Creasing Instability of Hydrogels and Elastomers

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CREASING INSTABILITY OF HYDROGELS AND ELASTOMERS

A Dissertation presented
by

DAYONG CHEN

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2014

POLYMERIC SCIENCE AND ENGINEERING
ACKNOWLEDGEMENTS

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ABSTRACT

CREASING INSTABILITY OF HYDROGELS AND ELASTOMERS
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Soft polymers placed under compressive stress can undergo an elastic creasing instability in which sharp folds spontaneously form on the free surfaces. This process may play an important role in contexts as diverse as brain morphogenesis, failure of tires, and electrical breakdown of soft polymer actuators. While the creasing instability has been used for collotype printing since as early as the 1850s, the scientific appreciation of this instability has become popular only recently and our understanding of this instability is still quite limited.

In chapter 2, we describe a simple experimental system to study creasing of thin elastomer films under uniaxial compression. The equilibrium depths, spacings and shapes of creases are characterized and found to show excellent agreements with numerical results. Further, we use this system to explore the important roles played by surface energy. Creases have been found to form in a nucleation and growth fashion, with surface energy providing a barrier in both processes.

While this process may play an important role in a variety of materials failures, it can also be harnessed to fabricate dynamic chemical patterns and as a new method for
lithography. To understand the role of creasing in materials failures or to engineer it for applications, the study of hysteresis in creasing is of vital importance. In Chapter 3, we review that different degrees of hysteresis have been observed in different systems. By changing the interface energy, we for the first time show that it is the self-adhesion at the folding region rather than plastic deformation that gives rise to hysteresis. We design a soft elastic bilayer that can snap between the flat and creased states repeatedly, with hysteresis. The strains at which the creases form and disappear are highly reproducible, and are tunable over a large range, through variations in the level of pre-compression applied to the substrate and the relative thickness of the film. The introduction of bistable flat and creased states and hysteretic switching is an important step to enable applications of this type of instability.

In chapter 4, we design experiments to show that creases can also form on the interface of two soft hydrogels. In comparison with surface creases, which form self-contact, interfacial creases take on a singular non-self-contacting "V" shape. Interfacial creases form at higher strain than surface creases, but always form prior to interface wrinkles.

In chapter 5, we show how the morphology and onset of creases depend on materials properties, geometry, loading history, as well as stress states. While several results are promising, we also propose better experimental setups to facilitate future studies and better control crease morphology.

In chapter 6, we introduce an application of the creasing instability, where we utilize creased hydrogels as a dynamic platform to apply tensile strain on cells. We have demonstrated that using temperature as a stimulus, cultured muscle cells can be mechanically deformed with different strain states and amplitudes. This experiment
also, for the first time, achieves local actuation of creasing instability with pneumatic/hydraulic pressure. Creases actuated by microfluidics offer potential for realization of high-throughput cell stretching devices on single cell level, through which different strain states, amplitudes, as well as loading rate and frequency could be modulated to mimic the mechanical environment cells experience in vivo.
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5.3 Lateral swelling ratio of hydrogel disk in PBS (containing 137 mM sodium chloride) as a function of temperature.

5.4 Creasing of elastomer film under equibiaxial compression. (a) a schematic of experimental setup showing gluing a soft thin PDMS film to an inflated stiffer PDMS substrate followed by deflation to put the thin film under equibiaxial compression, (b) optical micrographs showing the nucleation and growth of randomly oriented creases.

5.5 Creasing of pre-stretched hydrogel. With a pre-stretching ratio of $\lambda_1 = 1.3$, (a) at 33.5 °C, creases start to nucleate and grow along the pre-stretching direction. At 31.8 °C (b) and 29 °C (c), more creases form to equilibrate into quasi-periodic array. (d) at 29 °C, removing pre-stretch puts the hydrogel under equibiaxial compression, leading to the long crease stripe breaking into short dots, dashes and the formation of new creases in transverse direction.

5.6 Onset point of crease formation on hydrogel surface under different stress states. (a) onset temperature of creasing as a function of pre-stretching ratio $\lambda_1$, (b) lateral swelling ratio $\lambda_0$ of free swelling gel as a function of temperature, (c) a schematic of strain analysis, (d) experimental results plotted together with 'phase diagram' of flat surface, creasing and Biot's wrinkling. The symbols indicate different stress states (*: equibiaxial compression, &: plane strain and #: uniaxial compression).

5.7 Morphology of creases depending on loading history. (a) Stretching creased hydrogel leads to creases aligning along the stretching direction. (b) Stretching a swelling hydrogel below but close to the onset point of creasing leads to crease formation along the stretching direction. (c) Further swelling a pre-stretched hydrogel leads to the formation of well aligned creases along the pre-stretching direction. Scale bar: 200 μm.

5.8 Near threshold and far from threshold crease morphology. (a) Creases are randomly oriented curved stripes just above the onset point. At higher swelling ratio, creases evolve into quasi-hexagonally arranged triads and secondary creases form in between the primary creases, yielding a hierarchical surface pattern ((b) and a zoomed in image (c)). (d) A schematic of topographic pattern guiding crease formation. (e) Just above the critical point, creases form straight stripes on top of the topographic patterns. (f) At higher swelling ratio, secondary creases form short straight stripes perpendicular to the primary creases.

6.1 (a) Macroscopically deforming elastic cell culture substrates to apply deformation to cultured cells, (b) Nano-indentation on cells with AFM tip, (c) Micropipettes aspiration experiment on cells and (d) Stretching cells with Optical tweezers.

6.2 Procedure showing photo-patterning RGD peptide sequence onto the hydrogel surface between two neighboring creases, which are directed by topographic patterns on the rigid substrate, cell seeding and gel swelling to subject cells to stretching.

6.3 left: Scheme of benzophenone end-functionalized RGD peptide, right: A photo-patterned gel surface.
6.4 (a) C2C12 mouse myoblasts cultured on a standard PS substrate as a positive control. (b) C2C12 cells adhered to and spread on uniformly RGD-coated gel surfaces, albeit at lower density than for PS. (c) A non-RGD coated gel surface used as a negative control did not promote cell attachment. (d) C2C12 mouse myoblasts cultured on hydrogels patterned with stripes of RGD with 60 μm width and 300μm pitch. (e) For C2C12 mouse myoblasts cultured on gels patterned with circles of 60 μm in diameter, cells primarily stayed confined to a single dot, (f) while for 40 μm diameter circles spaced by 60 μm, cells occasionally bridged between neighboring circles.

6.5 Cells seeded between two parallel creases are put under plane strain condition. (a) Confocal cross-section micrograph showing relatively flat surface between two neighboring creases, (b) An experimental schematic showing cells seeding between two neighboring creases, (c) cells seeded at 37 °C are put under plane strain condition, with a tensile strain of \( \varepsilon_a = 0.20 \pm 0.04 \) and \( \varepsilon_b \approx 0 \).

6.6 Cells are seeded at the center of each ellipse at 37 °C. Reducing the temperature to 26 °C causes gel to further swell and applies a tensile strain to cells at single cell level. At 26 °C, cells are under four different stress states: (a) Nearly plane strain \( (\varepsilon_a \approx 0.22, \varepsilon_b \approx 0.02) \), (b) \( (\varepsilon_a \approx 0.15, \varepsilon_b \approx 0.08) \), (c) \( (\varepsilon_a \approx 0.15, \varepsilon_b \approx 0.10) \) and (d) equibiaxial stretching \( (\varepsilon_a \approx \varepsilon_b \approx 0.12) \).

6.7 Over the experimental time scale (~30 mins), temperature has negligible influence on the size of cells.

6.8 An experimental schematic showing inflation of microfluidic channels composed of an elastic membrane and a stiffer bottom to actuate creases on the attached hydrogel surface.

6.9 (a) Top view of the microfluidic channels, (b) Cross-section of the microfluidic channels showing the dimension of channels, (c) Randomly oriented creases form on unpatterned region, (d) while creases show some alignment along the microfluidic channels due to the different stiffness of the substrate.

6.10 Surface profiles of the substrate by Zygo Optical Profilometer under (a) inflation or (b) deflation of the membrane through syringe pump. (c) Inflation leads to stripe creases formation in between two neighboring channels, while (d) deflation leads to crease formation on top of each channel.
CHAPTER 1

INTRODUCTION

1.1 Mechanical instabilities

Historically, mechanical instabilities, such as Euler buckling of beams, the snapping through of dome building, or the cracking of painting, have long been regarded as modes of failure in structures. While the beautiful crack patterns have been appreciated for thousands of years as seen on ancient Chinese porcelain, Controlling and harnessing mechanical instabilities to serve specific functions has only become popular in the last decade. Governed by factors such as materials properties, geometry, stress state and stress amplitude, mechanical instabilities can be harnessed to realize geometrical patterns, to measure materials properties, as well as to function as sensors and actuators.

1.2 Wrinkling of bilayers, Biot’s wrinkling and creasing

Of all mechanical instabilities, wrinkling has been extensively studied in the context of composite materials as a mode of failure to be avoided, or in the reverse direction as a method to generate smart, responsive surface patterns for adhesion control, flexible electronics, tunable optics, etc., or as a method to probe materials properties such as Young’s modulus of thin films. Wrinkling instability happens when a stiff film attached to a soft substrate such as an elastomer is compressed beyond a critical strain. As shown in Figure 1.1, for the film with thickness of \( t \), the bending energy scales as \( U_{\text{bend}} \sim t^3 \), while the stretching energy scales as \( U_{\text{stretch}} \sim t \). For small \( t \),
$U_{\text{bend}} \sim t^3 \ll U_{\text{stretch}} \sim t$, thus thin film shows a strong preference for bending rather than stretching. When attached to a soft substrate, the small curvature bending of the top thin film is restricted by the out of plane stretching of the soft substrate. Balancing the bending energy of the film and the stretching energy of the substrate leads to an immediate wavelength of $\lambda = 2\pi (\bar{E}/3E_s)^{1/3}$, where $\bar{E} = E/(1 - \nu^2)$, is the plane strain modulus, with $E$ as the Young’s modulus and $\nu$ as the Poisson’s ratio. The energy comparison between flat state and wrinkled state gives rise to the critical strain

$$\varepsilon_w = 1/4((3E_s/\bar{E})^{2/3}.$$  

**Figure 1.1** Schematic illustrating wrinkles develop in a bilayer of a stiff skin (thickness $t$) attached to a soft substrate upon critical compression ($\varepsilon_c$). The wrinkles have a periodicity $\lambda$ and amplitude $A$.

While wrinkles form on soft elastic materials such as elastomers or hydrogels with a stiff skin, without a stiff skin, soft elastic materials are stable, and undergo homogeneous deformations at small strains, but are predicted to undergo a new mechanical instability upon a large amplitude compression. Using a linear stability analysis on a semi-infinite Neo-Hookean material in compression, Biot predicted that, upon a critical compression parallel to the surface, the free surface of an elastomeric half-space would become unstable to the formation of sinusoidal waves. If $\lambda_1$ is the extension ratio in the compression direction, $\lambda_3$ is the extension ratio in the direction
normal to the surface, the analytic solution for Biot’s point is $\lambda_3/\lambda_1 = 3.4$. To contrast with wrinkling of Bilayer films, we coined the term “Biot’s wrinkling instability” to describe this instability\textsuperscript{18,19}.

Figure 1.2 Schematic showing based on energetic analysis, creasing (onset strain $\varepsilon_c$) sets in before Biot’s wrinkling (onset strain $\varepsilon_B$) on the surface of soft elastic materials.

However, in reality, Biot’s wrinkling instability has never been observed. Instead, as illustrated in Figure 1.2, when soft elastic materials such as hydrogels or elastomers are placed under compression, above some critical compression, the free surfaces suddenly form sharp self-contacting features, a phenomenon we refer to as a "creasing instability"\textsuperscript{20,21}. Creases may play an important role in the development and function of the human brain\textsuperscript{21}, and can be seen in everyday contexts such as on a baby’s arm\textsuperscript{21} or on the surface of bread dough rising in a bowl\textsuperscript{22} (Figure 1.3).

Both creasing and Biot’s wrinkling represent a bifurcation from a state of homogeneous deformation. While the critical condition for the onset of wrinkles can be determined by a classical linear perturbation analysis, the critical condition for the onset of creases cannot\textsuperscript{23}.
A theoretical understanding of the creasing has only been realized recently, with a key contribution due to the numerical simulations of Hohlfeld and Mahadevan. In their work, a skin layer with finite bending stiffness was introduced to provide an energy barrier and thus break translational symmetry and yield a discontinuous transition from the flat state to a crease with finite depth. They found that at $\varepsilon_c = 0.35$ in plane strain, free surface of a Neo-Hookean solid will become nonlinearly unstable to formation of creases. Suo and coworkers subsequently generalized the non-linear analysis to all stress states. They break the translational symmetry by prescribing a small crease as the boundary condition. As shown in Figure 1.2, the critical point could be determined by comparing when the elastic energy of the creased states and homogeneously deformed are equal. By transferring an arbitrary deformation problem into a generalized plane strain problem, they generalized the critical conditions for creasing as $\lambda_3 / \lambda_1 = 2.4$. Cheng, et al. studied application of a point force at the free surface to break translational symmetry and trigger wrinkling and creasing. By varying the point

Figure 1.3 Crease-like patterns on a) human brain, b) infant baby’s arm, and c) confined risen bread dough (Credit: a to http://www.muskingum.edu, b to http://friendlytubes.blogspot.com and c to Michael D. Thouless).
perturbation amplitudes, they could recover both Biot’s wrinkling instability prediction and creasing instability analysis, yielding a conclusion that, in reality, creasing will be encountered first before wrinkling due to large inhomogeneities and imperfections on materials surface. We re-plot the theoretical prediction on creasing condition and Biot’s wrinkling instability into a “Phase diagram”, as shown in Figure 1.4.

![Figure 1.4 “Phase diagram” of flat surface, creasing and Biot’s wrinkling.](image)

### 1.3 Experimental observations of creases

While theoretical understanding of creases is in its nascent stage. Experimentally, creasing instability has been observed both on the surface of swollen soft polymer gels or elastomers supported on a rigid substrate and hydrogels or elastomers under true mechanical compression.

For surface attached soft polymer gels or elastomers films, upon osmotic swelling, they can only swell in the direction normal to the surface. As a result, they suffer in plane equibiaxial compression, in comparison with free standing gels or elastomers, which equilibrate into a stress free state. When the compressive strain is
sufficiently large and the film stays attached to the substrate, creases form on the free surface\textsuperscript{20}. While the swelling induced creasing instability of soft polymer gels has been known since 1855 in the context of a historical photographic printing technique\textsuperscript{25}, experimental studies on this are few.

Southern and Thomas found creases formation during the swelling of natural rubber vulcanizates in organic solvents\textsuperscript{26}. Later Tanaka, et al. reported the same phenomenon for swelling of charged poly(acrylamide) gels with water\textsuperscript{27}. Tanaka, et al. further quantitatively studied the morphological evolution of surface creases of gels during swelling\textsuperscript{28}. Specifically, as shown in Figure 1.5, initial micron scale patterns were observed and then coarsened in size as a function of the square root of time, showing the diffusive nature of gel swelling. In highly confined swollen state, the final morphology of creases is quasi-hexagonal. Trujillo, et al. studied creases formation on the surface of thin gel films attached onto rigid glass substrates\textsuperscript{20}. As shown in Figure 1.6 (c-e), they found the characteristic spacing of creases is linearly proportional to swelled layer thickness over a broad thickness range, since the thickness of swollen gel film is the only relevant length scale. As shown in Figure 1.6 (a-b), they also first systematically measured the effective critical compressive strain for crease formation. It was found to be virtually independent of film moduli with modulus in the range of $G=0.6-24$ kPa and film thickness in the range of $H=3\,\mu m-1$ mm ($\varepsilon_c = 0.30 - 0.37$)\textsuperscript{20}, this values agreed well with a measurement for rubber with modulus of order 1 MPa and thickness 1 mm ($\varepsilon_c = 0.35$)\textsuperscript{26}. Guvendiren, et al. investigated the morphological transition of creases on the surface of thin film gels with depth-wise crosslinking gradients with respect to solvent quality\textsuperscript{29}. Ortiz, et al. characterized creases in ultrathin photo-crosslinked gel coatings with thickness in the range of 30-1200 nm\textsuperscript{30}.
Figure 1.5 Crease pattern evolution during the swelling of a hydrogel\textsuperscript{31}.

While some experiments have hinted at the formation of creases by spinodal decomposition\textsuperscript{33-35}, some others found creases to form by the mechanism of nucleation
and growth. The reason could just be that for the former set of experiments, quenching depths are large enough to bypass the nucleation and growth zone. The latter focused on shallow step quench and thus could really approach the instability boundary in stability phase diagram.

Yoon, et al. have conducted the first detailed study of formation and disappearance of swelling-induced creases on surfaces of thin hydrogel layers attached to a rigid substrate. Under shallow quenching beyond the critical compressive strain, creases form by nucleation and lateral growth. Defects often serve as heterogeneous nucleation sites and also appear to pin the creases from reorganization. Thus heterogeneous defects often dominate the crease nucleation, morphology and cycle to cycle memory. Hysteresis between the onset and disappearance of creases is found to be the undercooling needed to overcome the nucleation barrier, which is suspected to be surface energy.

From these swelling experiments on surface attached polymer gels and elastomers, the critical onset strain of creasing is found to be $\varepsilon_c = 0.30 - 0.37$ for a broad modulus range. Remarkably, these measured effective compressive strains are very close to Biot’s calculated critical strain $\varepsilon_c = 0.33$ for equibiaxial compression. However, this finding shall only be fortuitous since Biot’s calculation was based on linear stability analysis of incompressible Neo-Hookean materials while the experimental results were for non-linear instability of compressible gels.

For elastomers or gels under true mechanical compression case, Gent and Cho have designed an elegant experiment by simply bending a rubber block. In this case, the elastomer suffers nearly plane strain in the inner surface. As shown in Figure 1.7 (a), crease formed transversely across the inner surface above a critical mechanical
compression of $\varepsilon_c = 0.35 \pm 0.07$, which is much lower than Biot’s calculation prediction $\varepsilon_c = 0.46$, in agreement with the result of $\varepsilon_c = 0.35$ under plane strain by non-linear analysis\textsuperscript{19,21,24}, yet with large uncertainty. Ghatak, et al. have put a hydrogel cylinder under mechanical compression, which first undergoes Euler buckling above some critical strain. As the compression increases to another critical point, a single crease forms on the inner side to release compression energy while the outside surface remains smooth\textsuperscript{39}. For both cases, a hysteresis is observed. For the former case, the creases leave visible faint lines when the rubber block is totally unbent, which gradually disappear over time. For the latter one, the crease disappears reversibly but at a smaller compression than the onset critical compression. And if the creased state is kept for ~3-10min, the crease was found to leave a defect, leading to a much lower onset point during reloading cycle.

\textbf{Figure 1.7} (a) Creases on the inner surface a bent rubber block\textsuperscript{38} and (b) formation of creases on initial flat surface of an elastomer film under high electric voltages\textsuperscript{40}.
As shown in Figure 1.7 (b), a set of experiments reports an ultrahigh electric field inducing creasing instability. This may be responsible for the electrical breakdown in soft polymer materials\textsuperscript{40,41}.

![Figure 1.8](image)

**Figure 1.8** Harnessing of creasing instability to make dynamic biomolecular patterns (a)\textsuperscript{42}, and to enhance adhesion (b)\textsuperscript{9}.

### 1.4 The organization of this thesis

While creasing instability may provide a limit on homogeneous swelling of anchored gels and explain the failure of materials from tires\textsuperscript{38} to dielectric elastomers\textsuperscript{40}, as shown in Figure 1.8, it can also be harnessed to make responsive patterns for biomedical application\textsuperscript{42}, or smart adhesion\textsuperscript{9}. To expand the applications of creasing instability, further detailed characterization of crease shapes, equilibrium depths and hysteresis during repeating loading cycles is both necessary and desired.
To predict the structure of creases, it is essential to make detailed comparisons between experiments and theory. The only reported agreement between experiments and theory is the onset compressive strain of $\varepsilon_c = 0.35 \pm 0.07$ for the formation of creases on bent rubber blocks by Gent and Cho$^{38}$, yet with large uncertainty. While more experiments have been conducted on the creasing of surface attached hydrogels, to quantitatively compare with theory requires the characterization of constitutive equations of gels in use in precision, which cause additional difficulties in both experiments and theoretical analysis. The detailed comparison between experiments and theoretical analysis is still lacking.

This thesis will focus on addressing the above mentioned questions. In chapter 2, we will characterize the equilibrium shape of creases, and make a comparison with numerical results based on neo-Hookean model. We demonstrate that creases form in a nucleation and growth mechanism due to surface energy. In chapter 3, we study the hysteric behavior of creasing during repeating loading/unloading cycles and develop an approach to control the hysteresis, yielding well-defined bistable states—flat state and deep creased state. In chapter 4, we develop a system to demonstrate that creases can also form on the interface between two elastic materials. In chapter 5, we show how the morphology and onset of creases depend on materials properties, geometry, loading history, as well as stress states. In chapter 6, we harness creasing instability to enable dynamic substrates for cell stretching.
1.5 References


CHAPTER 2

STRUCTURE AND FORMATION MECHANISM OF CREASES*

2.1 Introduction

While creases are commonly observed, their scientific understanding is in a nascent stage. Previous attempts to quantitatively analyze experimental data on crease formation\textsuperscript{1-3} have relied on Biot’s linear instability analysis of the surface of a compressed elastomer, which we refer to as a “Biot’s wrinkling” instability\textsuperscript{4}. Recent impetus comes from the realization that, for homogeneous elastic materials under compression, creases set in before wrinkles\textsuperscript{5,6}. For example, for neo-Hookean materials under plane-strain compression, nonlinear finite-element analyses\textsuperscript{5-9} predict that formation of creases is energetically favored at a critical strain of $\varepsilon = 0.35$, substantially below the value of 0.46 for wrinkling\textsuperscript{4}. Furthermore, Cao and Hutchinson carried out a post-bifurcation analysis of Biot’s wrinkling instability and found that the wrinkled state is extremely unstable, meaning that it is highly defect sensitive and once formed is dynamically unstable to formation of a crease\textsuperscript{10}. In practice, these results imply that: (i) the wrinkled state should never be an equilibrium solution for the surface of a compressed homogeneous material, and (ii) experimental observations on creases must be considered in the context of the nonlinear analysis, not the linear stability calculation.

While the measured onset of creasing on a bent elastomer surface, $\varepsilon = 0.35 \pm 0.07$, is in agreement with the nonlinear prediction, the large experimental uncertainty leaves doubt as to how closely the two values match. Further quantitative comparisons, for example on the spacings, shapes, or depths of folds, are completely lacking due to both modeling and experimental challenges. On the modeling side, the singularity of the creases and the necessity to break translational invariance have previously required introduction of a stiff skin whose thickness was gradually reduced in a limiting process, prescription of a small crease through boundary conditions, or application of a point force on the surface. Besides the inconvenience of these methods, they have so far limited analysis mostly to initiation of a single crease, with few predictions available for fully-formed folds. Experimentally, the study of creases on elastomeric blocks under simple compression is difficult since buckling or barreling instabilities usually occur at much lower strains. The solution to this problem has previously been to bend a rod or slab, providing nearly plane-strain compression on the inner bend surface. However, in this geometry quantitative characterization beyond crease initiation is complicated both by the inhomogeneous strain through the thickness of the specimens and the difficulty of measuring the spacing and shapes of the surface folds. Creases formed on swelling gel surfaces have received slightly more quantitative study, but the challenges inherent to modeling swelling have made quantitative comparisons with theory difficult.

In this chapter, we study both the initiation and development of creases in homogeneously compressed elastomer films through a combination of simple experimental and numerical methods. This allows for detailed quantitative comparisons between experimental measurements and numerical predictions. We find
that the onset, shape, and spacing of creases are very well described by calculations of the equilibrium elastic state for a Neo-Hookean material with no adjustable parameters.

While wrinkles form spontaneously upon a critical compression, creases form by nucleation and growth\textsuperscript{16}. The origin of this latter behavior, however, has remained unclear, as elasticity predicts a transition from the flat to creased states with no barrier.\textsuperscript{5-7}

In this chapter, we show here that the nucleation and growth behavior of creases can be understood in close analogy to classical nucleation theory for a thermodynamic phase transition\textsuperscript{17}. When the compression is high, the formation of a crease reduces elastic energy by an amount that scales with the deformed volume. However, the formation of the crease increases the surface area, and thus for a small incipient crease, surface energy provides a nucleation barrier. This behavior is also reminiscent of the formation of cracks\textsuperscript{18}, dislocations\textsuperscript{19} and cavities\textsuperscript{20}, phenomena that are of great technological significance, and present scientific challenges concerning issues of nucleation. While surface energy has been hypothesized to play a role in the formation of creases and wrinkles\textsuperscript{16,21}, past work has focused on swelling of hydrogels where the surface energy is small and difficult to measure, and quantitative verification has not previously been possible.

We study nucleation and growth of creases by compressing a soft elastomeric film on a stiff substrate, and by varying the surface energy using different environments. Creases nucleate at preexisting defects, and then grow—or channel—across the surface of the film. Due to the defect sensitivity, the strain for heterogeneous nucleation is not uniquely characterized, but the strain for channeling is. We design an experiment in
which channeling creases arrest in a film of gradient thickness, and find that measured channeling strains agree well with the predictions of a scaling analysis.

2.2 Experimental

2.2.1 Characterization of equilibrium shape of creases

The samples are prepared by gluing a thin soft film to a pre-stretched thick stiff substrate. The substrate and the film used in the experiment are polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning) elastomers of different crosslink densities (15:1 and 40:1 base: crosslinker by weight, respectively), with a shear modulus of 270 kPa for the substrate and 16 kPa for the film.22,23 The marked difference in stiffness, as shown below, leads to a nearly planar film/substrate interface, close to the simulation conditions. The substrate is prepared by pouring thoroughly mixed 15:1 Sylgard 184 PDMS into a plastic petri dish, followed by being fully cured at 70 °C for 8 hours, yielding an elastomer layer with thickness of 1-1.2 mm. The elastomer layer is then cut into 0.8 cm × 2 cm slabs. The film is prepared by spin coating thoroughly mixed 40:1 PDMS onto a glass wafer and being cured at 120 °C for 30 mins. After being cooled down to room temperature, the film is then bonded to the substrate by applying a thin adhesive layer of uncured 40:1 PDMS through spin coating, and subsequently crosslinking this layer prior to detachment from the glass wafer. To facilitate detachment, the glass wafer is pre-treated with oxygen plasma followed by vapor deposition of trimethylchlorosilane molecules. The thickness of adhesive layer is added into the total film thickness of \( H = 23 - 147 \mu \text{m} \), tuned by the rate of spin coating. While these materials display viscoelastic behavior, compression is performed slowly across
the range of strain $\varepsilon$ of interest (0.42-0.54) (~30 min between each incremental application of strain of ~0.01), and structures are measured only after allowing samples to equilibrate for at least 48 h, to ensure that the effects of viscous stresses are minimal.

While the formation of creases is monitored in situ using an upright optical microscope (Zeiss Axiotech Vario) in bright field reflection mode, structures of creases are characterized with laser scanning confocal microscopy (Zeiss 510 META). The film is labeled by incorporating a small amount of fluorescent monomer (4.5 µg fluorescein-o-acrylate per 1 g PDMS). The sample surface is immersed in a refractive index matched fluid of 72% by weight glycerol and 28% water.

### 2.2.2 Surface energy effects on creasing

To study the effects of surface energy on creases, we adopt the above described experimental setup. To enhance the influence of surface energy, we, however, reduced the undeformed thickness of the film to $H = 8 \sim 30$ µm by varying the rotation speed during spin coating. The surface tension is varied by conducting experiment in three environments: air, water, and an aqueous solution of the surfactant 3-[hydro(polyethyleneoxy)propyl] heptamethyltrisiloxane (Gelest) at a concentration above its critical micelle concentration (CMC). The values of the surface energies are 21, 40 and 0.8 mN/m, respectively, as measured by pendent drop tensiometry on uncured PDMS (Sylgard 184 base, Dow Corning) in contact with the corresponding fluid; the values for PDMS/air and PDMS/water match well with literature values\textsuperscript{24}. The CMC of the silicone surfactant is determined by Wilhelmy plate method to be ~0.1 mg/ml. In all experiments, concentration of the surfactant is always above ~0.5 mg/ml.
While compression is slowly applied onto the film by gradually releasing pre-stretch in the substrate, the nucleation and growth of creases is in situ observed via an upright optical microscope (Zeiss Axiotech Vario) in bright field reflection mode.

Preexisting defects serve as heterogeneous nucleation sites for creases, making it difficult to identify a unique critical strain for nucleation. To quantitatively test the effects of surface energy, we thus design an experiment in which channeling creases arrest in a film of gradient thickness (Figure 2.6). The films are made by first spin-coating uncured PDMS on a glass slide, placing the PDMS film on the pre-stretched substrate, and then curing. We find a variation in thickness from 10 \( \mu \)m at the edge to 0.5 \( \mu \)m in the center, likely because uncured PDMS is squeezed from the center to the edge prior to curing. To characterize the thickness of film at the frontier of arrested channeling creases, a small amount of fluorescent monomer (4.5 \( \mu \)g fluorescein-o-acrylate per 1 g PDMS) is incorporated into the film.

2.3 Results and discussions

2.3.1 Equilibrium shape of creases

Figure 2.1a illustrates the experimental approach, modified from a previous study of the snap-through instability of supported elastic membranes.\(^{25}\) We apply a uniaxial tension to stretch a thick substrate from the original length \( L_0 \) to a length \( L \), and then attach to the stretched substrate a stress-free film of thickness \( H \) that is much softer than the substrate. When the substrate is partially released to a length \( l \), the film is subjected to a compressive strain \( \varepsilon = 1 - (l/L) \). The film is in a state of uniaxial stress, because both the substrate and film are incompressible. The magnitude of the applied
strain can be varied continuously, but is limited by \(1 - \left(\frac{L_o}{L}\right)\), when the substrate is fully released.

Beyond a certain level of strain, short creases formed in the vicinity of defects or scratches on the film surface, as shown in Figure 2.1b, top left. At a higher level of strain, the creases extended laterally across the surface of the films, leading ultimately to an array of creases with fairly regular spacing (Figure 2.1b, bottom right). This behavior complicates unambiguous identification of a critical strain. However, the smallest strain at which creases were found to propagate across the surface for any sample was \(\varepsilon = 0.46\), providing an upper bound for the experimental value of the critical strain.

![Diagram](image.png)

**Figure 2.1** A schematic of the experiment by which an elastomeric film of initial thickness \(H\) is placed under uniaxial compressive strain by partial release of a much thicker and stiffer elastomeric substrate. (b) Reflectance optical micrographs show the nucleation and growth of creases for a film of \(H = 63\mu m\). At \(\varepsilon = 0.475\), short folds formed in the vicinity of defects but did not propagate, while at \(\varepsilon = 0.515\), lateral growth of creases (top right to bottom left) eventually led to formation of a parallel array of folds (bottom right).

The creasing instability may also be affected by the PDMS/air surface energy \(\gamma\), which, together with the modulus of the film \(\mu\), yields a material-specific length \(\gamma / \mu^{16}\) estimated as \(1.2 \ \mu m\) based on a value of \(\gamma = 20 \ \text{mN/m}^{22}\). As long as the dimensionless number \(\gamma / (\mu H)\), is sufficiently small, surface tension will have a negligible effect on the
shape and spacing of creases. For the experiments described here, we estimate $\gamma/(\mu H) = 0.009 \text{–} 0.054$, and thus we neglect the effect of surface energy in our calculations.

The onset of each crease is autonomous, occurring when any material point on the surface reaches a critical state of strain. Thus, the critical states of strain can be determined independent of the specific boundary conditions. For a neo-Hookean material, the conditions for the onset of creasing have been calculated under arbitrary states of strain. The general solution shows that under uniaxial stress the critical strain is 0.44 for the onset of creasing, while the critical strain is 0.56 for the onset of wrinkles.[26]

To analyze both the onset and subsequent development of creases, we used the commercial finite-element software ABAQUS. The film is assumed to form a periodic array of creases, so that half of a period is selected as a calculation cell, as illustrated in the inset of Figure 2.2, with $W$ being the period in the undeformed state. A symmetric boundary condition is applied on the right boundary of the cell, while a uniform horizontal displacement is prescribed on the left boundary. The top surface of the film is traction free. The substrate is taken to be much stiffer than the film, so that the bottom of the cell remains flat. The shear stress on the bottom surface is assumed to be negligible. Since a crease will emerge wherever the strain first exceeds the critical value, only a small perturbation is necessary to break translational invariance and specify the position of the crease. The small perturbation is introduced by placing in the finite-element mesh a defect—a quarter of a circle of a small radius; see the inset of Figure 2.2. To eliminate the effect of the size of the defect, the defect is made much smaller than the thickness of the film $H$. To resolve the field close to the tip of the crease, the defect is made much larger than the size of the finite elements around the defect. The surface of
the film is allowed to fold and self-contact. We also varied the size and shape of the defect and did not find any effect on the results we report, provided that the size was sufficiently large compared to the mesh and sufficiently small compared to the block thickness.

**Figure 2.2** The normalized elastic energy of the creased state plotted as a function of the uniaxial compressive strain. The creases are assumed to form a periodic array defined by the aspect ratio of the simulation cell (the inset illustrates half of the periodic cell). While the dependence on periodicity is rather weak, the elastic energy is nearly minimized by a value of $W/H \approx 3.5$ across the range of strains studied experimentally.

Figure 2.2 shows the calculated elastic energy of the cell in the creased state, $U$, normalized by the elastic energy of the uniformly compressed cell in the absence of the crease, $U_0$, as a function of the applied strain $\varepsilon$, for several values of $W/H$. When $\varepsilon < 0.44$, for all the values of $W/H$, the defect has negligible influence on the elastic energy. When $\varepsilon > 0.44$, the defect will induce a crease and reduce the elastic energy of the elastomer. The critical strain $0.44$ matches precisely the result previously obtained with a different numerical approach, and is in excellent agreement with the experimentally observed upper bound of 0.46 as described above.
The elastic energy is nearly minimized across the full range of applied strains covered by our experiment ($\varepsilon = 0.46 - 0.55$) for a ratio of $W/H \approx 3.5$. Since the spacing between creases in the deformed state is $w = (1 - \varepsilon)W$, we predict that the equilibrium spacing between creases is $w/H = 3.5(1 - \varepsilon)$. This prediction is plotted in Figure 3a, together with the experimental measurements. The magnitudes of the predicted and observed wavelengths are in good agreement, though the scatter in the experimental data precludes a more detailed comparison of the dependence on strain. While it has long been appreciated that the characteristic spacing between creases must scale as the film thickness, as this is the only relevant length scale in the problem, our results represent the first prediction of the pre-factor in this scaling relationship, as well as the first measurement of crease spacings for elastomers. Notably, experiments revealed a well-defined characteristic spacing of creases, but not perfectly regular packing (Figure 2.1b), and once a parallel array had formed, further compression led to only “affine” changes, never to annihilation or appearance of new creases. These observations are consistent with the relatively weak dependence of elastic energy on aspect ratio shown in Figure 2.2, and also indicate that creases are not able to fully equilibrate, thus yielding sensitivity of the observed spacing to sample history.

Figure 2.3b shows the calculated distance from the uppermost point on the surface to the bottom of the crease tip $d$, and the depth of the self-contacting region $a$. Experimentally, both the film and adhesive layer were doped with a small amount of fluorescent monomer (fluorescein acrylate) that labels both layers but also partitions preferentially to the film/air interface. As shown in Figure 2.4, this partition allowed unambiguous determination of the entire surface profile in the creased state by laser scanning confocal microscopy (of films immersed in a refractive index matched fluid of
72% by weight glycerol and 28% water)—including the self-contacting region of the surface and the film/substrate interface—details that have previously been unavailable from experiments on bent slabs or rods.\textsuperscript{1,3,5,6} Figure 2.3b shows close correspondence between the measured and predicted equilibrium values of $d$ and $a$, for all data points except those at $\varepsilon = 0.46$ (open symbols). This value is just slightly above the critical strain, and thus only isolated creases were formed, which have different shapes than those in an array.

![Image](image_url)

**Figure 2.3** (a) The equilibrium spacing of creases as a function of the compressive strain. The solid line is predicted by the calculation, and the symbols are experimental measurements, with error bars representing the standard deviation of average fold spacings measured at different positions on the sample surface. (b) The equilibrium depth of crease as a function of the compressive strain. The solid curves are predicted by the calculation, and symbols bars are experimental measurements. The open entries at a strain of 0.46 correspond to an isolated crease, while the filled symbols at higher strains are measured for parallel arrays of creases.

Figure 2.4 shows the calculated surface profiles overlaid on the experimental data for three values of strain, with only an isotropic scaling factor proportional to $1/H$ applied to each refractive-index-corrected cross-section. It can be seen that the calculations not only capture the depth and spacing of the creases, but also accurately
describe the shape of the free surface. In Figure 2.4c it can be seen that the film/substrate interface did not remain entirely planar, but the amplitude of corrugations was less than 3% of the film thickness at the highest applied strain of $\varepsilon = 0.55$. Thus, while the experimental geometry does not exactly match that of the simulation, any resulting deviations will be minor.

We emphasize that, apart from the choice of a Neo-Hookean strain energy function used to describe the elastomeric block, there are no adjustable parameters in our model. Thus, the agreement between calculations and experiment presented in Figure 2.3 and 2.4 is remarkably good.
Figure 2.4 Comparisons between calculated surface profiles (red dotted lines) and experimental cross-sections determined by confocal microscopy (green images), for elastomer surfaces in the creased state at three levels of strain. Initial film thicknesses $H$ were (a) 93 μm, (b) 91 μm and (c) 23 μm (scale bars represent 20 μm). For the thinnest film in (c), it is also possible to observe the film/substrate interface.

2.3.2 Surface energy effects on creasing

Creases form by nucleation and growth, in which surface energy has been hypothesized to play a role.$^{16,21}$ Past work, however, has focused on swelling of hydrogels where the surface energy is small and difficult to measure, and quantitative verification
has not previously been possible. Our experimental setup on PDMS elastomer under uniaxial compression provides a well measured shear modulus and well measured surface energy of PDMS in contact with different mediums, thus enables the quantitatively investigation of the effects of surface energy on creasing.

The surface tension $\gamma$ and shear modulus $\mu$ of the film together define a material-specific length $\gamma/\mu$, which is fundamental to many elastocapillary phenomena$^{28-30}$ and is closely related to the elastoadhesive length involved in contact$^{31}$ and fracture mechanics$^{18}$. In our experiments the length $\gamma/\mu$ varies from $\sim 50$ nm for the PDMS/surfactant interface to $\sim 2.5$ μm for PDMS/water.

For example, consider a film, thickness $H = 25$ μm, compressed in the surfactant solution (Figure 2.5). Compression is applied quasi-statically, with each increment in strain ($\sim 0.01$) followed by 30 min prior to the next increment. The creases nucleate at preexisting defects, and then channel across the surface of the film. The behavior of the creases bears remarkable resemblance to that of channeling cracks$^{32}$ and threading dislocations$^{33}$ in thin solid films. At larger strains, additional creases nucleate and grow, ultimately leading to a quasi-periodic array of parallel creases with spacing proportional to $H$. In Figure 2.5b, creases are first observed to grow across the surface of the film at a strain of $\varepsilon = 0.488$, which is well above the critical strain of $\varepsilon_c = 0.438$ in the absence of surface energy$^7$. As we show in detail below, this over-strain behavior is closely analogous to the supercooling of a clean liquid well below its melting point in that both phenomena are caused by the energy barrier due to surface energy.
Figure 2.5 An experimental setup to study nucleation and growth of creases. (a) A thick substrate of a stiff elastomer is stretched to length $L$, followed by attaching a stress-free thin film of a soft elastomer, thickness $H$. The bilayer is submerged in a medium to control the surface energy of the film. When the substrate is partially released to length $l'$, the film is in compression, and creases nucleate. When the substrate is further released to length $l$, creases channel across the surface of the film. (b) Nucleation and growth of creases as observed by reflection optical microscopy. The strain in the film is defined as $\varepsilon = (L-l)/L$.

Preexisting defects serve as heterogeneous nucleation sites for creases, making it difficult to identify a unique critical strain for nucleation. To quantitatively test the effects of surface energy, we thus design an experiment in which channeling creases arrest in a film of gradient thickness (Figure 2.6). The film is thicker at the edge and reduces in thickness towards the central region.
Figure 2.6 A comparison of experimental results and theoretical predictions for crease channeling. (a) A schematic illustration and reflection optical micrographs of creases channeling from thick (bottom) to thin (top) regions in a film of gradient thickness, in contact with air. (b) The measured over-strain required for channeling is plotted against the dimensionless elastocapillary number. The red filled symbols are experimental results for PDMS/surfactant interfaces (circles) and PDMS/air interfaces (squares), with experimental uncertainties being comparable to the symbol sizes. The red solid line represents the best-fit power law, while the blue dotted line corresponds to the theoretical prediction.

When the film is compressed, creases nucleate at the thick edge of the film, and channel toward the center. For a fixed applied strain, the creases arrest in the film at a position where the thickness becomes sufficiently small. Measuring the thickness of the film at the front where channeling is arrested as a function of the applied strain then provides a quantitative measure of the influence of surface energy, where the nature of the nuclei becomes irrelevant. The only geometric length is the thickness of the film, thus the system is characterized by a single dimensionless elastocapillary number $\gamma/\mu H$ that governs the strain required for channeling $\varepsilon_{\text{channel}}$ (Figure 2.6b). Motivated by the scaling analysis described below, we fit the experimentally measured over-strain to a power law, $\varepsilon_{\text{channel}} - \varepsilon_a = \alpha (\gamma / \mu H)^\beta$, with $\alpha = 0.17 \pm 0.01$ and $\beta = 0.49 \pm 0.06$. 

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Figure 2.7 Temporal evolution of creases channeling on a film of gradient thickness compressed to and held at a strain of $\varepsilon = 0.513$. In water, creases nucleate at the thick edge of the sample, channel a certain distance and then arrest. Flooding the surface with the surfactant solution reduces surface energy and causes arrested creases to rechannel, as well as the nucleation of new creases.

An additional experiment demonstrates that surface energy resists both nucleation and channeling of creases. As shown in Figure 2.7, a film of gradient thickness is compressed in water to a strain of $\varepsilon = 0.513$, causing creases nucleated at the thick edge of the sample to channel a certain distance and then arrest. Without changing the applied strain, the surface of the film is flooded with the surfactant solution, lowering $\gamma$ by a factor of 50. This causes the arrested creases to continue channeling into the thinner region of the film, and also leads to nucleation of new creases in the thinner regions of the sample. As creases channel from the thick to the thin regions of the film, the formation of additional creases is required to maintain the minimum-energy spacing of $W/H \approx 3.5$, and a hierarchical cascade of creases is indeed observed for a film of gradient thickness (Figure 2.8).
Figure 2.8 A film of gradient thickness forms a hierarchical cascade of creases. A film of gradient thickness in contact with air was put under uniaxial compression. At the edge of the film (left), the thickness was $H = 14 \ \mu m$. At the center of the film (right), the thickness was $H = 4 \ \mu m$. Creases nucleated from thick edge and channeled into thinner region at the center. As the creases propagated, new creases formed between the old creases to release elastic energy and maintain the equilibrium spacing of $W/H \approx 3.5$. This process resulted in a hierarchical cascade of creases.

We next perform a scaling analysis following Yoon, et al.\textsuperscript{16}, but here with coefficients determined by finite-element calculation. In a state of equilibrium, let $a$ be the length of the self-contacting region along the direction of the film thickness, and $\Delta U$ be the difference in energy per unit length of crease between the creased state and the homogeneously compressed state. We treat $\Delta U$ as the sum of two independent terms representing the surface energy $\Delta U_s$ and the elastic energy $\Delta U_e$. For a shallow crease, $a \ll H$, the length of contact $a$ is the only geometric length in the boundary value problem. That is, a crease is always of aspect ratio near one, with its lateral dimensions and depth both scaled with $a$, and therefore dimensional considerations give that

\vspace{1cm}

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ΔU_s \propto γa. We fit the calculated surface energy to the expression \( ΔU_s = Aγa \), with \( A = 0.45 \) (Figure 2.9a).

We ignore the contribution of the surface energy within the self-contacting region, assuming that the work of adhesion for the self-contacting surface takes on the thermodynamic limit of twice the surface tension. Consequently, the surface energy is

\[ ΔU_s = γ(s_c - s_h) \]

where \( s_c \) is the contour length of the free surface in the creased state, and \( s_h = W(1 - ε) \) is the corresponding value in the homogeneous state. The calculated excess surface energy is almost perfectly linear in the length of self-contact and furthermore is nearly independent of the applied strain over the range of 0.41–0.47 (Figure 2.9a).
Figure 2.9 Results of finite-element calculations. (a) The surface area, and (b) the elastic energy in the creased state relative to that in the homogeneous state, both plotted against the normalized length of contact at different levels of the applied strain.

We next consider the elastic energy due to the formation of a crease. For a shallow crease, \( a \ll H \), dimensional considerations suggest that the excess elastic energy scales as \( \Delta U_e = \mu a^2 f(\varepsilon) \), where \( f(\varepsilon) \) is a dimensionless function of the applied strain. In the absence of surface tension, a crease may form at the critical strain of \( \varepsilon_c = 0.43 \varepsilon \). That is, \( f(\varepsilon_c) = 0 \) and \( f(\varepsilon) > 0 \) when \( \varepsilon < \varepsilon_c \). Near \( \varepsilon_c \), the function \( f(\varepsilon) \) can be taken as linear in the over-strain, so that \( \Delta U_e \approx -B\mu(\varepsilon - \varepsilon_c)a^2 \), where \( B \) is a positive
constant. However, when the size of the crease $a$ is a significant fraction of the thickness of the film $H$, deepening of the crease is repelled by the rigidity of the substrate, which we capture through a third-order term in $a$: $\Delta U_c \approx -B\mu(\varepsilon - \varepsilon_o)a^2 + C(\mu / H)a^3$, where $C$ is a positive constant\textsuperscript{16}. We neglect terms of higher orders of $a$, and assume that $|\varepsilon - \varepsilon_o|$ is small, such that $B$ and $C$ are calculated at $\varepsilon = \varepsilon_o$. Fitting this expression to the calculated elastic energy (Figure 2.9b), we obtain $B = 13.5$ and $C = 2.4$.

The assumption that elastic and surface energies are independent is not strictly correct, as the shape of the crease can change to minimize the combined energy. Unfortunately, efforts to solve the coupled elastocapillary problem via finite element modeling have so far proven unsuccessful. While the simplifying assumption made here undoubtedly leads to errors in the calculated energy landscape especially for shallow creases, it does not change the qualitative behavior. Further, as we show later, even this simple treatment provides remarkably good agreement with experimental data.

For an incipient crease much smaller than the thickness of the film, surface energy provides a barrier to the nucleation of a crease, but the effect of the substrate is negligible. The excess energy then takes the form $\Delta U(a) \approx A\gamma a - B\mu(\varepsilon - \varepsilon_o)a^2$, which yields a dependence on length analogous to that in classical nucleation theory (Figure 2.10). The term due to surface energy resists formation of the crease, while the term due to elasticity motivates formation of the crease for $\varepsilon > \varepsilon_o$. For nuclei below the critical size, the increase in surface energy prevails, and the total energy is reduced when the nucleus shrinks. Above the critical size, the reduction in the elastic energy prevails, and the total energy decreases when the nucleus grows. Setting $\partial \Delta U(a) / \partial a = 0$, we obtain that
\[ a_{nuc} \approx \frac{A\gamma}{2B\mu(e - e_o)}. \]  

(1)

This expression becomes \( a_{nuc} = 0.017 \frac{\gamma}{\mu(e - e_o)} \) using the values of \( A \) and \( B \) from the finite-element calculations. For example, considering the film immersed in surfactant solution with an over-strain of \( e - e_o = 0.05 \) (Figure 1b), the predicted critical nucleus is of size \( a_{nuc} = 17 \text{ nm} \). However, a sizable energetic barrier to crease formation remains; in this case the barrier is about \( 12k_BT \) to form a crease whose length is also \( a_{nuc} \). Consequently, creases nucleate heterogeneously at defects within the sample, which are present with a distribution of sizes, shapes, and locations in the material, making it difficult to experimentally confirm the prediction of Eq. (1). We note that measuring critical nuclei in many thermodynamic phase transitions is a long-standing challenge.

By contrast, the effect of surface tension on channeling creases is well characterized. The condition for channeling creases to arrest in a film of gradient thickness is independent of preexisting defects, and is determined when the energy curve first touches zero for a finite crease depth, i.e. when \( \partial \Delta U / \partial a = 0 \) and \( \Delta U = 0 \) (represented in Figure 2.10 by the curve at \( e = 0.460 \)). Writing the excess energy in the form \( \Delta U = A\gamma a - B\mu(e - e_o)a^2 + C(\mu / H)a^3 \), we obtain the over-strain for channeling:

\[ e_{channel} - e_o = \frac{2\sqrt{AC}}{B} \left( \frac{\gamma}{\mu H} \right)^{1/2}. \]  

(2)

This expression becomes \( e_{channel} - e_o = 0.15(\gamma / \mu H)^{1/2} \) using the values of \( A, B \) and \( C \) from the finite-element calculations. The theoretically predicted pre-factor and the exponent both agree well with those determined from the experimental data, which can also be seen from the comparison in Figure 2.6b.
The combined elastic and surface energies in the creased state, relative to the homogeneously compressed state, are plotted against the normalized length of surface contact. Calculated curves are shown at different levels of the applied strain for a single value of the elastocapillary number.

For the largest value of the elastocapillary number considered, $\gamma/(\mu H) = 0.86$, the measured channeling strain is $\varepsilon_{\text{channel}} = 0.60$, which is far above the critical strain for the onset of creases in the absence of surface energy, $\varepsilon_c = 0.38$, and is even above Biot’s prediction of linear instability for wrinkling of the compressed surface, $\varepsilon_{\text{Biot}} = 0.56$. This raises the question of whether surface energy might ever suppress crease formation to the point that the surface becomes linearly unstable prior to the onset of creases. However, as summarized in the inset to Figure 2, when surface energy is included in the linear perturbation analysis for elastomer films, as studied previously by Huang and co-workers for gels, linear instability is suppressed even more strongly than creasing. Thus, while a large value of $\gamma/(\mu H)$ can delay the onset of creasing to much larger strains, it should not provide a qualitative change in the mechanism of formation.
2.4 Conclusions

In summary, we have introduced an experimental approach to place thin elastomeric films under homogeneous compression, leading to arrays of creases that can be characterized in detail, along with a numerical method that provides straightforward calculations of equilibrium crease structures. The excellent quantitative agreement obtained between the measured and calculated depths, spacings, and shapes of creases indicates that the onset and development of folds on the surface of a compressed elastomer is very well described by a simple nonlinear finite element analysis, so long as an appropriately sized defect is introduced to seed formation of a finite amplitude fold. Creases form by nucleation at preexisting defects and grow by channeling across the surface of the film. Surface energy provides a nucleation barrier and also resists channeling for finite values of the elastocapillary number. While the heterogeneous nucleation makes it difficult to characterize the critical strain for nucleation, the condition for channeling is well characterized and depends on the elastocapillary number.

2.5 References


CHAPTER 3

ORIGIN AND CONTROL OF HYSTERESIS BETWEEN FORMATION AND DISAPPEARANCE OF CREASES†

3.1 Introduction

While elastic instabilities, such as buckling of a column or wrinkling of a sheet, have long been regarded as modes of failure in architectural structures, electromechanical systems, and composite materials, they have increasingly been exploited for a variety of applications. An example of recent interest is the formation of surface creases when an elastic material is compressed beyond a critical value. Creases may look superficially like cracks, since both correspond to sharp, singular features. A significant difference, however, can be readily appreciated and will have practical implications. While repeated opening and closing of cracks often leads to fatigue and catastrophic failure, the elastic character of creases makes it possible to cycle a soft material repeatedly between flat and creased states without inducing damage.

The formation of creases corresponds to a pronounced change of state, reminiscent of a phase transition. This change of state has recently been used to connect diverse stimuli to multiple functions. Crease-inducing stimuli include temperature, light, and electric fields. Functions enabled by the formation of creases include the control of chemical patterns, enzymatic activity, cellular behavior, and adhesion. Each of these applications depends on how creases form.

and disappear. For a planar surface under in-plane compression, the creasing instability is supercritical, where creases appear and disappear at the same critical strain, with no hysteresis\textsuperscript{15}. In practice, however, widely varying degrees of hysteresis in different material systems have been observed, complicating the application of creases.

In this chapter, we first investigate the origin of hysteresis of creases observed during multiply loading/unloading cycles, with the experimental setup described in the previous chapter. We found that it is the adhesion at the self-contact region rather than plastic deformation or materials failure that gives rise to the hysteresis observed. Then we develop an approach, where we apply pre-compression in the substrate of a soft elastic bilayer, to realize tunable hysteresis between the formation and disappearance of surface creases.

### 3.2 Experimental

#### 3.2.1 Origin of hysteresis of creases on elastomer surface

With the experiment setup described in chapter 2, a film of a uniform thickness $H = 13 \, \mu m$ in contact with air is placed under uniaxial compression with step increases in strain, folding by holding at each strain for at least 30 min. Above a critical strain, creases nucleate and grow across the surface, forming quasi-periodic array. Then strain is step reduced at a rate of $\sim 0.01$ every 30 min in the range of $\varepsilon = 0.55 - 0.38$, and then reduced to $\varepsilon = 0.35$, $\varepsilon = 0.30$, $\varepsilon = 0.25$, and $\varepsilon = 0.18$, and held at each strain for at least 30 min. Then compression is totally removed and held at zero strain for at least 3 days. In the second loading cycle, compression is applied in the same way of in the first loading cycle. During loading/unloading, the sample surface is in situ monitored with an
upright optical microscope (Zeiss Axiotech Vario) in bright field reflection mode or with an optical profilometer (Zygo).

To make a comparison, a film of the same uniform thickness \( H = 13 \, \mu m \) in contact with an aqueous solution of the surfactant 3-[hydro(polyethyleneoxy)propyl] heptamethyltrisiloxane at a concentration (0.5 mg/ml) above its critical micelle concentration is placed under uniaxial compression in the same way. During loading/unloading, the sample surface is in situ monitored with an upright optical microscope (Zeiss Axiotech Vario) in bright field reflection mode.

### 3.2.2 Controlled formation and disappearance of surface creases

All experiments are performed on bilayers supported on a pre-stretched elastic ‘mounting layer’. The film layer and substrate layer consist of Sylgard 184 (Dow Corning) PDMS, while the mounting layer is prepared using a custom PDMS formulation from Gelest Inc. The mounting layer is prepared by first thoroughly mixing part A containing 99.997% fumed silica reinforced vinyl terminated PDMS (DMS-V31S15, Gelest Inc.) and 0.003% platinum catalyst (SIP6831.2) and part B containing 90% vinyl terminated PDMS (DMS-V31) and 10% trimethylsiloxy terminated methylhydrosiloxane-dimethylsiloxane copolymer (HMS-301) by a weight ratio 3 to 1. The mixture is then degassed, spread onto a silicon wafer, and cured at 120 °C for 8 h to yield a PDMS film with a thickness of ~1-1.2 mm. This PDMS film is then cut into 0.8 cm× 2 cm slabs and the shear modulus is determined by tensile experiments to be 260 kPa. This custom formulation of PDMS provides larger accessible pre-stretch in the mounting layer (up to 250%) without fracture, while maintaining a modulus.
substantially above that of the substrate and film. The substrate layer is prepared by spin coating degassed Sylgard 184 40:1 (by weight) base : crosslinker mixture onto a polystyrene support at 360 rpm for 120 s. After being cured at 70 °C for 1 h, the substrate layer is bonded to the mounting layer by spinning coating an adhesive layer of uncured 40:1 PDMS at 1200 rpm for 120 s and subsequently crosslinking this layer at 70 °C for 8 h prior to releasing pre-stretch in the mounting layer. Combining the pre-cured film with the adhesive layer gives rise to the substrate layer with an initial thickness of ~200 µm. Then the polystyrene is detached and the PDMS substrate layer is put under uniaxial compression (ε₀) by partially releasing pre-stretch. The top film is a Sylgard 184 40:1 PDMS film with a thickness of ~4 µm by spinning at 7000 rpm for 120 s. The top film is first partially cured at 70 °C for 15 min and then attached to the pre-compressed substrate; bonding between the layers is achieved by subsequently fully curing the film at 70 °C for 8 h. The lateral dimensions of the sample are at least 50 times as large as the combined thickness of the film and substrate, and thus in the central region of the film (where all measurements are conducted), the stress within each layer should be very nearly uniform along the thickness direction.

To measure the viscoelastic properties of our samples, compression stress relaxation experiments are conducted on Sylgard 184 40:1 PDMS cylinders with 12.5 mm in diameter and 15 mm in height molded in a syringe by fully curing at 70 °C for 8 h. The compression stress relaxation experiments are performed on an Instron 5800 compression test machine with 50 N loading cell by first loading the cylinder to a compressive strain of 0.45 with a strain rate 0.05 min⁻¹, and then tracking the compressive stress relaxation over 1 h while holding at this strain. Fitting the stress
relaxation curve with exponential decay function gives rise to the characteristic viscoelastic time $\tau = 1100$ s.

Over the strains of interest ($\varepsilon = 0.42 - 0.48$ for loading and $\varepsilon = 0.48 - 0.35$ for unloading), deformation is performed slowly by applying an incremental changes in strain of $\sim 0.01$ every 30 min, while the formation/disappearance of creases is monitored in situ using an upright optical microscope (Zeiss Axiotech Vario) in bright field reflection mode. Mechanical perturbation is performed with the sample held at a fixed strain by gently poking the surface with a rounded glass micropipette prepared by pulling a heated glass pipette until break and then forging the tip with a torch.

For laser scanning confocal microscopy (Zeiss 510 META), the top film is labeled by incorporating a small amount of fluorescent monomer (4.5 µg fluorescein-o-acrylate per 1 g PDMS). The sample surface is immersed in a refractive index matched fluid of 72% by weight glycerol and 28% water.

### 3.3 Numerical analysis

We use finite-element software ABAQUS to simulate snapping creases in a bilayer film-substrate structure subject to uniform external compression with the substrate under pre-strain. Both the film and the substrate are modeled as incompressible neo-Hookean materials. We write a user-defined material subroutine UMAT for the substrate to include the pre-strains in the free energy function. In order to break the translational symmetry, a small defect ($10^{-4}$ times the total thickness $H_f + H_s$ in size) is prescribed on the surface, and a crease will form on the position of the defect when the critical strain is reached. To eliminate the effect of the defect, its size is set much smaller than the thickness of the film. At the same time, to resolve the field close
to the defect, the size of the elements close to the defect is made much smaller than the size of the defect. The spacing of the creases is prescribed as 2.5 times of the total thickness of the film and substrate, which is similar to the experimental observations. Symmetry is assumed so that only half of a crease is simulated. Riks method based on arclength continuation is used to solve the boundary value problem so that not only the stable solutions, but also the unstable solutions can be captured. After the onset of a crease, the crease tip folds up and forms self-contact. The combination of the Riks method and contact makes the convergence of the simulation hard. A thick layer with extremely low shear modulus (1/100 of the film and substrate shear modulus) is added on the top of the film to prevent self-contact. The top boundary of the extremely compliant layer is constrained to be flat so that instability cannot form there, but can only form on the interface between the film and the extremely compliant layer. As shown in next chapter, when the modulus of the top layer is much smaller than that of the film and substrate, the result of the interfacial crease asymptotically approaches that of a surface crease. In order to realize the uniaxial compression condition as in the experiment by a 2D simulation, we model an axisymmetric ring under uniaxial compression parallel to the symmetry axis. The radius of the ring has to be much bigger than its thickness so that the curvature of the ring can be neglected. Element type CAX8H is used.

3.4 Results and discussions

3.4.1 Origin of hysteresis of creases on elastomer surface

In most experimental systems studied\textsuperscript{22-26} (with the notable exception of hydrogels with relatively low polymer concentration\textsuperscript{16,27,28}), it has been reported that
creases leave permanent “scars”, which allow creases to form at lower strains in the second and subsequent loading cycles. We observe similar behavior for PDMS films compressed in air (Figure 3.1a). During the first loading, a strain of $\varepsilon = 0.520$ is required for creases to nucleate and channel. The over-strain required to overcome the nucleation barrier provided by surface energy leads to a discontinuous jump from a smooth surface to creases of finite depth, as indicated by the solid black line. The depth of the creases (as estimated by optical profilometry of the free surface) decreases smoothly towards zero upon unloading, but scars remain even upon complete removal of compression ($\varepsilon = 0$). While these features diminish in amplitude to some extent over time, they remain visible even after several days at zero compressive strain (Figure 3.1b). During the second loading, the scars become creases (as judged by the change in slope of depth versus strain) at a lower strain ($\varepsilon = 0.485$) than that required for the nucleation of the creases during the first loading. Indeed, the scar-to-crease transition occurs at a strain comparable to the channeling strain.

One might expect that this scarring behavior reflects plastic deformation or material failure at the singular crease tip, thus leading to weak spots that facilitate crease initiation during subsequent cycles. However, strikingly different behavior is found for films compressed in the surfactant solution. In this case, scars are observed when compression is removed, but they completely disappear within 12 h of resting in the unloaded state. Reloading then leads to nucleation and growth of creases in essentially identical fashion as during the first loading.
Figure 3.1 (a) The depth of a crease for a PDMS/air interface shows large hysteresis between the first loading and subsequent unloading/reloading cycles due to formation of long-lived adhesion scars. (b) An optical surface profile shows that scars remain even after the complete removal of compression. The right inset shows a top view optical micrograph of the surface, while the left inset highlights a single scar (the self-contacting regions cannot be resolved in this method, and the profile is convoluted by the resolution of the instrument.)

This qualitative difference in behavior shows that scars are not due to plastic deformation, but instead arise from adhesion in the folded regions of self-contact. As a crease is peeled apart during unloading, the elastic driving force per unit length of crease diminishes with crease depth $d$. For a surface with significant self-adhesion, this force will ultimately fall below the critical strain energy release rate $G_c$ to propagate the “crack” between the self-contacting surface, thus leading to a finite steady-state scar
depth $d_c \sim G_c/\mu$. These experiments have demonstrated that adhesion, rather than plastic deformation, is responsible for the dramatic hysteresis between the first and subsequent cycles of compression.

3.4.2 Controlled formation and disappearance of surface creases

In the first part of this chapter, we have established that surface energy and therefore thermodynamic adhesion at the self-contact region is responsible for the varied degrees of hysteresis of creases observed on different material systems.

Next, we describe a strategy to create bistable flat and creased states, and to switch between the two states repeatedly, with hysteresis, at reproducible strains. We pre-compress a thick substrate, and then attach a thin film on top of the substrate. When we further compress the substrate-film bilayer, the difference in compression between the two layers defines an elastic energy barrier that separates the flat state from a state with deep creases that penetrate into the substrate. We use a combination of experiments and calculations to show that this approach yields well-defined bistable states, connected by a snap-through instability. The strains at which the creases form and disappear are tunable over a large range, through the pre-compression of the substrate and the relative thickness of the film.

The formation of creases can be either a supercritical or subcritical bifurcation. We sketch the bifurcation diagrams using the applied strain $\varepsilon$ as the control parameter, and the depth of crease $d$ as an indicator of state (Figure 3.2). The depth of a crease $d$ is defined as the distance between the uppermost point on the free surface and the bottom of the self-contacting region. For each type of bifurcation, a compressed solid has two
branches of equilibrium states: the flat and the creased states. In the bifurcation
diagram, the branch of flat states corresponds to the horizontal axis \( d = 0 \), while the
branch of creased states corresponds to a curve with \( d > 0 \).

![Bifurcation diagrams](image)

**Figure 3.2** Supercritical and subcritical creases. Bifurcation diagrams for (a) supercritical and
(b) subcritical creases. (c) Energy landscape corresponding to the subcritical bifurcation
diagram.

In the supercritical bifurcation, the creased branch is a monotonic function.
When \( \varepsilon \) exceeds a critical value \( \varepsilon_c \), the flat surface forms creases. The depth of the
creases \( d \) is infinitesimal initially, and then increases gradually as \( \varepsilon \) increases. When \( \varepsilon \) is reduced, the creases disappear at the same critical strain \( \varepsilon_c \), with no hysteresis. By contrast, in the subcritical bifurcation, the creased branch is not a monotonic function. When the applied compressive strain exceeds the strain \( \varepsilon_F \), the flat state becomes unstable, but no creased state of small depth exists; rather, the flat surface snaps forward to a state with creases of finite depth \( d_F \). When the applied compressive strain is reduced, the depth of the creases decreases gradually initially and then, at a finite depth \( d_B \) and strain \( \varepsilon_B \), the creased surface snaps backward to the flat state. That is, the switching between the flat and the creased state is hysteretic.

We can also describe the subcritical bifurcation by sketching the change in elastic energy \( \Delta E \) to form creases as a function of the depth of the creases \( d \) (Figure 3.2c). A minimum energy corresponds to a stable equilibrium state, and a maximum energy corresponds to an unstable equilibrium state. The shape of the energy landscape depends on the applied compressive strain \( \varepsilon \). At a very small strain, \( \varepsilon < \varepsilon_B \), creases of any depth raise the energy, and the flat state is stable. At a very large strain, \( \varepsilon > \varepsilon_F \), the flat state is unstable, and a creased state is stable. At an intermediate strain, \( \varepsilon_B < \varepsilon < \varepsilon_F \), the energy landscape has two local minima, one corresponding to a flat state, and the other to a creased state. Between the snap-forward strain \( \varepsilon_F \) and the snap-backward strain \( \varepsilon_B \) lies the Maxwell strain \( \varepsilon_M \), at which the two energy minima are equal. The flat state has a lower energy than the creased state when \( \varepsilon_B < \varepsilon < \varepsilon_M \), and the opposite is true when \( \varepsilon_M < \varepsilon < \varepsilon_F \).
Figure 3.3 Experimental setup. A mounting layer is stretched to length $L_0$, and a substrate of undeformed thickness $H_s$ is attached over the mounting layer. The mounting layer is partially relaxed to length $L$, and a film of undeformed thickness $H_f$ is attached over the substrate. The mounting layer is further relaxed to length $l$.

We design a system capable of tunable hysteresis of creases by using a multilayer setup (Figure 3.3). We stretch a mounting layer to a length $L_0$, and attach a substrate of undeformed thickness $H_s = 200\,\mu\text{m}$. We then partially relax the mounting layer to a length $L$, which compresses the substrate to a pre-strain $\varepsilon_0 = 1 - L / L_0$. On the pre-strained substrate we attach a film of undeformed thickness $H_f = 4\,\mu\text{m}$. When we relax the mounting layer to a length $l$, the film is under a compressive strain of $\varepsilon = 1 - l / L$. Both the film and substrate are poly (dimethyl siloxane) (PDMS; Sylgard 184, Dow Corning) elastomers of the same composition (40 : 1 base : crosslinker by weight), and thus possess identical elastic properties in the undeformed state (shear modulus $G = 16$ kPa). The mounting layer is a much stiffer and thicker PDMS slab ($G = 260$ kPa), which keeps the bottom boundary of the substrate nearly planar while enabling the application of large compressive strains. All experiments are conducted with the surface submerged under an aqueous solution containing 0.5 mg/mL 3-[hydro(polyethyleneoxy) propyl] heptamethyltrisiloxane (Gelest), which greatly reduces both surface tension (to $\sim 0.8$
mN/m) and self-adhesion, minimizing the importance of these effects compared to elasticity. As a result, the hysteresis arises predominantly from the elastic barrier due to the differential strain between the thin film and substrate, rather than the small residual surface energy and adhesion in the self-contacting region.

**Figure 3.4** Hysteresis of creases. The substrate is pre-compressed by a strain of $\epsilon_0 = 0.15$, and the film-substrate bilayer is then subjected to an additional compressive strain $\epsilon$. (a) Optical microscopy images show that (i) the surface is flat at $\epsilon = 0$, (ii) snaps into creases at $\epsilon = 0.45$, (iii) forms an array of creases at larger compressive strains, and (iv) becomes flat at $\epsilon = 0.36$. (b) Normalized crease depth as a function of the strain applied to the bilayer. The lines are predictions from the finite element method, with the solid line being the stable solution and the dashed line the unstable solution. The dots are experimental results, with the solid dots being on the snap-forward path and the open dots on the snap-backward path. The inset shows the confocal cross section at a strain of $\epsilon = 0.46$. (c) Cross sections (with only the top 2/3 simulation volume shown) generated from finite element simulation showing the distribution of normalized true stress in the compression direction ($2\sigma_{11}/G$) at three different strains: right before snap-forward ($\alpha$), right after snap-forward ($\beta$), and right before snap-backward ($\gamma$), as indicated in (b) with star symbols.

We use reflected light optical microscopy to obtain top-view images *in situ* while relaxing the mounting layer (Figure 3.4a). The substrate is under pre-strain $\epsilon_0 = 0.15$. 

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When the film is compressed, the flat surface snaps forward into the state of deep creases at a strain of $\varepsilon_F = 0.45$. Notably, the value of snap-forward strain $\varepsilon_F$ is very close to the anticipated value of 0.44, i.e., the critical strain for creasing of the film, since the barrier due to surface tension here is very low, and hence even small defects are sufficient to enable creases to nucleate. As compressive strain is further increased, additional deep creases nucleate and grow on the surface, eventually packing into a quasi-periodic array, as seen in Figure 3.4a, panel iii. The tendency of creases to adopt an average spacing proportional to the layer thickness, but without well-defined periodicity, is well known, and results from the difficulty of sliding creases laterally across the surface to adjust the crease locations initially defined by the nucleation and growth process. Once the quasi-periodic array is established, further compression causes the crease spacing to be reduced in an affine manner, i.e., such that the spacing between creases follows $\alpha(H_f + H_s)(1 - \varepsilon)$. Here, we measure a value of $\alpha$ that ranges from 1.9-2.8 between neighboring creases. Thus, we adopt a typical value of $\alpha = 2.5$ for the numerical simulations. When the compressive strain is reduced below the snap-backward strain, the surface becomes flat again. No scars or other visible signs of the creases remain.

We use finite-element software ABAQUS to simulate the formation of creases. To construct the entire branch of ceased states, namely, both the stable and unstable equilibrium states, we use the Riks method of arclength continuation. Due to the combination of the Riks method and issues associated with self-contact, the simulation often does not converge. To enable these calculations, we therefore place a much softer material on top of the film, which prevents surface self-contact and facilitates
convergence of the simulation. As the modulus of this top layer is made much smaller than that of the film and substrate, the result will asymptotically approach that for a free surface. As an example, we present the bifurcation diagram for the case $\varepsilon_o = 0.15$ and $H_f / (H_s + H_f) = 0.02$ (Figure 3.4b) obtained using this method. Also shown are cross-sections with the contour plots of the normalized true stress in the compression direction generated from the simulation (Figure 3.4c). The snap-forward strain is set by the condition to form a crease in the film, which should be the same as the critical strain for a crease to form in a homogeneous material under uniaxial compression, $\varepsilon_F = 0.44$.\textsuperscript{15} The result calculated here, $\varepsilon_F = 0.46$, is slightly higher than this value, reflecting the small influence of the soft material placed above the film. We focus on the case that the film is much thinner than the substrate, $H_f << H_s$. The equilibrium depth of this crease will be set by the substrate thickness—that is $d_f$ is a fraction of $H_s$. Over some intermediate range of strains, two (meta-)stable states exist, one corresponding to a flat surface ($d = 0$), and the other to a deep crease. In this regime, the film remains below the critical strain for creasing, and hence a shallow crease with $d << H_f$ raises the elastic energy, while the substrate is above the critical strain, and hence a deeper crease that penetrates into the substrate with $d >> H_f$ can lower the elastic energy.

To provide a detailed comparison with these predictions, we use laser scanning confocal microscopy (LSCM) to characterize the cross-sections of the samples. The film is stained with fluorescein, and the deep crease is clearly visible (Figure 3.4b inset). Experiments show that upon loading (solid symbols) the surface remains flat until a strain of $\varepsilon = 0.45$ before forming creases. Just beyond this point, a normalized crease
depth of \( d_f/(H_s + H_f) = 0.36 \) is measured, clearly indicating that the creases extend a distance many times the film thickness into the substrate. These values are in good agreement with numerical predictions. As mentioned above, the snap-forward strain \( \varepsilon_f \) obtained by the finite element simulations is around 0.46, which is slightly above the anticipated value of 0.44, due to the addition of the extremely compliant layer to help the numerical convergence. The snap-forward strain \( \varepsilon_f = 0.45 \) observed in experiments also represents a slight overestimate due to the small remaining barrier from surface tension.

Upon subsequently reducing the strain (open symbols), the creases become shallower, reaching a limiting depth of \( d_B = 0.12(H_f + H_s) \) before undergoing a discontinuous snap-through transition back to the flat state at value of \( \varepsilon_B = 0.38 \). The experimental results and numerics show good agreement, although the measured values of \( \varepsilon_B \) are slightly lower than the predictions. In the simulations, the snap back strain \( \varepsilon_B \) is slightly overestimated due to the soft layer placed above the film. We also suspect that the experimental value of \( \varepsilon_B \) may be reduced slightly due to a small amount of adhesion of the surface within the self-contacting region. Nevertheless, bistability between flat and creased states, and a well-defined window of hysteresis are clearly developed by applying a compressive pre-strain to a soft substrate underlying a soft film.
Figure 3.5 Switching between flat and creased states. The sample is switched between flat and creased states by cyclically increasing and decreasing the strain. The dots are experimental data. The dashed lines are the snap-forward strain $\varepsilon_F$ and snap-backward strain $\varepsilon_B$ calculated using the finite element method. The optical images show the surface in four states.

Our experimental measurements show that the snap-forward and snap-backward strains are reproducible (Figure 3.5). The measured values of $\varepsilon_F$ and $\varepsilon_B$ remain unchanged over several cycles within the precision of our measurements, once again indicating that no permanent scarring or damage to the material has occurred. The inset images in Figure 4 show the first cycle (a and b) and the third cycle (c and d) switching between creased states and flat states. During the third cycle, the sample is left creased (image c) for 2-3 days prior to snapping back at the same strain, indicating that even long-term aging does not damage the material. However, the creases do form at the same locations during each cycle, presumably due to the heterogeneities in the film that consistently serve as nucleation sites.

When the applied strain lies between the Maxwell strain $\varepsilon_M$ and the snap-forward strain $\varepsilon_F$, the flat state is metastable against the formation of creases, and hence it
should be possible to mechanically perturb the surface to overcome the elastic energy barrier and drive the formation of a deep crease. Figure 3.6 shows just this behavior on the surface of a bilayer with \( \varepsilon_0 = 0.15 \) and \( \varepsilon = 0.42 \) gently poked with a glass micropipette. Initially, a crease forms rapidly, and only in the vicinity of the perturbation. However, since the crease is lower in energy than the flat state, this localized crease spreads laterally, or “channels”, slowly from both ends over time. While this local snapping is fast, propagation of the short deep crease is slow. On the contrary, if the applied strain is below \( \varepsilon_B \), the flat surface is the global energy minimum and should be stable against perturbations. For bilayer with \( \varepsilon_0 = 0.15 \) and \( \varepsilon = 0.37 \), while poking with a glass micropipette induces formation of a transient crease, the flat state is quickly recovered.

**Figure 3.6** In the strain range of \( \varepsilon_M < \varepsilon < \varepsilon_F \), flat surface is metastable against mechanical perturbation. (a) When the substrate is subject to a pre-strain of \( \varepsilon_0 = 0.15 \) and the bilayer is subject to an additional compressive strain of \( \varepsilon = 0.42 \), between the Maxwell strain and the snap-forward strain, the flat surface is metastable. (b) A gentle poke overcomes the energy barrier and (c) the flat surface locally snaps into a deep crease. (d) The deep crease propagates at both ends and crosses the entire surface of the sample over time.
Figure 3.7 The zero-speed strain and the Maxwell strain. (a) The speed at which an isolated crease propagates or retracts is measured experimentally as a function of the applied strain. The interpolated zero-speed strain is $\varepsilon = 0.397 \pm 0.005$, which is close to the Maxwell strain $\varepsilon_M = 0.402$ calculated using the finite element method (indicated by the red open circle). (b) The energy difference between creased and flat states as a function of the applied strain is calculated using the finite element analysis. The Maxwell strain is the strain where creased state has the same energy as flat state (indicated by the red open circle).

This behavior allows us to experimentally determine the Maxwell strain, where the crease propagation speed should vanish, which is otherwise difficult to measure. As in Figure 3.6, an isolated crease is formed first by poking the surface of a sample.
compressed to $\varepsilon_M < \varepsilon < \varepsilon_F$. The compressive strain is then reduced stepwise and the crease propagation velocity characterized at each step. As plotted in Figure 3.7a, the growth velocity decreases as the applied strain is lowered, due to the reduction in the driving force for growth (i.e., the difference in elastic energy between the flat and creased states), just as in channeling of cracks$^{30}$. When the strain is reduced to the Maxwell strain, the crease ceases to propagate, and ultimately begins to retract from both ends with further decreases in strain. In Figure 3.7b, we plot the normalized energy difference between the creased state and the flat state obtained by simulations. The shallow crease solution always has higher energy than the flat state, while the deep crease solution has energy lower than the flat state when the strain is higher than the Maxwell strain. The predicted Maxwell strain, defined as the strain when the flat state and the deep creased state have the same elastic energy, is denoted by red open circles in Figure 3.7a and 3.7b. When $\varepsilon_0 = 0.15$ and $H_f/(H_f + H_s) = 0.02$, the Maxwell strain is predicted as $\varepsilon_M = 0.402$, while the measured value is $\varepsilon_M = 0.397 \pm 0.005$, very close to the prediction. However, we note that the predicted Maxwell strain is for periodic creases, while the measured Maxwell strain is for an isolated crease, thus the two should not agree perfectly. While the kinetics of crease channeling remain under study, we note that the slow propagation speeds of 0.54 μm/s to -0.14 μm/s (Figure 3.7a), likely reflect the viscoelastic relaxation of material elements near the front of the propagating crease, in a similar fashion as for propagating cracks$^{31}$. 
Figure 3.8 Tunable hysteresis of creases. (a) Snap-forward and snap-backward strains as a function of pre-strain for different thickness ratios. The black dotted line indicates the relationship $\varepsilon_B = (\varepsilon_F - \varepsilon_0)/(1 - \varepsilon_0)$ between snap-forward strain $\varepsilon_F$ and snap-backward strain $\varepsilon_B$, expected in the limit of vanishing film thickness. (b) Snap-forward and snap-backward crease depths as a function of pre-strain for different thickness ratios. Dashed lines (snap-forward) and solid lines (snap-backward) are calculated using the finite element method. The black solid symbols (squares for snap-forward and circles for snap-backward) are experimental results for thickness ratio $H_f/(H_f + H_s) = 0.02$, in good agreement with numerical results.

We use finite element simulations to characterize how the hysteresis of creases depends on the level of pre-strain and the thickness ratio of the film and substrate.
(Figure 3.8). The snap-forward strain $e_F$ has no dependence on either quantity, as it is simply determined by the stability of the film against forming a shallow crease. In contrast, the snap-backward strain $e_B$ increases with $H_f/(H_f+H_s)$ but decreases with $e_o$. Snapping back is determined by the difference between the energy reduction in the substrate and the energy increase in the film in the deep creased state with respect to the flat state. When the pre-strain $e_o$ is larger, the energy reduction in the substrate in the deep creased state is bigger and hence the snap-backward strain $e_B$ is lower. When $e_o$ is smaller, the snap-backward strain gets closer to the snap-forward strain $e_F$ and converges to $e_F$ when $e_o = 0$. In the limit of vanishing film thickness, the snap back strain $e_B$ should correspond to the point where the strain in the substrate drops to the critical strain for creasing. This would lead to the relationship $e_B = (e_F - e_o)/(1 - e_o)$, as plotted in Figure 3.8a (black dotted line). When the thickness ratio $H_f/(H_f+H_s)$ is larger, the energy increase in the film in the deep creased state is bigger and the snap back strain is higher. The snap-forward depth $d_F$ is primarily set by the thickness and strain of the substrate. Hence, $d_F$ is almost independent of the film thickness but increases with the pre-strain $e_o$. However, the snap back depth $d_B$ increases with the film thickness, for similar reasons as the effect on $e_B$ described above. The snap back depth $d_B$ also increases with the pre-strain $e_o$, since the depth of the crease increases with the strain in the substrate. With the decrease of $e_o$, $d_F$ gets closer to $d_B$. Finally both converge to $0$ when $e_o = 0$, and the instability becomes supercritical with no hysteresis. In the current study, we only consider pre-strains $e_o \leq 0.2$, because larger pre-strains yield wrinkles at
strain smaller than $\varepsilon_F$. However, we note that reducing the modulus of the film below that of the substrate allows the pre-strain $\varepsilon_0$ to be tuned over a larger range. We also include in Figure 6 the corresponding experimental results for the thickness ratio studied, $H_f/(H_f + H_s)=0.02$, which show rather good agreement with numerical results. These results provide detailed guidelines for fine-tuning both the extent of the hysteresis window in strain, as well as the amplitudes of both the snap-in and snap-out transitions.

3.5 Conclusions

In this chapter, we have identified varied degrees of hysteresis of creases observed on different material systems are due to surface energy and therefore thermodynamic adhesion at the self-contact region. We have also described a robust method for controlling the hysteretic behavior of surface creases through application of compressive pre-strain to the substrate of a soft bilayer. Over a well-defined range of strain, the system shows kinetic bistability between flat and deep creased states with snap-through transitions between these states at either extreme. Surfaces can be repeatedly snapped forward and backward between these states with little variation, and in good agreement with the predictions from numerical analysis. We anticipate that the greatly improved control over hysteresis, and the demonstration of bistability over a substantial range of strain will open new opportunities for applications of creases in sensors and responsive surfaces. This experimental system of a bilayer supported on a pre-stretched foundation provides great freedom to independently tune the modulus, thickness and pre-stretch/compression of both the substrate and film layers. While the current study has concerned only a very small range of parameter space with small
values of $H_f/(H_f + H_s)$, identical material properties for the film and substrate, and a narrow range of $\varepsilon_0$, we anticipate that the same approach will enable detailed studies of the rich landscape of behaviors in other regimes.

### 3.6 References


He, J., Xu, G. & Suo, Z. in AIP Conference Proceedings. 3.

CHAPTER 4

CREASES ON THE INTERFACE OF TWO SOFT MATERIALS

4.1 Introduction

Bonded materials with dissimilar properties are ubiquitous. They exist in composite materials, geological strata, electronic devices, biological tissues and soft actuators. In many cases, stresses arise due to differences in thermal expansion, chemical reaction, growth, swelling, or mechanical pre-strains. Such mismatches may cause buckling instabilities, which can reduce the strength of structures and lead to debonding of the interfaces.

Interfacial instability has long been regarded as a bifurcation from a state of flat interface. For example, Biot studied two elastic materials compressed along a direction parallel to the interface. He predicted that the interface forms wrinkles at a critical compression, similar to the formation of wrinkles on the free surface of a soft solid. These wrinkles have dynamic analogs: Stoneley waves on the interface between two materials, and Rayleigh waves on the surface of a homogeneous material. Wrinkles, however, have not been observed on surfaces of homogeneous elastic materials under compression; rather, creases have been observed. A recent theory shows that surface wrinkles and surface creases are two types of instability, and the critical strain for the onset of surface wrinkles is higher than that for the onset of surface creases. Notably, these phenomena occur at rather large compressive strains. While hard elastic materials generally cannot be loaded to such large strains without fracture,

soft materials such as gels and elastomers can easily be compressed to the point of instability.

Motivated by this recent understanding, in this chapter, we reconsider the stability of the interface between two soft materials. Our theory and experiment show an analogous localized, large-strain instability, which we call interfacial creases (Figure 4.1). Wrinkles and creases are two types of bifurcation from the state of flat interface. While wrinkles bifurcate by a deformation nonlocal in space and infinitesimal in amplitude, creases bifurcate by a deformation local in space and large in amplitude. In this regard, the wrinkling instability is of the same type as buckling of columns and plates, while the creasing instability is reminiscent of cracking, cavitation, shear banding, and phase transformation. Upon initiation, an interfacial crease corresponds to a field scaled by a single length scale. The critical strain is independent of this length scale and is scale-free. We calculate the critical conditions for the onset of the interfacial creases and find that, just like their surface counterparts, interfacial creases always form at lower compression than interfacial wrinkles. We show that interfacial creases are V-shaped. The presence of two materials prevents the interface from self-contact, but the tip of an interfacial crease is singular. Because the interface does not self-contact, the analysis of interfacial creases is simplified compared to that of surface creases. We demonstrate the existence of interfacial creases by experiments with hydrogels. By using differential swelling of two types of gels, we can form interfacial creases and surface creases independently.

4.2 Experimental

4.2.1 Experiment with hydrogels confined in a glass slit
A glass slit, thickness 1 mm and width 28 mm, is constructed by gluing glass slides together (Figure 4.4). The inner surfaces of the slit are treated with trimethylchlorosilane to reduce adhesion of the gels to the glass surfaces. A charged gel layer is first prepared by loading the slit with an aqueous pre-gel solution containing 700 mM \(N\)-isopropyl-acrylamide, 660 mM sodium acrylate and 45 mM \(N,N'\)-methylenbisacrylamide. Gelation is initiated by adding 1 \(\mu\)L of 10% w/w ammonium persulfate aqueous solution as the initiator and 0.3 \(\mu\)L \(N,N,N',N'\)-tetramethylenediamine as the catalyst into 200 \(\mu\)L of freshly degassed pre-gel solution immediately prior to loading the chamber. To stain the charged gel, a small amount \((3.2\times10^{-5}\text{ mmol})\) of a Rhodamine B-labeled methacrylate is incorporated into the 200 \(\mu\)L pre-gel solution. Next, a softer uncharged gel is prepared on top of the charged gel using the same procedure as above, but with a pre-gel solution containing 701 mM acrylamide and 19 mM \(N,N'\)-methylenbisacrylamide. Some interpenetration of the second gel into the existing charged gel does occur, and helps to bond the materials together, but based on the relatively rapid speed of gelation (~ 20 min), this length-scale is small compared to the ~ 1 cm dimensions of the gels. The contrast in modulus between the gels is not known, but based simply on the relative crosslinker concentrations, the charged gel should be at least ~ 2.4-fold stiffer than the uncharged gel.\(^{31}\) Following gelation, this confined gel sample is soaked in deionized water for 3 weeks to reach swelling equilibrium, and the shape of the interface is recorded using a digital camera.

### 4.2.2 Experiment with thin layers of gels on a glass substrate
This experiment uses a photo-crosslinkable poly(N-isopropylacrylamide-co-sodium acrylate-co-acrylamidobenzophenone) (poly(NSA)) polymer described in previous reports. A glass cover slip substrate is pretreated with [3-(methacryloxy)-propyl]trichlorosilane to provide covalently anchoring, then a copolymer film is solution cast from chloroform to yield a film thickness of \( H_2 = 6-8 \mu m \), followed by crosslinking by exposure to 365 nm UV light. A much softer uncharged gel is next formed by loading a freshly prepared de-gassed aqueous pre-gel solution (containing 701 mM acrylamide and 19 mM \( N,N' \)-methylenebisacrylamide; prepared as above) between the substrate-attached photo-crosslinked polymer film and a clean cover slip, and allowing 20 min for polymerization to proceed. The uncharged gel film thickness \( H_1 = 76 \mu m \) is defined using Kapton 300HN films (DuPont) as spacers. To prevent swelling of the photo-crosslinked poly(N-isopropylacrylamide) film by the pre-gel solution, the neutral gel is formed at 70 °C. Following polymerization, the cell is cooled to room temperature and the glass slides are separated. The surface-attached gel bilayer is then transferred to a phosphate buffered saline swelling solution containing 274 mM sodium chloride. Deionized water is then added drop-wise to dilute the swelling solution and thus increase the swelling ratio of the charged gel, while the formation of creases is monitored in situ using either an upright optical microscope (Zeiss Axiotech Vario) in reflected-light differential interference contrast mode or a laser scanning confocal fluorescence microscope (Zeiss). Based on a previous report, we estimate the Young’s modulus of the uncharged gel to be \( \sim 5 \) kPa, while that of the charged gel is estimated to be several hundred kPa based on the density of photo-crosslinking groups in the copolymer.
4.3 Results and discussions

We study the initiation of interfacial creases by comparing two states of equilibrium subject to the same applied strain (Figure 4.1). In the state of flat interface, the field in either material is homogeneous, and the elastic energy of the state is denoted by $U_0$. In the creased state, one point of the interface is prescribed with a downward displacement $L$, and the elastic energy of the state is denoted $U$. The magnitude of the displacement $L$ is arbitrary, so long as it is much smaller than any other length in the boundary-value problem (e.g., the thickness and width of the block used in computation). Once $L$ is prescribed, the creased state is determined by a boundary-value problem of large deformation. The two states of equilibrium differ by a deformation of large amplitude, but the difference is localized in a small region scaled by the length $L$. The two materials are taken to be incompressible and neo-Hookean, with shear moduli $G_A$ and $G_B$. We begin with the case that pre-strains are absent, and the block is compressed to reduce its width under plane strain conditions. The applied strain $\varepsilon$ is defined as the reduction in the width of the block divided by the width of the block in the undeformed state. Dimensional considerations dictate that the energy of the creased state should differ from that of the flat state by

$$U - U_0 = G_B L^2 f(\varepsilon, G_B / G_A).$$

(1)

As indicated, the dimensionless number $f$ is a function of the applied strain and the ratio of the shear moduli. The scaling relation (1) generalizes the result for surface creases.$^{34}$

Without loss of generality, we assume that $G_A < G_B$. We expect that interfacial creases form by growing into the stiffer material (B). In the absence of applied strain,
the energy of the state of flat interface vanishes, but the energy of the creased state is positive, so that the state of flat interface is stable. When a sufficiently large compressive strain is applied, the crease elongates the interface, so that the crease reduces energy in material B, but increases energy in material A. Because $G_A < G_B$, the crease can reduce the total elastic energy in the two materials. For a fixed ratio $G_B / G_A$, the function $f(\varepsilon, G_B / G_A)$ decreases monotonically with the applied strain $\varepsilon$. An interfacial crease sets in when the creased state has the same energy as the flat state, namely,

$$f(\varepsilon, G_B / G_A) = 0.$$  \hspace{1cm} (2)

This condition gives the critical strain for the onset of interfacial crease, $\varepsilon_c$, as a function of the modulus ratio, $G_B / G_A$.

![Figure 4.1](image)

**Figure 4.1** Materials A and B are bonded to each other along a flat interface. Subject to a compressive strain, the interface may either remain flat (a), or form creases (b).

The critical condition (2) for the onset of interfacial crease is independent of any length scale. This scale-free behavior results from two considerations. First, the prescribed displacement $L$ is assumed to be small compared to other lengths in the boundary-value problem, such as the thickness and width of the block used in the
calculation. The flat state differs from the creased state by a deformation localized within a region scaled with \( L \). Consequently, only the length \( L \) enters (1), and no length appears in the critical condition (2). Second, the theory of elasticity does not have any material-defined length scale. The situation would be different if we accounted for the interfacial tension \( \gamma \) between the two materials. The interfacial tension, together with the elastic modulus \( G \), would provide a length scale, the elastocapillary length \( \gamma/G \). This length scale can vary across many orders of magnitude depending on the material system, but typical values for elastomer/elastomer interfaces are \( \gamma \sim 1 - 10 \) mN/m and \( G \sim 100 \) kPa, while for gel/gel interfaces they are \( \gamma \sim 0.1 - 1 \) mN/m and \( G \sim 10 \) kPa, in both cases yielding \( \gamma/G \sim 10 - 100 \) nm. Incorporating interfacial tension will cause the tip of an interfacial crease to be rounded on a length scale of \( \gamma/G \), rather than being infinitely sharp. Interfacial tension would also provide a barrier against the initiation of interfacial creases, just as in the case of surface creases, thus requiring the application of a small amount of overstrain to drive crease nucleation.\(^3\) For simplicity, however, we ignore here the effects of interfacial tension and consider only elastic contributions, which is appropriate for understanding fully formed creases for samples much thicker than \( \gamma/G \).

In the above description, the creased state is determined by a boundary-value problem of large deformation, and the prescribed displacement \( L \) specifies the length scale. This particular way of specifying a length scale, however, does not affect the critical strain for the onset of the crease. Upon initiation, the creased state is scaled by one length, independent of how the length is specified.
Figure 4.2 Energy in both materials, $U_F$, energy in material A, $U_A$, and energy in material B, $U_B$, are plotted as functions of the applied strain. Each energy is normalized by the energy in the two materials in the state of flat interface, $U_0$.

We use finite element method to simulate the growth of an interfacial crease. In the reference state, two materials A and B are bonded with a flat interface. We make use of the symmetry condition, and only simulate the right half of a crease. After a crease initiates, its growth does depend on the size of the block used in the calculation. Here the two materials in the reference state have the same thickness $H$, and the lateral size of the simulation box (corresponding to half of the spacing between creases) is set to be $W = H$, close to what is observed in our experiments. To seed the crease, a small defect is prescribed on the left end of the interface. The size of the defect is much smaller than the thickness of either material, but is large compared to the size of the surrounding mesh. In the current state, a horizontal displacement is applied on the boundary on the right. The top and bottom boundaries are constrained to remain planar, so that they cannot form surface creases. The boundary on the left is a plane of mirror symmetry. The two materials are compressed in the horizontal direction and expand in the vertical direction, while the depth of the crease, $L$, evolves as a function of the applied displacement.
Figure 4.3 Interfacial creases under applied strain.  (a) The critical strain for the onset of creases as a function of the ratio of the shear modulus, $G_B / G_A$. Also plotted is the critical strain for the onset of wrinkles.  (b) The depth of a crease as a function of the applied strain for several values of $G_B / G_A$.  (c) Shapes of creased interfaces at applied strain $\varepsilon = 0.55$, for several values of the modulus ratio.
The elastic energy is a function of the applied strain (Figure 4.2). Let \( U_0 \) be the energy in the two materials in the state of flat interface, and \( U_F \) be the energy in the two materials calculated by using the finite element method of simulating crease growth. When the applied strain \( \varepsilon < 0.512 \), the interface remains flat, and the total elastic energy is the same as that in the two materials in the state of flat interface \( U_F / U_0 = 1 \). When \( \varepsilon > 0.512 \), a crease forms, reducing the total elastic energy below that in the two materials in the state of flat interface, \( U_F / U_0 < 1 \). Consequently, we identify \( \varepsilon = 0.512 \) as the critical strain for the onset of creases. After an interfacial crease forms, the elastic energy of the bottom material \( U_B \) decreases while the elastic energy of the top material \( U_A \) increases. Since the bottom material is stiffer than the top material, the decrease in elastic energy of the bottom material is larger than the increase in the energy of the top material. Consequently, the interfacial crease reduces the total energy \( U_F \).

Similarly, we can simulate the initiation and growth of interfacial creases for other modulus ratios. As expected, the critical strain for the onset of interfacial crease decreases as the modulus ratio \( G_B / G_A \) increases (Figure 4.3(a)). In the limit \( G_B / G_A \rightarrow \infty \), the critical strain for the onset of an interfacial crease recovers that of a surface crease, \( \varepsilon_c = 0.354 \). In the limit \( G_B / G_A \rightarrow 1 \), the two materials are elastically homogeneous, and an interfacial crease will not form under any compressive strain, so that \( \varepsilon_c \rightarrow 1 \). Also plotted in Figure 4.3(a) is the critical strain for the onset of interfacial wrinkles. While the onset of interfacial creases is determined by a boundary-value problem of large deformation, the onset of interfacial wrinkles is determined by a boundary-value problem of infinitesimal deformation superimposed on a known large
deformation. For any value of modulus ratio, the interfacial crease sets in at a critical strain lower than the interfacial wrinkles.

Figure 4.3(b) shows the evolution of interfacial crease depth with the applied strain for different modulus ratios. The limit $G_B/G_A \to \infty$ corresponds to a surface crease. At a lower value of $G_B/G_A$, material A retards the onset of the crease, and the interfacial crease is shallower than the surface crease under the same applied strain. The calculated shapes of the creased interfaces are V-shaped (Figure 4.3(c)). Under the same strain $\varepsilon = 0.55$, the interfacial crease is deeper for a larger value of $G_B/G_A$, and asymptotically approaches the shape of a surface crease with self-contact as $G_B/G_A \to \infty$.

We perform experiments to show the existence of interfacial creases. In one experiment, two hydrogels are confined between glass slides (Figure 4.4). The two gels are bonded to each other, but are not bonded to the glass slides. The colored gel is stiffer than the colorless gel. The former has a polymer network containing fixed charges, while the latter has an uncharged network (Figure 4.4(a)). After preparation, the two gels are nearly stress-free, and the interface is flat (Figure 4.4(b)). When placed in water and allowed to swell, the charged gel is subject to compressive stress due to its inability to expand laterally, leading to the formation of interfacial creases (Figure 4.4(c)). The uncharged gel swells negligibly, so that the top surface does not form surface creases.
Figure 4.4 Creases formed on the interface between two hydrogels. (a) A schematic of the experimental setup. Confined in a 1 mm thick glass slit are two gels, one with a charged network and the other with unchanged network. The gels are bonded to each other, but are not bonded to the glass. (b) After the preparation, the two hydrogels are relatively dry and stress-free, and the interface is flat. (c) When soaked in water, the charged gel swells much more than the uncharged gel, so that creases form on the interface between the two gels, but not on the free surface of the uncharged gel.

Figure 4.5 A comparison of surface creases and interfacial creases. (a) A charged gel is attached to a glass substrate, and is partially covered by an uncharged gel. (b) Cross-sectional schematic and (d) top-view micrograph when the charged gel swells by $H_2'/H_2 = 2.4$. Creases form on the free surface of the charged gel, while the interface between the gels remains flat. (c) Cross-sectional schematic and (e) top-view micrograph when the charged gel swells by $H_2''/H_2 = 3.3$. Creases also form on the interface. The creases on the interface have a smaller depth than the creases on the surface, as shown by the cross-sectional confocal images in the insets.

A second experiment is performed to compare interfacial creases and surface creases (Figure 4.5). A charged gel of thickness $H_2 = 6 - 8 \ \mu m$ is attached on a glass
substrate. A portion of the gel is then covered with an uncharged gel of thickness \(H_1 = 76\ \mu m\) (Figure 4.5(a)). When immersed in a phosphate buffered saline solution containing 274 mM sodium chloride, both gels swell slightly and generate in-plane equibiaxial compressive stresses, but the compression is insufficient to cause either surface or interfacial creases. Deionized water is then added drop by drop to reduce the concentration of the saline solution, so that the charged gel swells more and the uncharged gel swells negligibly (as characterized by fluorescence confocal microscopy). When the swelling ratio of the charged gel reaches \(\frac{H_2'}{H_2} = 2.4\pm0.1\), the uncovered portion of the charged gel forms surface creases, while the interface between the two gels remains flat (Figure 4.5 (b), (d)). This critical swelling ratio for the onset of surface creases is in good agreement with previous reports\(^{28}\). When the swelling ratio is increased to \(\frac{H_2''}{H_2} = 3.3\pm0.1\), the covered region of the gel forms interfacial creases (Figure 4.5 (c), (e)). At the same degree of swelling, the interfacial creases are shallower than surface creases, as shown by the cross-sectional confocal images in the insets of Figure 4.7 (e). Both surface and interfacial creases show a spacing of \(\sim 20\mu m\), or roughly 2.5 – 3 times \(H_2\). The gel of uncharged network swells negligibly, and its surface remains flat.

While these experimental observations qualitatively agree with our theoretical predictions, quantitative comparison between experiments and calculations would require that constitutive behavior of the gels be characterized with precision and used in the calculations. This task is beyond the scope of the present work.

Further, using the second experimental setup, we try to examine the hysteresis of creasing during multiple swelling-deswelling cycles. Without forming self-contact, the
interface creasing is expected to be totally reversible. However, we find interface creases could not disappear completely upon deswelling, leaving scars that seed creases during the following swelling cycles. The origin of the hysteretic behavior of interface creases remains a question to answer.

4.4 Conclusions

We present calculations and experiments to show that an interface between two soft materials under compression can form creases. A creased state deviates from a state of flat interface by a deformation large in amplitude and local in space. The critical condition for the onset of interfacial creases is scale-free. This critical condition is calculated in terms of elastic moduli, pre-stretches and applied stretches by allowing deviation from a flat state with a large deformation. By contrast, a wrinkled state deviates from a state of flat interface by a deformation infinitesimal in amplitude and nonlocal in space. The critical condition for the onset of interfacial wrinkles is calculated by a small-perturbation method. In all cases studied, the critical conditions for the onset of interfacial creases are reached before those for the onset of interfacial wrinkles.

4.5 References


CHAPTER 5
CREASING OF CONFINED SWELLING HYDROGELS WITH VARIED GEL THICKNESS, COMPOSITION OR STRESS STATE

5.1 Introduction

In previous chapters we have characterized the equilibrium structure of creases under uniaxial compression, explored the formation mechanism and hysteresis of creases, and developed a hydrogel system to demonstrate the formation of interfacial creases. In all these experiments and analysis, we assume a linear dependence of crease spacing on the initial film thickness, which should hold when surface energy is much smaller than elastic energy. However, the elastic energy decreases with decreasing initial film thickness, while surface energy has no dependence on the film thickness. For very thin films, where the elasto-capillary length becomes comparable with the film thickness, surface energy penalizes the formation of short wavelength creases. The linear dependence of crease spacing on the film thickness will break down\(^1\). In the first part of this chapter, we will characterize creases on confined swelling hydrogel film with film thickness ranging from a few microns to tens of nanometers. In the previous chapters, we have established that surface energy, and therefore thermodynamic adhesion at the self-contact region, is responsible for the varied degrees of hysteresis observed. While this argument is made based on experiments performed on an elastomer system, which is in general tough and resilient, it deserves close scrutiny when applied to the hydrogel systems on which the majority of literature on creasing instability concerns, which are known to be soft yet notoriously brittle\(^2\). In hydrogel
systems, the formation and disappearance of creases happens upon swelling and de-swelling, during which the gel volume fraction changes and hence the thermodynamic adhesion changes. While local material failure at the crease tip due to large local strain could pin creases, other sources of adhesion, such as entanglement of polymer chains in the hydrogel system upon de-swelling, could also give rise to memory\(^3\). In the second part of this chapter, we will examine hysteresis of creases on confined swelling hydrogels with varied initial gel volume fraction. From previous chapters, we know the morphology of creases depends on the stress state. Under uniaxial compression, creases form a quasi-periodic array\(^4\), while under equibiaxial compression, creases are randomly oriented due to in plane stress symmetry\(^5\). While the breaking of stress symmetry to direct crease formation has been achieved previously by using topographic patterns\(^6,7\) or micro-patterned electric field\(^8\), the systematic study of crease morphology dependence on stress state is still lacking. In the last part of this chapter, we attempt to address this problem.

5.2 Experimental

5.2.1 Wavelength /thickness ratio as a function of initial film thickness

All the samples are prepared with a photo-crosslinkable polymer poly(N-isopropylacrylamide-co-acrylic acid-co-acrylamidobenzophenone) poly(NAA). We synthesize this polymer by free radical copolymerization of 2 g N-isopropylacrylamide, 13 µL acrylic acid and 140 mg acrylamidobenzophenone in 30 mL 1, 4-dioxane. The reaction solution, together with 1.5 mg Azobisisobutyronitrile (AIBN) is put into a 100 mL gauge round-bottom flask, degassed by freeze-pump-thaw 3 times and then back filled with nitrogen. This reaction is initiated by heating the flask with oil bath to 80 °C
and proceeds for 12 hours refluxing at 80 °C. After cooling to room temperature, the reaction solution is diluted to 50 mL by adding 20 mL more 1, 4-dioxane, precipitated twice into diethyl ether, filtered and vacuum dried to yield 1.6 g polymer.

Acrylamidobenzophenone is synthesized by reacting 4-aminobenzophenone with acryloyl chloride. Specifically, 0.7 g 4-aminobenzophenone is dissolved into 15 mL anhydrous dichloromethane in a 50 mL gauge two-neck round-bottom flask, followed by syringe injecting 0.6 mL triethylamine into the capped flask. The flask is then cooled down to 0-5 °C with ice-water bath. 0.32 mL acryl chloride is added dropwise with a syringe over half an hour and stirred for 12 h at room temperature. The reaction is purified by washing 3 times with 1 M hydrochloride, 3 times with 1 M sodium bicarbonate and 3 times with pure water. The oil phase is dried over magnesium sulfate, filtered, rotary evaporated and dried under vacuum to yield a yellowish product, with structure confirmed by proton NMR.

Pre-gel films with thickness of 220 nm, 90 nm and 45 nm are spin-casted from poly(NAA)/cyclohexanone solution by varying polymer solution concentration and spin rate. Pre-gel films with thickness of 3-7 µm are drop casted from poly(NAA)/chloroform solution by varying polymer solution concentration. Silicon wafers, pre-treated with [3-(methacryloxy)-propyl]trichlorosilane to provide covalent anchoring, are used as substrates. Crosslinking is performed by exposure to 365 nm UV light. The thicknesses of films are determined by optical reflectometry or ellipsometry.

Samples are soaked in phosphine buffered saline (PBS) containing 137 mM sodium chloride to reach swelling equilibrium. They are then characterized by MFP-3D
AFM using low spring constant silicon nitride AFM probes with tapping mode. All the AFM measurements are conducted in PBS within a closed fluid cell.

5.2.2 Hysteresis of creases on confined swelling hydrogels with different polymer volume fraction

Two sets of samples are prepared for this experiment. Hydrogels with high polymer volume fraction are prepared in the same way as in the previous section. Specifically, pre-gel film with a thickness ~6 μm is drop casted out of poly(NAA)/chloform solution, and crosslinked with 365 nm UV light. Hydrogels with low polymer volume fraction are prepared from a freshly prepared aqueous pre-gel solution containing 785 mM N-isopropylacrylamide (NIPAM), 113 mM sodium acrylate (NaAc), and 4.5 mM N,N'-methylenebisacrylamide (BisAA). Gelation is initiated by adding 1 μL of 10% w/w ammonium persulfate aqueous solution as the initiator and 0.3 μL N,N,N',N'-tetramethylenediamine as the catalyst into 200 μL of freshly degassed pre-gel solution immediately prior to loading between a [3-(methacryloxy)-propyl]trichlorosilane pre-treated glass substrate and a clean cover slip separated by Kapton 30HN films spacers to define the gel thickness of 7.6 μm. The gelation cell is then put into a centrifugal tube under nitrogen atmosphere, allowing 30 min for the polymerization to proceed.

To measure hysteresis, AFM measurements are performed in PBS within a BioHeater™ Closed Fluid Cell (Asylum Research). Temperature is step changed between 60 °C and 25 °C, allowing system to equilibrate at each temperature for at least 30 min before the recalibration of AFM probe and measurement. Separate experiments are
performed with optical microscope (Zeiss Axiovert 200) to measure the swelling ratio of hydrogels as a function of temperature.

### 5.2.3 Morphology of creases under different stress state

Samples are prepared by spin coating poly(NAA)/cyclohexanone solution onto PDMS/Poly (2-hydroxyethyl methacrylate)(HEMA) interpenetrating polymer network (IPN) film substrate, followed by photo-crosslinking by exposure to 365 nm UV light. The sample is then carefully mounted onto a custom designed stretcher and soaked in PBS with controlled salt concentration or temperature to tune the swelling ratio. While strain is applied, the formation or morphologic change of creases is in situ monitored with inverted optical microscope (Zeiss Axiovert 200) in phase contrast mode.

PDMS/Poly (HEMA) IPN film substrates are prepared by soaking fully cured 15:1 Sylgard 184 PDMS film stripes with dimensions 0.8 cm × 2 cm × 0.7 mm into HEMA monomer/pyridine solution together with AIBN as initiator for 2 days. Then the solution is purged with nitrogen for 3 hours, followed by heating to 80 °C to initiate the polymerization. After the reaction, the stripes are collected and washed with acetone and pure water.

We also put elastomer film under equibiaxial compression by inflating a PDMS balloon of 20:1 Sylgard PDMS film with nitrogen, gluing a small thin 40:1 Sylgard PDMS film on the apex and deflating the PDMS balloon afterwards.

### 5.3 Results and discussions

#### 5.3.1 Wavelength /thickness ratio as a function of initial film thickness
Figure 5.1 Normalized crease spacing as a function of film thickness. (a) a schematic of creasing of substrate confined swelling hydrogel, creases on hydrogel surface characterized by AFM in fluid with varied initial film thickness: (b) 6.5 μm, (c) 3.5 μm, (d) 220 nm, and (e) 90 nm, (f) Normalized crease spacing is plotted as a function of initial film thickness.

When creasing experiments are conducted on elastomer or gel films with large film thickness, surface energy is much smaller than elastic energy. We observe a linear dependence of crease spacing on the initial film thickness. On confined swelling hydrogel surface with initial thickness ranging from 3 μm to 1 mm, the spacing : initial film thickness ratio ($\lambda / H$) is around 2, which agrees with a previous report, since the gel film thickness is the only relevant length scale. On uniaxially compressed elastomer film, the ratio in the un-deformed state is 3.5. However, as the film thickness is reduced, the influence of surface energy will increase and therefore $\lambda / H$ is expected to increase since surface energy will penalize the formation of short wavelength creases. Here we characterize the creases on the surface of confined swelling hydrogels with
initial film thickness in the micron and sub-micron range. As shown in Figure 5.1, surface creases are characterized by AFM in fluid and normalized crease spacing is plotted as a function of film thickness. As previously shown, when film thickness $H$ is large, the influence of surface energy on crease spacing is negligible. $\lambda / H$ is determined by minimizing elastic energy, which is independent of the film thickness. However, as film thickness $H$ approaches zero, the formation of short wavelength creases is penalized or even creasing instability is expected to be completely suppressed by surface energy. In the latter case, $\lambda / H$ will approach infinity. Figure 5.1f shows the data points and the trend curve. The Toomey group has characterized the crease spacing on swelled hydrogels with dry film thickness in the range of sub-micron and found the spacing/film thickness ratio reaches nearly 20, which is much higher than 2 for thick gel films, in agreement with our finding here.

5.3.2 Hysteresis of creases on confined swelling hydrogels with different polymer volume fraction

In chapter 3, we have established that, for creasing on elastomer surfaces, surface energy and adhesion at the self-contact region gives rise to varied degrees of hysteresis. The majority of literature on creasing concerns hydrogel systems, which are known to be soft yet brittle, compared to elastomer systems. It is thus of vital importance to examine the hysteretic behavior of creases on swelling hydrogels. For hydrogel systems, one of the most important physical factors is the polymer volume fraction.
Figure 5.2 Hysteresis of creases on hydrogels with different polymer volume fraction. Creases on hydrogel surface are characterized by AFM in fluid or optical microscope at varied temperature. The top row shows large hysteresis of creases on photo-crosslinked hydrogel surface with high polymer volume fraction by characterizing the surface at 27 °C (a), 45 °C (b) and 65 °C (c). The lower row shows low hysteresis of creases on free radical gelation hydrogel with low polymer volume fraction by characterizing the surface at 25 °C (d) and 45 °C (e). (f) Optical micrograph also shows low hysteresis with the same gel composition.⁶

In Figure 5.2, we perform an AFM in fluid measurement of creases on temperature responsive poly(NiPam)-based hydrogels with two different initial polymer volume fractions.

In the top row, the hydrogel is a photo crosslinked poly(NAA) glassy film prior to swelling, with the initial polymer volume fraction being 1. Above the critical swelling ratio, as shown in Figure 5.2a, randomly oriented creases form on the surface, the volume fraction is around 0.4. Significant hysteresis is observed upon gel de-swelling at higher temperature (Figure 5.2b and 5.2c). The swelling ratio of the photo-crosslinked gel films as a function of temperature is plotted in Figure 5.3. In the lower row, hydrogel films are prepared by free radical polymerization from monomer solution with only 0.1 initial volume fraction. At creased state (Figure 5.2d), the polymer volume fraction in hydrogel is only around 0.05. At slightly higher temperature, the hydrogel deswells and leaves only faint scars (Figure 5.2e). At even higher temperature, due to experimental difficulty, AFM fails to capture any scars on the surface (data not shown). While significant scars left from the 1st cycle tend to nucleate creases in the 2nd loading cycle, this low hysteretic behavior of creases on low polymer volume fraction hydrogels is in good agreement with previous observation by Yoon et al by overlaying the 1st and the 2nd cycle’s creases at the same location, which is illustrated in Figure 5.2f, showing
low degree of overlapping. We have previously identified that adhesion at the self-contact region is responsible for the hysteresis of creasing we observed in elastomer systems. The fact that hydrogels with lower volume fractions tend to have lower degrees of creasing hysteresis is in agreement with this conclusion. However, the agreement does not rule out other possible sources of hysteresis, such as temporary entanglement in gel network upon deswelling, occurring in gels with high enough volume fraction, or local damage/fracture of gel network, which, according to the Lake-Thomas model, depends on the crosslinking density and swelling ratio. Further investigation on the hysteresis of creasing in hydrogel systems will benefit from advancement in the study of adhesion between gel and gel interface, and failure of gel network upon confined swelling. While both topics have significant impact in the applications of gels, their studies are still in the nascent stage.

5.3.3 Morphology of creases under different stress state

In analogy to the rich morphologies of wrinkles occurring under different stress states or different geometric boundaries, creases are also expected to exhibit morphology dependence on the stress state. As we have shown previously, under uniaxial compression, creases form quasi-periodic array, while creases are randomly arranged under equibiaxial compression observed on confined swelling hydrogels. So far the comparison between experimental results and theoretical predictions has been limited to only plane strain or uniaxial compression. Here we study creasing of elastomer film under equibiaxial compression. We inflate a Sylgard 184 20:1 PDMS substrate into a spherical cap, followed by gluing a Sylgard 184 40:1 PDMS thin film to the spherical cap at the apex. We deflate the balloon stepwise by controlling the
nitrogen pressure to apply incremental compression to the film, and observe the formation of creases in situ with an optical microscope. The strain where the first crease nucleates is taken as the critical strain, calculated from the radius change of the circular film. As shown in Figure 5.4, the observed critical strain is \( \varepsilon_c = 1 - r_c/r_0 \approx 0.26 \), which is close to the theoretical prediction \( \varepsilon_c = 0.25 \) for equibiaxial compression.\(^{15}\) The small over strain is probably due to the surface energy as the nucleation barrier. While creases are randomly arranged globally due to the in plane stress symmetry, how creases are locally organized is worth a close examination in the future.

\[
\varepsilon_c = 1 - r_c/r_0
\]

**Figure 5.4** Creasing of elastomer film under equibiaxial compression. (a) a schematic of experimental setup showing gluing a soft thin PDMS film to an inflated stiffer PDMS substrate followed by deflation to put the thin film under equibiaxial compression, (b) optical micrographs showing the nucleation and growth of randomly oriented creases.
Figure 5.5 Creasing of pre-stretched hydrogel. With a pre-stretching ratio of $\lambda_i = 1.3$, (a) at 33.5 °C, creases start to nucleate and grow along the pre-stretching direction. At 31.8 °C (b) and 29 °C (c), more creases form to equilibrate into quasi-periodic array. (d) at 29 °C, removing pre-stretch puts the hydrogel under equibiaxial compression, leading to the long crease stripe breaking into short dots, dashes and the formation of new creases in transverse direction.

From the perspective of harnessing creases for applications, the precise control of crease morphology, and therefore the realization of arbitrary stress states is desired. While the design of biaxial stretching instruments is complex, here we realize arbitrary stress states by combining mechanical stretching with confined swelling. As shown in Figure 5.6, by tuning the mechanical stretching ratio and swelling ratio, we can achieve arbitrary stress states from uniaxial compression to equibiaxial compression.
Specifically, the experiments are performed with a temperature responsive poly(NIPAM)-based photo-crosslinked hydrogel which swells as temperature is decreased. We attach this gel to a PDMS/poly(HEMA) IPN elastomer, swell it slightly at high temperature, and apply a fixed stretching ratio. We then start to cool the gel to trigger creasing. As shown in Figure 5.5a and b, due to anisotropy of applied stress, creases nucleate at critical temperature 33.5 °C and grow along the pre-stretching direction, forming quasi-periodic array (Figure 5.5c). After releasing the pre-stretching, the gel is under equibiaxial compression. The long straight creases break into short ones and new creases form in the transverse direction (Figure 5.5d).

As plotted in Figure 5.6a, we measure a series of onset temperature of creasing as a function of the applied pre-stretching ratio. We characterize the lateral swelling ratio of this gel as a function of temperature, which is plotted in Figure 5.6b. As sketched in Figure 5.6c, the free swelling state is taken as the reference state and the stretching ratio \( \lambda_i = \lambda'_i / \lambda_0 \), is defined as the dimension in the current state over the dimension in the reference state. At each pre-stretching ratio \( \lambda'_i \), we observe one critical temperature which corresponds to a free swelling ratio \( \lambda_0 \) from Figure 5.6b.
Figure 5.6 Onset point of crease formation on hydrogel surface under different stress states. (a) onset temperature of creasing as a function of pre-stretching ratio $\lambda_1$, (b) lateral swelling ratio $\lambda_2$ of free swelling gel as a function of temperature, (c) a schematic of strain analysis, (d) experimental results plotted together with ‘phase diagram’ of flat surface, creasing and Biot’s wrinkling. The symbols indicate different stress states (*: equibiaxial compression, &: plane strain and #: uniaxial compression).

The elastomer is considered incompressible, thus $\lambda_2 = \sqrt{1/\lambda_1}$ under uniaxial pre-stretching. The experimental results on arbitrary stress states are summarized in Figure 5.6d, together with the ‘phase diagram’ defined by the theoretical prediction on critical strains for creasing and Biot’s wrinkling on incompressible elastomers.\(^\text{15}\) We can see the critical strain for equibiaxial compression is $\varepsilon_c = 0.36$, close to the previous results on
hydrogel systems, and far above the predicted critical strain $\varepsilon_c = 0.25$. The experimental critical strain shows a much smaller dependence on the strain anisotropy compared to theoretical prediction. We suspect the major possible reason for this discrepancy is the compressibility of hydrogels, while the theoretical prediction is based on an incompressible elastomer model. In Hong and Gao’s recent theoretical work considering hydrogels, they find that the critical strain does increase as the initial free swelling ratio increases, which they attributes to the finite compressibility of swollen hydrogels. While this finding agrees with our experimental results, they also point out that, due to the nucleation behavior of crease formation and the poroelasticity of gels, a dynamic model will be required to accurately capture creasing instability on swelling gels. Experimentally, our current setup is also not ideal. We spin coat the pre-gel polymer onto PDMS/poly(HEMA) IPN elastomer. After spin coating and UV crosslinking, the pre-gel glassy polymer film fractures into small pieces, indicating the existence of a high residual stress. The limited size of films pieces also amplifies the influence of the boundaries, which tend to serve as major defects to nucleate creases. While the residual tensile stress tends to raise the critical strain, the boundary defects may change the critical stain in the opposite direction.
Figure 5.7 Morphology of creases depending on loading history. (a) Stretching creased hydrogel leads to creases aligning along the stretching direction. (b) Stretching a swelling hydrogel below but close to the onset point of creasing leads to crease formation along the stretching direction. (c) Further swelling a pre-stretched hydrogel leads to the formation of well aligned creases along the pre-stretching direction. Scale bar: 200 μm.

In our previous studies on elastomers under uniaxial compression, creases form quasi-periodic array. While the PDMS elastomers we are using show viscoelastic properties, we take care to apply incremental strain slowly to minimize the viscous effect. We note that the final morphology may depend on the loading speed. To achieve the same final stress state, there are also different loading paths which could lead to different final morphologies. This is in analogy to the dependence of crystal structure on the thermal history.18,19 As shown in Figure 5.7, the three column optical micrographs show three different paths to achieve a similar final stress state yielding three different morphologies. In Figure 5.7a, a photo-crosslinked gel is attached to an elastomer substrate and swelled beyond the critical ratio, with randomly oriented short stripe creases formed on the surface (top). Subsequent stretching leads to the alignment of
creases along the stretching direction (bottom). However, these creases couldn’t merge into long straight stripes. In Figure 5.7b, gel with the same composition swelled to a degree below the onset point of creasing is subsequently stretched to increase compression in the transverse direction, leading to long stripes of crease along the stretching direction (bottom). In Figure 5.7c, gel with the same composition is slightly swelled and stretched to the same degree as in the first two columns. Further swelling leads to straight crease stripes along the stretching direction (bottom), with a smaller density of defects compared to in Figure 5.7b. The dependence of final morphology on loading history is due to the energy barrier existing between different morphologies. In analogy to the grain boundary migration in recrystallization where the energy barrier comes from the melting of crystal lattice, here the energy barrier comes from the unfolding of certain creases. Earlier in this chapter, we have shown unfolding of creases has a strong dependence on gel polymer volume fraction. To reduce the energy barrier, a low polymer volume fraction gel will be desired. The difficulty lies in gluing a free radical polymerization gel to a transparent elastomer. Due to its easy accessibility and transparency, PDMS elastomer is often used as stretching substrate in experiments. However, PDMS elastomer has high oxygen permeability. While this property has been harnessed to invent ‘stop-flow lithography’, it also makes mounting free radical polymerization gel onto PDMS quite difficult. PDMS also has a hydrophobic surface that is difficult to functionalize. Researchers have tried to tackle this problem by stretching gels crosslinked via non-free radical chemistry. All these approaches are problematic for the creasing study without reinventing the current gelation process. The alternative is to explore other elastomers. In the next chapter, we will introduce an option where we can use a type of polyurethane as an elastomer substrate for this purpose.
While previously have only been concerned with the near threshold region, crease morphology at the far from threshold region is also worth some effort. Before the discussion on creases, it is worthwhile to summarize the near threshold and far from threshold behavior of surface wrinkles. When a hard skin attached to a soft foundation is compressed beyond a critical strain, near the threshold, a sinusoidal surface wrinkle happens. As compression is further increased, secondary instabilities occur, forming periodic doubling, periodic quadrupling, folding or ridging.\textsuperscript{23-25} We have put an elastomer film under uniaxial compression where a quasi-periodic array of creases form on the surface in the near threshold region and period doubling is also expected as we further increase compression.\textsuperscript{26} However, what we have observed is the affine
deformation of periodic creases with increasing strain. The reason may be due to the limited strain range we could achieve with our current experimental system and the adhesion at self-contact regions, which provides an energetic barrier for the creases to unfold.\textsuperscript{27,28} On confined swelling hydrogel, at higher swelling ratio, creases evolve into quasi-hexagonally arranged triads and secondary creases form in between the primary creases, yielding a hierarchical surface pattern (Figure 5.8b and a zoomed in image Figure 5.8c). While the triad structure has been predicted by Tallinen, et al.\textsuperscript{29} the formation of secondary creases has yet to be explored. These secondary creases indicate a new characteristic length scale of the system, which is likely to be the depth of the exposed portion of the primary creases. As shown in Figure 5.8d, a topographic pattern could break the in plane stress symmetry, directing crease formation.\textsuperscript{6} Near the threshold, creases form straight stripes right on top of the topographic patterns. Further swelling leads to secondary creases forming short straight stripes perpendicular to the primary creases, yielding a ladder like pattern.

5.4 Conclusions

In this chapter we show that, for substrate-attached gel films with thickness in the range of micron and submicron, surface energy penalizes short wavelength creases. The equilibrium wavelength/initial film thickness ratio increases as the film thickness decreases. Hysteresis of creasing shows a strong dependence on the initial gel volume fraction. While gels with high polymer volume fraction show significant hysteresis, leaving permanent scars, gels with low polymer volume fraction show a low degree of hysteresis. This behavior could stem from surface energy and therefore thermodynamic adhesion at the self-contact region, material failure or other sources of adhesion, which
could be a topic of future work. Next, we study the morphology of creases under different stress states. We demonstrate that elastomer films under equibiaxial compression show similar morphology of creases as observed on the surface of substrate attached gel films upon swelling. Combining swelling and stretching, we achieve arbitrary stress states by gluing a gel film to an elastomer mounting layer. The critical strain of creasing shows less of a dependence on the stress anisotropy than as predicted by theories, likely due to the compressibility of hydrogels. We also show that the final morphology of creases has a dependence on the loading history, which could be due to the energy barrier existing between different crease patterns or hint at the influence of kinetics effects. While previous studies mainly concern the morphology of creases near the threshold, far from threshold behavior of creases is also studied, showing secondary creases formed perpendicularly between the primary creases. While the morphology of creases is a very important property for applications such as switchable adhesives and tunable optics, the precise control of it depends on materials properties, geometry, loading history, and stress states. Future study on this topic will benefit from the construction of better experimental setups and the use of exact constitutive equations of gels in modeling.

5.5 References


Hofeld, E. (Private communication, 2012).


Holfeld, E. (Private communication, 2012).


CHAPTER 6
CREASED HYDROGEL AS AN ACTIVE PLATFORM TO STUDY
MECHANICAL DEFORMATION EFFECTS ON MUSCLE CELLS

6.1 Introduction

Cells cultured in vitro using traditional substrates often change their behavior due to the lack of important cues they would naturally experience in vivo. One example is mechanical deformation, which is known to modulate cell behaviors including growth, differentiation, polarization, motility, contractility, and apoptosis (programmed cell death). 1-5

Mechanical deformation plays an important role in the life cycle of cells, especially muscle cells.4 In vivo, they are constantly under mechanical deformation due to motion of the body, breathing, and operation of the cardiovascular system. While the important influence of mechanical deformation on cell behavior is generally acknowledged,1 the characterization of it is still in its nascent stage due to the fact that research efforts tend to focus on the importance of chemical cues and genes for control of tissue physiology and the development of diseases. Cellular mechanotransduction refers to the process of converting mechanical stresses into biochemical signals and integrating these signals into the cellular responses. The cytoskeleton is believed to act as a mechano- and signal transducer. It includes a mesh of fibres made up of actin protein that lines the cell’s membrane, and tough ‘actomyosin bundles’ in which actin combines with the protein myosin II. Integrins protein spans the cell membrane,
griping the actomyosin filaments inside the cell and the extracellular matrix on the outside.6

To study mechanical deformation effects on muscle cells, a few methodologies have been developed to apply strain to cells either by macroscopically deforming elastic cell culture matrix/substrates (Figure 6.1a)7 or by microscopically applying force to cells using AFM tips, micropipettes or optical tweezers (Figure 6.1b, 6.1c, 6.1d).8-10 While it is difficult to integrate the former set of techniques with other in-situ characterization techniques, the later usually generates non-uniform and poorly characterized strain fields7,11. Another set of experiments to apply shear deformation on cultured cells is through fluid flow, although this represents a physiologically relevant state only for a few specific types of cells.12 Cells have also been put under bulk compression through osmotic pressure.13 Recently, dielectric elastomer has been utilized to fabricate micro-actuators for single-cell stretching applications.14 However, the break-down voltage, pull-in instability and buckling voltage exert a limit of the total strain that could be applied to single cells.

**Figure 6.1** (a) Macroscopically deforming elastic cell culture substrates to apply deformation to cultured cells, (b) Nano-indentation on cells with AFM tip, (c) Micropipettes aspiration experiment on cells and (d) Stretching cells with Optical tweezers.
For a thin layer of hydrogel attached on a rigid substrate, constrained swelling introduces equibiaxial compression. Above some critical strain, the hydrogel surface buckles into creases. While only recently this creasing instability has been appreciated, a few characteristics have already been characterized. First, it has been observed that the critical swelling ratio for onset of creasing doesn’t change much over a large range of hydrogel moduli (of ~ 100 Pa to MPa). Later, topographic micro-patterns have been used to break in-plane stress symmetry, directing crease formation. Next, creases on stimuli responsive gels could be reversibly formed and annihilated by a small variation in stimuli such as temperature, light, and electric field, solvent quality, pH value and salt concentration. Last, creasing is a local yet large amplitude deformation on the surface. When creases fold in, material points near the creases undergo in-plane displacement. All these merits make creased hydrogel a potential platform to apply mechanical strains to cells at single cell level and study, in-situ, the cells’ response to this strain.

Figure 6.2 Procedure showing photo-patterning RGD peptide sequence onto the hydrogel surface between two neighboring creases, which are directed by topographic patterns on the rigid substrate, cell seeding and gel swelling to subject cells to stretching.
To exploit this instability for use as shown in Figure 6.2, two challenges must first be overcome. First, and most importantly, cultured cells must be induced to adhere to the gel surface in the desired arrangement, such that folding and unfolding of a crease leads to the desired application of strain. As illustrated in Figure 6.2, the first challenge could be surmounted by employing a direct writing photolithography using a custom synthesized Benzophenone grafted Arg-Gly-Asp (RGD) peptide sequence. Second, the stimulus used to actuate deformation of the gel surface should be altered from global changes to one that ideally enables localized control of each fold (allowing a single substrate to house an array of independent micro-stretching devices) and does not elicit a pronounced biological response in its own right. Among the many stimuli that have been used to actuate creasing instability, the mildest stimulus to cultured cells, is temperature. In this chapter, we first demonstrate we can develop a potential high throughput platform, based on creased temperature-responsive hydrogels, to apply strains of different amplitudes and different stress states to cells at single cell level. Although considered as a mild stimulus, temperature in its own right is known to affect cell behavior. Further, the kinetics of crease actuation by temperature changes is limited by mass transport, which is determined by the poroelasticity of the gels. Next, we showcase a prototype of pneumatic/hydraulic actuation of creases, where both the strain rate and frequency can be modulated to be close to physiological levels. This hydraulic actuation will overcome the second challenge and can be programmed to independently control individual creases, thus enable an array of independent micro-stretching devices.
6.2 Experimental

6.2.1 Preparation of surface attached hydrogels

Hydrogels are prepared from degassed aqueous pre-gel solution containing 808.9 mM N-isopropylacrylamide (NIPAM), 80.6 mM sodium acrylate (NaAc), and 6.3 mM N,N’-methylenebisacrylamide (BisAA). For gels on substrates with parallel strip patterns, to initiate free radical polymerization, 0.3 µL of N,N,N’,N’-tetramethylethlenediamine as catalyst and 1.0 µL of a 10 wt% aqueous ammonium persulfate solution as initiator are added to 200 µL of pre-gel solution. The mixture is loaded by capillary force between a substrate and a release coverslip separated by spacers (Kapton 300HN films, DuPont) to define the thickness of the gel (76 µm). Gelation was carried out for at least 30 min in a nitrogen-filled sealed chamber. For gels on substrates with elliptical and circular patterns, the pre-gel solution is mixed with 10 µL of 3 wt% aqueous solution of 2,2’-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Wako Pure Chemical Industries, VA-086). The polymerization is initiated by applying 365 nm UV light, allowing 20 min for the reaction to proceed. To covalently attach gels to substrates, glass substrates were pretreated with the [3-(methacryloxy)-propyl] trimethoxysilane/ethanol solution for at least 6 h. Topographically patterned glass substrates are lithographically fabricated following a previous report. Specifically, SU-8 molds with a thickness of 40 µm are photo-lithographically patterned, from which PDMS (Sylgard 184, Dow Corning, base: crosslinker in a 10:1 mixing ratio by weight) negative replicas are casted and fully cured at 70 °C for 12 h. Then topographic patterns are molded from the PDMS replica with Norland optic adhesive (Norland 81), cured with 365 nm UV light.
6.2.2 Fabrication of microfluidics for the actuation of creases

Sealed Microfluidic substrate is composed of two parts: the stiffer bottom via soft lithography printing and the soft top film. To prepare the bottom, PDMS negative replicas (Dow Corning, Sylgard 184 5:1 base:crosslinker mixing ratio by weight) are cast from photo-lithographically patterned SU-8 molds (MicroChem, SU-8 2015). Polyurethane bottom is fabricated by pouring well mixed polyurethane (BJB enterprise, WC-540) onto the fully cured PDMS replica, degassing via vacuum, and curing at room temperature for 1 h followed by curing at 70 °C overnight. The top film is prepared by spin coating freshly mixed polyurethane (BJB enterprise, F-15) onto trimethylchlorosilane pre-treated glass substrate at 4000 rpm to yield PU films with a thickness of 16 μm. After being partially cured at room temperature for ~1 h, the top film is carefully laminated onto the stiffer bottom, with adhesion being achieved by fully curing at 70 °C overnight. The dimensions of the microfluidic channels are 80 μm in width, 40 μm in depth and ~1 cm in length.

To form gel on microfluidic substrates, gelation chamber is assembled with the microfluidic substrate and a release coverslip separated by spacers (Kapton 300HN films, DuPont) to define the thickness of the gel (76 μm). The pre-gel solution (~190 μL) containing 808.9 mM N-isopropylacrylamide(NIPAM), 80.6 mM sodium acrylate (NaAc), and 6.3 mM N,N’-methylenebisacrylamide (BisAA) is mixed with 10 μL of a 3 wt% aqueous solution of 2,2’-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Wako Pure Chemical Industries, VA-086). The gelation chamber, the pre-gel solution and a UV lamp are together put into a glove bag. The glove bag is purged with nitrogen for at
least 2 h before loading the chamber with pre-gel solution, triggering the initiation with 365 nm UV light and allowing 20 min for the polymerization to proceed.

6.2.3 Photopatterning RGD on hydrogels surfaces

A custom synthesized benzophenone grafted KGYSRGDSPAS peptide sequence (BP-RGD) (Figure 6.3) is obtained from Biomatik USA. Hydrogels surfaces are photopatterned with freshly made 1 mg/ml BP-RGD/ phosphate buffered saline (PBS, 137 mM NaCl) solution. Prior to photopatterning, hydrogel samples are taken out of the gelation chamber with release coverslip removed and soaked in PBS to remove unreacted small molecules during gelation. For photopatterning, a photomask is attached to the bottom side of standard 170 µm thick coverslip or a digital micromirror device (DMD) is used and the focal plane is adjusted to be on the hydrogel surface. About 50 µL of 1 mg/ml BP-RGD/PBS solution drop is put on the top of the coverslip and the hydrogel is put upside down with surface in direct contact with the droplet. With UV light (~365nm) shined from the bottom through the photomask, photopatterning is carried out for about 30 min. Then hydrogel samples are washed with ample amount PBS for 2 h to remove unreacted BP-RGD. To visualize RGD patterns, hydrogel samples are first soaked with 10 times concentrated PBS (1370 mM NaCl, adjusted to pH=9 by adding sodium carbonate) (10xPBS) for 1 h, then incubated with freshly made fluorescein isothiocyanate (FITC)/10XPBS solution for another 8 h. Then hydrogel samples are washed again with ample amount of 10xPBS and then PBS to remove unreacted FITC molecules. FITC labeled RGD patterns are imaged with 2.5x objective on a Zeiss inverted optical microscope (Zeiss Axiovert 200).
6.2.4 Cell culture

C2C12 myoblasts were obtained from the American Type Culture Collection (ATCC) and expanded and frozen down. Only early passage cells were used in these studies. For experiments, cells were plated at equal density (3\times10^5 cells per well) in 6-well culture plates that contained a glass slide coated with RGD. They were incubated in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10\% Fetal Bovine Serum (Atlanta Biologicals Norcross, GA). Cells were left to settle on RGD coated slides for 24 h prior to imaging. They were visualized and photographed with a 10X objective on a Zeiss inverted optical microscope (Zeiss Axiovert 200) and a Q-imaging camera (Retiga 2000R).

6.3 Results and discussions

While methods to pattern the surface chemistry of rigid substrates (plastic, glass, etc.) are widely used to spatially control cell attachment\(^{22,23}\) efforts to pattern biological ligands on soft gel substrates have so far been quite limited. Grainger and co-workers have photo-patterned Arg-Gly-Asp (RGD) peptide sequences on poly(ethylene glycol) (PEG) based polymer films, but their process is not easily adapted to the soft, stimulus-responsive gels considered here.\(^{24}\) Instead, we have modified the approach of Hebert, et al., in which peptides were directly patterned onto substrates coated with organic self-assembled monolayers using benzophenone (BP) photo-chemistry.\(^{22}\) Specifically, we used an end-functionalized peptide BP-KGYSGRGDSPAS(BP-RGD) shown in Figure 6.3. In our approach, a poly(N-isopropylacrylamide)-based hydrogel film supported on a glass substrate is immersed in phosphate buffered saline (PBS) containing BP-RGD.
Illumination with ~360 nm light through a photomask or a digital micromirror device (DMD) leads to patterned attachment of the peptide sequence to the gel through the well-known photo-grafting chemistry of BP. Confirmation of successful patterning was obtained by labeling the lysine (K) residue with fluorescein isothiocyanate (FITC), as shown in Figure 6.3 (the background fluorescence corresponds to FITC molecules that simply diffused into the hydrogel.).

**Figure 6.3** left: Scheme of benzophenone end-functionalized RGD peptide, right: A photo-patterned gel surface

Using this method, we fabricated a series of stripes with different widths and pitches and circular patterns with different diameters and center-to-center distances to test the critical RGD pattern size needed for C2C12 mouse myoblast cell adhesion to hydrogel surfaces. As controls, cells were also seeded on standard polystyrene (PS) culture dishes, hydrogels without RGD coating, and hydrogels uniformly coated with RGD. After 24 h, no cells were found to adhere to the hydrogel surface without RGD coating, while cells adhered to and spread on the uniformly RGD coated hydrogels much like the PS dishes. However, as shown in Figure 6.4, there was a lower cell density on
the RGD coated gels compared to PS, which we suspect reflects the relatively low density of RGD ligands compared to the level of protein adsorption on PS.

Figure 6.4 (a) C2C12 mouse myoblasts cultured on a standard PS substrate as a positive control. (b) C2C12 cells adhered to and spread on uniformly RGD-coated gel surfaces, albeit at lower density than for PS. (c) A non-RGD coated gel surface used as a negative control did not promote cell attachment. (d) C2C12 mouse myoblasts cultured on hydrogels patterned with stripes of RGD with 60µm width and 300µm pitch. (e) For C2C12 mouse myoblasts cultured on gels patterned with circles of 60 µm in diameter, cells primarily stayed confined to a single dot, (f) while for 40 µm diameter circles spaced by 60 µm, cells occasionally bridged between neighboring circles.

For stripe patterns, the critical stripe width was found to be ~ 60 µm for C2C12 cells to adhere in registry with surface patterns. When seeded on 60µm stripes (Figure 6.4), cells lined up “single file” along the stripe, and elongated along the stripe direction.
For circular patterns, the critical pad size was also found to be about 60µm in diameter. However, for circular patterns of 40µm diameter, with 60 µm spacing, cells were found to bridge between two or three neighboring pads (Figure 6.4, right). This result suggests that with fine-tuning, we can pattern cells at desired location at single cell level.

**Figure 6.5** Cells seeded between two parallel creases are put under plane strain condition. (a) Confocal cross-section micrograph showing relatively flat surface between two neighboring creases, (b) An experimental schematic showing cells seeding between two neighboring creases, (c) cells seeded at 37 °C are put under plane strain condition, with a tensile strain of $\varepsilon_a = 0.20 \pm 0.04$ and $\varepsilon_b \approx 0$.

As shown in Figure 6.5a, the prescribed topographical patterns break the in plane stress symmetry and direct a single crease formation on each pattern. While the surface at the crease area is highly curved, the surface between two creases is relatively flat. As illustrated in Figure 6.5b, cells are seeded between two neighboring creases. Cells are seeded onto a RGD peptide patterned temperature-responsive poly(N-
isopropylacrylamide)-based hydrogel at 37 °C (Figure 6.5c left column) and reducing temperature to 26 °C causes gel to further swell and applies a tensile strain to cells at single cell level (Figure 6.5c right column). When these parallel strip creases fold or unfold, material points on the gel surface between creases undergo displacement only in the direction perpendicular to the creases. Thus, at 26 °C, these cells are under plane strain condition, with a tensile strain of $\varepsilon_a = 0.20 \pm 0.04$ and $\varepsilon_b = 0$. While this strain is above the tensile strain of cells usually experience in vivo and previous studies show that strain above 0.20 leads to cell death\textsuperscript{26,27}, this large amplitude of strain suggests the capacity of our cell stretching device. Smaller strains could simply be achieved by tuning the temperature to a smaller range.

Cells in vivo undergo many different kinds of mechanical deformation. While cells are found to be viscoelastic and poroelastic\textsuperscript{28}, different stress states may have different influence on cell behavior, thus the generation of different stress states on cells is desired. To achieve different stress states, we redesign the topographic patterns on the substrates. As shown in Figure 6.6, we can pattern elliptical patterns with different anisotropicity on the substrates. On top of each pattern, a single strip of crease forms in good registry. Cells are seeded at the center of each ellipse at 37 °C. Reducing the temperature to 26 °C causes gel to further swell and applies a tensile strain to cells at single cell level. At 26 °C, cells are under four different stress states: (a) Nearly plane strain ($\varepsilon_a \approx 0.22, \varepsilon_b \approx 0.02$), (b) ($\varepsilon_a \approx 0.15, \varepsilon_b \approx 0.08$), (c) ($\varepsilon_a \approx 0.15, \varepsilon_b \approx 0.10$) and (d) equibiaxial stretching ($\varepsilon_a \approx \varepsilon_b \approx 0.12$). These results demonstrate that we can almost continuously tune the stress states from plane strain condition to equibiaxial stretching state.
Figure 6.6 Cells are seeded at the center of each ellipse at 37 °C. Reducing the temperature to 26 °C causes gel to further swell and applies a tensile strain to cells at single cell level. At 26 °C, cells are under four different stress states: (a) Nearly plane strain (\( \varepsilon_a \approx 0.22, \varepsilon_b \approx 0.02 \)), (b) (\( \varepsilon_a \approx 0.15, \varepsilon_b \approx 0.08 \)), (c) (\( \varepsilon_a \approx 0.15, \varepsilon_b \approx 0.10 \)) and (d) equibiaxial stretching (\( \varepsilon_a \approx \varepsilon_b \approx 0.12 \)).

One question we have to consider is the influence of temperature change on cells in its own right. A control experiment is performed on the flat unpatterned region of the same hydrogel surface coated with the same RGD peptide density. As shown in Figure 6.7, over the same period of observation time (~30 min), we have not noticed significant changes in the size of cells, indicating for the short experimental time, the size of cells is basically not influenced by the temperature change itself. Thus previous observations on the change of cells are due to mechanical deformations applied by the creased gel substrates. However, as we noted earlier, even as a mild stimulus, temperature is far from the ideal stimulus to actuate mechanical deformation on cells for real applications.
Normal human body temperature in adults is 36.5–37.5 °C, beyond which both hypothermia and hyperthermia could have detrimental effects on our health. An actuation stimulus which does not have biological influence in its own right is desired.

With temperature as stimulus, we have achieved the successful tuning of strain amplitude and different stress states on a single substrate. However, the applying strain rate or frequency is limited by poroelasticity of the hydrogel. The initial gel thickness of $H = 76 \mu m$ and the diffusion constant of $D = 1.5 \times 10^{-11} m^2 s^{-1}$ together define a swelling time scale of $\tau = H^2 / D \approx 6 \text{ min}^{29}$. While our heart rate and respiratory rate are in sub-second and a few second time scales, we need to find a new stimulus which can overcome the swelling/deswelling time limit.

![Figure 6.7](image.png)

*Figure 6.7* Over the experimental time scale (~30 mins), temperature has negligible influence on the size of cells.

Pneumatic/hydraulic actuation of soft robots has become a hot research topic in the last few years and shines light on our current stimulus searching$^{30,31}$. As shown in Figure 6.8, we design pneumatic/hydraulic channels with the top cover being a soft elastic poly(urethane) membrane and the bottom being a slight stiffer poly(urethane)
elastomer with troughs molded lithographically. We then form a thin hydrogel film on top of the cover by free radical polymerization. Swelling the hydrogel to a strain level just below the onset point of creasing, followed by inflation/deflation of the microfluidic channels is expected to mechanically activate/deactivate the creases. This deformation is local, elastic and expected to overcome the swelling/deswelling limits. Thus the rate or frequency of applying strains on cells is expected to approach physiological levels that cells experience in vivo.

Figure 6.8 An experimental schematic showing inflation of microfluidic channels composed of an elastic membrane and a stiffer bottom to actuate creases on the attached hydrogel surface.
Figure 6.9 (a) Top view of the microfluidic channels, (b) Cross-section of the microfluidic channels showing the dimension of channels, (c) Randomly oriented creases form on unpatterned region, (d) while creases show some alignment along the microfluidic channels due to the different stiffness of the substrate.

Figure 6.10 Surface profiles of the substrate by Zygo Optical Profilometer under (a) inflation or (b) deflation of the membrane through syringe pump. (c) Inflation leads to stripe creases formation in between two neighboring channels, while (d) deflation leads to crease formation on top of each channel.
As shown in Figure 6.9, microfluidic devices have been successfully fabricated with two types of polyurethane (transparent and stiffer PU as the bottom, translucent and highly stretchable PU as the top membrane). We make use of PU substrates, rather than PDMS, as the former allows for more robust gel/elastomer adhesion. This may be due to the reduced oxygen permeability of PU, as well as chemical and/or physical bonding between the elastomer and gel. Figure 6.9(c) shows randomly oriented creases formation on the surface of hydrogels seeded onto the unpatterned PU substrate, while Figure 6.9(d) shows some extent of crease alignment along the microfluidic channels, indicating that the contrast in out of plane substrate stiffness breaks in plane stress symmetry in the gel.

We further characterize the inflation/deflation of microfluidic membrane by optical profilometry while the inflation/deflation is actuated by syringe pump. One possible failure mode of this system is through balloon instability, which is due to the fact that inflation pressure is not monotonically related to the extension of elastic membrane.

By controlling the pressure, we could maintain the inflation pressure at the safe range. As shown in Figure 6.10(a), the inflation of membrane can be controlled to be roughly uniform throughout all the channels. When the gel is pre-swelled to just below the critical strain for creases formation, as shown in Figure 6.10(c), inflation of membranes applies additional compression to the gel portion between two neighboring channels, leading to stripe crease formation in between. While deflation subjects the gel portion on top of the microfluidic channels to higher compressive strain, yielding creases above channels. Further, the depth of creases could be tuned rapidly through programming the inflation/deflation via syringe pump. Preliminary results have shown
that the actuation of creases can achieve 1 Hz frequency, which is comparable to the strain rate cells experience \textit{in vivo}.

Other biophysical cues also have influence on cell behavior, such as substrate geometry\textsuperscript{23} and substrate stiffness\textsuperscript{32}. While we have shown the former can be controlled by varying the design of photomask, the latter can be tuned by adjusting the crosslinking density of hydrogels in use. Another advantage of utilizing creased hydrogel is that the onset strain of creasing is found to be almost independent of the hydrogel modulus, giving rise to the freedom of controlling the substrate stiffness while keep the other physical parameter the same. All of these merits together enable independent tuning of gel modulus, geometry, strain amplitude, strain states, as well as strain rates, in a high throughput way, providing a versatile platform to study the influence of physical cues on cultured cells.

\textbf{6.4 Conclusions}

This chapter has introduced an application of the creasing instability, where we utilize creased hydrogel as a dynamic platform to apply tensile strain on cells. We have demonstrated that using temperature as a stimulus, cultured muscle cells can be mechanically deformed with different strain states and amplitudes. This experiment also, for the first time, showcases actuation of a surface mechanical instability with pneumatic/microfluidic pressure. This actuation could be generalized to other surface or bulk mechanical instabilities for optical, wetting, adhesion, and soft robotic applications. Creases actuated by microfluidics offer potential for realization of high-throughput cell stretching devices, through which different strain states, amplitudes, as well as loading rate and frequency can be modulated to mimic the mechanical
environment cells experience *in vivo*. Another advantage with microfluidic actuation is that it can easily be programmed to independently tune individual creases. Compared to the current commercially available cell stretching devices, this construction enables the *in situ* observation of cultured cells at single cell level while programmable mechanical deformations are applied, thus introduces a versatile tool to the current tool kit for stem cells, cancer, gene transfection as well as kinesiology study.

### 6.5 References


CHAPTER 7

CONCLUSIONS

The main focus of this thesis is to deepen our understanding of creasing instability, which is important for understanding the role of creasing in materials failures or engineering it for applications. We have prepared silicone-based elastomers and stimuli-responsive hydrogels as our experimental systems to address the following three questions: 1) What are the equilibrium structures and formation mechanism of creases? 2) What is the origin of hysteresis of creasing and can we design a system to control it? 3) Can creases also form on the interface of two soft materials? Further, we have also showcased one application where creased hydrogels are utilized as a dynamic cell stretching platform.

In this thesis, we design simple experimental setups with well-defined materials properties, geometry, and strain states, which enable the first detailed characterization of the equilibrium depths, spacings and shapes of creases. On sufficient thick elastomer films, the equilibrium structure of creases is found to show excellent agreements with numerical results based on neo-Hookean materials model without any fitting parameter due to the negligible influence of surface energy. Using the same experimental setup with reduced film thickness where the influence of surface energy become significant, we have first established that creases form in a nucleation and growth fashion, with surface energy providing an energetic barrier. While creasing is found to be subcritical and hysteretic, we further established that it is the thermodynamic self-adhesion at the folding region other than plastic deformation that gives rise to hysteresis between the
formation and disappearance of creases during multiple loading cycles. We have designed a soft elastic bilayer system to show the hysteretic behavior can be controlled, yielding well-defined bistable flat and creased states connected by a snap through instability. We have also fabricated confined-swelling two soft hydrogels bonded on the interface to demonstrate for the first time the formation of “V” shape interfacial creases.

We have introduced an application of the creasing instability, where we utilize creased hydrogel as a dynamic platform to apply tensile strain on cells. We have demonstrated that using temperature as a stimulus, cultured myoblast cells can be mechanically deformed with different strain states and amplitudes. This experiment also, for the first time, showcases actuation of creasing instability with hydraulic pressure. Creases actuated by hydraulics offer potential for realization of high-throughput cell stretching devices on single cell level. The successful fabrication of cell stretching devices will enable the study of biological consequence of a variety of different mechanical deformations on cells. While pneumatic actuation of soft robots and hydraulic actuation of hard robots such as “big dog” by Boston Dynamics have become popular, the controlled actuation of mechanical instabilities by pneumatics or hydraulics could bring new functions to the current library.

Our new understanding of creasing instability will shine light on the study of patterns due to biological growth and provide guidance for harnessing creasing as a new lithographic method or for functional devices. The well characterized equilibrium structure and controlled hysteretic behavior of creases represent important steps towards applications for switchable flexible electronics, reversible adhesion or smart optical devices, such as tunable lenticular lens.
We have shown a few preliminary results of the morphology of crease dependence on materials properties, geometry, loading history, as well as stress states. While several results are promising and pointing out future research directions, we also propose some better experimental setups for future study to realize the study and precise control of crease morphology. The trilayer experimental setup, we introduce for the control of subcritical creasing, opens door to the study of other related surface mechanical instabilities such as wrinkling, folding and ridging. The hydrogel-elastomer bilayer setup we design will serve as a useful candidate system for exploring the rich morphology of creases. In this thesis, we only concern creasing of isotropic elastic materials. Switching to anisotropic elastic materials, such as nematic liquid-crystal elastomers, while keeping our current experimental setups, will both propose fundamental questions and also open avenues for new applications.

In this thesis we focus on the characterization of equilibrium structures of creases by adopting slow loading rates. While elastomers are in general viscoelastic, the viscous effects on crease morphology and the kinetics of crease formation could be important topics for future study. While the study of any nucleation event proves to be difficult, we have designed an experiment to characterize the channeling of creases. In future, proper design of experimental system may enable the study of nucleation behavior.

While creases on hydrogel systems have been actuated in response to a change in a variety of stimuli including temperature, electric field, pH, salt concentration and light, currently, on elastomer systems, creased state is only enabled through mechanical perturbation or high voltage close to the electric breaking down voltage. In future study, other stimuli for switching can be incorporated in the system. Particularly, with samples
pre-loaded to metastable states, a small change in stimuli such as electric field, light, or temperature change could be applied to switch on and/or off creases, which will enable fast elastic switching between creased state and flat surface, yielding mechanically robust devices based on creasing.
BIBLIOGRAPHY


