Instabilities as a measurement tool for soft materials†

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Mechanical instabilities such as wrinkles, creases, and folds have long been viewed as a source of frustration for engineers and often a point of curiosity among scientists. Scientists aspire to understand the underlying physics behind the formation of mechanical instabilities and how to manipulate them for various endeavours, while engineers use this same understanding to design materials that inhibit or impede the formation of instabilities in critical applications. In recent years, a new movement in this community has emerged: harnessing these instabilities to provide critical insight into the properties of soft materials. We describe here the foundation of one particular analytical tool based on surface wrinkling and how this approach has been used to measure materials and systems that are inherently difficult to characterize. We also highlight some of the specific challenges and opportunities we envision for this measurement tool. Within this framework, we believe that there is great potential for broadening the capabilities of wrinkling metrology as the field of instability-engineering continues to mature.

Introduction

Whether you realize it or not, wrinkling and related instabilities are pervasive in the natural world around us: the aging of human skin, the texturing of many citrus fruits, and the formation of mountains are just a few everyday examples. Consequently, numerous studies have focused on determining the conditions necessary to cause wrinkling.[1–6] In summary, wrinkling commonly occurs upon compression of a thin, stiff surface layer that is coupled to a thick compliant layer. The compressive stress can be applied *via* direct in-plane compression of the bilayer or indirectly *via* tension and the associated Poisson's compression orthogonal to the applied tensile stress. The origins of the compressive stress can be from a variety of sources: differences in coefficients of thermal expansion,[7,8] residual stresses due to processing or chemical reactions,[9] or differential growth processes in many natural systems,[10–12] to name a few.

While wrinkling in nature can be viewed as intriguing or awe-inspiring, modern engineering has been forced to deal with the deleterious effects of these instabilities: mechanical instabilities have caused the rippling of airplane wings, failure of microelectronic devices, and the unwanted wrinkling of protective coatings such as paint.[13] As a result, specific strategies to prevent or suppress wrinkling have been discovered, either through material design or processing changes.

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For example, composite/hybrid materials have been developed to mitigate the mechanical property mismatch between layers of dissimilar materials, allowing high loads to be sustained before deformation occurs.[14]

Of course, instabilities can also be beneficial: consider the folds found in lung tissue which allow for easy expansion and contraction and a rapid increase in exposed surface area required for efficient breathing.[15] Designed instabilities have been the focus of many scientific applications including patterned surfaces for tuning adhesion,[16] flexible electronics,[17,18] optical gratings,[19] platforms for enhanced cell growth,[20] aligned nanotube membranes,[21] or fabrication of microscale gears.[22] Occasionally such applications are developed *via* serendipity, but quite often the most robust applications of wrinkled surfaces rely on the foreknowledge of how and why wrinkles develop.

The motivations described above represent the wide array of advanced research efforts focused on wrinkling and related instabilities. Programs at the National Institute of Standards and Technology (NIST) have focused on the development of surface wrinkling as a metrology tool. While engineers apply the physics of wrinkling to create new applications or to design in safety factors, metrologists view this paradigm "through the looking glass" in which the physical phenomena (the wrinkles) and the governing equations (mechanics) are combined as a means to measure the material properties of unknown or otherwise difficult to measure components. Seminal work in this area revolved around the determination of the elastic modulus of thin and ultrathin polymer films.[23] The work was predicated on prior understanding of the underlying mechanics and physics of wrinkling instabilities. Likewise, advances in our understanding of wrinkling and other instabilities continue to inspire new possibilities for metrology development. In this context, we offer a brief outlook on the development and application of wrinkling-based metrologies, critical challenges that need to be addressed as this field moves forward, and opportunities for advancing the state-of-the-art in measurements *via* instabilities.

Background

Bilayer wrinkling has been studied as a measurement tool originating with work at NIST,[23] synthesizing the wrinkling pattern formation reported by Whitesides and coworkers[2] and the mechanics behind buckling of a plate.[24] The system was a simple bilayer consisting of a thin skin (polystyrene) adhered to a thick compliant substrate (polydimethylsiloxane network). The conclusion that wrinkle wavelength and amplitude, which can be easily characterized with a common optical microscope or an atomic force microscope (AFM), could be used to measure fundamental properties of the bilayer system inspired many researchers to re-examine how they think about measuring the mechanical properties of thin polymer films. The analytical basis for bilayer wrinkling can be summarized by eqn (1),[6,25] which relates the measured wavelength of wrinkles to the elastic modulus of the film ($\bar{E}_f$) and substrate ($\bar{E}_s$), and to the thickness (h) of the film:

$$\lambda = 2\pi h\left(\frac{\bar{E}_f}{3\bar{E}_s}\right)^{1/3} \quad (1)$$

where $\bar{E}$ is the plane-strain modulus and is related to the Young's modulus and Poisson's ratio by $\bar{E} = E/(1 - \nu_2)$. Additionally, the amplitude of the wrinkles (A) is correlated with the over-strain in the system ($\varepsilon - \varepsilon_c$), as well as the film thickness (h) as:

$$A = h\sqrt{\frac{\varepsilon - \varepsilon_c}{\varepsilon_c}} \quad (2)$$

where overstrain is defined as the applied strain (ε) in excess of the critical strain needed to induce wrinkling (ε_c).

The relationship between strain, amplitude, and wavelength is critical to the application of wrinkling as a metrology tool. Based on this foundation, the elastic modulus of either the rigid film[23] or the compliant substrate[26] can be measured using wrinkling metrology. Additionally, diffusion in soft materials,[27–29] mechanics of hydrogels,[26,30,31] mechanical properties of polymer brushes,[32,33] polymer dynamics of confined films,[34,35] and mechanics of nanocomposites[36] together represent a sampling of material measurements that have been elucidated with the wrinkling metrology. Some of the above metrology endeavors have been addressed at NIST, but many examples are also drawn from the larger scientific community.

We would like to draw particular attention in this perspective to three primary challenges for the standard wrinkling model. First, we address the treatment of constrained thin films using mechanics derived for macroscale materials. Next, we discuss how material heterogeneities may affect the metrology, as the basic analytical solutions are based on continuous homogenous films. Finally we address the assumption of ideal adhesion at the primary interfaces in the wrinkled system. These challenges are justifiably avoided in the context of most experimental wrinkling work. However, from a metrology point of view, these assumptions constrain the measurement capability and it becomes possible to detect where the model deviates from experimental observation. Therefore, in an effort to advance the wrinkling metrology model, we propose some experiments designed to address one or more of these primary challenges.

Thin film properties: confinement, relaxation, and process history

The analytical solutions defined in eqn (1) and (2) are based on descriptions of bulk material behavior and are valid if three conditions are met: (1) $\bar{E}_f \gg \bar{E}_s$, (2) $h_f \ll h_s$, and (3) perfect adhesion. It is certainly reasonable and necessary to use these bulk relationships as a starting point for deducing material properties, as there are no adequate alternative models available to describe thin and ultrathin film behavior. There will certainly be occasions where the bulk model fails to accurately capture the mechanical properties of the system, for example when $h_f \approx h_s$. The driving phenomena behind nanotechnology is that as feature size decreases, the influence of any material aberration such as grain boundaries, defects, and surface effects will exert a greater influence over the macroscopic material behavior. Any deviations from bulk behavior due to nanoscale features will directly impact the efficacy of the wrinkling model.

A clear example is the effect of confinement on thin film mechanical properties. It has been shown that the mechanical properties of ultrathin polymer films deviate significantly from their

bulk film counterparts,[34,35,37] similar to deviations in thin film T_g.[38–40] A two-layer T_g model was introduced to describe the behavior: a soft surface layer coupled to a bulk-like underlayer. The need to use a two-layer model illustrates the inability of a simple model based on bulk material properties to capture the complex material behavior of confined polymer films. Similarly, other dynamic properties of thin polymer films can be measured using surface wrinkling. For example, thermal wrinkling has been used to ascertain the viscoelastic properties of thin polymer films,[7,8,41] and solvent-based wrinkling has been leveraged to elucidate small molecule diffusion in thin films.[27–29] There are opportunities to apply surface wrinkling to the measurement of additional properties such as physical aging and relaxation dynamics in thin polymer films.

Similar to polymer films, the mechanical properties of metallic films have been studied using wrinkling as the primary measurement probe.[42–44] The elastic modulus of the metallic films exhibited a strong dependence on thickness of the metal film and residual stress due to deposition.[43] In the case of metal–polymer thin film bilayers, the microstructure of the deposited metal layer may have an effect on the mechanical response of the metal film.[44–46] Systematically varying the metal deposition conditions to mimic the well known "zone model"[47,48] could elicit variations in the characteristics of the metal film such as grain size and orientation of grain growth.[48] Similarly, variation in residual stress due to aggressive metal deposition techniques may be within the sensitivities of the wrinkling model.[49]

The interplay between processing history and material properties is critical for both metallic and polymer components of the wrinkling model.[37] Therefore it may be possible to use wrinkling to characterize residual stress in the film as a function of processing history.[50] Moreover, by quantifying the residual stress *via* wrinkling, researchers can ascertain the impact of residual stress on other behaviors and physical properties of thin and ultrathin polymer films. Just as residual stress may affect the measurement of material behavior, residual stress can also be utilized to pre-load a multilayer film such that it is able to wrinkle with very little external energy input. This draws a connection between the measurement of the critical energy required to induce wrinkling, and the application of wrinkling as a stimuli-responsive material. The ability to tune the stress-wrinkling response within a film by using residual stress provides an opportunity to generate a range of stimuli conditions in a single system both for manipulating the wrinkling-onset conditions and the resulting wrinkled morphology.[41,42]

Dynamic processes such as the swelling of gels,[30] relaxation of polymers,[51,52] or distribution of T_g in confined films[53] evoke models of heterogeneous layered systems. The layered film model was foreshadowed by de Gennes,[54] with regard to distribution of T_gs, and experimentally applied in recent work.[53,55] One larger implication of the confinement work is the likelihood of a distribution of material properties other than T_g through the thickness of a confined film. The reality of variable material properties in what is often assumed to be homogenous material is an issue to be addressed with respect to wrinkling experiments, especially as material dimensions approach confinement as well as when considering behavior at the interface. The following sections will address challenges associated with material heterogeneity and aberrations at the interface as they may affect wrinkling metrology.

Complex materials: heterogeneities and nanocomposites

The characterization of polymer-based nanocomposites involves many challenges for conventional material measurements, largely due to two factors: the tendency for uncontrolled nanoscale heterogeneities and the potential for significant portions of the polymer matrix to exist in a confined state. Together these qualities can obscure phenomena critical to material performance. Wrinkling of complex systems with designed heterogeneity has been investigated by measuring the mechanics of layer-by-layer film stacks of polymers. In this model, the analytical solution for wrinkling of a stiff plate on an elastic foundation had to be expanded to account for through-thickness (z-axis) variation in material properties.[56,57] Wrinkling studies on laterally heterogeneous films (x–y variation) demonstrated how patterned regions of elevated modulus would alter the appearance of wrinkles, as shown in Fig. 1.[58]

Together these studies illuminate opportunities for further work characterizing sub-surface heterogeneities in thin polymer films. Consider for example particle-based composite coatings, where wrinkling could be used as a detection mechanism of the dispersion of hard particles. Deviations in the wrinkle pattern similar to those observed by Tsukruk and co-workers due to local modulus variations[58] could serve as indicators of dispersion of hard particles or unwanted aggregates. Well dispersed particles would result in a wrinkle pattern that is homogenous, corresponding to the composite modulus of the film. However, regions of variation in modulus possibly due to aggregates or widespread absence of the higher modulus filler particle may

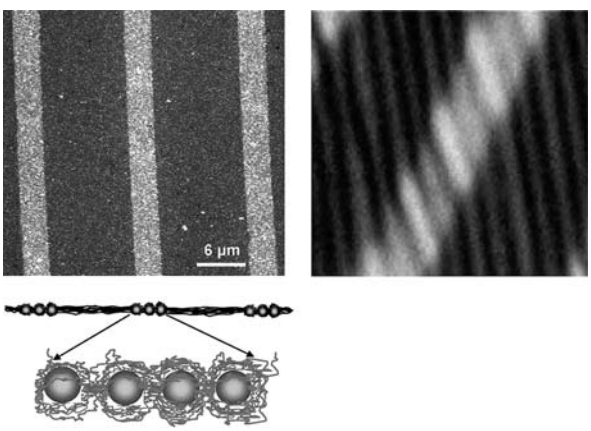

Fig. 1 Distortion of the wrinkling pattern due to in-plane heterogeneities of the film. Reproduced with permission.[58]

exhibit distortions in the wrinkle pattern. Micrometre-sized particles/aggregates may be the detection limit for a conventional bilayer system due to the typical wavelengths observed in wrinkling of polymer films. To circumvent this limitation, the distribution of wrinkle wavelengths, as indicated by the width of the scattering peak in a light scattering experiment, could capture subtle variations in particle distribution in the coating. Alternatively, the presence of two distinct wavelengths would be indicative of discrete regions having high and low concentrations of particles.

Another interesting possibility inspired by these studies is the application of surface wrinkling to characterize the physics of block copolymers (BCPs). Manipulation of BCP morphology from lamellar to lattice-type oriented cylinders is widely reported. To date the oriented block copolymer system has not been used in wrinkling studies for the primary reason that the domain spacing of many BCP systems is an order of magnitude smaller than the typical wavelength of observed wrinkles. Thus, it would be difficult to use the wrinkle pattern to elucidate nanoscale details of the BCP morphology. Instead, we propose that one could use BCP systems as models for in-plane heterogeneities, as the well defined morphology and domain spacing could serve as an ideal test-bed for probing mixed-material behavior. As such, heterogeneities could be designed to be on a periodic lattice or as a lamellar structure giving orientation specificity of the composite behavior.

Similarly, patterned surfaces beyond simple BCP systems could be very useful in the advancement of wrinkling metrology. For example, novel "zero CTE" (coefficient of thermal expansion, α) materials are often polymer/ceramic nanocomposites[59,60] in which thermal expansion is macroscopically depressed by combining a positive CTE matrix with a negative CTE filler. Wrinkling characterization of the thermo-mechanical behavior of such materials in ideally oriented systems may reveal useful structure–property relationships. For example, the critical length scales over which CTE mismatch is realized as macroscale mechanical deformation, or furthermore how stress is transferred in complex heterogeneous materials, are questions which could potentially be addressed *via* wrinkling metrology. Many CTE measurement methods such as wafer curvature capture the global CTE value for the film across the entire wafer; wrinkling-based CTE measurement would be more capable of characterizing discrete regions of the films for materials where CTE may be spatially varied. Along these lines, Oh and Ree measured the anisotropic CTE behavior of poly(methylsilsesquioxane) films with $\alpha_{\perp} : \alpha_{\parallel}$ on the order of 10 : 1 using a combination of spectroscopic ellipsometry, X-ray reflectivity and residual stress analysis.[61] Though it has yet to be applied in this manner, thermal wrinkling metrology can be used as a method to characterize the CTEs of thin films in instances where the elastic modulus is well known or can be measured using alternate techniques.

Challenges at the interface: adhesion

Adhesion at critical interfaces represents a special case of through-thickness variation in film properties and is the final challenge we discuss in this perspective. The wrinkling model assumes both a perfectly sharp interface with no material mixing and perfect interfacial adhesion, though these conditions are not always true in practice. Any slipping or delamination of material at the interface will distort the measured wrinkle amplitude and/or wavelength. Some investigation of the effect of adhesion at the substrate–film interface has shown that slip at this interface, though not central to the wrinkling phenomena, will distort the observed wrinkling pattern (Fig. 2).[62] Likewise, localized delamination can result in the formation of blister-like buckling instead of the expected wrinkling.[63] However, there has been no systematic study of the effect of adhesion at the film–substrate (bilayers) or film–superstrate (trilayers) interface or any detailed characterization of this interface for wrinkled systems, whether in the context of polymer–polymer or polymer–metal interfaces.

In the simple bilayer wrinkling model, the assumption is that all strain energy above a critical value is directly transferred to the creation of surface wrinkles. This assumption implies perfect adhesion at the critical bilayer interface, which for very thin films is likely to be valid. As the critical strain to wrinkle is rather low, the required minimum adhesion is also correspondingly low for thin films due to the minimal elastic energy stored in the film. However, as thickness of the rigid skin film increases, the bending stiffness also increases. Here, interfacial adhesion becomes more influential on the wrinkling behavior as the likelihood of delamination increases. As researchers expand the wrinkling metrology to thicker films, adhesion is going to be a greater concern. Strategies for generating sufficient adhesion may begin to impact the measurements through the introduction of mechanically stiff interlayers or intercalation of materials at the interface. The intercalation may be from polymer interdiffusion or the embedding of metal particles some depth into the free polymer surface during deposition. Either situation converts a simple bilayer problem

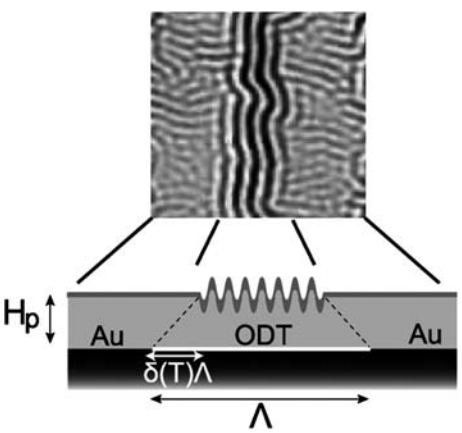

Fig. 2 Change in wrinkle pattern and orientation due to differences in adhesion at the substrate–film interface. Reproduced with permission.[62]

into a more complicated trilayer, similar to the layer-by-layer model discussed in the previous section. It is unlikely that the intercalated zone for most bilayers is large enough to significantly impact prior measurements. However, it does introduce an avenue of further study: using wrinkling to provide insight into materials that have material property variation in the z-direction, whether by alternating material layers or through the design of functionally graded materials. Instabilities in natural systems are found within complex graded materials, quite unlike the simple bilayer, which is admittedly, easier to study. The ability to apply a wrinkling model to such complex materials would provide great insight to the physics and design principles found in nature.

Conversely, it may be possible, though currently unexplored, to use wrinkling to measure the adhesion of two thin films. If there is delamination or slipping at the interface of the bilayer, the wrinkle pattern should be suppressed to an eventual boundary condition of full slip, where the stress mismatch in the thin films is able to be completely relieved through translation of the film along the interface rather than wrinkling. A simple experiment of a gradient fluoro-to-hydroxyl layer at the critical bilayer interface would demonstrate the potential to use wrinkling as an adhesion measurement. By using a gradient of surface energy, it would be possible to establish the critical adhesion energy at a surface required for the wrinkling–delamination transition.

Additionally, the modification of surface energy at a bilayer interface will likely involve functionalization *via* self-assembled or laterally bonded monolayers to alter adhesion. In such case, the monolayer will exert its own mechanical resistance and convolute the measurements of a bilayer system. The presence of the adhesion promoter could be problematic but could also be viewed as an opportunity: what are the mechanical properties of an ultrathin ($h \approx 1$ nm to 2 nm) self-assembled monolayer? The mechanical properties of monolayers have been extensively studied using the water supported Langmuir trough[64] and on rigid substrates using contact mechanics in conjunction with an AFM probe.[65] Both methods have clear advantages, but wrinkling metrology may be able to capture the behavior of monolayers in a relatively high throughput fashion with the ability to have macroscale film characterization. This would complement the AFM probe method which is advantaged by its nanoscale specificity.

Conclusions

Surface wrinkling affords a simple yet robust measurement tool to elucidate the properties of thin films and soft materials. There exist many challenges and opportunities as the field matures, specifically in the measurement of confined thin films, heterogeneous materials, and adhesion-related phenomena. The questions offered in this perspective highlight systems that will challenge the measurement accuracy and ultimate limits of the wrinkling metrology model. The advancement of the wrinkling metrology of soft materials and films is reliant on the capability to measure systems of increasing complexity. We are eager to see how researchers combine their creativity and scientific ingenuity to address these problems and uncover future challenges.

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