mu\text{m} \), respectively. The initial bilayer curvature in the hydrated state was measured to be \( 0.2 \text{ mm}^{-1} \). DNA hairpins were added to the bilayer bars to induce sequence-driven swelling. The average curvature of swollen bilayer bars under equilibrium was measured to be \( 1.0 \text{ mm}^{-1} \). The dimensions of both layers at equilibrium were also measured for calculation of the volumetric swelling ratios of the DNA and BIS gels, which were recorded to be 6.91 and 4.42 respectively. The sequence-induced swelling of the BIS gel was caused by the interpenetration of DNA and BIS gels during the layer-by-layer fabrication process, which was confirmed by confocal imaging.
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Figure 2.1: Fluorescence micrographs of photopatterned hydrogel bilayer beams (side-views) with a BIS hydrogel layer (green) and a DNA hydrogel layer (red), before (top) and after (bottom) sequence-driven curving. Scale bars are 1 mm. Reprinted with permission [2]. Copyright 2017, AAAS.
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

Figure 2.2: Finite element model of the BIS/DNA hydrogel bilayer. Green represents BIS hydrogel and red represents DNA hydrogel. Reprinted with permission [2]. Copyright 2017, AAAS.

2.2.2 Finite element model

2.2.2.1 Finite element geometry

The model geometry had the same dimensions as measured experimentally for the fully hydrated photopatterned bilayers (Fig. 2.2). The mesh was discretized using trilinear hexahedral elements. The dimensions of the elements were \( l_e = 61.6248 \, \mu m \) in length and \( w_e = 52.8 \, \mu m \) in width, and the thicknesses were \( t_e^{DNA} = 15.15 \, \mu m \), \( t_e^{BIS} = 17.9 \, \mu m \) for DNA and BIS gel elements, respectively. For boundary conditions, the displacements at the corner point of coordinates \( X = 0, Y = 0 \) and \( Z = 0 \) were restricted to zero.
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2.2.2.2 Material model

The material behavior of the DNA hydrogel and BIS hydrogel was described by a coupled chemo-mechanical model developed previously for the thermoresponsive behavior of hydrogels and described in detail in [3, 57, 68]. In our model, we neglected the kinetics of diffusion and assumed that the hydrogel remained in equilibrium throughout the deformation. This is a reasonable approximation since, in our experiments, we kept the hydrogel structures in DI water at the desired temperature for at least 24 hrs so that it can reach its equilibrium swollen state.

In our constitutive model, we first defined a deformation field \( \mathbf{x} = \mathbf{F}(\mathbf{X}) \), that maps from the material points \( \mathbf{X} \) in the initial undeformed dry polymer configuration to the spatial points \( \mathbf{x} \) in the current deformed hydrogel configuration. The total deformation gradient tensor \( \mathbf{F} \) was defined as \( \mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} \). To model the stress-free swelling of the hydrogel, the total deformation gradient tensor was further decomposed into two parts: a swelling part \( \mathbf{F}_s \) and a mechanical part \( \mathbf{F}_e \),

\[
\mathbf{F} = \mathbf{F}_e \mathbf{F}_s \tag{2.2.1}
\]

where \( \mathbf{F}_s = \phi^{-\frac{1}{3}} \mathbf{I} \). \( \phi \) is the polymer volume fraction of the hydrogel and defined as \( \phi = \frac{1}{1 + vc} \), where \( v \) is the volume per solvent molecule and \( c \) is the number of solvent molecules per polymer volume. We defined the stress-free swollen configuration as the reference configuration, and a deformation gradient tensor \( \mathbf{f} \) mapping from the
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

stress-free reference configuration to the final deformed configuration:

\[ f = \phi_0^\frac{1}{3} F \]  

(2.2.2)

where \( \phi_0 \) is the polymer volume fraction of the hydrogel in the reference configuration.

The left Cauchy-Green deformation tensor was defined as \( b = FF^T \). We expressed the \( b \) tensor in terms of its principle stretches \( \lambda_i \) and principle directions \( n_i \):

\[ b = \sum_{i=1}^{3} \lambda_i^2 n_i \otimes n_i \]  

(2.2.3)

and the corresponding principal stretches of \( f \) tensor are \( \bar{\lambda}_i = \phi_0^\frac{1}{3} \lambda_i \). The change of volume of the entire deformation process from the dry polymer configuration to the final hydrogel configuration was related to the mechanical part and the swelling part as:

\[ J = \text{det}(F) = \text{det}(F_e)\text{det}(F_s) = J_e\phi^{-1}. \]

We assumed that the free energy density of the hydrogel \( \Psi \) could be additively decomposed into two terms: a mechanical term arising from the stretching of polymer network \( \Psi_e \) and a chemical term arising from the mixing of the polymer network and solvent \( \Psi_m \):

\[ \Psi = \Psi_e(I_b, J_e) + \Psi_m(\phi) \]  

(2.2.4)

where \( I_b \) is the first invariant of \( b \) tensor: \( I_b = tr(b) \).

We used the quasi-incompressible Neo-Hookean model to describe the strain energy density of the polymer network with Gaussian chain statistics:

\[ \Psi_e(I_b, J_e) = \frac{G}{2}[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \ln(\lambda_1 \lambda_2 \lambda_3)] + \frac{K}{4}[(\phi \lambda_1 \lambda_2 \lambda_3)^2 - 2 \ln(\phi \lambda_1 \lambda_2 \lambda_3) - 1] \]  

(2.2.5)
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

where $G$ and $K$ are the shear modulus and bulk modulus of the polymer network respectively. To achieve the volumetric incompressibility of mechanical deformation, we assumed that the bulk modulus is 1000 times of the shear modulus.

We used the Flory-Huggins model [121] to describe the free energy density of mixing:

$$
\Psi_m(\phi) = \frac{RT}{v\phi}[(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)]
$$

(2.2.6)

where $R$ is the gas constant, $T$ is the temperature, and $\chi$ is the Flory-Huggins interaction parameter.

We calculated the Cauchy stress tensor from hyperelasticity theory as

$$
\sigma = \frac{1}{\det(F)} \frac{\partial \Psi}{\partial F} F^T,
$$

and we obtained the chemical potential using thermodynamics arguments as

$$
\mu = \frac{\partial \Psi}{\partial c},
$$

where $c$ is the number of solvent molecules per polymer volume. By substituting equations (2.2.4), (2.2.5), (2.2.6) into the above two relations, we obtained the equations of state for the hydrogel model:

$$
\sigma = \sum_{i=1}^{3} \left\{ \frac{G\phi_0}{\lambda_1\lambda_2\lambda_3}(\phi_0 - \phi_i^2) - 1 \right\} \frac{K\phi_0}{2\lambda_1\lambda_2\lambda_3} \left[ (\frac{\phi}{\phi_0} - \frac{\lambda_1\lambda_2\lambda_3}{\phi_0})^2 - 1 \right] n_i \otimes n_i
$$

(2.2.7)

$$
\mu = RT[\ln(1 - \phi) + \phi + \chi\phi^2] - \frac{K\nu\phi}{2} \left[ (\frac{\phi}{\phi_0} - \frac{\lambda_1\lambda_2\lambda_3}{\phi_0})^2 - 1 \right]
$$

(2.2.8)

The constitutive model was implemented in Tahoe (Sandia National Laboratories) for the finite element simulations of the hydrogel bilayers.

To determine the model parameters for the BIS hydrogel, we applied standard dynamic mechanical analysis tests (DMA Q800, TA instruments) to measure the elastic modulus $E_{BIS}$ of swollen BIS gel samples. Three BIS hydrogel samples of cubic
shape, each 8 mm x 8 mm x 8 mm in size, were fabricated via photopolymerization of 5% Am:BIS (19:1) pregel solution in a previously prepared PDMS mold. The hydrogel samples were then placed in buffer solution for two days to swell to equilibrium state via solvent uptake. To obtain elastic moduli values for the gels, the samples were subjected to an unconfined uniaxial compression test (Q800 DMA, TA instruments). The applied force was increased at a rate of 0.01 N/min until a maximum static force of 0.015 N was reached. The stress-strain curves were generated from the raw static force and displacement data. The elastic modulus was measured as the slope of the best-fit line to the stress-strain curves at 1% strain, and were determined to be 2.24 kPa, 2.18 kPa and 2.17 kPa for samples 1, 2 and 3, respectively Fig. 2.3. They are on the order of previously determined elastic moduli values for similar gels [122]. The average elastic modulus of the BIS gel in the fully hydrated state was calculated to be 2.2 kPa. Assuming that the gels were mechanically incompressible resulted in 733 Pa for the shear modulus $G_{BIS}$ of the BIS gel. The bulk modulus was set to $K_{BIS} = 1000G_{BIS}$ to enforce mechanical incompressibility of the polymer network. Though the BIS gel exhibited DNA interpenetration, we assumed that the shear modulus of the BIS gel did not change significantly during DNA-driven swelling. The Flory-Huggins interaction parameters were obtained by fitting the results of the equilibrium swelling ratio of the BIS gel domain within the bilayer before and after adding DNA hairpins. As described in the section 2.2.1, the average volumetric swelling ratio of BIS gel within the bilayer beams was calculated to be
Figure 2.3: Measurement of the elastic modulus for three BIS hydrogel samples. Reprinted with permission [2]. Copyright 2017, AAAS.

4.42 by dividing the volume of the gels after and before adding DNA hairpins. The material model parameters for the DNA and BIS gels are summarized in Table 2.1.

It was experimentally unpractical to use the unconfined uniaxial compression method to measure the elastic modulus of swollen DNA gel samples. First, it was difficult and expensive to prepare and fully expand a DNA-crosslinked hydrogel via hairpin incorporation large enough to perform a compression test using dynamic mechanical analysis. Further, handling expanded hydrogels was challenging due to the softening that occurs during DNA-driven swelling. Therefore, we tried different shear modulus values of DNA gel ranging from 2.29 Pa to 229 Pa in the finite element simulations. The Flory-Huggins interaction parameters were obtained by fitting the results of the equilibrium swelling ratio of the DNA gel domain within the bilayer which was calculated to be 6.91.

The simulation started from the initial hydrated configuration, where the ini-
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

<table>
<thead>
<tr>
<th>$G (Pa)$</th>
<th>$\chi$ for the hydrated state</th>
<th>$\chi$ for the DNA-actuated state</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNA gel</td>
<td>2.29 - 229</td>
<td>0.55</td>
</tr>
<tr>
<td>BIS gel</td>
<td>733</td>
<td>0.55</td>
</tr>
</tbody>
</table>

**Table 2.1:** The constitutive model parameters determined for DNA and BIS hydrogels

tial curvature of bilayer was 0.2 mm$^{-1}$ as measured in the experiments. The initial polymer network volume fraction $\phi_0$ was obtained by solving equations (2.2.7) and (2.2.8) with the conditions $\sigma = 0$ and $\mu = 0$. The DNA sequence-driven swelling was simulated by decreasing the Flory-Huggins interaction parameter $\chi$ in the DNA and BIS gel domains continuously from 0.55 to 0.51 to achieve the experimentally measured volumetric swelling ratios within the different layers and then solving for the displacement field in the bilayer.

We performed the finite element simulations while varying the shear modulus of the DNA gel from 2.29 to 229 Pa, and calculated for each case the equilibrium curvature of the bilayer bar at the equilibrium swelling. To calculate the equilibrium curvature of the bilayer, the deformed positions of the points on the midline of the bilayer inner surface were obtained from the simulation result. We determined the radius of the best fit circle to the points using the method of least squares. The curvature was then calculated by taking the inverse of the radius.
2.2.2.3 Parameter study

To explore the design space of the DNA/BIS bilayer beams, we applied the finite element model to investigate the effect of the thickness $t_{DNA}$, shear modulus $G_{DNA}$ and volumetric swelling ratio $\theta_{DNA}$ of the DNA gel, and the shear modulus of BIS gel $G_{BIS}$ on the curvature of folding BIS/DNA gel bilayer beams. Each parameter was varied one-by-one over a wide range to evaluate the individual effects of the geometric and material factors. The simulation parameter values for the finite element parameter study are summarized in Table 2.2. The DNA gel layer thickness was first varied from 13 $\mu$m to 70 $\mu$m while keeping the DNA gel shear modulus, volumetric swelling ratio, the BIS layer thickness and shear modulus unchanged. Next, we adjusted the DNA gel shear modulus from 2.29 to 850 Pa, and kept the DNA gel thickness, DNA gel volumetric swelling ratio, and BIS gel thickness constant, for the BIS gel shear modulus values of 633, 733 and 833 Pa, respectively. We then kept the DNA gel thickness, shear modulus, BIS gel thickness and shear modulus unchanged, and varied the DNA gel volumetric swelling ratio from 5 to 12. Last, we changed the BIS gel shear modulus from 233 Pa to 1433 Pa, and kept the DNA gel thickness, shear modulus, volumetric swelling ratio, and BIS gel thickness constant.
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

<table>
<thead>
<tr>
<th>$t_{DNA}$</th>
<th>$G_{DNA}$</th>
<th>$\theta_{DNA}$</th>
<th>$G_{BIS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 13 – 70$\mu$m</td>
<td>229Pa</td>
<td>6.91</td>
<td>733Pa</td>
</tr>
<tr>
<td>(b) 60.6$\mu$m</td>
<td>2.29 – 850Pa</td>
<td>6.91</td>
<td>633, 733, 833Pa</td>
</tr>
<tr>
<td>(c) 60.6$\mu$m</td>
<td>229Pa</td>
<td>5 – 12</td>
<td>733Pa</td>
</tr>
<tr>
<td>(d) 60.6$\mu$m</td>
<td>229Pa</td>
<td>6.91</td>
<td>233 – 1433Pa</td>
</tr>
</tbody>
</table>

**Table 2.2:** The simulation parameters for the finite element parameter study

2.2.3 Modified Stoney’s formula

Theoretical solutions for the curving of thin film-thick substrate bilayer system have been derived based on the century-old Stoney formula [123]. This formula assumes small strains and rotations, and that the material of each layer is isotropic, homogeneous, and linear elastic. The Stoney formula can be used to calculate the bilayer curvature when the substrate is much thicker than the film. For the case where the thicknesses of each layer are comparable (and the other assumptions of the Stoney formula hold), Freund et al. [118] derived the modified Stoney formula for the bilayer curvature $\kappa_F$,

$$
\kappa_F = \frac{M_f t_f \epsilon_m}{M_s t_s} \left(1 + \frac{t_f}{t_s}\right)
+ \frac{4M_f t_s^2 M_f}{t_s M_s} + 6\left(\frac{t_f}{t_s}\right)^2 \frac{M_f M_s}{t_s M_s}
+ 4\left(\frac{t_f}{t_s}\right)^3 \frac{M_f M_s}{t_s M_s}
+ \left(\frac{t_f}{t_s}\right)^4 \left(\frac{M_f M_s}{t_s M_s}\right)^2
$$

where $t_f$ and $t_s$ are the thicknesses of the film and substrate, $M_f$ and $M_s$ are the biaxial moduli of the film and substrate (the biaxial modulus $M$ is related to the elastic modulus $E$ and the Poisson ratio $\nu$ as $M = \frac{E}{1-\nu}$), and $\epsilon_m$ is the mismatch strain between the film and substrate $\epsilon_m = \epsilon^f - \epsilon^s$. $\epsilon^f$ is the strain in the free-
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

standing film, and $\epsilon^s$ is the strain in the free-standing substrate.

For the film, the relationship between the volumetric swelling ratio $\theta_f$ and the strain $\epsilon_i^f$ in each direction $i$ was derived by neglecting higher order terms,

$$\theta_f = \frac{V_{f\text{final}}}{V_{f\text{initial}}} = (1 + \epsilon_1^f)(1 + \epsilon_2^f)(1 + \epsilon_3^f) \approx 1 + \epsilon_1^f + \epsilon_2^f + \epsilon_3^f \quad (2.2.10)$$

where $V_{f\text{initial}}$ and $V_{f\text{final}}$ are the volume of the film in the undeformed and deformed states. Similarly, for the substrate, the relationship between the volumetric swelling ratio $\theta_s$ and the strain $\epsilon_i^s$ in each direction $i$ was derived,

$$\theta_s \approx 1 + \epsilon_1^s + \epsilon_2^s + \epsilon_3^s \quad (2.2.11)$$

The difference of the volumetric swelling ratios between the film and the substrate is:

$$\Delta \theta = \theta_f - \theta_s = 3\epsilon_m \quad (2.2.12)$$

Substituting eq. (2.2.12) into eq. (2.2.9), the modified Stoney’s formula for the bilayer curvature when the film and substrate thicknesses are comparable becomes:

$$\kappa_F = 2 \frac{M_f t_f M_s}{1 + 4t_f t_s M_f M_s + 6(t_f t_s)^2 M_f M_s + 4(t_f t_s)^3 M_f M_s + (t_f t_s)^4 M_f M_s} \left(1 + \frac{t_f}{t_s}\right) \frac{\Delta \theta}{E_{fB}} \quad (2.2.13)$$

Inspired by this, we defined the bilayer ratio $\eta$ of the DNA/BIS bilayer beam as,

$$\eta = \frac{E_{DNA} t_{DNA}^{\Delta \theta}}{E_{BIS} t_{BIS}^{\Delta \theta}} \frac{1 + \frac{t_{DNA}}{t_{BIS}}}{1 + 4\frac{t_{DNA}}{t_{BIS}} E_{DNA} E_{BIS} + 6\left(\frac{t_{DNA}}{t_{BIS}}\right)^2 E_{DNA} E_{BIS} + 4\left(\frac{t_{DNA}}{t_{BIS}}\right)^3 E_{DNA} E_{BIS} + \left(\frac{t_{DNA}}{t_{BIS}}\right)^4 E_{DNA} E_{BIS}^2} \quad (2.2.14)$$

for the case when the two layers (DNA gel and BIS gel) have the same Poisson ratio $\nu$. $E_{DNA}$ and $E_{BIS}$ are the elastic moduli of DNA and BIS gels (Pa); $t_{DNA}$ and $t_{BIS}$ are the film thicknesses of DNA and BIS gels (mm); and $\Delta \theta$ is the difference
in the volumetric swelling ratio between the DNA and BIS gels. For an initiallylat DNA/BIS gel bilayer where the DNA layer thickness is similar to the BIS layer
thickness, the modified Stoney formula (eq. (2.2.13)) gives us an estimate of the
equilibrium bilayer curvature as, $\kappa = 2\eta$.

### 2.3 Results and discussions

To estimate the elastic modulus of DNA gel in the fully swollen state, we first ap-
plied the finite element model while varying the shear modulus of the DNA gel from
2.29 to 229 Pa to determine the shear modulus of the DNA gel needed to obtain the
experimentally measured curvature for the actuated bilayer. The calculated equilib-
rium curvatures of the bilayers from the simulations for different values of DNA gel
shear modulus were summarized in Table 2.3. We compared the simulation curva-
tures to the curvature of the actuated bilayer measured in experiments (1.0 mm$^{-1}$). A
shear modulus of 229 Pa for the DNA gel produced the best fit to the experimentally
measured bilayer average curvature at the steady state.

We next investigated the effect of the material and geometric factors on the equi-
librium curvature of the DNA/BIS bilayer beams. The simulation results from the
finite element parameter study are shown in Fig. 2.4. The plots showed the variation
of the equilibrium bilayer curvature with the DNA gel shear modulus, BIS gel shear
modulus, DNA gel thickness and volumetric swelling ratio. From the simulation re-
results, we found that increasing the DNA gel thickness or shear modulus increased the
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

<table>
<thead>
<tr>
<th>DNA gel shear modulus, $G_{DNA}$ (Pa)</th>
<th>Calculated equilibrium bilayer curvature, $\kappa$ (mm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.29</td>
<td>0.2</td>
</tr>
<tr>
<td>6.87</td>
<td>0.26</td>
</tr>
<tr>
<td>22.9</td>
<td>0.45</td>
</tr>
<tr>
<td>49.3</td>
<td>0.64</td>
</tr>
<tr>
<td>77.7</td>
<td>0.75</td>
</tr>
<tr>
<td>106.1</td>
<td>0.83</td>
</tr>
<tr>
<td>229</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 2.3: DNA gel shear moduli and corresponding equilibrium curvatures calculated from FEA.

The modified Stoney’s formula $\kappa = 2\eta$ provided a poor prediction of the simulation results for the curvature of the DNA/BIS gel bilayers, likely because the simulations exhibited large deformation and nonlinear elastic behavior, which vio-
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Figure 2.4: Computational predictions of bilayer curvature as DNA gel volumetric swelling ratio, DNA gel thickness, and DNA and BIS gel shear moduli are individually varied. The simulation parameters for each parameter study are summarized in Table 2.2. Reprinted with permission [2]. Copyright 2017, AAAS.
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lated the assumptions of the theory. However, we found that the simulation results for the curvature change scaled with the bilayer ratio \( \eta \). For each case of the simulation parameter study when varying the DNA gel thickness, shear modulus and volumetric swelling ratio, we applied the geometric and material parameters to calculate the bilayer ratio \( \eta \) in eq. 2.2.14. Plots of the curvature \( \kappa \) calculated from the finite element analysis as a function of the bilayer ratio \( \eta \) for all these cases of the parameter study fell on a straight line of the form \( \kappa = C\eta + \kappa_0 \) (Fig. 2.5). A linear regression returned \( C = 0.21 \) for the proportionality constant and \( \kappa_0 = 0.2 \text{ mm}^{-1} \) for the initial curvature, which agreed with the average initial curvature of the bilayers measured in the hydrated state 0.2057 mm\(^{-1}\).

This analysis showed that the effects of varying DNA gel thickness, modulus, and the degree of swelling can be described by a simple design rule \( \kappa = 0.21\eta + 0.2 \) for the curvature of the bilayer. The bilayer ratio \( \eta \) depends nonlinearly on the modulus and thickness ratio of the DNA and BIS gels, and depends linearly on the difference in the volumetric swelling ratio. This design rule indicates that the curvature is more sensitive to the DNA gel swelling ratio (\( \Delta \theta \)) than to the shear modulus or thickness of the DNA gel layer. The high degree of swelling was thus essential for extensive shape change.

Further, there is an optimum thickness of the DNA gel for which the curvature is maximized. In Fig. 2.6, we plotted the equilibrium bilayer curvature calculated from the design rule as a function of the DNA layer thickness \( t_{DNA} \) for BIS layer
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**Figure 2.5:** Computational finite element parameter study of bilayer curvature. The baseline case (white circle) corresponds to the experimentally measured bilayer curvature and swelling ratios. The bilayer ratio $\eta$ (Eq. 2.2.14) captures the effects of the shear moduli, thickness, and volumetric swelling ratios of the gel layers. Illustrated bilayers in the inset show the predicted final shapes for different volumetric swelling ratios from finite element simulations. Reprinted with permission [2]. Copyright 2017, AAAS.
CHAPTER 2. MODELING THE SHAPE CHANGING BEHAVIOR OF DNA HYDROGEL BILAYERS

thicknesses of 51.6 $\mu$m, 71.6 $\mu$m, and 91.6 $\mu$m. In these cases, the DNA gel shear modulus, volumetric swelling ratio, and BIS gel shear modulus were kept constant at 229 Pa, 6.91, and 733 Pa. From Fig. 2.6, we found that increasing the BIS gel thickness resulted in a lower curvature due to the increased flexural stiffness of BIS layer. However, the effect of varying the thickness of the DNA gel was more complicated. For each BIS gel thickness, there was an optimum thickness of DNA gel for which the bilayer curvature was maximized. For example, the optimal DNA gel thickness was 60.6 $\mu$m for a BIS gel thickness of 71.6 $\mu$m. The bilayer curvature decreased for larger and smaller values of DNA gel thickness. A DNA gel layer that is too thin did not exert enough force to bend the bilayer, while a DNA gel layer that is too thick was negligibly affected by the BIS gel layer and underwent uniform swelling rather than inducing folding. The optimal thickness increased with the BIS gel thickness. For the BIS gel thicknesses of 51.6 $\mu$m, 71.6 $\mu$m, and 91.6 $\mu$m, the optimum DNA gel thicknesses were 42, 60.6 and 69.8 $\mu$m, respectively.

The design rule also showed that the high degree of swelling of the DNA gel should allow millimeter to centimeter sized bilayer structures to achieve a large shape change. For example, we asked whether a 10 mm long flat bilayer beam that was also several millimeters thick (as opposed to 0.1 mm or less as we had studied previously) could fold into a complete circle. The relation obtained from the parameter study was $\kappa = 0.21 \eta + 0.2$ where 0.2 mm$^{-1}$ represents the initial curvature of the bilayers in the hydrated state. Using the relation $\kappa = 0.21 \eta$ and assuming the 10 mm long
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Figure 2.6: Analytical predictions of curvature change using the design rule $\kappa = C\eta + \kappa_0$, where $C$ and $\kappa_0$ were fit to the simulation results in Fig. 2.5. Reprinted with permission [2]. Copyright 2017, AAAS.

bilayer beam was initially flat, we determined that the 10 mm long bilayer with the optimum DNA gel thickness can be as thick as 7.23 mm and still fold into a complete circle for the maximum experimentally measured swelling ratio of $3.72 \pm 0.11$.

There are two limitations to the FEM and theoretical model for the DNA gel bilayer. First, in the bilayer swelling experiments, the curvature in the swollen state is nonuniform along the contour length of the bilayer, and we took the average of the measured curvatures as the equilibrium curvature. However, in the finite element simulations without contact, the tips of the bilayer overlapped with each other and the curvature of the swollen bilayer was uniform. This resulted in a discrepancy between our FEM and experiment results. Second, to validate the theoretical model,
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we only carried out experiments with one set of design parameters (Fig. 2.1). More experiments are needed to carry out with different design parameters to validate our analytic design rule.

2.4 Conclusions

Biological tissues demonstrate the versatility and functionality of shape change driven by biomolecules, where different cues and their concentrations determine which responses occur [124]. We have demonstrated how specific DNA biomolecular signals can also determine the large shape change of hydrogels. To estimate the elastic modulus of this novel hydrogel that cannot be measured by traditional experimental approach, we used finite element analysis to study the curving of DNA/BIS gel bilayer beams. By comparing the finite element simulations to the experiment result, the DNA gel shear modulus was estimated to be 229 Pa. Then, we applied the finite element model to conduct a parameter study on the influence of bilayer geometric and material properties on the equilibrium curvature. Inspired by the modified Stoney formula for the curving of film/substrate system, we further developed a simple design rule for the equilibrium curvature of DNA/BIS bilayer beams. This simple design rule provides a powerful method for predicting the bilayer curvatures for gel layers of similar thicknesses and designing chemo-mechanical devices that require no batteries and can easily be miniaturized and integrated with other devices.
Chapter 3

Dual-gel 4D Printing of Bioinspired Tubes

The distribution of periodic patterns of materials with radial or bilateral symmetry is a universal biological design principle. Amongst the many biological forms, tubular shapes are a common motif in many organisms, and they are also important for bioimplants and soft robots. However, the simple design principle of strategic placement of 3D-printed segments of swelling and non-swelling materials to achieve widely different functionality has yet to be demonstrated. Here, we demonstrate the design, fabrication, and characterization of segmented 3D printed gel tubes composed of an active thermally responsive swelling gel (poly N-isopropylacrylamide; pNIPAM) and a passive thermally non-responsive gel (polyacrylamide; pAAM). Using finite element simulations and experiments, we design the variety of shape changes including uniaxial
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elongation, radial expansion, bending, and gripping based on two gels. Actualization and characterization of thermally induced shape changes are of key importance to robotics and biomedical engineering. This study presents rational approaches to engineering complex parameters with a high level of customization and tunability into additive manufacturing of dynamic gel structures.


3.1 Introduction

The radial or bilateral distribution of chemicals during growth and morphogenesis is a widely observed feature in biology, seen in more than 99% of modern animals, and across diverse species ranging from humans to microorganisms [125]. Tubular biological species and their functional components including nematodes, flowers, marine animals and elephant trunks also show symmetric and/or periodic arrangements

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of different material segments. The organisms exploit the swelling mismatch and mechanical instabilities inherent in these structures to enable complex shape change and motion. It is noteworthy that tubular shapes are essential in human engineering due to the need for bioimplants such as vascular grafts [126] and continuum robots [127]. Apart from static designs, controllable shape change in tubular shapes such as elongation, lumen expansion and bending could facilitate smart or autonomous behaviors, but such features are challenging to incorporate especially in an unwired, external-power-free, and customizable manner [128, 129].

Stimuli-responsive polymers offer significant opportunities for implementing a range of smart, adaptive and dynamic behaviors in response to temperature, light, electromagnetic fields, and chemicals [2, 4, 16, 22, 119, 130, 131]. As one of the most widely used stimuli-responsive materials, thermally responsive poly N-isopropylacrylamide (pNIPAM) has been utilized to create a range of shape-changing structures including grippers [57, 132], propellers [133, 134], and actuators [135–137]. When coupled with 3D printing, a high level of customization, tunability and adaptability can be achieved.

4D printing which introduces a new dimension of time [9, 11, 12, 79–81, 138] has been previously utilized to create shape-changing structures and devices [8, 13, 82–89, 139–142]. Besides the well-recognized advantage of easy programmability as a path-based additive manufacturing method, 3D printing also offers excellent potential in material integration and switching of dissimilar materials on demand (in a manner
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that is analogous to weaving). Among the different types of 3D printing, direct ink writing (DIW) of gels has notable advantages over alternative 3D gel printing methods such as stereolithography in terms of low cost implementation and the ease of incorporating multiple gels at the same time.

Inspired by symmetrical and periodic tubular structures in biology and motivated by the need to create untethered, thermally responsive bioimplants and continuum robots, we explored the 4D printing of tubes with alternating segmental patterns of an active thermoresponsive gel (poly N-isopropylacrylamide; pNIPAM) and a passive thermally non-responsive gel (polyacrylamide; pAAM) based on direct ink writing. The essential challenge in our work was to elucidate, rationalize and validate design principles by which sequential arrangements of segments of high and low swelling stimuli-responsive gels could elicit dramatically different shape change of functional importance.

The similar acrylamide composition of the gels is essential to ensure interfacial adhesion in segmented designs. First, printable inks were made by blending monomers of these gels with a clay (Laponite) that alters the rheological characteristics of the gels and enables shear thinning behaviors. Using finite element modeling and bioinspiration, we generated standard tessellation language (STL) to make tubes with different periodic vertical and horizontal arrangement of active and passive segments that could generate a diverse range of shape changes including uniaxial elongation, bending, radial expansion, and gripping. Further, inspired by coral polyps, we designed and
printed tubes with self-folding fingers at one end, and these structures display more complex dual-function thermally responsive shape change involving both uniaxial expansion of the tube and finger gripping. We anticipate that this novel bioinspired approach utilizing segmented placement of active and passive stimuli-responsive materials, when combined with finite element simulations and the versatility of customizable 3D printing designs, offers the possibility of producing a range of multi-functional shape-changing structures with broad applicability.

3.2 Methods

3.2.1 Ink development, 4D printing, and imaging

3.2.1.1 Development of active and passive hydrogel inks

To be 3D printed via Direct Ink Writing (DIW), a material must display unique rheological or shear thinning characteristics [90, 143]. Hence, the first step was to create thermoresponsive NIPAM and non-thermoresponsive AAM inks for DIW. pNIPAM has a lower critical solution temperature (LCST) above which it transforms from a hydrophilic to hydrophobic state and expels water with a significant reduction in volume [144]. pAAM lacks the critical isopropyl group and shows no LCST.

Both NIPAM and AAM have previously been printed using stereolithography [12] and DIW [9, 11, 79, 80]. We blended the monomer NIPAM with different shear-
thinning agents including Xanthan Gum, Gellan Gum, and Laponite nanoclay. All of the three agents showed shear-thinning properties (the rheology measurements of our NIPAM inks are shown in Fig. 3.1) and could be printed by direct ink writing. We attribute this observation to dissociation of the ink network under applied shear stress. Consequently, the ink could be extruded out of the printing nozzle, and when the shear stress was removed after printing the network reassembled and the extruded ink retained its shape [143]. The rheology of the inks was measured using a rheometer (Modular Compact Rheometer MCR 302, Anton Paar, Austria) with a 1° cone-plate geometry. The temperature of the plate was kept at 23°C. Ink viscosities were measured via a logarithmic sweep of shear rates ranging from 0.01 s$^{-1}$ to 1000 s$^{-1}$. Oscillatory experiments were performed at a constant frequency of 1 Hz.

We observed however, that the Laponite-blended ink had a higher storage modulus than the other two inks (Fig. 3.1B), and could be used to print taller structures. The AAM-blended inks showed similar rheological and modulus trends. Therefore, we chose Laponite as the shear-thinning agent for both our active NIPAM and passive AAM inks. Also, a free radical curing agent Irgacure was added to both inks to facilitate photocuring with ultraviolet (UV) light. It has been previously reported, and we confirmed, that the Laponite-NIPAM-Irgacure mixture was photocrosslinkable and retained its shape in water [145, 146]. However, it was necessary to add a crosslinker, N,N$'$/-methylenebis(acrylamide) (BIS), to the AAM inks, so that they did not dissolve in water after printing and curing (Fig. 3.2). The UV-Vis absorbance
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Figure 3.1: Rheological measurements of the NIPAM inks. Log-log plots of, (A) Ink viscosity as a function of shear rate, (B) Storage modulus as a function of oscillation strain, and (C) loss modulus as a function of oscillation strain for NIPAM inks blended with different shear thinning agents: (black) 3 wt% Xanthan gum ink, (red) 2 wt% Gellan gum ink, and (blue) 6.77 wt% Laponite ink. Reprinted with permission [14]. Copyright 2019, ACS.
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**Figure 3.2:** Schematic representation of the molecular and microstructure of the inks: (A) active NIPAM ink and (B) passive AAM ink. Reprinted with permission [14]. Copyright 2019, ACS.

and FTIR measurements of active and passive inks before and after photocuring are shown in Fig. 3.3.

The detailed preparation procedures and recipes for the active NIPAM and passive AAM inks are described as follows.

Active NIPAM ink: Laponite XLG (Southern Clay Products) was first mixed with DI water using magnetic stirring, followed by a planetary mixer (Mazerustar KK-250S, Kurabo Industry Ltd.) 10 vol% of a 0.12 mg ml$^{-1}$ solution of Methacryloxyethyl thiocarbamoyl Rhodamine B (Polysciences, Inc.) was used as the dye for fluorescence imaging. The aqueous dye solution was added to the Laponite solution and mixed with the planetary mixer. Subsequently, N-Isopropylacrylamide (NIPAM, Scientific Polymer Products Inc.) monomer and Irgacure 2959 (BASF) as a UV photoinitiator
Figure 3.3: UV-Vis absorbance and FTIR measurements of active and passive inks before and after photocuring. (A) UV-Vis absorption spectra of NIPAM ink and AAM ink before and after photocuring. The inks were transferred into cuvettes and the absorption spectra were measured using a PerkinElmer UV/VIS/NIR Spectrometer Lambda 950 with readings acquired in 6 nm increments. (B- C) FTIR spectra of the NIPAM and AAM ink before and after photocuring. The main features are similar with small differences before and after curing. The FTIR spectra were measured using a Bruker Hyperion FTIR Microscope. Reprinted with permission [14]. Copyright 2019, ACS.
was added to the Laponite-dye solution and mixed again using the planetary mixer. The final concentrations (by weight) of each component in the active NIPAM ink were as follows: 84.6% DI water, 8.46% NIPAM, 6.77% Laponite, 0.17% Irgacure, 0.001% Methacryloxyethyl thiocarbamoyl Rhodamine B. The NIPAM concentration was chosen based upon literature precedent and our empiric data.

Passive AAM ink: Laponite solution was prepared in the same way as the active ink. 10 vol% of a 0.3 mg ml$^{-1}$ solution of Fluorescein o-methacrylate (97%, Sigma-Aldrich) was used as the dye for the passive ink. The dye solution also contained 2 mg ml$^{-1}$ NaOH (Fisher Scientific) since the dye monomer is dissolvable in base conditions, and was mixed by magnetic stirring. Subsequently, acrylamide (AAM, Sigma-Aldrich) monomer, Irgacure 2959 and N,N$'$/methylenbisacrylamide (BIS, Sigma-Aldrich; BIS functions as a crosslinker) was added to the Laponite-dye solution and mixed using the planetary mixer. The final concentrations (by weight) of each component in the passive ink were: 82.97% DI water, 7.88% AAM, 6.64% Laponite, 0.83% Irgacure, 1.66% BIS, 0.0025% Fluorescein o-methacrylate, 0.017% NaOH.

3.2.1.2 3D printing of pNIPAM and pAAM dual-hydrogel structures

The NIPAM and AAM inks were loaded into syringes, transferred to UV-shielded cartridges and centrifuged to remove any bubbles present in the cartridges. The inks were kept at room temperature for at least 24 hrs to allow thorough hydration needed
to achieve the desired shear thinning properties. The cartridges were then attached to the Direct Ink Writing 3D Printer (Inkredible+ 3D Bioprinter, Cellink) and connected to an air pump pressure control. We chose nozzles 22G (diameter 0.41 mm) which ensures smooth and clog-free printing. All the computer-aided-design (CAD) and STL files were generated in Solidworks (Dassault Systèmes). Then, the G-code for each design was generated using the software Slic3r (layer height 0.4 mm, printing speed 10 mm s\(^{-1}\)). Before printing the final designs, we printed test structures to calibrate the two printing nozzles so that they were perfectly aligned with each other. The structures were printed on silicon wafers at room temperature in air. The printing pressures were optimized for each ink to ensure smooth printing at a speed of 10 mm s\(^{-1}\). The pressures used for printing active and passive inks were 90-100 kPa and 110-130 kPa, respectively.

Printing tall structures of dual materials requires a number of challenges to be overcome. First, switching between the two materials needs to be seamless, which necessitates that the two nozzle tips be perfectly aligned with each other. Even a small misalignment of the nozzles accumulates recurring errors in each layer resulting in significant defects in the final structure. Moreover, printing 3D tall structures are more technically demanding than printing shorter 2D structures. The tall structures we printed require approximately 50-100 layers of printing, and a single perturbation (such as an air bubble or clog) in the printing process ruins the entire print.

To overcome these challenges, we developed the following calibration procedure to
implement before printing the final dual-gel structure. First, we made sure that both
print heads were leveled with each other in the Z direction. Then, for calibration in the
X and Y directions, we printed a calibration structure consisting of a pNIPAM tube
on top of a pAAM tube. The objective of this step was to check whether there was
any misalignment between the two print heads because even a small misalignment
will accumulate recurring errors in each layer, resulting in defects in the structure
and undesired shape change. If any misalignments were observed, we added preset
values in the X and Y directions for the print heads in the g-code files. This step was
repeated multiple times until the print heads were aligned to ensure seamless printing
of the two inks.

3.2.1.3 UV photocuring

After 3D printing, we photocured the structures using an Omnicure UV source (LX
500, Lumen Dynamics). We designed a rotating platform that rotates slowly at 9.6
rpm to enable relatively uniform exposure of UV light and consequently uniform
curing of gel tubes. Two UV LED heads with 365 nm wavelength were used to cure
the tubular structures, and we used a lens of diameter 12 mm for each UV LED head
and a resulting intensity of 0.4 W/cm² at a distance of 3 cm. We cured the tubular
structures with 100% power and section by section depending on the structural height.
Each section was cured for 9 mins using two UV LED heads at the same time.

Uniform UV curing of tall 3D structures was essential to achieve the desired shape
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Figure 3.4: Schematic showing the microstructure of the active NIPAM and passive AAM inks and different steps in the 4D printing process including formulation of the inks, 3D direct ink writing and photocuring. Reprinted with permission [14]. Copyright 2019, ACS.

change. While many researchers cure their structures from above, we found that this strategy resulted in significant crosslink gradients. We built a new rotating platform which facilitated the uniform photocrosslinking of the entire structure. We placed the 3D printed structures in the center of a table that was rotated at 9.6 rpm, and used the LX 500 Omnicure system (Lumen Dynamics) with two UV LED heads (wavelength 365 nm) for the curing process. The two UV heads were pointed towards the outer and inner surfaces of the structures simultaneously at a distance of 3 cm. The homogeneous pNIPAM tubes and pAAM tubes were cured as a single section. For the uniaxial elongation tube, bending tube, radial expansion tube, and gripper, the top, and bottom sections were cured successively. The coral polyp inspired dual-shape change tube was cured as three sections.

The conceptual schematic of the 4D Printing process is shown in Fig. 3.4.
3.2.1.4 Macro-imaging

After printing and photocuring in air, the structures were soaked in deionized (DI) water which induced swelling and releasing from the substrate. All optical images were taken with a digital camera (Canon EOS 70D) and a broad spectrum UV light source (Spectroline Model EF-160C, Spectronics Corporation, USA) to excite the fluorescent dyes in the inks. The images of photocured tubes were taken at room temperature in air after UV curing. Then, the structures were placed in DI water and put into an incubator (MODEL 1575, Sheldon Manufacturing, INC., USA) set at the desired temperatures for 24 hours to reach the equilibrium swollen state at each temperature. The photographs of the transformed structures were taken in DI water. We started the time-lapse study of the tubes after immersion in DI water at room temperature. We connected the Pixel T3/E3 Timer Shutter Release Remote Control to the camera and took pictures every 50 seconds for 6 hours.

3.2.2 Finite element model

3.2.2.1 Finite element geometry

Finite element modeling was applied to design the dual-gel tubes with desired shape changes and functions. Inspired by nature, we arranged the two hydrogels with different mechanical properties and swelling capabilities in two categories of 3D patterns: horizontal segments and vertical segments. The finite element geometries of the hor-
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Horizontal and vertical gel segments are shown in Fig. 3.5. The dimensions of each
model geometry were the same as measured from the structures’ experimental pic-
tures in the photocured state. The mesh was discretized using trilinear hexahedral
elements. As boundary conditions, one point of the structure’s bottom plane was
fixed. The displacement boundary conditions of the uniaxial elongation tube and the
radial expansion tube were set as:

\[ u_x(x = 10, y = 0, z = 0) = u_y(x = 10, y = 0, z = 0) = u_z(x = 10, y = 0, z = 0) = 0 \]  

(3.2.1)

The displacement boundary conditions of the bending tube were set as:

\[ u_x(x = 7.5, y = 0, z = 0) = u_y(x = 7.5, y = 0, z = 0) = u_z(x = 7.5, y = 0, z = 0) = 0 \]  

(3.2.2)

The displacement boundary conditions of the gripper were set as:

\[ u_x(x = 9, y = 0, z = 0) = u_y(x = 9, y = 0, z = 0) = u_z(x = 9, y = 0, z = 0) = 0 \]  

(3.2.3)

3.2.2.2 Constitutive model

pNIPAM hydrogel:

The material behavior of the pNIPAM segments was described by a coupled
chemo-mechanical model developed previously for the thermoresponsive behavior of
hydrogels and described in detail in Ch. 2. Briefly, the stress response of the gel
Figure 3.5: Finite element geometries of the functional dual-gel tubes. (A) Horizontal gel segments, and (B) Vertical gel segments. Green represents passive pAAM hydrogel and red represents active pNIPAM hydrogel. The model geometries are the same as those measured experimentally in the photocured state. Reprinted with permission [14]. Copyright 2019, ACS.
was assumed to be the sum of an elastic component for the entropic response of the polymer network and the solvent pressure acting on the network derived from the Flory-Huggins theory [121]. To model the thermoresponsive behavior, we assumed that the Flory-Huggins interaction parameter \( \chi \) in eq. (2.2.6) had the following form [93],

\[
\chi = \frac{1}{2}(\chi_L + \chi_H) + \frac{1}{2}(\chi_H - \chi_L) \tanh\left(\frac{T - T_{trn}}{\Delta T}\right)
\]

(3.2.4)

where \( \chi_L \) and \( \chi_H \) are the Flory-Huggins interaction parameters at low and high temperatures respectively, \( T_{trn} \) is the transition temperature, and \( \Delta T \) is the width of transition region. The equations of state for the hydrogel model are eqs. (2.2.7) and (2.2.8). The hydrogel constitutive model was implemented into TAHOE (Sandia National Laboratories) for finite element simulation of horizontal and vertical gel segments.

To determine the model parameters for the pNIPAM segments, we 3D printed pNIPAM hydrogel square plates of side length 10 mm and thickness 2 mm. After photocuring, the hydrogel samples were placed into DI water at room temperature for 24 hours to reach the free swollen equilibrium state. We used a DMA (Dynamic Mechanical Analyzer Q800, TA Instruments) to carry out unconfined compression tests on the hydrogel samples with a maximum applied static force of 6 mN at a rate of 1 mN min\(^{-1}\). The static force and displacement data output from the DMA were converted to engineering stress and engineering strain. We tested three pNIPAM hydrogel square plate samples and calculated the average Young’s modulus \( E_{Gel}^{pNIPAM} = 2.53kPa \) from
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Figure 3.6: Results of stress-strain measurements of 3D printed and photocured pNIPAM hydrogel. Elastic moduli measurements were obtained for fully hydrated hydrogel square plates to determine the stiffness of the hydrogels used in this study. The elastic modulus of the pNIPAM gel sample was measured using unconfined compression test at room temperature (DMA Q800; TA instruments) with a maximum applied static force of 6 mN at a rate of 1 mN min$^{-1}$. Reprinted with permission [14]. Copyright 2019, ACS.

The slopes of engineering stress-engineering strain curves (Fig. 3.6), which corresponds to a shear modulus of $G_{pNIPAM}^{\text{gel}} = \frac{1}{3}E_{pNIPAM}^{\text{gel}} = 0.84\text{kPa}$ assuming mechanical incompressibility.

We then measured the volumetric swelling ratio of the pNIPAM hydrogel from the dry state to the equilibrium swollen state at room temperature in order to calculate the polymer’s elastic modulus. We measured the average weight $M_{\text{hydrated}}$ of three pNIPAM square plate hydrogel samples in the equilibrium swollen state at room temperature. The hydrogel samples were then put into incubator (MODEL 1575, Sheldon Manufacturing, INC., USA) in air at 50°C for 24 hours to reach completely dry state,
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and weighted again ($M_{\text{dry}}$). The volumetric swelling ratio of pNIPAM hydrogel from the dry state to the equilibrium swollen state at room temperature was calculated by $Q_{p\text{NIPAM}} = \frac{M_{\text{hydrated}}}{M_{\text{dry}}} = 21.14$. The pNIPAM polymer shear modulus $G_{p\text{NIPAM}}^{\text{Polymer}}$ is related to the hydrogel shear modulus as [68]:

$$G_{p\text{NIPAM}}^{\text{Polymer}} = G_{p\text{NIPAM}}^{\text{Gel}} Q_{p\text{NIPAM}}^{\frac{1}{3}} = 2.32 \text{kPa}.$$

The Flory-Huggins interaction parameters $\chi_L$, $\chi_H$, $T_{\text{tran}}$, and $\Delta T$ of the pNIPAM segment were obtained by fitting the results of the equilibrium swelling tests of the printed pNIPAM homogeneous tubes at different temperatures (between 25°C and 50°C). For the swelling tests, three homogeneous pNIPAM hydrogel tubes of diameter 2 cm and height 2 cm were 3D printed and photocured. After photocuring, the three pNIPAM hydrogel tubes were placed into DI water in the incubator at 50°C, 41°C, 33°C, 25°C, 33°C, 41°C, and 50°C for 24 hours to reach the equilibrium swollen state at each temperature. We took optical images of the pNIPAM hydrogel tubes at different temperatures, and measured the average tube outer diameter $D$ using the ImageJ software. We plotted the fractional change in diameter ($\frac{\Delta D}{D_0}$) of the pNIPAM hydrogel tubes at different temperatures in Fig. 3.7, where $D_0$ represents the average pNIPAM tube outer diameter in the photocured state, and $\Delta D$ represents the average change of outer diameter under different temperatures. We observed dramatic increases (38%) and decreases in the diameter of the pNIPAM tubes on cooling and heating, respectively. This swelling behavior agrees with prior swelling data from photolithographically patterned pNIPAM gel [68]. Consequently, we consider the
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pNIPAM portion of the structure to be the active gel that drives shape change by swelling or deswelling. We attribute the hysteresis to a variety of factors including reorganization of chains of crosslinked and uncrosslinked polymer, as well as documented differences in intra- and intermolecular hydrogen bonding that occur between heating and cooling [147–149]. The parameters \( L \), \( H \), \( T_{\text{tran}} \), and \( \Delta T \) were obtained by fitting the simulation equilibrium swelling data under different temperatures to the experimental cooling curve.

**Passive hydrogel:**

We used the quasi-incompressible Neo-Hookean model to describe the pAAM segment, because the swelling of the 3D printed homogeneous pAAM hydrogel tubes was negligible and independent of temperature. For the swelling tests, three homogeneous pAAM hydrogel tubes of diameter 2 cm and height 2 cm were 3D printed and photocured, and the same swelling tests were conducted. No significant change (1.2%) in the diameter of pAAM tubes was observed for different test temperatures (Fig. 3.7). Thus the pAAM hydrogel served as the passive material in the segmented tubes. To determine the shear modulus of pAAM, we conducted all of the same experiments described above on three 3D printed pAAM hydrogel square plate samples. The pAAM polymer shear modulus was calculated to be 11.9 kPa.

The simulation started from the high temperature \( T = 50^\circ \text{C} \) to approximate the un-swollen photocured state. The initial polymer fraction \( \phi_0 \) was obtained by solving equations (2.2.7), (2.2.8) with the condition \( \sigma = 0 \) and \( \mu = 0 \). The temperature of the
Figure 3.7: A plot showing the experimentally measured normalized diameter change ($\frac{\Delta D}{D_0}$) in water at different temperatures between 25°C and 50°C for 3D printed and photocured tubes composed of pNIPAM and pAAM. $D_0$ is the diameter of the 3D printed and photocured tube in air. Bars indicate standard deviation with a sample size of three and data at each temperature was taken at equilibrium after 24 hours. Inset shows several snapshots of the pNIPAM (yellow) and pAAM (green) tubes recorded at different temperatures. Scale bars indicate 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
model was linearly decreased to different temperatures (25°C, 35°C) to simulate the equilibrium shape changes of the structures. At each step, the deformation gradient $f$ and polymer volume fraction $\phi$ were updated to satisfy the momentum balance and chemical potential equilibrium.

### 3.3 Results and discussions

As discussed previously, symmetric composite materials are widely found in nature. When the constituent materials have different mechanical properties such as the extent of swellability in our two gels, this can lead to predictable and controllable shape change, that is amenable to modeling by finite element methods (FEM). Applying the FEM and experiments, we explored the rational design of shape-changing gel tubes by the symmetric placement of horizontal or vertical segments of active pNIPAM gels interspaced with passive pAAM gels. After 3D printing and photocuring, the structures were soaked in DI water at 25°C, 35°C, and 50°C for 24 hours to reach the equilibrium state. Bilaterally symmetric tubes with equally spaced, alternating cylindrical-disk-shaped segments of pNIPAM (three segments), and pAAM (four segments) showed elongation as high as 32%, with good agreement between FEA simulations and experiments (Fig. 3.8A-B and Fig. 3.9). As compared with homogeneous tubes of pNIPAM that elongate by approximately the same extent (38%, Fig. 3.7), the introduction of passive segments constrained radial expansion of the tube, so that its predominant shape change was uniaxial elongation.
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Figure 3.8: Bilaterally symmetric tubes with horizontal, periodically-spaced segments. (A-B) Results showing thermoresponsive uniaxial elongation of tubes with alternating cylindrical discs of active pNIPAM (red) and passive pAAM (green) segments. (A) Optical and FEA snapshots of shape change of tubes at different temperatures. $H$ indicates the height of the tube which is plotted against temperature in panel (B). (C-D) Results showing thermoresponsive bending of tubes with alternating cylindrical wedge shaped segments of active pNIPAM (red) and passive pAAM (green) segments. (C) Optical and FEA snapshots of shape change of tube at different temperatures. $\theta$ indicates the bending angle of the tube which is plotted against temperature in panel (D). The experimental snapshots of all tubes were obtained after soaking them in water and allowed to equilibrate at the desired temperature over 24 hours. The simulation snapshots and plots are in agreement with the experiments. The printing of tube designs was repeated 2-3 times and no significant variation was observed (we estimate less than 10%) in height and bending angle change. All scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
Figure 3.9: Shape change snapshots of the uniaxial elongation tube with different aspect ratios ($\frac{h_{pNIPAM}}{h_{pAAM}}$). $h_{pNIPAM}$ and $h_{pAAM}$ represent the height of the active and passive rings respectively. Increasing the aspect ratio from 1 (bottom) to 3 (top) resulted in an increase of elongation ($\frac{\Delta H}{H_0}$) from 15.5% to 32.4%. Scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
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Figure 3.10: Time-lapse shape change snapshots of the bending tube in DI water at room temperature. Scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.

When the same number of alternating pNIPAM and pAAM segments were placed at angles with respect to each other (Fig. 3.8C-D and Fig. 3.10), like cylindrical wedges, the tube bent by approximately 25°. The bending angle decreased as we increased temperature, and at 50°C, it reversed to the photocured state (θ = 0°), in agreement with simulation snapshots.

We next printed tubes with twelve alternating vertical segments of pNIPAM and of pAAM (six of each), on top of a constraining ring of pAAM. The tubes expanded radially by 75% but did not elongate. Constrained by the nonswelling strips of pAAM, the tube buckled and folded downwards to accommodate the elongation of the pNIPAM strips by swelling (Fig. 3.11A-B and Fig. 3.12A). The tubes recovered their original shapes when we increased the temperature to 50°C.

We also designed tubes with wedge-shaped alternating pNIPAM and pAAM vertical segments and overhanging pNIPAM “fingers” constrained by pAAM edges. The pNIPAM “fingers” are more constrained at their bottoms than at their tops. As a
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result, the “fingers” bent by approximately, \( \omega = 35^\circ \) when the pNIPAM gel swelled at 25\(^\circ\)C (Fig. 3.11C-D, Fig. 3.12B). The side-view comparison of experimental results and FEA for the uniaxial elongation tube, bending tube, and radial expansion tube are shown in Fig. 3.13.

Advanced biomedical or soft robotics applications often require a library of parts that may transform in shape. Nature is replete with such complex shape-change organisms. For example, the coral polyp [15] is an aquatic animal with a cylindrical vase-shaped body with radially distributed tentacles capable of capturing prey (Fig. 3.14A). Our design, simulation, and 3D printing approach is amenable to the creation of such complex shape-change devices. Inspired by the coral polyp, we designed dual shape-change tubes, composed of a uniaxial elongation tubular base (Fig. 3.8A) and a bending three finger gripper module (Fig. 3.11C). A 3D printed passive ring at the bottom of the base served as a handle (Fig. 3.14B-C). After 3D printing and photocuring, the structure was suspended in air on top of a cuboidal object placed at the bottom of the tank (Fig. 3.14D). When the tank was filled with water at 25\(^\circ\)C, the polyp-inspired tube showed two shape-change events by simultaneously elongating and bending its fingers to grab onto the cube (Fig. 3.14E, Fig. 3.15). It is noteworthy that the fingers were able to firmly grasp the cube so that it could be lifted from the bottom of the tank (Fig. 3.14F). Upon heating to 50\(^\circ\)C, the fingers opened up, the base contracted and the cube was released (Fig. 3.14G).
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![Figure 3.11: Radially symmetric tubes with vertical, periodically-spaced segments. (A-B) Results showing thermoresponsive radial expansion of tubes with alternating vertical segments of active pNIPAM (red) and passive pAAM (green) segments. (A) Optical and FEA snapshots of shape change of tubes at different temperatures. \( D \) indicates the diameter of the tube at the point of maximal expansion which is plotted against temperature in panel (B). (C- D) Results showing thermoresponsive folding of fingers on tubes with vertical segments of active pNIPAM (red) and passive pAAM (green) segments. (C) Optical and FEA snapshots of shape change of the tube at different temperatures. \( \omega \) indicates the folding angle of the fingers which is plotted against temperature in panel (D). The experimental snapshots of all tubes were obtained after soaking them in water and allowed to equilibrate at the desired temperature over 24 hours. The simulation snapshots and plots are in agreement with the experiments. All scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.](image-url)
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**Figure 3.12:** Time-lapse shape change snapshots of the (A) radial expansion tube, and (B) the gripper in DI water at room temperature. Scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
Figure 3.13: Side-view comparison of experimental results and finite element method (FEM). (A) Uniaxial elongation tube, (B) Bending tube, and (B) Radial expansion tube. Scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
Figure 3.14: Dual-shape change tubes. (A) Schematic of the basic anatomy of the coral polyp; the image was created based on encyclopedic depictions of the polyp [15]. (B-C) CAD model and image of a 3D printed and photocured tube with cylindrical base and three fingers. (D-G) Optical snapshots of shape change of the tube at different temperatures. The tube was suspended over a part placed in a tank. When water was added to the tank, the tube shows uniaxial elongation and gripping of the part. Upon heating to 50°C, the tube shortened and the fingers opened to release the part back to the bottom of the tank. Scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
**Figure 3.15:** Time lapse of the coral polyp inspired dual-shape change tube reaching inside a box to grab a hexagonal prism. The shape change occurred in DI water at room temperature. Scale bars are 1 cm. Reprinted with permission [14]. Copyright 2019, ACS.
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3.4 Conclusion

We utilized bioinspired principles of symmetric and segmented arrangements of high-swelling and low-swelling gels in tubular geometries to achieve uniaxial elongation, radial expansion, bending, and gripping. The use of symmetry and segments combined with numerical modeling enables rational design of shape-changing primitives and their combinations to produce significantly complex motions of practical importance. We designed a dual-function tube capable of simultaneous elongation and gripping inspired by coral polyp; this polyp inspired tube can reach into a tank and grab an object (Snapshots are shown in Fig. 3.15). We incorporated advanced multi-material integration in the direct ink writing process to achieve interweaving of active and passive materials with a 3D structure and with a high spatial resolution of approximately 400 microns. Additive manufacturing with multi-material integration permits direct printing of the assembly of shape-changing primitives and potentially of functional grading. It is conceivable that this approach could be extended to the 4D printing of more complicated assemblies, including those with soft and rigid segments [3] or those with multiple temperature responsive gels [150] to enable sequential motions for more complicated tasks. For example, shape-changing tubular constructs which elongate, bend or increase in size are important for pediatric tissue and vascular implants to accommodate and adjust to the effects of growth of the surrounding tissues [151, 152]. Alternatively, tubes that elongate and grip are important for soft-robotic endoscopic
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applications [153]. Coupling our methodology with materials that respond to alternative and/or additional stimuli such as biochemicals [119], light [77], or magnetic fields [154] would further enhance programmability and complexity, and facilitate realization of multistage, goal-oriented control of broad relevance to soft-robotics and biomedical engineering.
Chapter 4

Periodic Buckling of Soft 3D Printed Bioinspired Tubes

Buckled surfaces induced by mismatched swelling and elastic properties of materials are commonly observed in nature, such as on cacti and euphorbias. The rational design and mimicry of such buckling surfaces could lead to the development of smart, adaptive, and stimuli responsive devices. We designed a 4D printed tubular structure, composed of soft swellable poly N-isopropylacrylamide (pNIPAM) segments and stiff non-swellable poly acrylamide (pAAM) segments. Similar to the shape change of Saguaro stems after rainfall, the tubes show tunable periodic buckling modes in water at the room temperature. The buckling behavior was harnessed through the development of compressive stresses in the soft swellable segments induced by the constraint of the stiff non-swellable segments. We developed a finite element model
to explore the design space of this periodic buckling behavior for the tube, and used a chemo-mechanically coupled constitutive model to describe the swellable hydrogel. Inspired by the classic bar buckling problem, we constructed a phase diagram and discovered a universal design parameter that combines the effects of geometric and material properties to guide the design of periodic buckling tubes for bioinspired functional gel structures.


4.1 Introduction

Cacti and euphorbias are two families of plants that grow in the arid desert environments of North America and Africa, respectively. To survive the harsh arid conditions, many of these plants have evolved stems with longitudinal ribs that can shrink and expand like an accordion. The ribs contract during periods of dry hot weather, which shades large areas of the plant and reduces water loss [155, 156]. The ribs also serve to increase the mechanical stability of the plants during rapid expansion. The plants

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imibe a large volume of water after a heavy rain fall, which increases the weight and compressive loading on the stems. The expanding ribs allow the large volume increase to be accommodated through a large expansion of the cross-sectional area rather than elongation. This decreases the slenderness ratio of the stems and increases the stability against buckling [157]. As cacti grow, the stems become taller and more slender [157], and develop more longitudinal ribs. Saguaro cacti usually have 6-20 ribs and the number of ribs is proportional to the height of the stem to provide mechanical support and improve the stability of the plants [158].

Inspired by the anisotropic periodic swelling of the ribbed stems, we designed 4D printed hydrogel tubes with alternating vertical segments of a thermoresponsive swelling poly N-isopropylacrylamide (pNIPAM) gel, representing the longitudinal ribs, and a passive polyacrylamide (pAAM) gel [14]. The thermoresponsive pNIPAM experiences a lower critical solution temperature (LCST) transition that causes it to transform from a hydrophilic to hydrophobic material when heated above the LCST and deswell [144]. The transformation is reversed by cooling to below the LCST allowing the material to swell. We found that the swelling of the vertical pNIPAM segments constrained on both sides by the nonswelling gel segments caused the tube to buckle and develop periodic circumferential folds. The axisymmetric buckling mode allows the tube to accommodate the large volume increase by area expansion with little axial elongation, in a manner similar to the longitudinal ribs in the stem of cacti and euphorbia plants. The circumferential folds can also be found on cacti with long...
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Figure 4.1: A ribbed and buckled Saguaro stem in Arizona; reprinted with permission from Dave McShaffrey, Marietta College.

columnar stems, such as the saguaro (Fig. 4.1), and may have developed from the axisymmetric buckling of the stems after a large water uptake.

The aim of this work was to investigate the axisymmetric periodic buckling of 4D printed hydrogel tubes with alternating vertical segments of soft swelling and stiff non-swelling hydrogels using a combined theoretical and computational approach. The role of mechanics in the pattern formation and function of plants is widely accepted [159] and many investigators have applied beam, plate, and shell buckling theories to explain the shape and surface patterns on plant structures. Liu et al. [102] applied a chemo-mechanical model for the coupled swelling and elastic deformation of hydrogels in finite element simulations to show how the growth and drying of a thin surface layer on a thick substrate can induce the buckling formation of regularly spaced lon-
CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES

gitudinal ridges and wrinkle patterns found in a wide array of squashes, bitter gourd and fruits. Chen et al. [160, 161] established a quantitative mechanics framework for stress-driven buckling of spheroidal thin film/substrate system to explore the morphologies of biological systems and the possibilities of manipulating the undulations. Shipman et al. and Steele et al. [107, 162–165] used the energy-minimizing buckling patterns of a compressed shell on an elastic foundation to study the formation of phyllotaxis, the patterns seen in plants shoots and flowers. Amar et al. [166, 167] adopted Föppl-von Kármán theory to investigate the growth-induced morphogenesis of plants. Mahadevan et al. [110, 112, 113] used a combination of mathematical model, stability analysis and numerical simulation to examine a variety of plant growth processes, including the snap buckling of Venus flytrap, the deformation of long leaf, and the origin of tendril coiling. Yang et al. [168] studied a soft shell sliding on a rigid cylinder and revealed the smooth-wrinkle-ridge-sagging pattern transitions of rolling up a sleeve. Holmes et al. [169] investigated the periodic buckling patterns of elastic shells when subjected to different geometric confinement and found a geometric parameter to predict the number of lobes formed. In this study, we applied finite element analysis that used a chemo-mechanical model for hydrogels, to evaluate the effect of geometry and material properties of the swelling and non-swelling vertical segments on the periodic buckling mode. We next analyzed the buckling of a bar on an elastic foundation to develop a design parameter for the buckling mode of the tube. The design parameter combines the effects of geometry of the tube and material proper-
ties of segments to predict the periodic buckling modes and the associated number of buckles. We applied the design parameter to construct a phase diagram to guide the design and application of the anisotropic swelling properties of periodic buckling of the hydrogel tubes. We observed good agreement between simulations and experiments and uncovered a buckling parameter that can be used to predict the number of buckles. Our studies provide a framework for rational design of tubular mechanical structures of relevance to biomedical implants and soft robotics [170].

4.2 Method

4.2.1 Material synthesis and 4D printing

The self-morphing accordion structures were fabricated using 4D printing process described in detail in a prior publication [14] (Fig. 4.2). First, active NIPAM ink and passive AAM ink with shear-thinning properties were prepared by mixing shear-thinning agent (Laponite nanoclay), photo-initiator, chemical crosslinker, corresponding monomers and fluorescent dyes using magnetic stirring followed by planetary mixing (Mazerustar KK-250S, Kurabo Industry). The inks were transferred to UV-shielded cartridges and centrifuged to remove air bubbles. The inks were kept at room temperature for at least 24 hrs to allow thorough hydration needed for the desired shear thinning properties. The cartridges were attached to the dual-nozzle Direct Ink Writing 3D Printer (Inkredible+ 3D Bioprinter, Cellink) and connected to an air
pump pressure control. Printing nozzles 22G (diameter 0.41 mm) were used to ensure smooth and clog-free printing. The computer-aided-design (CAD) and STL files were created in SolidWorks (Dassault Systèmes), and the G-code files were generated using an independent software project Slic3r (http://slic3r.org/) with layer height 0.4 mm and printing speed 10 mm/s to control the movement of printing nozzles. Before printing, the two printing nozzles were carefully calibrated in $x$, $y$, and $z$ directions to ensure seamless switching of two materials. This is essential for printing tall 3D structures because small recurring misalignments over 50-100 printing layers result in significant defects in the final structure. The structures were printed on silicon wafers at room temperature in air at a speed of 10 mm/s. The pressures used for printing the active and passive inks were 90-100 kPa and 110-130 kPa, respectively. After printing, the tubular pregel structures were crosslinked by photocuring using a rotating platform (9.6 rpm) and an Omnicure UV source (LX500, Lumen Dynamics) to enable uniform exposure of UV light and crosslinking. Two UV LED heads (365 nm wavelength) were used to cure the tubular structures with intensity of 0.4 W/cm$^2$. The tubular structures were photocured section by section and exposure time of nine minutes on each section.

For the actuation experiments, the photocured tubular structures were immersed in deionized (DI) water at room temperature. The structures were allowed to swell for at least 24 hrs to reach a swollen equilibrium state. All optical images were taken in a dark room with a digital camera (EOS 70D, Canon) and a broad spectrum

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**CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES**

**Figure 4.2:** Schematic of materials synthesis and 4D printing process for the dual-gel accordion structure.

UV light source (EF-160C, Spectronics) to excite the fluorescent dyes in the inks. The photographs of the photocured tubes were taken in the air and those of the transformed structures were taken in DI water.

### 4.2.2 Finite element model

#### 4.2.2.1 Finite element geometry

The finite element geometry was developed using the dimensions measured from the tubes after photocuring (Fig. 4.3). The baseline model was a $L = 20$ mm long tube composed of alternating vertical active segments of width of $W_a = 5.2$ mm and passive segments of width of $W_p = 5.2$ mm. The inner and outer radii of the tube...
CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES

**Figure 4.3:** Finite element geometry of the baseline accordion structure with inner radius $A$, outer radius $B$, height $L$, active strip width $W_a$, and passive strip width $W_p$. Red represents the active pNIPAM hydrogel and green represents the passive pAAM hydrogel. were $A=9.1$ mm and $B=10$ mm, respectively. The mesh was discretized using trilinear hexahedral brick elements of height 0.6 mm, width 0.7 mm and thickness 0.18 mm. The following boundary conditions were applied on three points located on the outer rim of the tube’s top and bottom surfaces to prevent rigid body motion: $u_x = u_y = u_z = 0$ at $x = B, y = 0, z = 0$ ($P_1$); $u_x = u_y = 0$ at $x = B, y = 0, z = L$ ($P_2$), and $u_y = 0$ at $x = -B, y = 0, z = L$ ($P_3$).

4.2.2.2 Material model

The material behavior of the pAAM segments was described by a quasi-incompressible Neo-Hookean model (Eq. (4.2.1)). The shear modulus of the pAAM gel, $G = 11.9$ kPa, was measured using a dynamic mechanical analyzer (DMA Q800, TA instru-
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Samples with a shape of a square disk were 3D printed using the process described in the previous section. We ensured that the samples reached equilibrium swelling by immersing them in DI water at the room temperature for at least 24 hrs. The samples were then measured at room temperature in air by uniaxial compression tests to a 2% applied strain. Stress-strain curves were generated from the raw static force and displacement data. The elastic modulus $E$ was calculated as the tangent to the linear fit of stress-strain data, and the shear modulus $G$ was calculated as $\frac{1}{3}E$ assuming mechanical incompressibility. The bulk modulus $K$ of the pAAM gel was set to 1000 times of the shear modulus to achieve the nearly incompressible response, which is a commonly used assumption for modeling polymeric hydrogel materials.

Equilibrium swelling tests of printed pAAM hydrogel tubes in DI water at different temperatures confirmed that the pAAM does not swell in response to a temperature change, which validates the choice of the hyperelastic Neo-Hookean model for pAAM.

The behavior of the pNIPAM segments was described by a coupled chemo-mechanical model developed previously for the thermoresponsive behavior of hydrogels and described in detail in [3, 57, 68]. The model can accurately predict the equilibrium configuration of pNIPAM gels and composite structures in response to different temperature and mechanical stimuli. The limitation of the model is that we neglected the kinetics of diffusion and could not capture the process of shape change at a given temperature. Briefly, the free energy of the hydrogel $\Psi = \Psi_e(F, \phi) + \Psi_m(\phi)$ was assumed to be composed additively of a mechanical part $\Psi_e$ for the stretching of polymer net-
work and a chemical part $\Psi_m$ for the mixing of the polymer network and solvent, where $F$ is the deformation gradient tensor and $\phi$ is the polymer volume fraction of the hydrogel at the final deformed swollen state. We used a quasi-incompressible Neo-Hookean model to describe the strain energy density of the polymer network,

$$\Psi_e(F, \phi) = \frac{G}{2} [\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \ln(\lambda_1 \lambda_2 \lambda_3)] + \frac{K}{4} [(\phi \lambda_1 \lambda_2 \lambda_3)^2 - 2 \ln(\phi \lambda_1 \lambda_2 \lambda_3) - 1]$$

(4.2.1)

where $G$ and $K$ are the shear modulus and bulk modulus of the polymer network, and $\lambda_1$, $\lambda_2$, and $\lambda_3$ are the principal stretches of the deformation gradient tensor. The bulk modulus was assumed to be 1000 times of the shear modulus to achieve near mechanical incompressibility ($J_e = \phi \lambda_1 \lambda_2 \lambda_3 \approx 1$).

The Flory-Huggins model was used to describe the free energy density of mixing [121],

$$\Psi_m(\phi) = \frac{RT}{v_\phi} [(1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi)]$$

(4.2.2)

where $R$ is the gas constant, $T$ is the temperature, $v$ is the volume per solute molecule, and $\chi$ is the Flory-Huggins interaction parameter. To model the thermoresponsive swelling of hydrogel, we assumed that the Flory-Huggins parameter depended on the temperature as follows [93],

$$\chi = \frac{1}{2} (\chi_L + \chi_H) + \frac{1}{2} (\chi_H - \chi_L) \tanh \left( \frac{T - T_{\text{tran}}}{\Delta T} \right)$$

(4.2.3)

where $\chi_L$ and $\chi_H$ are the Flory-Huggins parameters at low and high temperatures, $T_{\text{tran}}$ is the LCST temperature, and $\Delta T$ is the width of temperature transition region.
CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES

From the free energy density of the hydrogel, the Cauchy stress tensor of the hydrogel $\sigma$ can be calculated from hyperelasticity theory, and the chemical potential of the hydrogel $\mu$ can be derived from the thermodynamics argument,

$$\sigma = \frac{1}{\det(F)} \frac{\partial \Psi}{\partial F} F^T$$

$$\mu = \frac{\partial \Psi}{\partial c}$$

where $c$ is the number of solute molecules per polymer volume in the final deformed swollen state, and is related to $\phi$ through $\phi = \frac{1}{1+vc}$. The constitutive model was implemented in Tahoe (Sandia National Laboratories) for the finite element simulations of the hydrogel tubular structures.

To determine the model parameters for the pNIPAM gel, we applied standard dynamic mechanical analysis tests (DMA Q800, TA instruments) to measure the shear modulus $G$ of 3D printed gel samples. Square disk shaped pNIPAM gel samples were 3D printed and allowed to swell in DI water at the room temperature for 24 hrs. Uniaxial compression tests were conducted on the printed gel samples in the same manner as described above for the pAAM gel samples. The Flory-Huggins interaction parameters $\chi_L$, $\chi_H$, $T_{tran}$, and $\Delta T$ were obtained by fitting the results of the equilibrium swelling tests of the printed gels at different temperatures (between $25^\circ$C and $50^\circ$C). For the equilibrium swelling tests, circular tubes of pNIPAM gel were 3D printed and photocured. The photos of the printed pNIPAM tubes were taken in a dark room using a digital camera (EOS 70D, Canon) and a broad spectrum UV light source (EF-160C, Spectronics) after photocuring and after immersed in DI
water at the test temperature for 24 hours. The diameters of the printed pNIPAM tubes were measured manually using ImageJ software, and the volumetric swelling ratios of the pNIPAM gel at each test temperature compared with the photocured state were calculated. A small volumetric swelling ratio of 0.94 was obtained at the highest temperature 50°C. The equilibrium volumetric swelling ratio increased to 1.33, 2.05, and 2.6 as the temperature was decreased to 41°C, 33°C and 25°C, respectively [14]. The material model parameters for the printed pNIPAM and pAAM gels are summarized in Table 4.1.

The simulation was started from the high temperature $T = 50°C$ to approximate the un-swollen photocured state. The initial polymer volume fraction $\phi_0$ at this reference state was determined by solving the mechanical and chemical equilibrium equations (4.2.4)-(4.2.5). The swelling induced shape-change was simulated by linearly decreasing the temperature from 50°C to the room temperature 25°C and solving the mechanical and chemical equilibration equations at each step.

<table>
<thead>
<tr>
<th></th>
<th>$G$(kPa)</th>
<th>$\chi_L$</th>
<th>$\chi_H$</th>
<th>$T_{\text{tran}}$(°C)</th>
<th>$\Delta T$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D Printed pNIPAM</td>
<td>2.32</td>
<td>0.5</td>
<td>0.9</td>
<td>34</td>
<td>4</td>
</tr>
<tr>
<td>3D Printed pAAM</td>
<td>11.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1: The constitutive model parameters for 3D Printed pNIPAM and pAAM hydrogels
Chapter 4. Periodic Buckling of Soft 3D Printed Bioinspired Tubes

4.2.2.3 Parameter Study

A parameter study was performed to investigate the effects of material properties and geometrical factors on the periodic buckling mode of the 4D printed hydrogel tubes. The five geometrical properties of the tube structure $A$, $B$, $L$, $W_p$, and $W_a$ were combined into four dimensionless structural parameters: $\frac{B}{L}$, which describes the slenderness ratio, the diameter ratio $\frac{B}{A}$, the segment width ratio $\frac{W_p}{W_a}$, and $\frac{B}{W_p+W_a}$, which describes the number of alternating passive and active segments. The material behavior is described by two additional dimensionless parameters, the ratio of the Young’s moduli of the passive and active segments $\frac{E_p}{E_a}$ and the volumetric swelling ratio $\Delta \theta$ of the pNIPAM hydrogel.

The six dimensionless parameters in the study were varied one-by-one over a wide range to evaluate the individual effect of the geometric and material factors (Table 4.2). The baseline values $\frac{E_p}{E_a} = 5$ and $\Delta \theta = 2.6$ were obtained from the experimental measurements as described in the prior section. Specifically, the ratio of $\frac{B}{L}$ (Table 4.2(a)), was varied by varying $L$ to keep all other parameters constant. The diameter ratio and modulus ratio were changed by varying the parameter $A$ and $E_p$ respectively to keep all other parameters unchanged. The segment width ratio was varied by changing $W_p$ and setting $W_a = \frac{2\pi B}{n} - W_p$, where $n = 6$ is the number of segments, to maintain all other parameters constant. The $\frac{B}{W_p+W_a} = \frac{n}{2\pi}$ was varied by changing the number of alternating passive and active segments from $n = 6$ to $n = 15$, while all other parameters were kept unchanged. The number of alternating segments were
CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES

chosen based on the number of ribs on saguaro cacti (6 - 20) [158].

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</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.2 - 1</td>
<td>1.1</td>
<td>1</td>
<td>$\frac{6}{2\pi}$</td>
<td>5</td>
</tr>
<tr>
<td>(b)</td>
<td>0.5</td>
<td>1.04 - 1.5</td>
<td>1</td>
<td>$\frac{6}{2\pi}$</td>
<td>5</td>
</tr>
<tr>
<td>(c)</td>
<td>1</td>
<td>1.1</td>
<td>0.25 - 5</td>
<td>$\frac{6}{2\pi}$</td>
<td>5</td>
</tr>
<tr>
<td>(d)</td>
<td>0.5</td>
<td>1.1</td>
<td>1</td>
<td>$\frac{6}{2\pi} - \frac{15}{2\pi}$</td>
<td>5</td>
</tr>
<tr>
<td>(e)</td>
<td>0.5</td>
<td>1.1</td>
<td>1</td>
<td>$\frac{6}{2\pi}$</td>
<td>5 - 250</td>
</tr>
<tr>
<td>(f)</td>
<td>0.5</td>
<td>1.1</td>
<td>1</td>
<td>$\frac{6}{2\pi}$</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.2: The simulation design parameters for the parameter study

4.2.3 Buckling of bar sitting on an elastic foundation

Swelling of the pNIPAMs strips against the constraints of the adjacent elastic passive strips causes compressive stresses to develop in the swelling strips that are released by the buckling of the strip into a sinusoidal shape. The constrained swelling of a pNIPAM strip can be approximated as a beam supported by equally spaced elastic supports, subjected to a compressive load in the axial direction (Fig. 4.4). Timoshenko and Gere [171] provide a detailed theoretical analysis for the buckling of this structure.

The concentrated axial force of the beam on the elastic foundation is given by:

$$F = \frac{\pi^2 EI}{l^2} \left( m^2 + \frac{\beta l^4}{m^2 \pi^4 EI} \right)$$

(4.2.6)
where $E$, $I$, and $l$ represent the Young’s modulus, second moment of inertia, and length of the bar, $\beta$ is the Young’s modulus of the elastic foundation, and $m$ is the number of half sine waves of the buckling mode. The number of half sine waves ($m$) is calculated by minimizing the critical load $F$ in Eq. (4.2.6) with respect to $m$. Thus the number of half sine waves at buckling of the bar depends on the geometry dimension of the bar, and the elastic moduli of the bar and the foundation. Considering the special case when $\beta = 0$, there is no elastic foundation and minimizing Eq. (4.2.6) gives $m = 1$. For flexible foundation ($\beta$ is very small), $m$ is constant at 1 meaning that the bar buckles without an intermediate inflection point. By gradually increasing the elastic modulus of the foundation $\beta$, we can reach a situation where $m = 3$ gives

**Figure 4.4:** Schematic of buckling of a bar on an elastic foundation.
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a smaller $F$ than $m = 1$. Setting $F$ to be at the same at $m$ and $m + 2$ gives the following buckling coefficient of the bar, which signifies the ratio of the structural stiffness of the foundation and bar, at the transition between two buckling modes,

$$\omega_{bar} = \frac{\beta l^4}{\pi^4 EI} = m^2(m + 2)^2 \quad (4.2.7)$$

Equation (4.2.7) can be used to determine the buckling mode, characterized by $m$, for given a dimension of the bar and elastic moduli of the bar and the foundation. For values of $\omega_{bar}$ smaller than $m^2(m + 2)^2$, the deflection curve of the buckled bar has $m$ half sine waves; for $\omega_{bar}$ larger than $m^2(m + 2)^2$, the bar will be buckled into $m + 2$ half sine waves (Table 4.3).

<table>
<thead>
<tr>
<th>Buckling coefficient, $\omega_{bar}$</th>
<th>Number of half sine waves at buckling, $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{bar} \leq 9$</td>
<td>$m = 1$</td>
</tr>
<tr>
<td>$9 &lt; \omega_{bar} \leq 225$</td>
<td>$m = 3$</td>
</tr>
<tr>
<td>$225 &lt; \omega_{bar} \leq 1225$</td>
<td>$m = 5$</td>
</tr>
<tr>
<td>$1225 &lt; \omega_{bar} \leq 3969$</td>
<td>$m = 7$</td>
</tr>
<tr>
<td>$3969 &lt; \omega_{bar} \leq 9801$</td>
<td>$m = 9$</td>
</tr>
</tbody>
</table>

**Table 4.3:** The buckling coefficient and number of half sine waves for a bar on elastic foundation.

For the vertical segments in the tube of length $L$, width $w = \frac{\pi B}{6}$ and thickness $h = B - A$, $E = E_a$ and $\beta = E_p$, the second moment of area can be approximated as $I = \frac{1}{12} wh^3 = \frac{\pi B}{72}(B - A)^3$ by neglecting the curvature of the segments. Then the
buckling coefficient in Eq. (4.2.7) can be expressed as,

$$\omega_{\text{tube}} = C \frac{72E_p L^4}{\pi^5 E_a B (B - A)^3}$$  \hfill (4.2.8)

where $C$ is a constant that accounts for the effects of finite deformation and of geometrical features not considered in the theoretical beam model. For example, the active segments in the tube were supported by adjacent elastic passive strips, while in the original theory the bar was sitting on the elastic foundation.

### 4.3 Results and discussions

We first simulated the equilibrium buckling deformation of the baseline 4D-printed tube observed in experiments (Fig. 4.5a). The swelling tests subjected the printed tube immersed in DI water to stepwise temperature changes from 50°C to 25°C. The temperature was held constant for 24 hrs to achieve the equilibrium swelling shape. In the simulations, the temperature was decreased continuously from 50°C to 25°C, and the equilibrium shape was evaluated at each temperature by solving Eq. (4.2.4)-(4.2.5) for mechanical and chemical equilibrium. The constrained swelling of pNIPAM strips during cooling caused compressive axial stresses to build up in the pNIPAM strips (Fig. 4.5b) until periodic buckling of mode $m = 3$ was initiated at 36°C. Buckling allowed the compressive axial stresses to be relieved by the lateral deflection of the strip into a full sine wave characteristic of mode 3 buckling. The amplitude of the buckling mode increased with decreasing temperature, which results
CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES

**Figure 4.5:** (a) Experimental pictures of the actuation tests of the printed baseline accordion structure. $2B_{\text{initial}}$ and $2B_{\text{swollen}}$ represent the outer diameter of the tube in the initial unswollen state and swollen state at 25°C, respectively. Scale bar indicates 1 cm. (b) Contour plots of the axial stress ($\sigma_{zz}$) developed in the active segments until the initiation of buckling at 36°C for the simulated baseline accordion model. (c) Contour plot of the pNIPAM volumetric swelling ratio $\theta$ for the simulated equilibrium shape at 25°C.

in an increase in the maximum diameter of the swollen tube by 53% at 25°C (Fig. 4.5c), which agreed quantitatively with experimental measurements of the diameter ratio $\frac{B_{\text{swollen}}}{B_{\text{initial}}}$ in the equilibrium swelling tests (Fig. 4.5a).

We next investigated the effect of the material and geometric factors on the buckling mode of the 4D-printed tube. Decreasing $\frac{B}{L}$ from 1 to 0.2 caused the tubes to become more slender and more susceptible to higher buckling modes. The number
of half sine waves predicted by the finite element simulations increased from 1 to 9 (Fig. 4.6a). Decreasing $B/A$ reduced the thickness of the tube, which decreased flexural stiffness and caused the tubes to experience higher buckling modes (Fig. 4.6b). Varying the ratio of the segment widths $W_p/W_a$ from 0.25 to 5 changed the amplitude of the buckling mode but did not induce a higher bucking mode (Fig. 4.6c). We calculated the axial force $f$ on the passive segments exerted by the active segments, by integrating the normal axial stress $\sigma_{zz}$ on the $z = L/2$ plane surface of the passive segments at $25^\circ$C. The axial load on the passive segments was defined by dividing $f$ with passive segment width $W_p$. When the segment width ratio $W_p/W_a$ increased from 0.25 to 5, the axial load $f/W_p$ decreased by 81%, and the narrow pNIPAM strips could not exert enough force to buckle the whole tube structure. As a result, the diameter change from the unswollen to the swollen buckled state decreased by 71%. Increasing the number of alternating segments $B/(W_p+W_a)$ did not affect the buckling mode, but increased the swelling ratio of active segments needed to initiate buckling. From finite element simulations, we found that for tubes with $n = 6, 9, 12, 15$ alternating active and passive segments, the volumetric swelling ratio $\Delta \theta$ needed for the initiation of buckling were 1.9, 2.9, 6.1, and 10.9 respectively.

Increasing the modulus ratio $E_p/E_a$ had a similar effect to decreasing the slenderness ratio and diameter ratio. Increasing the modulus of the passive pAAM strips produced a higher compressive loading on the pNIPAM strips resulting in higher buckling mode with a larger number of half sine waves at buckling (Fig. 4.6d). The elastic
Figure 4.6: The effects of dimensionless material and geometric parameters on the periodic buckling modes: (a) slenderness ratio $B/L$ (pink), (b) diameter ratio $B/A$ (maroon), (c) segment width ratio $W_p/W_a$ (purple), and (d) modulus ratio $E_p/E_a$ (grey). The parameters were varied one by one in the parameter study. Contour plots of the volumetric swelling ratio $\theta$ of the hydrogel in the swollen configuration at 25°C are included in the inset.
modulus of the hydrogel layers can be made larger through higher shear-thinning agent concentration, higher polymer concentration, or higher crosslinking density. As expected, varying the swelling ratio \( \Delta \theta \) of pNIPAM had the same effect as varying the temperature. Increasing \( \Delta \theta \) from 2.6 to 24 caused the diameter swelling ratio to increase by 78\%, but did not affect the buckling mode.

The finite element modeling study showed that the number of half sine waves of the buckled tube can be tuned by varying \( \frac{B}{L} \), \( \frac{B}{A} \), and \( \frac{E_p}{E_a} \). Changing the segment width ratio \( \frac{W_p}{W_a} \), number of segments \( \frac{B}{W_p+W_a} \), and volumetric swelling ratio \( \Delta \theta \) did not alter the buckling mode. The fitting parameter \( C = \frac{4}{350} \) of the critical buckling coefficient for the tubes in Eq. (4.2.8) was determined to satisfy \( \omega_{\text{tube}} = m^2(m+2)^2 \) for the cases of the parameter study (Fig. 4.7). The resulting \( \omega_{\text{tube}} = \frac{72 E_p L^4}{350 m^2 E_a B (B-A)^3} \) provides a design parameter for the periodic folding of the composite tube that combines the effects of geometry and material properties of the active and passive segments.

The modeling outcomes were validated by 3D printing three selected cases from the parameter study and performing the swelling experiments in DI water at the room temperature (Fig. 4.8). The three cases were: \( \frac{B}{L} = 0.5, \frac{B}{A} = 1.04, \) and \( \frac{E_p}{E_a} = 5 \) (Fig. 4.8a); \( \frac{B}{L} = 0.33, \frac{B}{A} = 1.1, \) and \( \frac{E_p}{E_a} = 5 \) (Fig. 4.8b); and \( \frac{B}{L} = 0.25, \frac{B}{A} = 1.1, \) and \( \frac{E_p}{E_a} = 5 \) (Fig. 4.8c). The printed tubes were immersed in DI water for 24 hours and the deformed configuration showed the same buckling mode with the same number \( m \) of half sine waves as predicted by the FEA simulations and the critical buckling coefficient \( \omega_{\text{tube}} \). The experiment was repeated 2-3 times for each case with the same
Figure 4.7: Phase diagram for the periodic buckling modes of tubes with different structural geometries and material properties. Pink, maroon, and grey dots represent the simulation results in the parameter study when varying the slenderness ratio $\frac{B}{L}$, diameter ratio $\frac{B}{A}$, and modulus ratio $\frac{E_p}{E_a}$ one at a time. The transitions between the buckling mode (−) occurs at $\omega_{tube} = m^2(m + 2)^2$. 

Buckling coefficient, $\omega_{tube} = \frac{72E_p L^4}{350 \pi^5 E_a B (B - A)^3}$
result.

4.4 Conclusions

We designed stimuli responsive periodic buckling tubes composed of alternating soft active segments and stiff passive segments. We investigated the buckling modes of the tube using a combination of theoretical and finite element modeling and verified the buckling modes with 4D printing experiments. The model included six dimensionless design parameters that describe the geometry and material properties of the active and passive segments. From the simulations, we observed that the number of half sine waves at buckling varied with three design parameters individually: slenderness ratio $B/L$, diameter ratio $B/A$, and modulus ratio $E_p/E_a$. The other three design parameters, segment width ratio $W_p/W_a$, number of alternating segments $B/(W_p + W_a)$, and volumetric swelling ratio $\Delta \theta$, did not affect the buckling modes. Approximating the buckled segment as the buckling of a bar on an elastic foundation, we developed a universal design parameter, $\omega_{tube}$, that combines the effects of geometry dimensions, modulus and swelling ratio, and constructed a phase diagram of the periodic buckling modes of the tubes, that were validated by experiments. The design parameter provides an efficient rule for the design of self-morphing tubes that can expand radially with negligible axial elongation that have potential applications to deployable and morphing biomedical implantable devices and actuators for soft robotics. The combined theoretical and computational approach represents a powerful framework to develop analytical design
CHAPTER 4. PERIODIC BUCKLING OF SOFT 3D PRINTED BIOINSPIRED TUBES

Figure 4.8: Images from the photocured and the actuated tubes exhibiting different periodic buckling modes along with simulation snapshots. Tubes with different design parameters were printed: (a) $\frac{B}{L} = 0.5$, $\frac{B}{A} = 1.04$, and $\frac{E_p}{E_a} = 5$; (b) $\frac{B}{L} = 0.33$, $\frac{B}{A} = 1.1$, and $\frac{E_p}{E_a} = 5$; and (c) $\frac{B}{L} = 0.25$, $\frac{B}{A} = 1.1$, and $\frac{E_p}{E_a} = 5$. In the experimental pictures, the active pNIPAM and passive pAAM hydrogels show fluorescent orange and green colors, and the scale bar indicates 1 cm. In the simulation snapshots, the contour plots of the volumetric swelling ratio of the hydrogel are shown for the deformed equilibrium configuration at 25°C.
parameters for tailoring buckling instabilities of active hydrogel structures.
Chapter 5

Conclusions and future work

Programmable shape changing of stimuli-responsive hydrogels has potentially a wide range of applications, including drug delivery [25–31], soft robotics [32–37], and biomedical devices [4, 38, 39]. In this work, we aimed to achieve complex stimuli-responsive shape changes that are of key importance to robotics and biomedical engineering. The current challenges of advancing stimuli-responsive devices into real-life applications lie in both the design and fabrication stage. In the design perspective, several coupled diffusion-deformation models have been developed recently for describing the material behavior of hydrogels. However, the level of complexity involved for implementing the constitutive model in FEA limited their application when guiding the device design. The majority of the modeling work did not show quantitative experimental verifications. Simple mechanics-based design rules are needed to guide the community when designing stimuli-responsive devices with more complex shape
CHAPTER 5. CONCLUSIONS AND FUTURE WORK

changes and functionalities. In the fabrication perspective, traditional fabrication methods for programmable shape changing structures such as 2D lithography limits the number of achievable 3D geometries, restraining the application of these materials. Even with the recent developments in 4D printing, the majority of this field manufacture 2D shapes that fold into 3D structures, with a few exceptions in simple 3D-to-3D shape changes. Advanced 3D shape changes is important for achieving gel devices for real-life applications.

The unique contribution of this work is that we developed a hybrid modeling design methodology combining computational analysis and theory-based design rules, which was also experimentally validated. We first used FEA to explore the shape change of different patterns of hydrogels with different moduli and swelling capabilities. Once a pattern has been identified to produce the desired shape change and function, parameter study was conducted to explore the design space and investigate the effects of key design parameters on the structure response. In order to help the design of future devices, we used theoretical analysis to develop analytic design rules that combines the effects of geometry and material properties to tailor the shape change. These simple design rules are efficient to implement for designing stimuli-responsive hydrogel structures and devices. We also experimentally validated the design rules by fabricating the structures and quantitively measuring the shape change to compare to design predictions. The 3D shape changing designs were validated with a custom-made 4D printing platform capable of printing tall 3D devices
CHAPTER 5. CONCLUSIONS AND FUTURE WORK

with complicated geometries and segment arrangements. Our methodology provides a powerful framework to design and fabricate stimuli-responsive functional devices for biomedical implants and soft robotics.

5.1 Summary of this work

In Chapter 2, we investigated the shape changing behavior of DNA hydrogel bilayers by finite element models. In order to estimate the elastic modulus of DNA hydrogel that cannot be measured by traditional experimental approach, we used finite element analysis to study the curving of DNA/BIS gel bilayer beams. By comparing the finite element simulations to the experiment result, the DNA gel shear modulus was estimated to be 229 Pa. Then we applied the finite element model to conduct a parameter study on the influence of bilayer geometric and material properties on the equilibrium curvature. Inspired by the modified Stoney formula for the curving of film/substrate system, a simple design rule was developed for predicting the equilibrium curvature of bilayer beams with different dimensions and material properties. This simple design rule provides a powerful method for predicting the bilayer curvature for gel layers of similar thicknesses and designing chemo-mechanical devices that require no batteries and can easily be integrated with other devices.

In Chapter 3, we utilized bioinspired principles of symmetric and segmented arrangements of high-swelling and low-swelling gels in tubular geometries to achieve uniaxial elongation, radial expansion, bending, and gripping. The use of symmetry
and segments combined with numerical modeling enables rational design of shape-changing primitives and their combinations to produce complex motions of practical importance. We incorporated advanced multi-material integration in the direct ink writing process to achieve interweaving of active and passive materials with a 3D structure and with a high spatial resolution of approximately 400 microns. Depending on the shape and orientation of the segments (i.e., vertical or horizontal), tubes with different primitive shape changes have been achieved. Additive manufacturing with multi-material integration permits direct printing of the assembly of shape-changing primitives and potentially of functional grading. It is conceivable that this approach could be extended to the 4D printing of more complicated assemblies, including those with soft and rigid segments or those with multiple temperature responsive gels to enable sequential motions for more complicated tasks. Coupling our methodology with materials that respond to alternative and/or additional stimuli such as biochemicals, light, or magnetic fields would further enhance programmability and complexity, and facilitate realization of multistage, goal-oriented control of broad relevance to soft-robotics and biomedical engineering.

In Chapter 4, we designed stimuli responsive periodic buckling tubes composed of alternating soft active segments and stiff passive segments. We investigated the buckling modes of the tube using a combination of theoretical and finite element modeling and verified the buckling modes with 4D printing experiments. The model included six dimensionless design parameters that describe the geometry and material proper-
ties of the active and passive segments. From the simulations, we observed that the number of half sine waves at buckling varied with three design parameters individually: slenderness ratio $\frac{B}{L}$, diameter ratio $\frac{B}{A}$, and modulus ratio $\frac{E_p}{E_a}$. The other three design parameters, segment width ratio $\frac{W_p}{W_a}$, number of alternating segments $\frac{B}{W_p+W_a}$, and volumetric swelling ratio $\Delta \theta$, did not affect the buckling modes. Approximating the buckled segment as the buckling of a bar on an elastic foundation, we developed a universal design parameter, $\omega_{\text{tube}}$, that combines the effects of geometry dimensions, modulus and swelling ratio, and constructed a phase diagram of the periodic buckling modes of the tubes, that were validated by experiments. The design parameter provides an efficient rule for the design of self-morphing tubes that can expand radially with negligible axial elongation that have potential applications to deployable and morphing biomedical implantable devices and actuators for soft robotics.

5.2 Limitations of this work

Though our combined computational, theoretical, and experimental approach has achieved considerable success in developing smart, adaptive, and stimuli responsive devices, some limitations of this work should be acknowledged. To begin with, our constitutive model for hydrogels is an equilibrium model. The model can accurately predict the equilibrium configuration of stimuli-responsive gels and composite structures in response to different temperatures and mechanical stimuli. However, the model neglected the kinetics of diffusion and could not capture the process of shape
CHAPTER 5. CONCLUSIONS AND FUTURE WORK

change at a given temperature. There are several setbacks to this limitation. First, the time required for solvent molecules to diffuse into or out of hydrogels to achieve a desired deformation ranges from hours to days depending on the thickness of the structure. Without the kinetics of diffusion, we can only predict the device function at the end of process, but not the time needed for the device to complete the function. Such information is important for translating the stimuli-responsive hydrogel devices into real-life applications, and optimizing production variables, such as structural thickness and methods for introducing environmental stimuli, before manufacturing. Second, achieving a well-defined sequence of shape changes with multiple actuation steps can greatly improve the complexity of stimuli-responsive shape change. For example, a functional soft robot that can walk requires a set of well-choreographed movements of different parts. The addition of diffusion kinetics to the hydrogel model will allow us to design stimuli-responsive components with different thicknesses to control the actuation time and thus achieve sequential motions. This will further expand the achievable shape changes and functionalities.

The materials that we used here also have several drawbacks. First, our inks undergo isotropic swelling/deswelling under environmental stimuli, which produce isotropic material/structural response. To overcome this, we arranged different isotropic materials with varying properties in segments in order to produce overall anisotropic shape changes, such as bending, twisting and buckling. This macroscopic anisotropy requires multiple materials to be precisely arranged and patterned, increasing the
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design challenge and technical difficulties. However, the anisotropy of the materials can be directly introduced by embedding anisotropic particles such as fibers [9] or platelets [13] in the inks. This microscopic anisotropy could broaden the design space and enable more complicated shape changes. Therefore, with the same manufacturing settings, anisotropic materials could provide more tunability with more economical use of materials. Second, shear-thinning agent is an essential component for 3D printable inks. Several considerations are needed to be taken into account when choosing the appropriate shear-thinning agent, including its elastic modulus and biocompatibility. The laponite-based inks that we used in this work have a high modulus which is suitable for printing 3D tall devices, but are not biocompatible. The xanthan gum-based and gellan gum-based inks can be used for cell-related applications, but have a low elastic modulus and can only be used for printing short structures. More work is needed in developing appropriate shear-thinning agent to enable more complicated applications.

There are some technical challenges for the printing platform that we developed. First, we observed that more defects appeared in the top part of the structure, especially for structures over 20 mm (Fig. 4.8c). These defects are a result of recurring errors accumulated during each layer of printing even with the careful calibration steps that we developed. The success rate of printing also decreased significantly with increasing structure height. A more precise method of calibration is needed for reducing the printing errors and manufacturing taller devices. Second, the resolution
of direct ink writing (DIW) that we used in this work is limited by the diameter of
printing nozzle, and is usually on the order of 0.4 mm. The relatively low resolution
limits the size of devices that can be printed and their applications. Compared to
DIW, stereolithography, where UV laser beam is used to draw a pre-programmed
shape on to the surface of the photopolymerizable resin pool for fabrication of each
layer, has more potentials. The resolution is limited by the UV beam spot diameter,
which can be as high as 80 μm. The combination of stimuli-responsive hydrogels and
stereolithography will enable devices with smaller sizes and more precise functional
features.

5.3 Future directions

Future directions will focus on improving current constitutive model, enriching the
3D printable stimuli-responsive materials, and reducing the response time.

Our current equilibrium constitutive model for hydrogels can be improved by in-
corporating the kinetics of solvent diffusion. Some of the literature has modeled the
diffusion as passage of a fluid in a porous elastic solid using Darcy’s law [172]. Darcy’s
law assumes that fluid flows in the pores of the solid, and the permeability is propor-
tional to the square of the pore size. The mesh size of the polymer network changes
significantly as the gel swells, and implementing Darcy’s law for gels is a nontrivial
task [114]. More recent models with diffusion assume that self-diffusion of solvent
molecules is the dominating kinetic process in the gel [93, 114–117]. However, it also
CHAPTER 5. CONCLUSIONS AND FUTURE WORK

has certain limitations. For example, the assumption may fail when macroscopic flow or convection of solvent molecules prevails in the gel. We should not only consider the self-diffusion migration, but also include other mechanisms of migration, when incorporating the solvent diffusion in the constitutive model. This will allow us to take advantage of the diffusion to design active hydrogel structures with predictable response times, such as a soft walking robot with sequential motion of each part.

It remains a challenge in hydrogel-based systems to achieve a well-defined sequence of multiple actuation steps using materials that respond differently in time to different levels of stimuli [4, 10]. One of the approaches that addressed this challenge used selective reduction of metals to chemically control sequential folding of hinges ionoprinted with two metals [173]. This represents an important improvement, but it requires reprinting of hinges to achieve subsequent shape changes. To improve our current thermo-responsive system (pNIPAM) which has the LCST between 32°C and 36°C [16, 20–22, 68], we are developing 3D printable stimuli-responsive materials with tunable LCST. In a recent work [150], the LCST of poly-oligo (ethylene glycol) methyl ether methacrylate (pOEGMA) gels was adjusted by varying the side chain length and the extent of copolymerization. pOEGMA gels that swelled at three different temperatures were demonstrated. We are currently working on introducing shear-thinning property to the pOEGMA gels with multiple LCST to make them 3D printable for smart, adaptive devices with sequential shape changes.

Response speed represents another key challenge for stimuli-responsive hydrogels,
as actuation is typically limited by diffusion of water or ions \[4, 172, 174\]. For our 4D printed hydrogel structures, the diameter of printable gel filament is limited by the size of the printing nozzles (typically on the order of 0.4 mm). The resulting mm-thick gel structures required at least 6 hrs to reach their equilibrium shape. This low actuation speed limits the application of these materials. There are several approaches to address this challenge. First, microscopically, introducing porosity in the polymer networks can effectively reduce the response time, as demonstrated by Ionov et al. who used electrospun hydrogel fibers for fabricating superfast bilayer actuators \[175\]. Printing architectured hydrogel structures with controlled macroscopic pores will also accelerate the diffusion and increase the actuation speed \[176\]. Second, the development of stereolithography of stimuli-responsive hydrogels will allow sub-mm or even \(\mu\)m-scaled devices to be printed, as the printing precision is limited by the size of the UV beam \[177\]. The diffusion time is proportional to the square of the thickness of the structure \[114\]. Furthermore, the diffusion can be enhanced by introducing convection or macroscopic flow. The models incorporating the kinetics of diffusion can help us design stimuli-responsive hydrogel devices and engineer external environmental conditions to achieve faster response speed.
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