Effect of Processing History and Material Properties on the Growth of Wrinkle Amplitude

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EFFECT OF PROCESSING HISTORY AND MATERIAL PROPERTIES
ON THE GROWTH OF WRINKLE AMPLITUDE

A Dissertation Presented

by

YU-CHENG 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

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Polymer Science and Engineering
EFFECT OF PROCESSING HISTORY AND MATERIAL PROPERTIES ON THE GROWTH OF WRINKLE AMPLITUDE

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To my parents, for supporting me without reservation.
ACKNOWLEDGMENTS

This thesis cannot be done without the mentoring of my research advisor Professor Al Crosby. While I was a clueless first year student listening to the research talks, all the researches in this department seems very far away from me except Al’s. Since then I have been fascinated with his ability to inspire his audience. During the years of my PhD, Al’s advising style has been very inspiring as well. He is always excited in my ongoing work, and that encourages me to move forward. Not just asking for experiment results, Al is very patient with training me with how to effectively convey and organize my research, which I think is the most valuable skill to learn in the PhD training. I appreciate everything Al has taught me.

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ABSTRACT

EFFECT OF PROCESSING HISTORY AND MATERIAL PROPERTIES ON THE GROWTH OF WRINKLE AMPLITUDE

SEPTEMBER 2015

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Wrinkling has been employed by many organisms to form unique topography, such as fingerprints, gut villi, and surface of flower petal cells. The wavy wrinkle structure provides friction enhancement, surface area increase, optical, and wetting properties improvement. Inspired by Nature, scientists have created wrinkles synthetically and proposed numerous uses for them. However, wrinkling surfaces encounters limitations on achieving massive area and high amplitude-to-wavelength ratio (aspect ratio).

The three phase contact line wrinkling technique creates well-defined wrinkles in a continuous fashion, and has great potential to scale-up for massive production. In addition to the velocity dependent adhesion force, we find the film deformed by the surface tension also contributes to the wrinkle amplitude and pattern. We refine the contact line mechanics with the material properties for the wrinkle aspect ratio and the pattern. (Chapter 2)

It has been known the aspect ratio of wrinkles is a function of the square root of applied strain until the wrinkling transitions into the strain localization modes. The
localization modes, e.g. folding, have very different topographical structures and distinct properties to the wrinkles, and are undesired for wrinkling applications. This restricts the aspect ratio of the wrinkles reported in literature to be less than 0.3, limiting the functionalities of the wrinkling surfaces. To understand the transition to the localization mode, we create inhomogeneous wrinkled surfaces that have alternating flat and wrinkling regions, and study the distribution of applied global strain. We find that the distribution of the applied strain is neither localized nor homogenized by the initial inhomogeneity. (Chapter 3)

We further explore the limitation of the aspect ratio. In this thesis, delaying the localization transition to larger strains is the main strategy to access high aspect ratio wrinkles. We use two approaches to influence the onset of the strain localization. The first approach is the substrate prestretch, a practical method as it is also popular to create wrinkles. The amount of prestretch is found to delay localizations, and appropriate material properties are selected to avoid surface fractures. (Chapter 4) The second approach demonstrated a concept inspired from living organisms, which stabilizes wrinkles by reducing the stress. We rearranging the crosslinking network to minimize the traction forces during the growth of aspect ratio. This is described by the reduction of the strain energy in the substrate. (Chapter 5) These approaches allow us to achieve an aspect ratio three times larger (0.9) than that reported previously in the literature.
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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Project Overview

In Nature, many organisms developed wrinkling surfaces to improve the surface properties. For instance, fingerprints and wrinkles on wet fingers enhance friction and fluid draining for better grip,\textsuperscript{1,2} inner intestines feature villi grown from wrinkles to provide large surface area for more efficient absorption,\textsuperscript{3} and some plant cells form wrinkling structures to obtain surface hydrophobicity and structural colors.\textsuperscript{4,5} (Figure 1.1) Inspired by Nature, researchers have been interested in utilizing wrinkling for advanced surface technologies. To achieve this, understanding the wrinkling mechanics become important.

![Figure 1.1 Examples for wrinkling features in living organisms.](image)

Wrinkling occurs when a compressive strain is imposed on a stiff thin film bounded to a soft substrate.\textsuperscript{6,7} Under the compression, the compromise between film bending and substrate stretching results in smooth, wavy, highly periodic sinusoidal profile across the surface. The wrinkle wavelength has been found to be governed mainly by the material properties,\textsuperscript{6,8} while the amplitude has been shown to be sensitive to the compressive strain.\textsuperscript{9} Wrinkling provides an unique surface patterning method with low-cost experimental process and has unique topography with excess surface area and continuous curvature. Moreover, the strain dependence of amplitude allows strain-responsive surfaces. Taking advantage of these features, researchers have proposed numerous wrinkle-based technologies, such as controlled adhesion,\textsuperscript{10,11} optical surfaces,\textsuperscript{12,13} and flexible electronics.\textsuperscript{14,15} (Figure 1.2) The functionalities of these applications are controlled by the aspect ratio of wrinkles. The aspect ratio is defined by the amplitude normalized by the wavelength. Therefore, effectively fabricating and tuning the aspect ratio is the key for wrinkle-based technologies.

Unlike the high aspect ratio features observed in living organisms, artificial wrinkles have limited aspect ratio under 0.3, restricting the development of wrinkle-based technology.\textsuperscript{16} This limitation is caused by a transition of wrinkling surfaces into localization modes, such as folds or ridges,\textsuperscript{17,18} as the wrinkling film is under large strains. Since the strain distribution and the structures of localization modes are rarely uniform and very different from the wrinkles, the localization transition is considered to be failure of the wrinkling mode.
The goal of this research is to create wrinkles with controlled aspect ratios, even beyond the current limit. Specifically, we study how process and materials influence the aspect ratio and the localization, and optimize the process and materials to achieve high aspect ratio wrinkles. This knowledge will impact the development of wrinkle technology and will give insight into the formation of high aspect ratio features observed in living organisms.

This thesis is divided into an introductory section, four experimental projects and a conclusion section. We start with understanding the mechanics of the contact line wrinkling process as it is not only an important experimental technique throughout this thesis, but also a potentially useful technique for large scale roll-to-roll process. The strain sources for wrinkling induced by this unique technique is discussed. (Chapter 2) Then we utilize this technique to explore the wrinkling on a inhomogeneously pre-wrinkled surface. This understanding gives us information about the distribution of applied strain on a surface with pre-defined inhomogeneous strain fields. (Chapter 3) Since the localization has been linked to the stress nonlinearity of materials, we propose controlling the stress state in the substrate effectively influences the localization. With optimized mechanical substrate prestretch, the localization is significantly delayed and yield the aspect ratio as high as 0.65. Surface fractures are suppressed at large strains required by high aspect ratio wrinkles by using appropriate materials. (Chapter 4) Inspired from living organs, reducing stresses in the substrate is demonstrated to influence the localization. Crosslinking networks in the soft substrate are chemically rearranged to relieve the stresses while maintaining the wrinkling aspect ratio. With this approach, aspect ratios as high as 0.9 are achieved. (Chapter 5)
1.2 Wrinkling Mechanics

Wrinkling is a buckling instability, in which multiple bifurcation modes of deformation are possible for the material. A buckling instability occurs when a compressive axial strain exceeds a critical value, putting the material in the unstable state. The unstable state is often illustrated as a ball sitting on the peak of a hill, and any small perturbation would cause the ball to fall down from its current state. A material in the unstable state cannot recover its current state after a small lateral perturbation is applied and then removed, instead, it transforms into another deformation state.\(^{19}\)

Wrinkling as defined in this thesis is caused by the buckling instability, and has symmetric up and down amplitude about the undeformed lateral plane and the characteristic period. In this thesis, we focus on the wrinkling system consisting of a thin stiff film bounded on a softer substrate, as it has been widely employed and studied extensively.\(^{6,7,20,21}\) When a small compressive strain (\(\varepsilon\)) is developed in the system, the thin film tends to buckle into a large radius of curvature, costing stretching energy for the substrate. Thus, the substrate inhibits the out-of-plane deformation, and the system deforms in-plane. When \(\varepsilon\) exceeds the critical wrinkling strain (\(\varepsilon_c\)), the in-plane deformation mode becomes unstable, and wrinkling occurs as the other bifurcation mode. \(\varepsilon_c\) can be calculated by the governing equation for bending a stiff film on a soft substrate.\(^{6,22}\)

\[
\bar{E} I \frac{d^4 w}{dx^4} + F \frac{d^2 w}{dx^2} + qw = 0 \tag{1.1}
\]

where \(I\) is the moment of inertia of the film, \(F\) is the external force, \(x\) is the axis parallel to the wavelength, and \(q\) is the Winkler’s modulus of the substrate. For an uniaxially
strained wrinkling system, the out-of-plane deformation \( w \) is a sinusoidal function of the peak-to-valley amplitude \( A \) and wavenumber \( k \).

\[
w = \frac{A}{2} \cos(kx_1)
\]  

(1.2)

Substitute Equation (1.2) into Equation (1.1), the critical strain \( \varepsilon_c \) for wrinkling is obtained by minimizing the external force \( F \) by \( k \).

\[
\varepsilon_c = \frac{1}{4} k^2 t^2
\]  

(1.3)

The competition between film bending and substrate stretching governs the characteristic wavelength \( \lambda \) (Figure 1.3).\(^{7,23,24}\)

Figure 1.3 Mechanism of wrinkling. (a) An applied strain is applied onto a system consisted of a thin film bounded on a soft substrate. (b) The bilayer system is deformed in-plane when \( \varepsilon < \varepsilon_c \). (c) Unfavorable state which the buckled film stretches the soft substrate out of plane. (d) The competition between the bending and the stretching determines the wrinkle wavelength. (e) Schematic of the peak-to-peak wavelength and the peak-to-valley amplitude.
The total energy per area \((U_T)\) in this system can be written as the summation of the film bending energy per area \((U_B)\) and the substrate stretching energy per area \((U_S)\).

\[
U_T = U_B + U_S
\]  \(\text{(1.4)}\)

\(U_B\) and \(U_S\) will be obtained by integrating the energy densities of an elastic Von Karman plate,\(^{8,23}\) respectively.

\[
U_B = \frac{\bar{E}_f t^3}{48} k^4 \frac{A^2}{4}
\]  \(\text{(1.5)}\)

\[
U_S = \frac{\bar{E}_S}{8} k^4 \frac{A^2}{4}
\]  \(\text{(1.6)}\)

where \(t\) is the thickness of the film, \(\bar{E}_f\) is the plane modulus of the film, and \(\bar{E}_S\) is the plane modulus of the substrate. Assuming an inextensible film, \(A\) can be related to the wrinkling strain \((\varepsilon)\) by the sinusoidal wave geometry under small \(\varepsilon\).

\[
\varepsilon \approx \left(\frac{kA}{4}\right)^2
\]  \(\text{(1.7)}\)

Therefore,

\[
U_T = \frac{\bar{E}_f t^3}{12} k^2 \varepsilon + \frac{\bar{E}_S}{2k} \varepsilon
\]  \(\text{(1.8)}\)

By minimizing \(U_T\) with respect to \(k\), and use the relationship \(k = 2\pi/\lambda\), the characteristic wavelength is

\[
\lambda = 2\pi t \left(\frac{\bar{E}_f}{3\bar{E}_S}\right)^{1/3}
\]  \(\text{(1.9)}\)

and Equation (1.3) becomes

\[
\varepsilon_c = \frac{1}{4} \left(\frac{3\bar{E}_S}{\bar{E}_f}\right)^{2/3}
\]  \(\text{(1.10)}\)

The wavelength is often considered to be insensitive to \(\varepsilon\) in the low strain condition. Assuming the top film is inextensible and the contour of the film is fixed, the wrinkle amplitude is determined by the excess contour of the film at \(\varepsilon\):\(^{17,22,24}\)
\[
\frac{A}{2} = t \sqrt{\frac{\varepsilon}{\varepsilon_c}} - 1 \quad (1.11)
\]

Therefore, the aspect ratio of the wrinkle is proportional to the square root of strain:

\[
\frac{A}{\lambda} = \frac{2}{\pi} \sqrt{\varepsilon - \varepsilon_c} \quad (1.12)
\]

This analysis has been verified by experiments with \( \varepsilon < 0.15 \), but it is worth noting that it only applies to the small strain condition. The behaviors of wavelength and amplitude under large strains are still elusive.

### 1.3 Wrinkle Morphology and Straining Mechanism

Researchers have demonstrated creating wrinkle patterns across large surface area by controlling the strain field in different methods. For uniaxial strain field, wrinkles are aligned into one dimensional (1D) straight parallel lines, orthogonal to the strain direction. (Figure 1.4a) The mechanics of the 1D pattern are discussed in the previous section. Uniaxial compression can be applied by mechanical compression on the system.\(^{25}\) Prestretching the substrate before a strain-free film is formed/coated then release the prestretch imposes compressive strain into the film.\(^ {20,26}\) Since the wrinkles created by prestretch method maintain aspect ratio without needing to apply external strain to the system, this method becomes very useful for many applications.

Equal-biaxial strain field results in two dimensional (2D) patterns. Scientists have demonstrated several straining methods, including thermal treatment,\(^ {6,27,28}\) solvent swelling,\(^ {29-34}\) and mechanical compression.\(^ {17,26,35}\) Several distinct patterns have been observed depending on the amount of stress and the modulus mismatch \((E_f/E_S)\).\(^ {36}\) At low stress and low modulus mismatch conditions, dimple and segment patterns dominate.\(^ {36}\)
At high stress and large modulus mismatch, labyrinth and herringbone dominate. (Figure 1.4bc)

![Image of wrinkle patterns](image)

Figure 1.4 Wrinkle patterns. (a) 1D wrinkle pattern created by uniaxial strains. (b) 2D labyrinth pattern created by equal-biaxial strain. (c) 2D herringbone pattern created by aligning the labyrinth pattern. (d) Unique wrinkle pattern formed with circular holes. The scale bar in (a) is applicable to (b) and (c). (a)(b)(c) Reprinted with permission from Lin, P.-C.; Yang, S. Spontaneous Formation of One-Dimensional Ripples in Transit to Highly Ordered Two-Dimensional Herringbone Structures through Sequential and Unequal Biaxial Mechanical Stretching. Appl. Phys. Lett. 2007, 90, 241903. Copyright 2007, AIP Publishing LLC. (d) Reprinted by permission from Macmillan Publishers Ltd: Nature, copyright 1998.

In addition to the methods homogeneously creating wrinkle patterns described above, complicated and inhomogeneous wrinkle patterns can be created by substrate patterning and material inhomogeneity. Boundaries of holes or steps on the substrate
change the strain field, allowing design of unique 2D wrinkle patterns.\textsuperscript{27} (Figure 1.4d) Locally forming stiff film by lithography or focus ion beam is also an approach for pattern design.\textsuperscript{37} However, these methods require complicated experimental processing and expensive instrument. Recently developed contact line wrinkling technique shows interesting ability to locally pattern wrinkling surfaces and induce strain inhomogeneity with one step and low cost experiment.\textsuperscript{38} This technique is discussed in Chapter 2 and Chapter 3.

1.4 Strain Localizations

As the aspect ratio increases, the deformation in the substrate increase and the stored strain energy increases (Equation (1.5) (1.6)). At a critical point, the localization transition occurs, where the shape of surface profile significantly alters. Localizations concentrate the strain to small fractions of surface. As the applied strain increases, the localization structures increase in amplitude by consuming the amplitudes of neighboring wrinkles, suppressing the growth of the wrinkle aspect ratio.\textsuperscript{25,39} Therefore, understanding the onset of localization modes is important to improve the aspect ratio of wrinkles.

Several localization modes have been observed and gained increasing attention. Crease is a sharp in-to-the-surface structure occurring around a strain of 0.3 when the modulus mismatch is small (Figure 1.5a).\textsuperscript{40–42} It has been demonstrated to dynamically manipulate cells on the surface.\textsuperscript{43} Fold\textsuperscript{44,45} (Figure 1.5b) and period-doubling (Figure 1.5c),\textsuperscript{46,47} in which the film forms into-the-surface structures, is observed when the modulus mismatch is significant ($E_f/E_S > 10$). Folds are demonstrate to provide useful light guidance properties\textsuperscript{45} and have potential to be used as microfluidic channels.\textsuperscript{48}
Ridges are out-of-surface structures and are proposed to modify surface hydrophobicity and adhesion (Figure 1.5d).49

Some theoretical and experimental works have investigate these localization modes. Pocivavsek and coworkers study a thin film transitions from wrinkled to folded on water and gel surface.\textsuperscript{25} They show the folds suppress the wrinkle aspect ratio, and claim the transition occurs when the energies of wrinkling becomes greater than folding. Damman and coworkers derive an quadratic equation to describe the period-doubling event.\textsuperscript{46} Recently, Hutchinson and coworkers model the thin film bounded on a nonlinear soft material, and suggest that the imbalanced up-and-down traction forces cause the folds and ridges.\textsuperscript{50} More detail of this model is reviewed in Chapter 4. An integrated study from Zhao and coworkers has summarized the localization modes, including creasing, folding, period-doubling, and ridging, along with the delamination mode.\textsuperscript{51} These modes are found to dominate in different mismatch strains, material moduli and interfaces.\textsuperscript{51} Although these studies provide limited information about the wrinkle amplitude, the fundamental knowledge of localization from these studies is important for resolving the questions in this thesis.

1.5 Thesis Organization and Governing Questions

The wrinkle amplitude (aspect ratio) is focused in this thesis. The goal is to develop processes that are able to create controlled amplitude not only in the current accessible range but also beyond. This problem is closely related to the localization transition since the localization suppresses the aspect ratio.

Chapter 2 studies a newly developed contact line wrinkling technique to control the wrinkle amplitude. When a thin film is laminated onto a soft material, wrinkles form at the contact line of the thin film and the soft material. We investigate the wrinkling and the
mechanics of this technique as a function of the moduli of the film and substrate. The deformation of the substrate by adhesion force and the deformation of the film by the surface energy difference are the main sources of the strain. The contact line geometry is used throughout this work to laminate the film.

- How do the film modulus and the substrate modulus influence the wrinkling?

Chapter 3 studies the influence of strain inhomogeneity on wrinkling. The contact line technique is used to create inhomogeneous wrinkle patterns on the surface without any nonuniform material properties or geometry. We study the wrinkle aspect ratio as a function of strain on an inhomogeneous pre-wrinkled surface, and investigate whether the global strain will be localized by strain inhomogeneity, giving us information about the onset of strain localization.

- How does the wrinkle aspect ratio depend on the applied strain on an pre-defined inhomogeneous surface?
- Can an inhomogeneously wrinkled surface transform into homogeneously wrinkled?

Chapter 4 demonstrates the process of making high aspect ratio wrinkling surface with the prestretch method. Optimal amount of prestretch set the substrate at the most linear region and stabilizes the wrinkling at high aspect ratio as large as 0.65. We aim to find the relationship between the localization transition and the amount of prestretch, and optimize the material properties to avoid surface fractures.

- How does the localization mode depend on the amount of prestretch?
- How do we avoid surface fractures by optimal material properties?
- How high the wrinkle aspect ratio can be using substrate prestretch?
Chapter 5 continues the efforts in making high aspect ratio. Inspired by living organs, we demonstrate a new approach by reducing the stress in the substrate. By forming or rearranging the crosslinking network, the wrinkled substrate releases strain energy, ultimately influencing the localization transition. We achieve high aspect ratio wrinkles as high as 0.9.

- How is the localization influenced by stress reduction in the substrate?
- How high the wrinkle aspect ratio can be using stress relaxation?
- What is the localization mode for the stress-relaxed wrinkles?
CHAPTER 2

MECHANICS OF CONTACT LINE WRINKLING

2.1 Introduction

Wrinkling has received intensive attentions for its effective patterning ability.\textsuperscript{27} Conventional methods, such as thermal expansion,\textsuperscript{6,27,28} substrate prestretching\textsuperscript{20,26} and solvent swelling,\textsuperscript{29–34} are usually two-step processes that includes separated steps of forming or laminating a stiff film on the substrate, and then applying a compressive stress. While these methods show ability to globally pattern the surface, the wrinkle fabrication encounters the limitation to locally pattern the designed regions and to scale-up for massive continuous process. Inspired by the phenomenon that wrinkling is often observed during thin film lamination, the contact line wrinkling technique is proposed.\textsuperscript{38}

The contact line wrinkling technique is an one-step wrinkling process that has unique mechanism to create wrinkles.\textsuperscript{38} In this technique, the wrinkles form parallel to the contact line successionally as oppose to simultaneously across the whole surface with other wrinkling methods. The unique wrinkling mechanism provides possibility to microscopically pattern wrinkling surfaces, while having the potential to be scaled up for macroscopic roll-to-roll process. We aim to understand the fundamental mechanisms of the wrinkling. To resolve the contact line wrinkling, the previous work has demonstrated the strain depends on the velocity due to the velocity dependence of adhesion.\textsuperscript{38} However, the current model lacks description for the material properties, specifically, the film modulus ($E_f$) and the substrate modulus ($E_S$).

In this chapter, the understanding of the contact line wrinkling mechanics is refined considering $E_f$ and $E_S$. With lower $E_S$, we observe the wrinkling pattern transition from
one-dimensional (1D) to two-dimensional (2D), suggesting a biaxial strain is involved. In addition to the substrate deformation discovered previously, we find the film contour area changes two-dimensionally after the film is laminated onto the substrate, creating the biaxial strain. The substrate deformation is built upon the previous work and further observed to relate to the substrate modulus. The film deformation is found to depend on the film modulus, and is the main parameter to the 1D to 2D transition (Figure 2.1).

![Figure 2.1 Typical wrinkle patterns by the contact line wrinkling.](image)

(a) 1D pattern with 80 nm polystyrene film. (b) 2D pattern with 1MPa film.

2.2 Contact Line Wrinkling Mechanics

2.2.1 Current Understanding of the Contact Line Wrinkling

In this technique, a soft substrate is immersed into water, and a thin film is floated onto the water surface. One edge of the film is then attached to the substrate, creating a three-phase contact line. The film attaches to the substrate with good adhesion since both of them are hydrophobic. (Figure 2.2) At the contact line, the surface tension of water and the adhesion pull the film and cause local deformation on the substrate. The substrate and the film are set to move with a velocity \( V \), and the contact line sweeps across the substrate
surface. Wrinkles form parallel to the contact line if the deformation is greater than the critical value of wrinkling.

![Figure 2.2 Schematics of the contact line wrinkling technique.](image)

(a) The film and the substrate are lifted out from the water bath. (b) The film and the substrate are dipped into the water bath.

An important feature of this method is that the magnitude of strain, hence the wrinkle amplitude, strongly depends on $V$. The previous work proposes that the strain of wrinkling is resulted from the difference of the contour between the locally deformed substrate and the undeformed substrate. To model the contact line problem, the “knife edge” geometry is considered (Figure 2.3a). Assuming the shape of the substrate deformation is $f(x) = (P/E) \ln(x_0/x)$, where $P$ is the surface tension of water, and $x_0$ is the distance at which the perturbation becomes negligible. Importantly, when the local deformation is much smaller than the other dimensions, $x_0$ is assumed to equal to the elastocapillary length, $x_c = G_c/E$, where $G_c$ is the critical energy release rate which corresponds to the medium between the film and substrate. Therefore, the strain of wrinkling ($\varepsilon$) is
where $G_0$ and $V^*$ are constants. In the previous work, glassy polystyrene film and two substrate moduli, 120 kPa to 400 kPa, are used. Equation (2.1) fits the experimental data with $(P^2/G_c^2) = 0.106 \text{ m}^2$. (Figure 2.3b)

Although the previous work has demonstrated the velocity dependence of the strain, many other experiment parameters such as the film modulus ($E_f$) and the substrate modulus ($E_S$) are still unexplored.

![Figure 2.3](image)

Figure 2.3 Substrate deformation at the contact line. (a) The scheme of deformation of the substrate at the contact line in the case of $V > 0$. (b) Strain calculated from wrinkle aspect ratio. The solid line represents Equation (2.1). Reproduced in part from Ref 38 with permission of The Royal Society of Chemistry.

### 2.2.2 Influence of Material Moduli on the Contact Line Wrinkling

Here, in addition to the current understanding, we propose a biaxial strain mechanism to describe the 2D wrinkle pattern. For the contact line wrinkling, the total strain in the film ($\varepsilon$) is the summation of $\varepsilon_S$ and $\varepsilon_F$.

$$\varepsilon = \varepsilon_S + \varepsilon_F$$  \hspace{1cm} (2.2)
where $\varepsilon_S$ is the strain from the changes in the projection dimension of film imposed by the substrate, and $\varepsilon_F$ is the strain from changes in the interfacial area imposed by the film. Since $\varepsilon_S$ involves changes in lateral projection dimensions of the film, we estimate $\varepsilon_S$ by the lateral projection displacement using strain markers. On the other hand, $\varepsilon_F$ is from the surface tension difference between water and PDMS, involving no lateral dimension changes but changes in the interfacial area of the film and the substrate, ultimately influencing the wrinkle amplitude without changing the lateral dimensions. (Figure 2.4)

![Diagrams for two mechanisms of wrinkling.](image)

Figure 2.4 Diagrams for two mechanisms of wrinkling. The triangles mark the edges of the film. (a) The substrate is deformed while the film remains its surface area. $\varepsilon_S$ involves changes in the projection dimensions. (b) The edges of the film are fixed while the film expands in contour.

We consider the strains in 2D and discuss the $x$ component and $y$ component of $\varepsilon$ separately.

\[
\varepsilon_x = \varepsilon_{S,x} + \varepsilon_{F,x} \tag{2.3}
\]
\[
\varepsilon_y = \varepsilon_{S,y} + \varepsilon_{F,y} \tag{2.4}
\]

where the $x$ axis being parallel to the contact line and the $y$ axis being parallel to the moving direction of the substrate. We relate $\varepsilon_{S,x}$ and $\varepsilon_{S,y}$ by the Poisson’s effect of the substrate.
\[ \varepsilon_{S,x} = -\nu_S \varepsilon_{S,y} \]  
(2.5)

where \( \nu_S \) is a prefactor. \( \varepsilon_S \) is insufficient to induce the 2D patterns because the opposite sign of \( \varepsilon_{A,x} \) means tensile strain in the \( x \) direction. This suggests the 2D pattern is determined by another straining source involving no lateral displacement.

In our system, surface tension difference causes the biaxial compressive strain \( (\varepsilon_F) \) required for the 2D wrinkles as other mechanisms, such as thermal contraction, water swelling, residual stress by film preparation and chemical reactions, are expected to be negligible. \( \varepsilon_F \) is considered to be an equal-biaxial strain,

\[ \varepsilon_{F,x} = \varepsilon_{F,y} \]  
(2.6)

By the force balance at the edge of the film, we find

\[ tE_f \varepsilon_{S,y} = tE_f \varepsilon_{S,x} = \Delta \gamma \]  
(2.7)

where \( \Delta \gamma \) is the surface tension difference between the water and the substrate, \( E_f \) is the film modulus and \( t \) is the film thickness. Therefore,

\[ \varepsilon_{S,y} = \varepsilon_{S,x} = \frac{\Delta \gamma}{tE_f} \]  
(2.8)

Therefore, the wrinkling strain in \( x \) direction and \( y \) direction are

\[ -\varepsilon_x = \varepsilon_{A,x} - \frac{\Delta \gamma}{tE_f} \]  
(2.9)

\[ -\varepsilon_y = -\varepsilon_{A,y} - \frac{\Delta \gamma}{tE_f} \]  
(2.10)

where the negative sign represents compression.

We consider a stress-controlled mechanism for \( \varepsilon_S \) as the driving force being the pulling force from the liquid phase. Therefore, \( \varepsilon_S \) is inversely proportional to the substrate modulus \( (E_s) \)

\[ \varepsilon_{S,y} = f \left( \nu, \frac{1}{E_s} \right) \]  
(2.11)

as the previous work has demonstrated the velocity dependence of \( \varepsilon_S \).
2.3 Experimental Approach

To investigate the influences of $E_f$ and $E_S$ on the contact line wrinkling, we use custom-built instrument equipped with a linear nanopositioner (EXFO Burleigh Inchworm motor 8200) and a bath of reverse osmosis (RO) water (Figure 2.5). The thin film is cut into squares (10×10 mm$^2$) and floated onto the RO water and the substrate was made in a plastic dish fixed on the nanopositioner. After the film is attached onto the substrate, the substrate is lifted out or immersed into the water by the nanopositioner at a constant speed with the film attached on (Figure 2.2). The angle of the substrate and water surface is fixed at 45 degree. After the whole film is laminated onto the substrate, the sample is taken out from the water bath and dried at the room temperature (20 °C).

Figure 2.5 Picture of the contact line wrinkling setup. A nanopositioner is set at 45 degree, and a substrate is moving into or out of the water bath.
2.3.1 Film preparation and characterization

To study the influence of $E_f$ on the wrinkling pattern, we change $E_f$ by adjusting the crosslinking density of the crosslinked polydimethylsiloxane elastomers (PDMS) and by using polystyrene (PS) to prepare glassy, high modulus films.

Glassy films are made of polystyrene purchased from Polymer Source Inc. with $M_n = 130$ kg mol$^{-1}$ and $M_n / M_w = 1.05$. The PS is dissolved into 3 wt% solution in toluene, then spun-coat on a silicon wafer with 3000 rpm for 30 seconds. Before spin-coating, the silicon wafer is rinsed with toluene and isopropanol and cleaned with UV-ozone cleaner for 20 minutes. The film is used immediately after spun-coat. The film thickness of $130 \pm 10$ nm is measured by the interferometry profilometer (Filmetrics F-20 Thin Film Analyzer). The elastic modulus, $E_f = 3.5$ GPa is obtained from literature.$^{53}$

Elastomeric films are made of crosslinked vinyl terminated PDMS, Dow Corning Sylgard$^{\text{TM}}$ 184, Momentive$^{\text{TM}}$ LSR7070, and Momentive$^{\text{TM}}$ LSR2080. The film thickness is measured by optical profilometry (Zygo NewView 7300). The thickness is $2.5 \pm 0.5$ μm. The film modulus is calculated by comparing the wrinkle wavelength to the PS film wrinkles.$^{22,54,55}$

The mixture of 1.86g vinyl terminated PDMS, DMS-V00 (Gelest Inc.), 1.6g trimethylsilyl terminated PDMS, HMS-991 (Gelest Inc.), and 0.2g 1.7wt% Platinum-divinyltetramethyldisiloxane (Pt catalyst) complex solution in tetramethyldivinylcyclooctasiloxane ($D_4^V$, Gelest Inc.) is spun-coated onto a polyacrylic acid (PAA) layer on a glass slide with 1000rpm for 30 seconds. The PAA is purchased from Aldrich Inc. with $M_w = 1800$ g mol$^{-1}$ and diluted into 2 wt% solution in water. The PAA solution is spun-coat on a UV-ozone treated (10 minutes) glass slide.
with 500 rpm for 60 seconds. After being spun-coat, the PDMS film is cured in 70 °C for at least 6 hours, and then used immediately after cooling to room temperature (~20 °C).

The mixture of 2g DMS-V05 (Gelest Inc.), and 0.4g HMS-991 and 0.05g Pt catalyst solution is spun-coated onto the PAA layer on a glass slide with 2500rpm for 30 seconds. After being spun-coat, the PDMS film is cured in 70 °C for at least 6 hours, and then used immediately after cooling to room temperature (~20 °C).

The mixing ratio of prepolymer:crosslinker are 5:1, 10:1 and 20:1 by weight for Sylgard™ 184. The mixture is then diluted into 25 wt% in hexane. The solution is spun-coat on the PAA/glass with 3000 rpm for 30 seconds. After being spun-coat, the PDMS film is cured in a 70 °C oven for at least 3 hours, and then used immediately after cooling to room temperature (~20 °C).

LSR7070 purchased from Momentive Inc. are diluted into 20wt% solution in hexane, then follow the same spin-coating and thermal curing process described for Sylgard™. LSR2080 follows the same dilution, spin-coating and thermal curing process described for LSR7070.

2.3.2 Substrate preparation and characterization

The soft substrates are crosslinked polydimethylsiloxane (PDMS), made from Dow Corning Sylgard™ 184 elastomer kit. The prepolymer to crosslinker mixing ratio is 40:1 by weight. The mixture is degassed in a moderate vacuum for 40 minutes, poured into polystyrene petri dishes, then cured in a 70 °C oven for 60 minutes. Cured samples are immediately used after cooling to room temperature (20 °C). The elastic modulus ($E_S$) for each substrate is calculated from the wavelength$^{22,54,55}$ of 120 nm PS film wrinkles, taking $E_f = 3$GPa, $\nu_S = 0.5$ and $\nu_f = 0.33$. 

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2.3.3 **Wrinkle characterization**

The wrinkles are measured after 24 hours for equilibrium. The amplitude and wavelength are measured by the optical profilometer. The amplitude is taken as the mean peak-to-valley distances from a cross-section of the scanned area consisting of 3-5 wrinkles, and the wavelength is taken as the mean peak-to-peak distances from these wrinkles. The error bars of aspect ratio values are calculated from this measurement at four different locations of the sample surface. The optical images are taken by the Zeiss AxioTech Vario optical microscope with 2.5x, 5x, 10x, and 20x optics, equipped with Pixel Link CCD camera. The FFT images are generated by the ImageJ software.

2.4 **Results and Discussion**

2.4.1 **Analysis of Strain by Strain Markers**

To estimate $\varepsilon_S$, we measure the lateral projection displacement. We spray florescent particles on the film as strain markers. The distances between the particles are measured through fluorescent microscopy images when the film is on water and when the film is laminated onto the PDMS substrate. (Figure 2.6) As the particles (diameter = 1 $\mu$m) are 20-50 times smaller than the wrinkle wavelength, no influences on wrinkles are observed.
Figure 2.6 Fluorescent microscopy images for tracking displacements by particles. Each column represents one sample. The first row was taken when the films were floating on water. The second row was taken when the films were wrinkled. Although there are some different in the pattern and the wavelength between each samples, similar strains are observed. Strains measured from the images are (a)(b) $\varepsilon_x = 1\%$ and $\varepsilon_y = -2.8\%$. (c)(d) $\varepsilon_x = 0.8\%$ and $\varepsilon_y = -2.2\%$. (e)(f) $\varepsilon_x = -0.8\%$ and $\varepsilon_y = -1.8\%$. (g)(h) $\varepsilon_x = 0.6\%$ and $\varepsilon_y = -1.9\%$. (i)(j) $\varepsilon_x = 1.6\%$ and $\varepsilon_y = -2.8\%$.

We use the flow coating technique\textsuperscript{56,57} to assemble the florescent CdSe nanoparticles into grids on the film. The grids conform to the wrinkling topography as shown in the confocal microscopy image (Figure 2.7). The nanoparticle grids have well-defined spacing ($100 \ \mu m$ or $200 \ \mu m$) (Figure 2.8). With the thickness of 10 nanometer, no influences on the wrinkles by the grids are observed.
Figure 2.7 Nanoparticle grids for tracking displacement. (a) Schematics of preparing the PDMS films with nanoparticle grids. (b) Confocal microscopy image of the nanoparticle grids. The fluorescent lines are nanoparticle grids pre-patterned onto the film. The top inset is the cross section along the horizontal green line, and the right inset is the cross section along the vertical red line.

The lateral displacements in $x$ and $y$ direction are calculated using the film floating on water as the reference. The lateral displacements represent the strain imposed by the substrate, hence, $\varepsilon_S$. We find $\varepsilon_{S,y} < 0$ (compression) and $\varepsilon_{S,x} > 0$ (tension) for not only 1D but also 2D wrinkles. This confirms Equation (2.5) and the hypothesis that an additional biaxial strain mechanism is involved.
Figure 2.8 Microscopy images for tracking displacements by nanoparticle grids. Each column represents one sample. The first row was taken when the films were floating on water. The second and third rows were taken when the films were wrinkled. Although there are some different in the pattern and the wavelength between each samples, similar strains are observed. Strains measured from the images are (a) $\varepsilon_x = 1.1\%$ and $\varepsilon_y = -2.5\%$. (b) $\varepsilon_x = 1.1\%$ and $\varepsilon_y = -0.97\%$. (c) $\varepsilon_x = 1.1\%$ and $\varepsilon_y = -0.56\%$. (d) $\varepsilon_x = 1.5\%$ and $\varepsilon_y = -1.8\%$. (e) $\varepsilon_x = -1.2\%$ and $\varepsilon_y = -2.0\%$. (f) $\varepsilon_x = 2.4\%$ and $\varepsilon_y = -1.3\%$.

2.4.2 Influence of Film Modulus

To investigate $E_f$, we prepare films with different $E_f$ (500kPa-3GPa) by changing the crosslinking density of PDMS. The PDMS film thickness of 2-3 μm is used. The substrate is prepared with PDMS with low crosslinking density ($E_S = 6kPa$, 17kPa and 20kPa), providing sufficient modulus mismatch ($E_f/E_S$) for wrinkling. When the film and substrate are immersed into the water with $V = 10 \mu m/s$, the 2D wrinkles are observed at $2 < tE_f < 300$, and the 1D wrinkle pattern dominates for $tE_f < 2$ and $tE_f > 300$. The ordered 2D wrinkle pattern, herringbone, is observed at $tE_f = 20$. Transition from 1D to 2D pattern causes the slightly buckled 1D pattern as $tE_f$ is close to 20. For $V = 1500 \mu m/s$, 

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2D wrinkles emerge with \( tE_f < 300 \). Beyond \( tE_f < 300 \), no wrinkle is observed. (Figure 2.9)

![Figure 2.9 Wrinkle patterns at various \( tE_f \) for two velocities. All the images share the same scale bar. The insets represent the fast Fourier transform of the corresponding image.]

In Figure 2.10, \( \varepsilon_y \) is calculated from the wrinkle amplitude \( (A) \), wrinkle wavelength \( (\lambda) \) and the critical wrinkling strain \( (\varepsilon_c) \).\(^{24,38,58}\)

\[
\varepsilon_y = \left( \frac{\pi A}{2 \lambda} \right)^2 + \varepsilon_c
\]  
(2.12)

Both the short wavelength and the intermediate wavelength\(^{35}\) are used to calculate the strain and reported, respectively.
Figure 2.10 The strain in the y direction for different $tE_f$. The data points are calculated from the wrinkle aspect ratio. The curves represent $\varepsilon_y = \varepsilon_S + \Delta\gamma / tE_f$ with fitting parameters $\Delta\gamma = 0.45 \text{ N/m}$ and $\varepsilon_S = 0, 0.02$ or $0.06$. (a) Strain calculated with the intermediate wavelength. (b) Strain calculated with the short wavelength.

The wrinkling strain calculated from the wrinkle aspect ratio (Equation (2.12)) increases as $tE_f$ decreases for $tE_f > 4$ (Figure 2.10). When $v = 1500 \text{ µm/s}$, $\varepsilon_{S,y}$ is small and $\varepsilon_y \approx \varepsilon_{F,y}$. $\varepsilon_{S,y}$ becomes non-zero when $v = 10 \text{ µm/s}$. The experimental results agree with Equation (2.10) until $tE_f < 4$, where the strain deviates from the prediction and the wrinkles recover 1D pattern. This can be contributed by the film compression in the contour plane with low $E_f$ and low $E_f/E_S$, resulting the underestimate of strain as inextensible films are assumed in Equation (2.12).$^{24,38,58}$ We note that the most well-ordered 2D wrinkle pattern, herringbone, emerges at $tE_f = 20$, rather than $tE_f = 60$ where corresponds to the largest $\varepsilon_y$. Further understanding to the 2D wrinkle mechanics is needed to explain the deviation at $tE_f < 4$ and the formation of herringbone pattern.
2.4.3 Substrate Modulus Dependence

When $tE_f > 500$, $\varepsilon_y \approx \varepsilon_{S,y}$, and we find $\varepsilon_y$ for $E_S = 6\text{kPa}$ is three times greater than $\varepsilon_y$ for $E_S = 20\text{kPa}$, implying the scaling of $\varepsilon_{S,y} \sim 1/E_S$. To study the effect of $E_S$, we prepare PDMS substrates with different moduli ranging from 10kPa to 2MPa. The film is made of PS for high $E_f$ to minimize $\varepsilon_F$. A constant speed is set to be smaller than 10 μm/s since the strain is predicted to plateau at this region in the previous work, and we find the strain is insensitive to $V$ for $V < 10$ μm/s. We also perform an experiment utilizing the curing kinetic of the PDMS. An under cured PDMS substrate is slowly lifted out with a speed of 0.4 μm/s for the distance of 10 mm. During the process, the substrate crosslinks and stiffens, providing continuous change in $E_S$ at where each wave of wrinkles is formed. Using this experiment, we obtain the aspect ratio for various $E_S$ value on a single wrinkled film.
Wrinkle strain at different $E_S$ is plotted in Figure 2.11, having an agreement with Equation (2.11).

### 2.4.4 Enhancing 2D Wrinkles by Thermal Curing

In addition to $\varepsilon_F$, biaxial strain can be applied by thermal curing in 70°C for a few hours. For the PDMS/PDMS wrinkles, the jogging angle of the 2D wrinkle pattern decreases and the aspect ratio increases after the thermal curing. On the other hand, the
PS/PDMS wrinkles show limited area of 2D pattern and the aspect ratio remain unchanged (Figure 2.12).

![Image](image_url)

Figure 2.12 Enhance 2D wrinkles by thermal curing. (a) Wrinkling pattern before thermal curing. (b) Wrinkling pattern after thermal curing for four hours. The jogging angle decreases. (c) The aspect ratio increases by the thermal curing for the PDMS films (open data points). The aspect ratio remain unchanged for the PS films (filled data points). The scale bar represents 200 μm.

With this thermal curing step, 2D wrinkles with enhanced 2D characteristics and enhanced aspect ratio are obtained. The enhancement of pattern and aspect ratio maintains after the wrinkles are cooled to room temperature. This can be caused by
mechanisms such as stress relaxation and crosslinking network rearranging during the thermal curing, as we will discuss more in Chapter 5.

The major mechanism for the enhancement is expected to be the biaxial expansion of the PDMS film rather than substrate shrinkage, as the PS film shows less effects. Insignificant change in $\varepsilon_S$ by this curing step using the particle experiment further confirms this mechanism (Figure 2.13).

![Figure 2.13 Tracking displacement after curing.](image)

(a)-(c) Microscopy images for particles when the film is on water, wrinkled and cured, respectively. (d) Particle distances in the $x$ direction (brown bars) and the $y$ direction (black bars). No significant change between sample that is just wrinkled and after cured.

We visualize the dramatic displacement field in these thermal cured 2D wrinkles by the largely distorted nanoparticle grids (Figure 2.14).
2.5 Summary

In summary, we find the strain imposed by the substrate deformation is inversely proportional to the substrate modulus, observed with the glassy PS film. In addition to the strain by substrate, a biaxial strain caused by the surface tension difference is found in the film and to contribute to the contact line wrinkling. This biaxial strain is inversely proportional to the film modulus, allowing us to create 1D and 2D wrinkles with the contact line wrinkling technique through changing the film modulus. Precisely quantifying the film thickness will provide direct measurement for $\varepsilon_F$, as significantly expansion of film required to generate $\varepsilon_F$ is expected to associate with shrinkage in thickness. For example, when $\varepsilon_{F,y} = 0.08$, the thickness decreases 4% (0.12 μm for an originally 3 μm film) with the Poisson’s ratio of 0.5.
This work not only further understands the contact line wrinkling, but also provides insights for problems related to the three phase contact line, such as the lamination, rolling transfer, peeling and the deformation of soft material by water droplets.

2.6 Acknowledgement

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CHAPTER 3

WRINKLING OF SURFACES WITH STRAIN INHOMOGENEITY

3.1 Introduction

For wrinkles made with a polymer film supported on a soft elastomer, the amplitude is directly proportional to the wavelength and the square root of the applied strain. This dependence has been confirmed with ideal substrates where the global strain is homogeneously distributed, but the influence of strain inhomogeneity has not been considered previously. Strain inhomogeneity has also been shown to relate to localization events where the localization structures grow in amplitude by consuming neighboring amplitude. Pre-existing strain inhomogeneity on a surface can be caused by defects or residual strains that are not trivial to eliminate in non-ideal systems. Will the inhomogeneity lead to strain localization or will the system try to homogenize the subsequent strain globally?

We use the contact line wrinkling technique to prepare strain inhomogeneity without local property or geometry modifications to the materials. Periodic regions of different wrinkle amplitudes, hence strains, are created on the polystyrene thin films on the soft substrates. We observe the change in wrinkle amplitude when a global strain is applied, and find that an inhomogeneously strained surface approaches amplitude homogeneity globally upon the application of sufficiently large strains. We derive relationships to describe this process, providing fundamental knowledge of the wrinkling mechanism.
3.2 Background

While it has been shown that a homogeneous strain field will result in a homogeneously wrinkled surface, it has also been shown that inhomogeneous topographical features, such as creases or folds, will develop beyond a critical strain. The onset of this secondary transition, or strain localization, has been associated with an inhomogeneity in the strain field. Such localizations have received increased attention in recent literature due to their relevance in Nature processes of morphogenesis, as well as their implications in the fidelity of thin film devices. Although inhomogeneities or defects have been qualitatively linked to strain localization events, a systematic understanding of pre-existing strain homogeneity has remained elusive.

While homogeneous wrinkles across the entire surface are largely demonstrated by global straining methods such as thermal expansion mismatch, solvent swelling, and mechanical straining, inducing controlled inhomogeneous wrinkles is challenging and is usually achieved by non-uniform material properties or geometry. For example, selectively forming films with photolithography or ion beam gives wrinkles at designed locations, but the material property across the surface is no longer uniform. This creates difficulties to study inhomogeneous wrinkling. A recently developed fabrication method allows three types of wrinkling surface to be made with a single fabrication process on uniform materials: flat, continuously wrinkled, and periodically wrinkled films.

3.3 Approach

To understand the influence of strain homogeneity on wrinkling surfaces. Three types of wrinkling surface are prepared. By applying global mechanical strain to each of
these three types, we investigate how initial strain inhomogeneity influences amplitude growth of these wrinkling surfaces upon global compression.

Figure 3.1 Schematic of the experimental process. A polystyrene film is laminated onto a soft substrate. The wrinkle amplitude is varied by controlling the velocity of the pull out process.

To prepare initial structures, we apply a recently developed contact line technique previously discussed in Chapter 2. In brief, a soft substrate is immersed into water, and a thin film is floated onto the water surface. The deformable soft substrate is made of crosslinked polydimethylsiloxane (PDMS), and the inextensible thin film is made of polystyrene. One edge of the film is then attached to the substrate, creating a three-phase contact line. The substrate, as well as the film, are slowly lifted from the water and the contact line sweeps across the substrate surface with a controlled velocity \( V \) (Figure 3.1). Wrinkles form parallel to the contact line, if the deformation is larger than the critical value of wrinkling.
(a) By setting $V$ larger than a critical velocity $V^*$, wrinkle-free flat surface is made. (b) By setting $V$ lower than $V^*$ wrinkling surface with homogeneous aspect ratio is made. (c) By oscillating $V$ larger and lower than $V^*$ inhomogeneous wrinkling surface is made. (d) Optical microscopy of the homogeneous wrinkling surface. (e) Optical microscopy of the inhomogeneous wrinkling surface.

An important feature of this method is that the magnitude of strain, hence the amplitude, strongly depends on $(V)$ due to the velocity dependence of the interfacial adhesion energy between the film and substrate. When $V$ exceeds a critical value, the water at the contact line wets the interface between the film and substrate. The water coating prevents strain from developing due to adhesion, and the film remains wrinkle-free. This
allows us to fabricate different initial structures by controlling the velocity profile. By setting the velocity beyond the critical value, films remain flat. In contrast, films form uniform wrinkles when the velocity is constant and lower than the critical value. We vary the velocity of the contact line beyond and below the critical value, fabricating initial structures with periodically wrinkled regions (Figure 3.2). The wavenumber for the pre-wrinkled region can be controlled by the velocity profile. By precisely controlling the velocity of the contact line, the wavenumber as few as 4 wrinkles can be made (Figure 3.3). Due to the experimental difficulty to make low wavenumber, the wavenumber larger than 10 is used in this work.

![Microscopy image for low wavenumber](image)

Figure 3.3 Microscopy image for low wavenumber. Wavenumber as low as 4 is found.

We then carefully mount each of the three types of wrinkled samples on a customized strain stage. A linear actuator on the strain stage allows us to apply uniaxial global compression ($\varepsilon_{\text{app}}$) on the samples. Amplitude and wavelength at each strain step (~0.5%) were characterized by the optical profilometer. The amplitude data are normalized
by the respective wavelength at each strain state. Both the amplitude and wavelength are averaged over 10-20 waves on an arbitrary spot far from film edges. For the inhomogeneously strained films, the data are the average values in a fixed area that is initially wrinkled or flat.

3.4 Experimental

3.4.1 Film preparation and characterization

The stiff polymeric thin films were made with polystyrene (PS) purchased from Polymer Source Inc. ($M_n = 130$ kg/mol, $M_n/M_w = 1.05$). An 80 nm film was made from dissolving bulk PS in toluene at 2wt%, then spun-coated onto a silicon wafer at 3000 rpm for 30 seconds. 200 nm and 300 nm films were made from 4% solution in toluene, then spin-coated onto a silicon wafer for 30 seconds at 3000 rpm and 1000 rpm, respectively. No any further treatment such as annealing is applied. Prior to spin-coating the PS solution, the silicon wafer is cleaned with toluene and isopropanol, then treated with UV-ozone cleaner for 20 minutes. The film thickness was measured using the one point thin film profilometer (Filmetrics Optical Profilometer F-20). The Young’s modulus of the film ($E_{PS} \approx 3.5$ GPa) was retrieved from literature.53

3.4.2 Substrate preparation and characterization

Crosslinked polydimethylsiloxane (PDMS) was prepared by mixing Dow Corning Sylgard™ 184 elastomer base and curing agent. First, a mixing ratio of base/agent 10:1 was used as a supporting material, and the mixture was degassed for 40 minutes. It was then cured in a rectangular mold ($30 \times 25 \times 7$ mm or $44 \times 25 \times 7$ mm) in 70°C oven for 1 hour. Mixing ratio of 30:1 or 40:1 was spin-coated (500 rpm for 60 seconds) onto the
10:1 PDMS supporting material to make the substrate layer (~250 μm thick). The supporting material and the substrate were again cured in 70°C oven for 2 hours. The substrate was then used immediately after cooling to room temperature (~23°C). The Young’s moduli of the PDMS substrates were measured separately with thick (> 5mm) 30:1 or 40:1 PDMS. A contact mechanics setup,\textsuperscript{65} which probes the force as a function of displacement of a 2 mm diameter cylindrical silica probe, provided the moduli of PDMS ($E_{PDMS, 30:1} \approx 130\pm10\text{kPa}$ and $E_{PDMS, 40:1} \approx 50\pm10\text{kPa}$).

### 3.4.3 Wrinkle process and characterization

The substrate was immersed into the water and the film was attached to the substrate surface. The substrate and the film was then pulled out from water at a velocity of 10 μm/s and a angle of 45°. Instead of pulling continuously, a “stop-and-go” process was used, where the stopping time was 6 seconds followed by 300 μm, 500 μm, or 800 μm spacing at a velocity of 800 μm/s to prepare the periodically wrinkled samples.

The samples were then mounted onto a customized strain stage with a linear actuator. The contact interface of the sample and the stage was appropriately lubricated to allow the sample to slide freely. The mounting was conducted under a microscope in order to assure good alignment. Compressive strain was applied on the samples in the direction of the pre-strain by the strain stage. The amplitude, wavelength, and contour length were measured by an optical profilometer (Zygo NewView 7300, 10x and 50x objective) with MetroPro software. Optical microscopy images were taken by an optical microscope (Zeiss AxioTech Vario, 5x or 10x objective, Pixel Link CCD camera). Approximately 10% strain was applied over 2 hours. Manual and motorized stages were
both used after verifying that the strain rate had little effect on the amplitude measurement results.

3.5 Results and Discussion

3.5.1 Wrinkling of Homogeneously Strained Surfaces

For an initially flat film (Figure 3.4a, open data points), we find that the aspect ratio, \( A/\lambda \), increases with the square root of the applied global strain (\( \varepsilon_{\text{app}} \)). Here, \( \varepsilon_{\text{app}} = \varepsilon \).

From Equation (1.12):

\[
\frac{A}{\lambda} \propto \sqrt{\varepsilon} \tag{3.1}
\]

As evident in our data for three films of different thickness (\( t = 80\pm5 \) nm, \( 200\pm10 \) nm, \( 300\pm10 \) nm), the aspect ratio growth with strain is independent of film thickness. Also, in accordance with classical wrinkling theory, the aspect ratio will only be non-zero at strains greater than a critical wrinkling strain, which is independent of film thickness. The observed slight variation in the critical wrinkling strain for our data is attributed to experimental error in the alignment of samples with the strain stage.

In contrast to a vanishing aspect ratio at a finite strain, materials that are pre-wrinkled homogeneously have a finite aspect ratio at infinitely small globally applied strains (Figure 3.4a, solid data points). As strain is applied globally, the aspect ratio is found to increase at an initially slower rate until \( \varepsilon_{\text{app}} \) approaches the strain applied by the contact line method for pre-wrinkling the surface (\( \varepsilon_0 \)). As \( \varepsilon_{\text{app}} \sim \varepsilon_0 \), the aspect ratio grows according to \( \varepsilon_{\text{app}}^{1/2} \). The continuous growth of aspect ratio over all strains can be understood according to Equation (3.1), if the initial strain of the pre-wrinkles is known such that
\[ \varepsilon = (1 - \varepsilon_0) \varepsilon_{app} + \varepsilon_0 \]  

accordingly, replotting both data sets as a function of \( \varepsilon \), defined by Equation (3.2), allows them to collapse onto a single growth curve. This implies that the strain associated with both the contact line method and subsequent global mechanical strain are applied in the linear regime, such that superposition can be applied.

Figure 3.4 Plots of the aspect ratio growth for homogeneous wrinkling surfaces. The inset shows the direction of strain. The solid data points denote pre-wrinkled films while the open data points denote the initially flat films. Different colors represent different samples. (a) The aspect ratio of wrinkles as a function of \( \varepsilon_{app} \). The wrinkles from initially flat films increases more rapidly than pre-wrinkles. The lines are guidelines for the two types of samples. (b) The same data being re-plotted as a function of \( \varepsilon \) with Equation (3.2). The two types of wrinkles both follow the square root scaling. The solid line has the slope of 0.5. Used with permission: Soft Mat. 2013.66

3.5.2 Wrinkling of Inhomogeneously Strained Surfaces

For inhomogeneous wrinkled surfaces that have periodically alternating pre-wrinkled regions and flat regions (width of the flat region > 5\( \lambda \)) (Figure 3.2e), the results show that the pre-wrinkle amplitude grows (Figure 3.5) while new wrinkles initiate,
demonstrated by an increase in the total number of wrinkles on the surface (Figure 3.6). We further find that the growth of newly-formed wrinkles is identical to globally flat samples, and the growth of pre-wrinkles is identical to homogeneously wrinkled samples (Figure 3.7). In other words, Equation (3.1) well describes the amplitude growth regardless of initial structures on films. In addition, the wrinkle initiation and growing process is reversible as long as the materials are in their linear elastic regions. That is, when the surface is released from an applied strain, the initially flat region reverts to wrinkle-free and the pre-wrinkles relax to their original $A/\lambda$. Good adhesion at the film-substrate interface prevents the pre-wrinkles from re-distributing, and the homogeneity of the substrate allows the global compressive strain to be uniformly distributed. It should be noted that although we expect that new wrinkles form simultaneously on an ideal flat surface, Figure 3.5 indicates a progressive wrinkle formation. This is caused by a pre-existing strain gradient induced by the contact line technique.
Figure 3.5 Optical profilometry of a inhomogeneous wrinkling during compression. Left column shows 3D contour maps for applied strain of 0%, 4.5%, 5.6%, and 6.7% from top to bottom. The image width is 350 μm. Right column shows height profiles of the cross section indicated by dashed lines. New wrinkles are initiated at the initially flat regions. The wrinkle amplitude becomes homogeneous across the entire region at $\varepsilon_{app} \sim 6\%$. Used with permission: Soft Mat. 2013.66
Figure 3.6 Number of wrinkles across the whole surfaces. Used with permission: Soft Mat. 2013.66

Figure 3.7 Plots of the aspect ratio growth for inhomogeneous wrinkling surfaces. The inset shows the direction of strain. The solid data points denote pre-wrinkles while the open data points denote the initially flat regions. Different colors represent different samples. (a) The aspect ratio of wrinkles as a function of $\varepsilon_{app}$. The lines are the same guidelines from Figure 3.4. (b) The same data being re-plotted as a function of $\varepsilon$ with Equation (3.2). The two wrinkling regions both follow the square root scaling. The solid line has the slope of 0.5. Used with permission: Soft Mat. 2013.66
3.5.3 Homogeneity of Wrinkling Surfaces

From Equation (1.12), the aspect ratio in the initially flat region is described as

$$\frac{A}{\lambda} \approx \sqrt{\varepsilon} = \sqrt{\varepsilon_{app} - \varepsilon_c}$$

(3.3)

In the pre-wrinkled region,

$$\frac{A}{\lambda} \approx \sqrt{\varepsilon} = \sqrt{(1 - \varepsilon_0)\varepsilon_{app} + \varepsilon_0}$$

(3.4)

Equation (3.3) and Equation (3.4) are plotted in Figure 3.8.

Figure 3.8 Calculated aspect ratio as a function of applied strain. The red line represents Equation (3.1), where $\varepsilon_c$ and $\varepsilon_0$ are 0. The curves below the red line represent the initially flat surface with $\varepsilon_c = 1\%$, 2\% and 3\%, respectively. The curves above the red line represent the pre-wrinkled surface with $\varepsilon_0 = 0.5\%$, 1\% and 4\%, respectively.

By equating Equation (3.3) and Equation (3.4), $\varepsilon_{app}$ needed for the inhomogeneous wrinkling surface to transition to a homogeneous wrinkling surface is calculated to be 100\%, implying that homogenization of wrinkle aspect ratio is not possible. However, the optical profilometry data in Figure 3.5 indicates that the aspect
ratio of wrinkles across the entire surface becomes similar. We describe this homogenization by considering the rate of growth for wrinkle aspect ratio as a function of strain. Taking the derivative to Equation (3.1) gives the amplitude growth rate:

$$\left(\frac{\partial A}{\partial \epsilon}\right) \propto \epsilon^{-1/2} \propto A^{-1} \quad (3.5)$$

Equation (3.5) is plotted in Figure 3.9.

![Figure 3.9 Calculated wrinkle growth rate. The red curve represents the wrinkle growth rate for surfaces with $\epsilon_c = \epsilon_0 = 0$. The growth rate decreases drastically within 2%.

The growth rate is a decreasing function of amplitude. Therefore newly-formed wrinkles, which are smaller in amplitude, grow faster than the pre-wrinkles, which are greater in amplitude. Since newly-formed wrinkles quickly approach the amplitude of pre-wrinkles, the surface appears to be homogeneous.

The difference between the growth rates of pre-wrinkles and newly-formed wrinkles causes the system to approach a nearly homogeneous amplitude at $\epsilon_{app} < 6\%$, 49
which is significantly earlier than the predicted strain ($e_{app} = 100\%$) for uniformity. Since the wrinkle growth is only governed by Equation (3.1) regardless of the initial structure, the homogenization strain (6%) is expected to be insensitive to the separation distance of pre-wrinkle regions and the number of pre-wrinkles in each region. By taking advantage of this growth rate difference, surfaces can switch between homogeneous and inhomogeneous wrinkle amplitude by only a small applied global strain (Figure 3.10), demonstrating great potential for optical applications.

![Figure 3.10](image_url) Optical images of the inhomogeneous to homogeneous transition. (a) surface with inhomogeneity. (b) The inhomogeneity is reduced by 6% applied strain.

### 3.5.4 Patterning Localization Structures

At large strains, wrinkling transition to localization modes. For a homogeneously wrinkled surface, the emerging location of localization structures is unpredictable. Here, we briefly demonstrate patterning the fold structure onto designed location with pre-wrinkles. Since the wrinkling strain in the pre-wrinkled region is larger than the wrinkling strain in the initially flat region, pre-wrinkled region transition to the folding mode while the initially flat region remains in the wrinkling mode (Figure 3.11). This
interesting surface mixes the localization mode and the wrinkling mode while preserving periodicity of surface structures. We predict the pre-wrinkled region with low wavenumber can precisely pattern localization structures.

Figure 3.11 Optical microscopy of controlled folding location. The pre-wrinkled region (bottom half) reaches the localization transition earlier than the initially flat region (top half). The vertical lines are crazes caused by Poisson’s effect.

3.5.5 Wrinkling Surfaces with Multiple Orientation

Incorporating with mechanical compression, off-angled wrinkles are generated in the initially flat region (Figure 3.12b). With higher strain, the wrinkles are ultimately aligned by the strain field. This morphology can be useful to study the re-orientation of the wrinkles. This wrinkled surface has interesting morphology and can have unique properties for wrinkle-based technology.
In this chapter, we have considered the influence of strain inhomogeneity on the formation of wrinkles under a compressive strain. A recently developed contact line technique was applied to fabricate three different initial structures: flat, continuously wrinkled, and periodically wrinkled films. By applying compressive strain to the inhomogeneous, periodically pre-wrinkled surfaces, we tracked the amplitude as a function of applied global strain. We found that the growth of both the pre-wrinkles and the newly-formed wrinkles independently followed the classical amplitude-strain theory, regardless of pre-existing strains. We also observed that the total strain stored in wrinkles neither homogenized nor localized. Although the system will theoretically achieve uniform amplitude when $\epsilon_{app} = 1$, the inhomogeneous amplitudes approach a single, uniform amplitude at small strains ($< 6\%$) due to the growth rate differences of newly-formed and pre-existing wrinkles. Incorporating with other straining methods, the contact line

Figure 3.12 Optical microscopy of off-angled wrinkles. (a) Wrinkles with two orientations. The vertical wrinkles are created by the contact line technique, and the oblique wrinkles are induced by a oblique compression. (b) A strain about 5% is applied to align the wrinkles to the compression direction.
technique is able to create unique inhomogeneous wrinkle patterns without complicated experimental processes.

3.7 Acknowledgement

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CHAPTER 4

HIGH ASPECT RATIO WRINKLES BY SUBSTRATE PRESTRETCH

4.1 Introduction

Wrinkle aspect ratio is a very critical parameter for many promising wrinkle-based technologies since it directly corresponds to surface roughness, local curvature, and strain field. Although the aspect ratio of wrinkles can grow with increasing compressive strain, currently accessible aspect ratios are still low and restricted to less than 0.35, severely limiting the impact to these technologies. This limit results from a critical strain at which localization modes or surface failure modes replace wrinkle structures and significantly change the topography of surfaces. Building upon recently developed models which link the localization transition to the asymmetric traction forces between the wrinkle peaks and valleys for non-linear strain energy functions, we experimentally quantify the critical strain for both folding and ridging as a function of initial prestretch ratio. We also integrate the current knowledge of surface failures and demonstrate that not only prestretch but also material properties are important to fabricating high aspect ratio wrinkling surfaces. Collectively, we demonstrate the ability to delay the localization modes such as folding and ridging, and avoid surface failure such as crazing, cracking, and delamination, ultimately doubling the accessible aspect ratio to 0.65, demonstrating significant promise for future wrinkle-based applications.
4.2 Background

Although aspect ratio is potentially the key control parameter for many of proposed applications, the range of demonstrated wrinkle aspect ratio has been limited severely. In fact, a survey reveals the wrinkles are usually shallow (aspect ratio 0.1-0.2), and limited to 0.35 (Figure 4.1a). Shallow wrinkles correspond to low surface roughness, low local curvature, and low stored strain energy (Figure 4.1b), resulting in a considerably hindered impact for wrinkled surfaces to modern technology. Even though wrinkles with aspect ratios higher than 0.35 have remained unexplored, high aspect ratio wrinkles are expected to largely influence surface area, surface friction, adhesion and the other research fields. For instance, by enhancing aspect ratio from 0.3 to 0.6, the surface contour area improves from 9% more than the projection area to 36%; the local curvature doubles; the stretch ability of wrinkle-based flexible electronics improves from 20% to 40%.

As a compressive strain ($\varepsilon$) is applied to the film, the wrinkle aspect ratio ($A/\lambda$) grows according to Equation (1.12) until upper limits where other modes replace the wrinkling mode. Current upper limits in wrinkle aspect ratio are associated with the transition to localization modes such as creasing, period-doubling, folding and ridging; or to surface failures such as cracking and delamination. These modes and failures correspond to non-homogeneous strain fields that break the wrinkle structure. In order to expand the capability of wrinkle-based devices, the wrinkling mode needs to be stabilized in a wider range of strain.
During the localization transition, the surface transforms from homogeneous topography to a surface with sharp discontinuities in surface height, local curvature, and local strain. Further, in the localization modes, surface strain is localized, and the growth of wrinkle aspect ratio is suppressed. To date, detailed strain localizing mechanisms have not been widely understood. A recent study by Cao and Hutchinson involves numerical simulations to demonstrate that substrate prestretch, a commonly used method of wrinkle fabrication, significantly influences the critical wrinkling strain ($\varepsilon_c$) and the critical strain for transforming the wrinkling mode to localization modes ($\varepsilon_L$). These critical strains are found to vary as a function of substrate prestretch, as well as a

Figure 4.1 Aspect ratios in literature and wrinkle shape in true scale.  

(a) Summary of reported wrinkle aspect ratios in 38 published research articles. The star represents the result demonstrated in this chapter.  

(b) Simulated wrinkle profile with aspect ratios of 0.1 (dotted line) and 0.3 (solid line) in true scale. Used with permission: Adv. Mat. 2014.16
function of the film/substrate shear modulus mismatch \((\mu_f / \mu_s)\). The prestretch \((\lambda^0)\) is defined as the length at the prestretched state divided by the length at the strain-free state.

They propose the sinusoidal symmetry of wrinkles is broken by the localization modes when the out-of-surface traction force imbalances with the into-surface traction force due to non-linear strain energy functions. Since the prestretch influences the stress state in the substrate and the strain required for anisotropic traction, it changes the onset of the localization modes. Although only three prestretch values, \(\lambda^0 = 1.0, 1.3,\) and 2.0, were reported by Cao and Hutchinson, interestingly, they observed that the modest prestretch of 1.3 results in the largest \(\varepsilon_L\), implying an optimized prestretch is required for achieving the largest accessible wrinkle aspect ratio. Inspired by these studies, we investigate how this commonly used prestretch method can impact the accessible range of wrinkle aspect ratio.

Beyond localization transitions, surface failures can cause a complex strain field and affect the homogeneity of wrinkles. These surface failures are closely related to the strengths of the composite. Fracture occurs when stresses in the film exceed a critical value related to the toughness of the film \((\sigma_f)^{92-97,104}\) and delamination occurs when stresses in the interface exceed the interfacial strength \((\sigma_{int}))^{79,98-103}\). Although these failures have individually drawn lots of attention in the field of materials science, integrated discussions regarding the impact of these failures on wrinkle aspect ratio are still elusive.

4.3 Approach

In this project, we build upon recent theories and study transitions restricting the wrinkle aspect ratio to develop strategies for maximizing aspect ratio. Localization modes and surface failures are discussed separately: the localization modes are discussed following Cao and Hutchinson’s model, and the surface failures are analyzed regarding
material and interfacial strengths. This knowledge allows us to fabricate homogeneous, high aspect ratio wrinkled surfaces.

A schematic of the experimental process is shown in Figure 4.2. $\lambda_S$ represents the current stretch ratio of each step. The substrate is first prestretched with an amount of $\lambda^0$, and a thin film is floated onto the water. A dip-coating process is then used to laminate the film onto the substrate with sufficient adhesion between the two layers.

Figure 4.2 Schematic of the experimental process of prestretch. (a) The substrate is prestretched to $\lambda^0$ from $\lambda_S = 1$. (b) The film is laminated onto the prestretched substrate by the dip-coating method. (c) Small residual strain developed at dip-coating. (d) The end-to-end distance of the substrate is gradually decreased, resulting a compressive strain in the film. Used with permission: Adv. Mat. 2014.16
4.3.1 Analyzing the Previous Theoretical Calculation

Theoretical work by Cao and Hutchinson, predicts the $\varepsilon_c$ and $\varepsilon_L$ as a function of $\mu_f/\mu_s$. From Equation (1.12), we calculate the aspect ratios for the three values of prestretch, 1.0, 1.3, and 2.0 (Figure 4.3). Considering a plateau aspect ratio at $\mu_f/\mu_s \geq 60$ in Figure 4.3,

4.3.2 Quantifying Residual Strain from the Laminating Process

During the dip-coating process, a small residual strain ($\varepsilon_r$) can develop on the film. This residual strain is evident by the formation of wrinkles after coating, as discussed in the previous chapters. We use these wrinkles to quantify $\varepsilon_r$, which is equal to the summation of the critical wrinkling strain, and the strain stored in these shallow wrinkles.

$$
\varepsilon_r \approx \frac{1}{4} \left( \frac{3E_s}{E_f} \right)^{2/3} + \left( \frac{\pi A}{2\lambda} \right)^2
$$

(4.1)

Figure 4.3 Predicted maximum aspect ratios from Cao and Hutchinson’s simulation. Data analyzed using Equation (1.12). (a) Maximum aspect ratios for different modulus mismatches. (b) Maximum aspect ratios at the large $\mu_f/\mu_s$ end for three values of prestretch. Used with permission: Adv. Mat. 2014.16
where $\bar{E} = 2\mu/(1 - \nu)$; $\mu$ is the shear modulus; $\nu$ is Poisson’s ratio; the subscripts $f$ and $s$ correspond to film and substrate, respectively. Residual strain ($\varepsilon_r$) is typically less than 0.06 from observation (Figure 4.4).

![Image](image.png)

Figure 4.4 Optical profilometry of a polystyrene film laminated on PDMS substrate. ($\mu_s = 1\text{kPa}$). The profile is taken from the solid line. The residual strain is caused by the three phase contact line mechanics. $\varepsilon_r$ of this profile is 0.02 according to Equation (4.1). Used with permission: Adv. Mat. 2014.

### 4.3.3 Quantifying Compressive strain on the Film

The compression to the film is applied by decreasing the end-to-end distance of the substrate. Owing to the modulus mismatch between top film and substrate, the strain of substrate $(1 - \lambda_S/\lambda^0)$ does not unnecessarily to completely transfer into the top film. Thus, we experimentally quantify the "true strain" in the film, which accounts for the actual displacement at the edges of the film.

Particle tracking method is used to determine the true strain: After the film is laminated onto the substrate, few droplets of small polystyrene particles (diameter = 1 $\mu$m) in water suspension are sprayed onto the film and let dry. These particles act as markers that allow us to measure the true strain of the film under a microscope.
A factor $m$ is applied to convert the strain of substrates to the true strain. Therefore,

$$\text{true strain} = m\left(1 - \frac{\lambda_s}{\lambda^0}\right)$$ \hspace{1cm} (4.2)

For samples with large modulus mismatch ($\mu_f / \mu_s = 10^6$), $m$ is smaller than 1, showing the substrate strain is partially transferred to the film. For samples with smaller modulus mismatch, $m$ is very close to unity (Figure 4.6). Therefore, the strain of film ($\varepsilon$) is defined as

$$\varepsilon = \varepsilon_r + m\left(1 - \frac{\lambda_s}{\lambda^0}\right)$$ \hspace{1cm} (4.3)

![Figure 4.5](image1.png)

Figure 4.5 True strain as a function of $(1 - \lambda_s / \lambda^0)$ for three representative $\mu_f / \mu_s$ (a) When $\mu_f / \mu_s = 10^6$, $m = 0.7$ at $(1 - \lambda_s / \lambda^0) > 0.2$. (b) $\mu_f / \mu_s = 10^4$ (c) $\mu_f / \mu_s = 333$. Used with permission: Adv. Mat. 2014.\textsuperscript{16}
4.3.4 Growth of Wrinkle Aspect Ratio and Strain Localization

The average $A$ and average $\lambda$ across the surface are tracked as a function of $\varepsilon$. Figure 4.6 shows a representative plot of aspect ratio for a polystyrene (PS) thin film wrinkled on crosslinked polydimethylsiloxane (PDMS). $A/\lambda$ in the Figure 4.6 represents average aspect ratio across the surface, and the error bars represent standard deviations of amplitude normalized by average $\lambda$. As $\varepsilon$ increases, the aspect ratio is found to monotonically increase until a maximum value where localization modes or surface failures are observed optically. Figure 4.6 clearly shows that the maximum aspect ratio depends on the amount of prestretch and also suggests an aspect ratio larger than 0.35 can be achieved.

![Figure 4.6 Average aspect ratio under steps of strain.](image)

The error bars represent the standard deviation of amplitude values. Representative samples of a 150 nm polystyrene thin film ($\mu_f = 1.1$ GPa) on a thick PDMS substrate ($\mu_s = 1$ kPa). The points corresponding to a maximum aspect ratio and localization strain are marked with solid data point. The solid line represents Equation (4.5). The dashed line represents the conventional small strain model Equation (1.12). Used with permission: Adv. Mat. 2014.\textsuperscript{16}
Due to the high strains associated with the high aspect ratio wrinkles, conventional models assuming small strain and constant wavelength\textsuperscript{22,74} are insufficient to describe the growth of high aspect ratio wrinkles. Instead, we consider an accordion bellow mechanism which corrects the wavelength change at large strain,\textsuperscript{22,74}

\[
\lambda = 2\pi t \left( \frac{\bar{E}_f}{3E_s} \right)^{1/3} (1 - (\varepsilon - \varepsilon_c))
\]  
(4.4)

The aspect ratio can be written as

\[
\frac{A}{\lambda} = \frac{2}{\pi} \sqrt{(\varepsilon - \varepsilon_c)(1 - (\varepsilon - \varepsilon_c))^{-1}}
\]  
(4.5)

Equation (4.5) well describes the increase of aspect ratio up to $\varepsilon = 0.65$, while the conventional small strain model, indicated by the dashed line, is restrained to $\varepsilon < 0.25$. At the transition where localization modes or surface failures appear, the aspect ratio drops and the error bar significantly expands. Thus, the maximum aspect ratio ($A/\lambda_{max}$) of each prestretch corresponds to $\varepsilon_L$ for the given conditions. Histograms plotting the distribution of wrinkle amplitude as a function of applied strain serve as a supplementary method for determining this transition point. (Figure 4.7 and Figure 4.8)

On every step of strain, the amplitude distribution across the whole surface is plotted. While the wrinkling mode has only one narrow peak, localization modes often have either a broad peak or several peaks. Note that the width of peak directly relates to the magnitude of error in Figure 4.6. The strain where one narrow peak broadens or splits into several peaks is marked as the localization strain or surface failure strain.

The histograms are plotted with MATLAB\textsuperscript{TM} code. First, height data of a surface (640 x 480) obtained by the optical profilometer is imported and saved into 480 cross-sectioned height profiles. Next, the “Findpeaks” function is employed to determine
the peaks and valleys for each cross section. Then, the distances between peaks and valleys are saved as amplitudes. Finally, the distribution of amplitude is plotted by “hist“ and “bin“ functions.
Figure 4.7 Histogram analysis for localization strain. All the plots have the same scales as the very bottom left plot. All the data presented here correspond to $\mu_f/\mu_s = 10^6$. (a) The strain at which the wrinkling mode ends for $\lambda^0 = 1$ is $\varepsilon = 0.26$. (b) The strain at which the wrinkling mode ends for $\lambda^0 = 1.5$ is $\varepsilon = 0.44$. Used with permission: Adv. Mat. 2014.16
Figure 4.8 Histogram analysis for localization strain. All the plots have the same scales as the very bottom left plot. All the data presented here correspond to $\mu_y/\mu_c = 10^6$. (a) The strain at which the wrinkling mode ends for $\lambda^0 = 1.8$ is $\varepsilon = 0.40$. (b) The strain at which the wrinkling mode ends for $\lambda^0 = 2.1$ is $\varepsilon = 0.15$. (c) The strain at which the wrinkling mode ends for $\lambda^0 = 2.6$ is $\varepsilon = 0.05$. Used with permission: Adv. Mat. 2014.\textsuperscript{16}
4.4 Experimental

4.4.1 Film preparation and characterization

Glassy films were polystyrene (PS) films prepared with the same procedure described in Chapter 2. The elastic modulus $E_f = 3.5$ GPa was obtained from literature and the shear modulus $\mu_f = 1.1$ GPa was calculated assuming $\nu = 0.33$.\(^{53}\)

Elastomeric films were made of crosslinked PDMS, Dow Corning Sylgard™ 184 elastomer kit. The prepolymer:crosslinker mixing ratios of 5:1, 10:1 and 20:1 are used. The preparation procedure and characterization are described in Chapter 2.

4.4.2 Substrate preparation and characterization

The soft substrates were crosslinked polydimethylsiloxane (PDMS), made from Dow Corning Sylgard™ 184 elastomer kit. The prepolymer to crosslinker mixing ratio was controlled between 40:1 to 10:1 by weight to vary the substrate modulus. The mixtures were degassed in a moderate vacuum for 40 minutes, poured into polystyrene (PS) petri dishes, then cured in a 70 °C oven for 60 minutes. Cured samples were immediately used after cooling to room temperature (20 °C). Part of the cured PDMS was reserved for wrinkling experiments, while the other part of PDMS was punched into the dogbone shape (20×5 mm) for modulus measurement. The elastic modulus, $E_S$, for each sample was measured using tensile tests on an Instron™ 5564 with a 50 N load cell, with a stretching rate 100 mm/min. A stress-strain curve for each sample was fitted with the Neo-Hookean model, $\sigma = (E_S / 3)(\lambda_S - 1 / \lambda_S^2)$, where $\sigma$ is the stress and $\lambda_S$ is the stretch ratio. The full curve is used to fit to the Neo-Hookean model, except for the two highest modulus substrates, in which half of the curve is used to fit to the Neo-Hookean model. The shear modulus ($\mu_S$) was calculated by $\mu_S = E_S / 3$, assuming $\nu_S = 0.5$. 
The lightly crosslinked 40:1 PDMS (60 minute thermal curing) is more extensively characterized. Both the tensile and compressive tests are used to construct the full stress-strain curve (b). Since excess crosslinkers are remaining in the network, the PDMS crosslinking reaction continues slowly, showed by the stiffening after 50 days under room temperature (20 °C) (a).

Figure 4.9 Stress-strain data for the used substrates. The colors represent different substrates. The red solid line is fitted using the Neo-Hookean model, and the numbers are the fitted $E_S$. (a) Data for all the substrates. (b) Zoom in to show the softest three curves.
The shear rheology test is also performed for the 40:1 PDMS to characterize its viscoelasticity. A PDMS disk (diameter = 30 mm, thickness = 3 mm) is mounted between the parallel plate geometry on a rheometer (TA Instruments AR2000). The test was under the oscillatory mode. The strain sweep and the frequency sweep are performed (Figure 4.11). In this thesis, the experiments are performed within the low strain rate region, where $G'/G'' > 10$. Only elastic properties are considered for the wrinkling throughout this thesis because no significant viscous properties are observed.

Figure 4.10 Stress-strain response of PDMS. (a) The red data points represent PDMS with mixing ratio of 20:1 and the black data points represent PDMS with mixing ratio of 40:1. The tensile test and the compression test are performed separately. The dogbone shaped samples are used for the tensile tests while cylindrical samples are used for the compression tests. The tensile tests are under 0.08 s$^{-1}$ and the compression tests are under 0.001 s$^{-1}$. The stress is normalized by the initial slope for each sample. The initial slope for the tensile tests is 63kPa for 20:1 and 4kPa for 40:1. The initial slope for the compression tests is 177kPa for 20:1 and 10kPa for 40:1. (b) The 40:1 PDMS stiffens over 50 days.
An extraction process is performed to estimate the gel fraction of the 40:1 PDMS. The 40:1 PDMS is weighed right after crosslinked for 1 hour, and then is swollen in toluene to dissolve uncrosslinked chains. In the first toluene bath, 300ppm 1-dodecanethiol is added to deactivate the crosslinking catalyst. The 40:1 PDMS is kept immersed in toluene for 72 hours and the toluene is changed for at least 9 times through this process. After 72 hours, the PDMS is washed with methanol and then dried in gentle vacuum for 24 hours to remove solvents. After the extraction, the elastic modulus
decreases (a), and the sample stops stiffening over time (b). The weight ratio of the extracted PDMS to the fresh PDMS is the gel fraction. The gel fraction of the sample is 55%~65%.

Figure 4.12 Stress-strain curve for the extracted PDMS. (a) The modulus of the PDMS decreases after being extracted. (b) The extracted PDMS does not stiffen after 50 days.

### 4.4.3 Wrinkle process and characterization

The soft substrate was cut into long slabs (70×20×3 mm) and prestretched with a custom-built strain stage with a motorized/manual linear moving stage. A prestretch was performed at a strain rate of approximately 0.15 s⁻¹. The top film (PS or PDMS film) was cut into squares (10×10 mm²), and floated onto a water bath. PS films separated from the silicon wafer instantaneously. PDMS films were separated from the glass slide by dissolving the PAA layer. After the film was attached onto the substrate, the prestretched substrate and the film were dipped into the water bath at 45° in relation to the water surface at a velocity of 2 mm s⁻¹. After the whole film was laminated onto the substrate, the strain stage and the substrate were taken out from the water bath and dried. The initial surface of
the film was scanned with the optical profilometer to quantify the residual strain. The prestretch was released to apply \( \varepsilon = 0.05 \) on the film with a strain rate of approximately 0.15 s\(^{-1}\). Approximately 30 seconds was allowed for equilibrating and for measurement. The surface was scanned every \( \varepsilon = 0.05 \) with the optical profilometer until the localization was observed optically. In case that the surface did not localize before the complete release of prestretch, the substrate was trimmed to 25 mm long and carefully attached on a thick PDMS slab (30×25×7 mm\(^3\)) to perform further compression. The compression was performed at the same rate and step.

Residual strain along the stretch direction from the laminating process was calculated based on the surface wrinkling and the theoretical critical wrinkling strain. For each strain, the amplitude was taken as the mean peak-to-valley distances from a cross-section of the scanned area consisting of 20-40 wrinkles, and the wavelength was taken as the mean peak-to-peak distances from these wrinkles. The error bars of aspect ratio values were determined by dividing the standard deviation of amplitude values by the mean wavelength.

Since the optical profilometer detected only the peaks and valleys for large aspect ratios features, the full surface profiles shown in figures were fitted using spline interpolation. The optical images were taken by the Zeiss AxioTech Vario optical microscope with 2.5x, 5x, and 10x optics, equipped with Pixel Link CCD camera.
4.5 Results and Discussion

4.5.1 High Aspect Ratio Wrinkles with Substrate Prestretch

The localization transition is quantified with the maximum aspect ratio \((A/\lambda)_{\text{max}}\) and the critical strain \(\varepsilon_L\), respectively, and is plotted as a function of prestretch \(\lambda^0\). Experimental studies performed with PS films and PDMS substrates (\(\mu_f = 1.1\) GPa and \(\mu_s = 1\) kPa, respectively) indicate \(\varepsilon_L\), \((A/\lambda)_{\text{max}}\) and the structure of localization modes are strongly influenced by the substrate prestretch (Figure 4.13). In the range of moderate prestretch, \(1 < \lambda^0 < 1.8\), the folding mode dominates the localization mode. These folds sharply dip into the substrate (Figure 4.14a), suggesting a large into-surface traction. In this range, the transition to folding is delayed and \((A/\lambda)_{\text{max}}\) is linearly increased by increasing \(\lambda^0\). Beyond this range of prestretch (\(\lambda^0 > 1.8\)), another localization mode, ridging, emerges. The ridges protruding out of surface suggest the out-of-surface traction force surpasses the into-surface traction force at this strain and prestretch condition (Figure 4.14b). Different
from the folds, $\varepsilon_L$ of these ridges is very close to $\varepsilon_c$ and cannot be delayed by $\lambda^0$, resulting in considerably suppressed $(A/\lambda)_{\text{max}}$. From Figure 4.13b, we find the optimized prestretch being the largest value before ridge emerges, $\lambda^0 = 1.8$. With this optimized prestretch, we are able to achieve the aspect ratio as large as 0.65.

Figure 4.14 Optical microscopy images of the folds and ridges. The thicker features are the localizations, while the finer features are wrinkles. The inset shows the height profile of a fold or ridge, measured with optical profilometry. (a) Folds of the PS film. (b) Ridges of the PS film. (c) Folds of the PDMS film. (d) Ridges of the PDMS film. Used with permission: Adv. Mat. 2014.
Theoretical calculation by Cao and Hutchinson is plotted along our results, and shows agreement with our experimental results. In addition, our substrate shows similar nonlinearity used in the calculation, suggesting the model they proposed applies to our system as our substrates exhibit similar non-linear stress-strain response (Figure 4.10a).

4.5.2 Localization Modes with Various Film Moduli

When $\mu_f/\mu_s$ remains in the plateau region, the onset and the structure of localization modes are found to be insensitive to the films (Figure 4.13 and Figure 4.14). Quantitatively identical localization events are observed on the same substrate $\mu_s = 1$ kPa with different films, including glassy films ($t = 150$ nm, $\mu_f = 1.1$ GPa), elastomeric films ($t = 3$ μm, $\mu_f \approx 0.3$ MPa), and soft elastomeric films ($t = 3$ μm, $\mu_f \approx 0.07$ MPa). This result confirms that the localization events depend on the interaction of film and substrate rather than the film itself.

4.5.3 Surface Failure Modes and Substrate Modulus

Although $\mu_f/\mu_s$ does not influence the localization transition in the region we studied, interestingly, we find $\mu_s$ to be a critical control parameter for the fabrication of high aspect ratio wrinkles. Rather than localization modes, $\mu_s$ controls the surface failures such as film fractures (crazing (Figure 4.15a) or cracking (Figure 4.15b)) and delamination (Figure 4.15c). These failures affect the homogeneity of the strain field and therefore wrinkles. Thus, fabricating high aspect ratio wrinkles not only requires appropriate prestretch but also requires appropriate material properties to avoid surface failures.
Figure 4.15 Surface failure modes.  (a) Optical microscopy image of crazing of a 150 nm PS film ($\mu_f = 1.1$ GPa) laminated on a PDMS substrate ($\mu_s = 20$ kPa). The horizontal features are crazes. (b) Optical microscopy image of the cracking surface of a 150 nm PS film laminated on a PDMS substrate ($\mu_s = 20$ kPa). The cracking occurs at a higher strain than the crazing. The large stripe on the top right is a crack. (c) Optical microscopy image of the delaminated 150 nm PS film from the PDMS surface ($\mu_s = 100$ kPa). The inset shows a magnified image of the delamination structure. (d) Maximum aspect ratio under a different amount of prestretch for various substrate moduli, and a polystyrene film modulus, $\mu_f = 1.1$ GPa. Different failure modes are observed on different substrate moduli. Used with permission: Adv. Mat. 2014.16
Fracture occurs when a resultant Poisson’s stress exceeds the critical stress of fracture for the film. While the end-to-end distance of the substrate is reduced and the compressive strain is applied to the film, Poisson’s effect expands the substrate in the orthogonal direction. Due to the modulus difference of the two layers, we propose that a slight global curvature is induced to the surface and a tensile stress is imposed to the film. When the tensile stress exceeds the critical stress of the film (σ_f), crazing followed by the cracking occurs. The tensile stress in the film is described by the Stoney’s equation. The global curvature (K) from a strain mismatch between the bilayer (ε_fS) is given as\(^{106,107}\)

\[
K \approx \frac{6(ε_fS)}{h_s} \left( \frac{tE_f}{h_sE_s} \right) \left[ \frac{1 + \frac{t}{h_s}}{1 + \frac{tE_f}{E_s} + \frac{4t}{h_s} + \frac{4t^2}{h_s^2} + \frac{(\frac{4t}{h_s})^2}{E_s^2}} \right] \tag{4.6}
\]

where \(h_s\) is the thickness of the substrate and \(E\) is the elastic modulus. Assuming \(t / h_s\) to be very small, Equation (4.6) can be simplified to

\[
K \approx \frac{6(ε_fS)}{h_s} \left( \frac{tE_f}{4tE_f + h_sE_s} \right) \tag{4.7}
\]

When \(t << h_s\), the average stress in the film is accordingly\(^{108,109}\)

\[
\bar{σ} \approx \frac{K}{6} \frac{E_s}{(1 - ν_s)} \frac{h_s^2}{t} \tag{4.8}
\]

Substituting Equation (4.7) into Equation (4.8), we find

\[
\bar{σ} \approx \frac{E_f(ε_fS)}{1 + 4tE_f} \frac{1}{h_sE_s} \frac{1}{(1 - ν_s)} \tag{4.9}
\]

Assuming the film fractures when \(\bar{σ}\) equals \(σ_f\), and the strain mismatch (ε_fS) equals the Poisson’s strain, \(ε_fS = ν_sε_{fracture}\)

\[
ν_sε_{fracture} \approx \frac{σ_f}{E_f} \left( 1 + \frac{4tE_f}{h_sE_s} \right) \tag{4.10}
\]

where \(ε_{fracture}\) is the critical strain required for film fracture. Substitute \(ε_{fracture}\) and the critical wrinkling strain into Equation (4.5), the aspect ratio when the film fractures is
where

\[ S = \varepsilon - \varepsilon_c = \frac{\sigma_f (1-u_s)}{2 \mu_f v_s (1+u_f) (1+v_f) \mu_f h_s \mu_s} \left( 1 + \frac{(1+u_f) 4 t \mu_f}{(1+u_s) h_s \mu_s} \right) - \frac{1}{4} \left( \frac{3 \mu_s (1-u_f)}{\mu_f (1-u_s)} \right)^{2/3} \]  (4.12)

When \( \mu_s << \mu_f \) and \( \mu_s h_s << \mu_f t \), \( S \sim \mu_s^{-1} \) and \( (A/\lambda)_{max} \) for film fracture scales as \( \mu_s^{-1/2} \).
The main difference arises when the evolution of surface features is observed. While ridges always emerge ridge by ridge, delaminations nucleate from an impurity (dust between the film and the substrate) then elongate. The other quantitative difference is associated with the distribution of amplitude. Utilizing the histogram analysis, we find

Figure 4.17 Differentiating the ridge and the delamination. (a) Optical microscopy image of ridges. The dark vertical features are ridges. Ridges usually instantaneously form across the surface. (b) Optical microscopy image of delamination. The delaminations nucleate from impurities and then propagate. The dark vertical features are delaminations. (c) Amplitude histogram for the ridging mode. Two peaks from small amplitude to large amplitude represent the shallow wrinkles and the ridges. (d) Amplitude histogram for the delamination mode. Three peaks from small amplitude to large amplitude represent the wrinkles next to the delaminations, the wrinkles far from the delaminations, and the delaminations. Used with permission: Adv. Mat. 2014.16
that a ridging surface consists of two peaks of amplitude (Figure 4.17ac) while a
delamination surface consists of three (Figure 4.17bd). These differences provide solid
evidence for differentiating the two structures.

Previous research has derived the critical delamination strain ($\varepsilon_d$) at which the
interfacial normal traction force in a wrinkled system exceeds the interfacial strength
($\sigma_{int}$).\cite{101, 110, 111}

$$\varepsilon_d \approx \varepsilon_c + \left( \frac{3-4\mu_s}{4(1-\nu_s)^2} \frac{\sigma_{int}}{\bar{E}_s} \right)^2 \quad (4.13)$$

Substituting $\varepsilon_d$ into Equation (4.5) and assuming small strains, the aspect ratio when
delamination occurs is

$$(A/\lambda)_{max} \approx \frac{(3-4\mu_s)\sigma_{int}}{4(1-\nu_s)\pi} \mu_s^{-1} \quad (4.14)$$

Equation (4.14) indicates that $(A/\lambda)_{max}$ before delamination appears is proportional to $\mu_s^{-1}$
with the fitting parameter being the interfacial strength ($\sigma_{int}$).

In our experiments with PS films, fracture and delamination are observed to
suppress $(A/\lambda)_{max}$ (Figure 4.15d). With a selected prestretch $\lambda^0 = 1.6$, Figure 4.18 shows an
example of $(A/\lambda)_{max}$ and the corresponding modes as a function of $\mu_s$ for PS films. The
$(A/\lambda)_{max}$ of the folding mode depends only on $\lambda^0$ and behaves insensitively to $\mu_s$ within this
material region. With reasonable fitting values $\sigma_f = 20 \text{ MPa}$\cite{53, 96, 112} and $\sigma_{int} = 0.07 \text{ MPa}$,
$(A/\lambda)_{max}$ at film fracture as well as $(A/\lambda)_{max}$ at delamination are well described by Equation
(4.11) and (4.14), respectively. Figure 4.18 provides a prediction of surface failures as a
function of the simple material property, $\mu_s$, when fabricating high aspect ratio wrinkle
surfaces. Collectively, with an appropriate prestretch of 1.8 and low substrate modulus
($\mu_s = 1 \text{ kPa}$), we successfully create homogeneous, non-fractured, and high aspect ratio
wrinkled surfaces.
In summary, we demonstrate the ability to create high aspect ratio wrinkles across a large surface using optimized substrate prestretch conditions and substrate modulus, effectively delaying strain localization transitions and avoiding surface failures. (Figure 4.19) We find that the prestretch can enhance the maximum aspect ratio and delay the localization transition strain until the ridging mode emerges at a prestretch of 2.0. We also find low modulus substrates are able to maintain the wrinkled films free from crazing, cracking and delamination. Our results with $\lambda^0 \approx 1.8$ and $\mu_s = 1$ kPa provide wrinkles with
an aspect ratio 0.65, twice as high as previously reported values. With large surface roughness, large local curvature at the peak and the valley, and large strain energy stored, high aspect ratio wrinkles have potential to impact many fields such as adhesion, optics, and flexible electronics.

Figure 4.19 Pictures of high aspect ratio wrinkles. (a) Macro scale picture of the high aspect ratio wrinkle sample. This sample is made with an elastomeric film ($\mu_f = 0.33$ MPa) and a soft substrate ($\mu_s = 1$ kPa). (b) Height profile of the sample shown in (a). (c) Optical microscopy image of the sample shown in (a). (d) Cross-section of a sample with the wrinkle aspect ratio of 0.65. To slice and image the cross-section without damaging the wrinkles, this particular sample is stiffened by a further curing. The aspect ratio has been confirmed to be 0.65 with the optical profilometry. Used with permission: Adv. Mat. 2014.16
4.7 Acknowledgement

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CHAPTER 5
TO ACHIEVE HIGH ASPECT RATIO FEATURES BY MODIFYING THE
MATERIAL NETWORK

5.1 Introduction

Although we have improved the wrinkle aspect ratio to 0.6 with the prestretch
method in Chapter 4,\textsuperscript{16} it is still insufficient to achieve the extremely high aspect ratio
structures (>1) created by living creatures, for example, gut villi\textsuperscript{3} and structures on flower
petal cells (Figure 1.1).\textsuperscript{5} These high aspect ratio structures provide excellent surface area
enhancement, hydrodynamic properties, and photonic properties to the creatures. The
mechanics for forming these structures while avoiding localizations remain undiscovered.
Inspired by the living creatures, we hypothesize growth involves reduction of the stress
accumulated in the structures. In other words, large undulations in living systems can be
stabilized by reconfiguring the primary mechanical network of a system with the current
shape configuration. This process reduces the strain energy in the system as shapes,
typically associated with large deformations, are achieved.

We explore this idea with synthetic silicone materials. The stress is independently
changed while the aspect ratio remain fixed. We first fabricate wrinkled surfaces with
negligible stress energy by molding the substrate from wrinkling surfaces, and study the
localizations on these wrinkles. Then we consider localizations on the substrate with a
secondary crosslinking network. By this approach, we not only achieve wrinkle aspect
ratio as high as 0.9, but also derive a model for how stress reduction influences the
localization. Finally, using a special chemical stress relaxation reaction,\textsuperscript{113,114} we
demonstrate stress reduction is promising for making high aspect ratio wrinkles. This
project provides a new perspective to understand wrinkles in both biological and synthetic systems.

5.2 Background

As discussed in Chapter 4, the localization transition is mainly due to the non-linearity when the substrate is at large strains. Therefore, we reduce the stress in the substrate to delay the localization from occurring.

Equation (1.6) gives the strain energy of wrinkling in the substrate.

\[ U_S = \frac{\bar{E}_S}{8} \kappa \frac{A^2}{4} \]  

Rewrite \( U_S \) as a function of the wavelength and amplitude, we find \( U_S \) strongly depends on \((A/\lambda)\).

\[ U_S \sim E_S \lambda \left(\frac{A}{\lambda}\right)^2 \]  

We will use this relationship to quantify the amount of stress in a given aspect ratio.

In a crosslinked polymer network, the macroscopic stress-strain response is related to the microscopic polymer chain conformation. These polymer chains are fixed at chemical or physical junction points and the extension of the chains causes strain energy.\(^{115,116}\) The configuration of the crosslinking points and the conformation of the polymer chains determine the stress state in the material.

5.3 Approach

Using crosslinked polydimethylsiloxane (PDMS) based elastomers as the wrinkle substrate, we demonstrate an approach that alters the strain energy of a wrinkled surface, to achieve high aspect ratio features, by redefining the primary network of a material in
the shape of a current deformation. First, we mold the substrate from wrinkled surfaces and deposit thin films onto these substrates. The molded wrinkles have wrinkled topography but have minimal stress. We demonstrate the localization occurs at higher aspect ratio with the molded wrinkles than with the conventional wrinkles. Then we use this knowledge to develop a processing technique that forms a secondary network in a instability-induced wrinkling substrate. We also utilize the living silicone that has been proven to undergo chemical stress relaxation to reducing strain energy in wrinkles.\textsuperscript{113} The living silicone allows us to eliminate the strain energy multiple times, and more closely mimic the growth of wrinkles in the biological systems.

5.3.1 Wrinkling on Molded Wavy Substrates

To prepare stress-free wrinkles, we mold the substrate from conventional wrinkling surfaces, and deposit a stiff polymer film of poly(allylamine hydrochloride) and poly(styrene sulfonate) onto the wavy substrate using the layer-by-layer deposition (LbL).\textsuperscript{117,118} The deposition method yields thin films with well-defined thickness and conformity without bending (Figure 5.2). The thickness of the polymer film ($t$) is determined using the molded substrate wavelength and Equation (1.9). The process of molding and deposition allows us to create wrinkles with negligible stresses, and to study the localization transition.
Comparing the film/substrate bilayer with the bare wavy substrate without the film, we find the bare substrate localizes to creasing at a small strain (~10%) (Figure 5.2ab) as oppose to 30% for flat substrates. This suggests the strain is more significantly localized at the wrinkle valleys. We demonstrate the strain localization by depositing a film with a thickness $t/3$. On these films, small wrinkles with a wavelength around 1/3 to the molded wavelength appear only at the valleys of the primary wrinkles (Figure 5.2cd).

By mechanically compressing the films with thickness $t$, we find the localization transition occurs at higher aspect ratio than that of the regular flat substrates (Figure 5.3), and at larger strain than the bare substrates, showing the film distributes the strain to the valleys and peaks and stabilizes the wrinkle profile. Interestingly, the aspect ratio is able to grow even when the substrate is molded at a value larger than the localization point of a initially flat surface, suggesting the localization transition is influenced by the absence of stress in the molded crosslinking networks.

Figure 5.1 SEM image of the LbL film on a wavy substrate. The film is composed of 100 layers. The wide vertical stripes are cracks intentionally induced to show the film thickness.
Figure 5.2 Wrinkling on molded bare substrates and $t/3$ films.  
(a) Aspect ratio of a bare wavy substrate. Creasing occurs at relatively small strain (~10%). (b) Optical profilometry of the creasing on a bare substrate. The height scale bar scales from $-31 \mu$m to 15 $\mu$m. (c) Optical microscopy image of wrinkling at the valleys of a $t/3$ film. (The peaks are out of focus.) (d) No wrinkle is observed on the peaks of a $t/3$ film. (The valleys are out of focus.)
In this experiment, an one-time network stress modification is performed to the substrate. Wrinkles are created with a stiff silicone thin film bounded on an undercured flat silicone substrate. The undercured substrate contains unreacted crosslink agent for subsequent rearrangement of the crosslinking network. The stiff silicone thin film is attached onto the undercured substrate with the substrate being prestretched (Figure 5.4a). When the prestretch is being released, wrinkling instability occurs and the wrinkle aspect ratio grows as the applied strain increases (Figure 5.4b). In Figure 5.4b, localization is observed as the wrinkle aspect ratio reaches the maximum value of 0.55, consistent with published results (Process A in Figure 5.4a). To study the role of the internal stress in the substrate network acting on the localization event, samples at the wrinkling state are thermally post-cured (Process B in Figure 5.4a). During this post-curing process, a secondary crosslinking network forms at the presence of wrinkles, having the shape of

Figure 5.3 Aspect ratio growth on film thickness $t$ on various molded aspect ratios. The surfaces are molded into wavy shapes with aspect ratios of 0, 0.06, 0.27 and 0.45. The localization transition occurs at the largest aspect ratio observed, 0.25, 0.3, 0.4 and 0.6, respectively.

5.3.2 Post-curing the Silicone Network

In this experiment, an one-time network stress modification is performed to the substrate. Wrinkles are created with a stiff silicone thin film bounded on an undercured flat silicone substrate. The undercured substrate contains unreacted crosslink agent for subsequent rearrangement of the crosslinking network. The stiff silicone thin film is attached onto the undercured substrate with the substrate being prestretched (Figure 5.4a). When the prestretch is being released, wrinkling instability occurs and the wrinkle aspect ratio grows as the applied strain increases (Figure 5.4b). In Figure 5.4b, localization is observed as the wrinkle aspect ratio reaches the maximum value of 0.55, consistent with published results (Process A in Figure 5.4a). To study the role of the internal stress in the substrate network acting on the localization event, samples at the wrinkling state are thermally post-cured (Process B in Figure 5.4a). During this post-curing process, a secondary crosslinking network forms at the presence of wrinkles, having the shape of

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wrinkles but with minimal stress. This secondary crosslinking network stabilizes the wrinkles and suppresses the localizations since an aspect ratio as large as 0.9 is observed with the post-cured wrinkles (Figure 5.4bc). A into-the-plane localization mode is observed after the aspect ratio achieve 0.9 (Figure 5.4d).

Figure 5.4 Wrinkling with a further curing of substrate. (a) Experimental process of the curing experiment. Process A is identical to the prestretch experiment discussed in Chapter 4. Process B introduces a post-curing step to form the secondary network. (b) The aspect ratio as a function of applied strain. The error bars represent the standard deviation for the wrinkles across the whole surface. This set of results is performed with a prestretch of 1.6. The filled data points represent Process A, and the localization transition happens when the aspect ratio reaches the maximum value 0.6. The open data points represent Process B, and the post-curing is applied at the aspect ratio of 0.55. The localization transition happens when the aspect ratio reaches the maximum value of 0.9. (c) Optical profilometry of the wrinkles with the aspect ratio of 0.9. The figure is drawn to scale. (d) Optical microscopy of the localization mode observed after the aspect ratio reaches 0.9.
5.3.3 Chemical Stress Relaxation in the Wrinkle Substrate

In this approach, we utilize the living silicone to demonstrate the importance of the internal stress in the substrate. The living silicone contains active catalysts for breaking and reforming chemical crosslinking bonds, allowing multiple-time network modifications.\textsuperscript{113,114} Macroscopically, the material relaxes stress while maintaining the strain, demonstrated by the permanent deformation of a bulk sample (Figure 5.5a). We laminate a thin film of regular silicone on the top of the living silicone, and relax the stress at 110°C after the film is wrinkled by a global strain. We test the ability of stress relaxation by re-stretching the substrate. Instead of relieving the primary wrinkles, the sample forms orthogonal wrinkles by the Poisson’s strain while the primary wrinkles remain, creating the checkerboard pattern. The checkerboard pattern indicates the substrate has relaxed the stress and has been permanently shaped by the primary wrinkles (Figure 5.5bd).\textsuperscript{64}

After confirming the ability of stress relaxation, the aspect ratio is increased by performing substrate relaxation between each global compressive strain step of 0.1. Taking advantage of the ability of chemical relaxation, the substrate maintains minimal internal stress when the wrinkle aspect ratio increases, and the wrinkle aspect ratio is able to reach 0.7 with no prestretch (Figure 5.5c), significantly higher than the reported wrinkle aspect ratio limited at 0.3. Further increasing is hindered by the material stability under high temperature and the straining method for high strains (up to 0.6). To more closely represent the continuous stress reducing by the living systems, the top film can be replaced by living silicones and the straining/relaxation process can be improved to a continuous fashion in the future. The strategy using the living silicone
indicates the relaxation of internal stress delays the localization to higher aspect ratio, and is promising for explaining the high aspect ratio structures on living creatures.

Figure 5.5 The aspect ratio growth for the living silicone. (a) Macroscopic picture of the bulk living silicone. The living silicone was made into a cylinder (left). The cylinder was then deformed and stress-relaxed (right). Both of the silicone are under no stress. (b) Wrinkles made by a vertical strain. (c) The network rearranges at the strains of 0.2, 0.3, 0.4 and 0.5. The two data points at these strains represent the aspect ratios before and after the network rearranges. (d) Checkerboard wrinkles by stretching (b) in vertical direction after stress relaxation. The inset is the optical profilometry. The amplitude is about 6 μm.
5.4 Experimental

5.4.1 Post-curing experiment

The top film is made of polydimethylsiloxane (PDMS), Dow Corning Sylgard™ 184 elastomer kit. The prepolymer and the crosslinker are mixed in the weight ratio of 5:1. The preparation procedure and characterization are described in Chapter 2.

The soft substrates are polydimethylsiloxane (PDMS) made from Dow Corning Sylgard™ 184 elastomer kit. The prepolymer and the crosslinker are mixed in the weight ratio of 40:1. The mixture is degassed in a moderate vacuum for 40 minutes, then molded into a 100 × 25 × 3 mm slab in a 70°C oven for 40 minutes. This undercured substrate is immediately used after cooled down to room temperature (20°C). The elastic moduli of the undercured PDMS is obtained with the tensile test in the dogbone shape. The elastic modulus is 40 ± 10kPa.

The undercured soft substrate is prestretched to 1.6 times of its original length with a custom-built strain stage equipped with a micrometer. The prestretch is performed manually at a strain rate of approximately 0.14 s⁻¹. The top film is cut into square (15×15 mm), and floated onto water surface. After a part of the substrate is immersed into the water, the film is attached onto the substrate, then the substrate and the strain stage and the film are immersed into the water bath in 45° at a velocity of 1 mm/s. After the whole film is laminated onto the substrate, the strain stage and the substrate are taken out from the water bath. The initial surface of the film is scanned with the optical profilometer to quantify the residue strain. The prestretch is then released manually with a strain rate of approximately 0.14 s⁻¹. Approximately 30 seconds is allowed for the surface to equilibrate. The surface is scanned with the optical profilometer to obtain the wrinkle amplitude and wavelength.
In Process A (with no post-curing), after the prestretch is fully released, the sample is trimmed to 25 mm long and carefully attached onto a thick PDMS slab (25×20×7 mm) to perform further compression.

In Process B (with post-curing), after the prestretch is fully released, the sample is trimmed to 25 mm long and carefully attached onto a thick PDMS slab (25×20×7 mm) with a thin layer of 20:1 PDMS as adhesive. Then the sample is post-cured in 70°C for 10 hours before further compression.

5.4.2 Molding experiment

Wrinkled surfaces are made following the process of post-curing experiment. Two mixing ratios, 30:1 and 40:1, are used. Different wrinkle aspect ratios are made with different amount of prestretch. These surfaces are duplicated by the UV-curable polymer Norland Optical Adhesive 60 (NOA 60). The NOA 60 samples are vapor-coated by a thin layer of parylene (~100nm). The prepolymer/crosslinker mixture of Sylgard™ 184 with the mixing ratio of 40:1 is cured on the top of the NOA 60/parylene duplicates, giving the wrinkle-shape wavy substrates.

These wavy substrates are then coated with polymer multi-layers by the layer-by-layer deposition. The PDMS substrate is dipped back-and-forth into the poly(allylamine hydrochloride) (PAH) solution and the poly(styrene sulfonate) (PSS) solution by a customized automatic instrument. The wavy substrate is first dipped into the PAH solution and a gentle vacuum is applied to ensure good contact between the PDMS and the solution. After the vacuum, the substrate is immersed in the PAH solution for 3 minutes, rinse in DI water for 1 minute for three times, immersed in the PSS solution for 3 minutes, then rinse in DI water for 1 minute for three times again. This process yields two
mono-layers of the two polymer, and is repeated for 80 to 120 times to deposit the desired thickness.

PAH solution: poly(allylamine) ($M_w \sim 65,000, 10\text{wt}\%$ in water purchased from Sigma-Aldrich) is diluted to 0.01M in DI water. The poly(allylamine) solution is adjusted to pH ~ 3 with 0.1N hydrochloride to yield the PAH solution. PSS solution: Polystyrene sulfonate, sodium salt ($M_w \sim 70,000$ purchased from Scientific Polymer Products, Inc.) is dissolved to 0.01M in DI water. The solution is adjusted to pH~3 with 0.1N hydrochloride.

5.4.3 Living silicone experiment

The top film is made from Momentive LSR7070. The A and B parts are mixed with hexane in the ratio of 1:1:6. The same fabrication process to the Sylgard™ 184 thin film is followed to yield the Momentive LSR 7070 thin film with a thickness of ~8 ± 0.6 μm.

Octamethylcyclotetrasiloxane (D4) and 2.5 wt% benzoyl peroxide (BPO) were heated together with stirring at 120 °C for 2 hours. The resulting yellow solution was passed through alumina to remove BPO-derived byproducts and yield a clear mixture of D4 and 2.4 wt% bis(heptamethylcyclotetrasiloxanyl)-ethane (bis-D4). The anionic polymerization initiator, bis(tetramethylammonium)oligodimethylsiloxanediolate (0.1 wt%), was added to (dissolved in) this monomer/cross-linking agent, and the solution was poured into the cylindrical mold and heated at 90 °C for 12 hours.

The living silicone substrate and the Momentive thin film are attached to each other and heated in 70°C to chemically bonded to each other. A strain of 0.1 is applied every steps. Between each straining, the wrinkle amplitude and wavelength are measured by the optical profilometer, then the sample is heated in 100°C for 10 hours to relax the stress.
Residue strain along the stretch direction from the laminating process is calculated based on the critical wrinkling strain and the residue wrinkling. For each profilometry, the amplitude is taken as the mean of peak-to-valley distances from a cross section of the scanned area consisted of 20-40 wrinkles, and the wavelength is taken as the mean of peak-to-peak distances from these wrinkles. The standard deviations of the amplitudes of these wrinkles are divided by the mean wavelength then used as the error bars of aspect ratios.

Since the optical profilometer can only detect the peaks and valleys for features with large aspect ratios, some surface profiles are interpolated by the MetroPro software. The optical image is taken by the Zeiss AxioTech Vario, Pixel Link CCD camera optical microscope.

5.5 Results and Discussion

5.5.1 Scaling of Strain Energy in Wrinkling Substrate

The experimental results show the wrinkles are stabilized by substrate stress modification. We estimate the elastic energy in the substrate to analyze these results since it has been proposed to dominate the localization transition. When the surface is wrinkled, the elastic energy of the substrate scales as \( U_S \sim E_s \lambda \left( \frac{A_f}{\lambda_f} \right)^2 \) \(^{(5.1)}\)

and the elastic energy of the substrate required for localization transition can be written as

\[ U_F^0 \sim E_s \lambda_F^0 \left( \frac{A_F^0}{\lambda_F^0} \right)^2 \] \(^{(5.2)}\)

where \( A_F^0 \) and \( \lambda_F^0 \) are the wrinkle amplitude and wavelength, respectively, when the localization takes place without any post-curing or chemical relaxation. Although more
sophisticated localization transition mechanism has been developed, here, we use a simplified localization transition criteria, $U = U_F^0$. In Chapter 4, we have discussed the onset of localization is insensitive to the modulus mismatch, $E_f/E_S$, when $E_f/E_S > 60$. Thus, we assume $(A_F^0/\lambda_F^0)$ remains constant for all the material systems we use, and only depend on the amount of prestretch.

For the post-curing experiment, the substrate starts from the elastic modulus $E_1$. When the wrinkles with amplitude and wavelength $A_m$ and $\lambda_m$ are formed, the post-curing is performed and a secondary crosslinking network with the elastic modulus $E_2$ is created (Figure 5.6a). As a result, the elastic modulus of the whole sample, $E_c$, is modeled by the Voigt’s model, where $E_c = \phi E_1 + (1-\phi) E_2$, with $\phi$ being the volume fraction of the $E_1$ network.

Therefore, when the localization transition occurs on the post-cured wrinkles, the elastic energy is written as

$$E_c \lambda_F \left(\frac{A_F}{\lambda_F}\right)^2 - E_2 \lambda_m \left(\frac{A_m}{\lambda_m}\right)^2 = E_c \lambda_F^0 \left(\frac{A_F^0}{\lambda_F^0}\right)^2$$

(5.3)

Where $A_F$ and $\lambda_F$ is the amplitude and wavelength, respectively, when the localization transition occurs on the post-cured sample. The right-hand side of the equation is the energy required for the corresponding modulus. The left-hand side of the equation summarizes the energy in the wrinkles, and indicates the idea that the absence of the secondary network before post-curing reduces the total energy in the wrinkles, ultimately influences the localization transition. Rearrange Equation (5.3),

$$\frac{\lambda_F}{\lambda_m} \left(\frac{A_F}{\lambda_F}\right)^2 = \frac{E_2}{E_c} \left(\frac{A_m}{\lambda_m}\right)^2 + \frac{\lambda_F^0}{\lambda_m} \left(\frac{A_F^0}{\lambda_F^0}\right)^2$$

(5.4)

Figure 5.6b shows the influence of the amount of energy reduction on the localization transition. This plot shows our experimental data for both the post-curing experiments and
molding experiments agree with Equation (5.4). The intercept of the y-axis indicates the localization transition for surfaces starting from flat, and depends on the amount of substrate prestretch. The slope represents the ratio of $E_2$ and $E_c$, predicted to be larger or equal to unity by the Voigt’s model for the post-curing experiments and the molding experiments, respectively.

Figure 5.6 Model for the aspect ratio of substrate stress reduction. (a) Schematic of the proposed mechanism. The secondary network is shaped at an amplitude and wavelength of $A_m$ and $\lambda_m$, then the whole sample is localized at $A_F$ and $\lambda_F$. (b) Plot for the final localization aspect ratio and the molded aspect ratio. The open data points represent the post-curing experiments. The filled data points represent the molding experiments.
5.5.2 High Aspect Ratio Feature and Localization Mode

As shown in Figure 5.4, the aspect ratio as high as 0.9 is observed with the post-curing process. By forming a secondary network at an aspect ratio of 0.6, the aspect ratio is able to grow to 0.9. Further compressing the high aspect ratio wrinkles results in collapse of two wrinkle ridges, causing the doubling in period. Although more studies are needed, we attribute this localization mode to the nonlinearity of the materials, since it has the similar structure to the period-doubling, which the trough in between the collapsed ridges is deeper than its neighboring troughs. The adhesion force between two ridges is expected to be minor because the elastocapillary distance for this material is much smaller than the wavelength. The collapsing of ridges forms cylindrical channels that are potentially interesting for microfluidic applications (Figure 5.7).

Figure 5.7 Cross section images for aspect ratio 0.9 and the localization. (a) Image of the wrinkles with an aspect ratio of 0.9. The red dashed line outlines the surface profile. In this image, some of the wrinkle ridges are close to transitioning to localizations. (b) The localized surface. Further compressing causes the wrinkle ridges collapse and form channels.
In Equation (5.4), since the aspect ratio at localization for flat surfaces \( (A_F^0/\lambda_F^0) \) and the applied strain are relatively constrained, the slope of Equation (5.4) \( (E_2/E_c) \) becomes the main parameter for the aspect ratio at localization transition \( (A_F/\lambda_F) \). Optimizing \( E_2/E_c \) can result in higher aspect ratio wrinkles. A more controlled material system is needed to investigate and optimize \( E_2/E_c \) ratio. Double network crosslinking materials with independently controlled moduli and distinct crosslinking mechanisms for both networks can be a useful material system.

Although the living silicone can be considered as fluid or an elastic material depending on different time scale, interestingly, the living silicone shows significant larger aspect ratio for localizations comparing to either water or elastic materials. We suspect the shear traction acting on the film from elasticity and the up-and-down traction symmetry from the viscosity inhibit the occurring of localization. The time scales in the experiment is expected to control the balance between elasticity and the viscosity.

### 5.6 Summary

We have demonstrated a mechanism for creating high aspect ratio wrinkles, and the mechanism is promising to explain high aspect ratio structures found in living organs. The modification of the substrate stress stabilizes the wrinkles as the elastic energy becomes insufficient to trigger the localization transition. The finding extends current understanding of wrinkling and the localization transition. By successfully creating the high aspect ratio wrinkles, we demonstrate a further step toward bio-inspired surface property modifications.
5.7 Acknowledgement

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CHAPTER 6

CONCLUSION

6.1 Contributions

This work provides new approaches to create high aspect ratio wrinkles in large area. The contact line wrinkling technique is able to yield one dimensional and two dimensional wrinkle patterns by two straining mechanisms, deformation in the substrate and the deformation in the film. Two dimensional patterns are observed with the film stiffness ($tE_f$) is close to 20 mPa when the substrate modulus ($E_S$) is 10kPa. (Chapter 2) In addition to the interesting ability of patterning, the contact line wrinkling technique allows us to study the influence of initial strain inhomogeneity on wrinkling with its unique ability to induce inhomogeneously wrinkled surfaces. The growth of wrinkle aspect ratio is found to be insensitive to the initial strain inhomogeneity, and each wrinkle follow the geometrical equation for aspect ratio, $A/\lambda \sim \epsilon^{1/2}$, independent of the aspect ratios of the neighboring wrinkles. This result implies the strain localization is insensitive to defects of strain field. (Chapter 3) To further increase the aspect ratio beyond the current limit, we delay the onset of the localization transitions by the substrate prestretch method. We experimentally demonstrate the onset of localization and the structure of localization depend on the amount of prestretch, and find the optimal prestretch, $\lambda^0 = 1.8$. We use soft substrates ($E_S < 20$ kPa) to avoid the thin polystyrene film from cracking and delamination caused by the large compression required by the high aspect ratio wrinkles, ultimately allowing us to fabricate large areas of high aspect ratio (0.65) wrinkles. (Chapter 4) Moreover, wrinkling structures with more significant aspect ratio (0.9) are achieved by reducing the strain energy in the substrate, inspired from living creatures.
Three experiments are performed to control the stress in the substrate: molding substrates to create stress free wrinkling surfaces, secondary curing to form secondary crosslinking network, and using living silicone material to relax stresses. We find the localization is delayed to larger strains determined by the amount of stress relaxation. The aspect ratio when the localization occurs directly relates to the aspect ratio of the relaxed substrate network. (Chapter 5) The high aspect ratio wrinkled surfaces achieved in this work not only will impact the wrinkle based technologies, but also help us reveal the fundamental mechanisms of high aspect ratio features observed in living organisms.

6.2 Future Studies

The success in achieving high aspect ratio wrinkles open new research directions, including wrinkling mechanics and possible applications. This work will impact the research fields listed below and is promising to the wrinkle-based technologies.

6.2.1 Wrinkling mechanics

- Understand high aspect ratio features in living organisms.

  The questions that how Nature achieves the high aspect ratio features and the morphology still remain. Understanding the growth of the substances in the cells involved in the wrinkle formation can be very useful for this problem.

- Creating higher wrinkle aspect ratio

  For the artificial wrinkles, the localization modes is the major factor that hinders the growth of aspect ratio. Is it possible to eliminate the localization modes by selecting ideal materials or by creating ideal geometry to maintain the up and down traction forces perfectly symmetry? If the localization modes are avoided, are there other mechanisms restricting the aspect ratio?
6.2.2 Possible applications

- Large scale wrinkling fabrications

  Although the concept of the contact line wrinkling is promising to be used in the roll-to-roll process, experimental details such as the use of water need to be improved.

- High aspect ratio applications

  It is very interesting to apply the high aspect ratio wrinkles in this work to the proposed wrinkle-based technologies. Since the aspect ratio is significantly different to the conventional wrinkles, we expect improved results and even new mechanisms.


