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Osmotically-driven surface buckling is a simple method for introducing controlled micro- and nanoscale topography onto material surfaces. To achieve a fundamental understanding of the buckling process and a library of the equilibrium and kinetically-trapped structures that can be attained, we observe the growth processes of a buckling silicate plate rigidly attached to an elastomeric substrate. The primary variable is the lateral extent of the silicate plate which is shown to dictate the location of buckle initiation, and thus the resulting morphology of the final buckled structure. We present a model to qualitatively describe the radial stress profile within the plate, based on both the diffusion-controlled local osmotic stress and the ability of the plate to transfer this stress to the relatively unconfined region surrounding it. These results and insights provide lessons for controlling the order and arrangement of buckled microstructures.

Introduction

When a compressive stress is applied to a material bilayer consisting of a stiff skin bound to a soft substrate, a mechanical instability develops whereby the surface undergoes out-of-plane deformation as a stress relief mechanism known as buckling. This phenomenon is related to the Euler buckling of a rod and has been used to introduce controllable microscale surface topography for a number of different material systems. Such surfaces are suitable for a wide array of applications, including anti-reflective surfaces, enhanced adhesives, and cell culture surfaces. Surface buckling offers many advantages over alternative patterning processes, including ease of preparation, cost-effectiveness, and the ability to pattern large areas.

Despite the variety of successes, understanding of the mechanisms by which buckling occurs and their influence on the resulting buckle morphologies remains incomplete. Several papers predict the emergence of the zigzag herringbone morphology at equilibrium for systems subjected to equibiaxial stresses well above the critical buckling stress. Although achievable, the observed morphology is often wrought with defects, causing the overall structure to grossly deviate from the predicted herringbone pattern. To fundamentally understand the mechanisms that give rise to these observed morphologies, we must examine the transitions that arise during buckle formation, when the applied stress only fractionally exceeds the critical buckling stress, and as the stable surface structure evolves. This paper seeks to extend our understanding of the phenomena which govern the formation of buckled patterns at the point of initiation and throughout the entire buckling process until no further development is seen.

In recent work, Chan and Crosby demonstrated the buckling of an oxidized polydimethylsiloxane (PDMS) surface under stress applied through absorptive swelling of a liquid solvent into the PDMS layer. The stiffer oxide surface resists this swelling, putting the elastomeric PDMS near the oxide interface into a compressive stress state. Once this stress reaches a material-defined critical stress, buckles form across the oxidized portion of the sample. This simple approach provides great versatility and tunability of the buckle dimensions and order through control of the thickness of the oxide layer, the choice of solvent, and the size and geometry of the silicate plates that can decorate the material surface. Specifically, finite lateral dimensions of the oxidized plate can allow access to wrinkle-based patterns ranging from the dominant buckling modes of the semi-infinite oxidized surface down to arrays of single, half-wavelength convex microlenses for sufficiently small plates.

Fig. 1 Herringbone patterns resulting from buckling of a flat plate in the absence of edge effects. (a) Unusually ordered herringbone buckling morphology radiating outward from a single point defect at the center. (b) Typical herringbone pattern characterized by numerous pattern defects. (c) Schematic depicting sample preparation and the buckling process.
In this paper, we modified the approach of Chan and Crosby by replacing the liquid monomer with solvent vapor as the swelling agent to generate buckled features in such a way that their evolution may be monitored and recorded (Fig. 1c). Samples of PDMS elastomer were selectively oxidized using a UV-ozone oxidation process in conjunction with stencil masks to produce circular oxidized regions with radii ranging from 0.83 mm to 8.6 mm. The UVO-treated PDMS was placed on a transparent pedestal inside a sealed glass chamber at room temperature. Immediately before sealing the chamber, a liquid solvent was placed in a reservoir surrounding the pedestal such that it did not directly contact the PDMS sample. The resulting vapor pressure acted as an osmotic driving force, allowing solvent to swell the PDMS. The oxidized surface of the PDMS was imaged over time through optical microscopy.

Results

Initially, the oxidized PDMS is in a solvent-free state. Upon exposure to the solvent-rich atmosphere, solvent molecules enter the sample through the exposed top surface. The oxidized regions slow the rate of solvent uptake relative to the unoxidized PDMS, forming an effective barrier layer. As a result, a temporary concentration gradient forms beneath the oxidized plates. Due to the constraint imposed on the PDMS by the stiff oxidized layer, the swelling expansion of the PDMS network is restricted, thus placing the PDMS into a state of compression. This compressive stress $\sigma$ becomes greater over time as the solvent concentration within the PDMS increases. After sufficient time, $\sigma$ reaches a critical value where the stress may be relieved through buckling of the stiff layer. This material-defined critical stress is given by:

$$\sigma^C = \frac{E_f}{4} \left( \frac{3E_s}{E_f} \right)^{2/3}$$  \hspace{1cm} (1)$$

where $E_f$ and $E_s$ are the plane strain moduli ($E = E/(1-\nu^2)$) of the stiff layer and the soft substrate, respectively, with $E$ as the material Young’s modulus and $\nu$ as the Poisson’s ratio. Although eqn (1) is best known for describing $\sigma^C$ for a uniaxial stress state, it has also been shown to describe the critical stress for any buckling mode whose wavenumbers ($k$) satisfy:

$$\sqrt{k_1^2 + k_2^2} = \left( \frac{3E_s}{E_f} \right)^{1/3}$$  \hspace{1cm} (2)$$

which includes the equibiaxial case ($k_1 = k_2$) as well as the uniaxial case ($k_1 = 0$ or $k_2 = 0$).5,12,26

Most of the published experiments and theory regarding buckle morphology has focused on the case when the applied stress is much greater than this critical buckling stress ($\sigma/\sigma^C \gg 1$). In contrast, our system possesses the advantage that the morphology may be characterized at values of $\sigma/\sigma^C$ ranging from just above unity up to the maximum value attainable with a given solvent.

Fig. 2(a–c) shows the observed buckle evolution over time for the experiment involving a circular oxidized plate with $a = 1.0$ mm. For this example, the wrinkle morphology in later stages (Fig. 2c) arises through the development of dimple structures that coalesce to form locally elongated wrinkle structures. Optical profilometry measurements (Fig. 2d) confirm that the hexagonally arranged dark regions observed in transmission light microscopy are dimples, or axisymmetric depressions in the oxide surface.

Buckle initiation plays a key role in determining the morphology at both short and long timescales, as demonstrated in Fig. 3, where the dominant buckling mode changes as both a function of time and of the radius of the oxidized plate. The largest plate ($a = 8.6$ mm) first reaches $\sigma^C$ near its perimeter, resulting in radially aligned initial buckles and indicating a dominant stress state in the $0$-direction. As plate size decreases, the region of initiation shifts radially inward until, for sufficiently small $a$, the buckle initiation collapses from an annular to a circular region at the plate center. Here, the stress state is equibiaxial rather than $0$-dominated, and the initial buckles appear in an isotropic morphology: a hexagonal array of dimples.

These initial buckling states dictate the evolution of the pattern that emerges as higher stresses are applied with the continued absorption of solvent into the PDMS (Fig. 3). The uniaxial buckling near the edges quickly propagates towards the center, with the buckles aligned perpendicular to the propagating wavefront of the buckled region. Further swelling and stress development leads to deformation of the isotropic wrinkle structures into one of two patterns (see Fig. 3a-III): (1) the zipper morphology reported by Chan and Crosby² near the region of buckle initiation, and (2) the herringbone morphology, near the plate’s center.

In contrast, further buckling of a dimple array is dictated by the hexagonal lattice formed by the dimples. Neighboring dimples coalesce into a single, oval-shaped depression. As this occurs across the array, two patterns are observed locally: (1) a cage-like structure consisting of six coalesced pairs of dimples in a hexagon surrounding a single dimple (Fig. 2c, circled section), and (2) a structure resembling the herringbone style of...
brick-laying (Fig. 2c, rectangular section)—not to be confused with the zigzag herringbone morphology. The cage structure represents the dominant morphology, with the brick-like pattern only appearing in smaller, localized areas. Some areas where neither of these patterns is evident also exist, but hexagonal origins are still observed.

As Fig. 3 demonstrates, the final surface structure of the buckled oxide plate is dependent on the conditions of buckle initiation. Buckle initiation must occur where the local in-plane stress first exceeds \( \sigma_c \); therefore, we can understand the radial shift of the buckle initiation site by examining the radial stress profile of the circular oxidized plate under diffusive swelling conditions. This stress profile is dependent upon the concentration gradient of the swelling agent and the positional constraint imposed by the vanishing radial displacements at the oxide/PDMS interface.

As mentioned above, the silicate plate acts as a barrier to solvent absorption causing a lateral concentration gradient beneath the plate. Considering only the stress imparted by the swelling material in the direct vicinity of the plate (i.e. \( C_0 \) is constant with respect to time and depth into the sample) and ignoring absorption through the plate and the impact of stress on diffusive processes, we can model the lateral solvent transport as diffusion into a cylinder from a constant edge concentration \( C_0 \):\(^ {27} \)

\[
C / C_0 = 1 - 2 \sum_{n=1}^{\infty} \frac{\exp(-D \alpha_n^2 t) J_0(\alpha_n r)}{\alpha_n J_1(\alpha_n a)}
\]  \hspace{1cm} (3)

where \( r \) is the radial position, \( D \) is the solvent diffusion coefficient, \( J_0 \) and \( J_1 \) are the first- and second-order Bessel functions of the first kind, respectively, and \( \alpha_n \) are the solutions to \( J_0(\alpha_n a) = 0 \). Fig. 4a shows the normalized concentration as a function of \( r/a \) for different values of \( D / a^2 \). Thus, for a fixed materials system at a given point in time, the concentration profile of the swelling agent is defined by the lateral extent of the barrier plate.

The development of the compressive stress that leads to surface buckling is dictated by the rigid radial boundary conditions at the oxide/PDMS interface, i.e. radial displacement at this interface is near zero. Although an exact model has not been developed to define the local lateral stresses for a given concentration with these rigid boundary conditions, we invoke a simple convolution to provide insight into our experimental observations. The convolution involves the concentration profile
described above and the stress distribution for a uniformly swollen elastomer rigidly attached to a finite plate. Due to the release of swelling constraints radially from the edges of the finite plate, we hypothesize that the stresses near the boundary of the plate will take a general parabolic form with maximum stresses in the center and vanishing stresses at the plate’s edge. From this assumption for a normal stress distribution near the oxide/PDMS interface, we use solutions for the radial distribution of radial and circumferential stresses:

\[
\frac{\sigma_r}{p_0} = \frac{1 - 2\nu}{3} \left( \frac{a^2}{r^2} \right) \left[ 1 - \left( 1 - r^2/a^2 \right)^{3/2} \right] - \left( 1 - r^2/a^2 \right)^{1/2}
\]

(4)

where \(p_0\) is 3/2 times the mean applied pressure. The mean pressure may be thought of as the effective osmotic pressure within the PDMS under uniform swelling conditions. Radial profiles of these stresses are plotted in Fig. 4b. It is interesting to note that for a compressible system, \(\sigma_c\) becomes noticeably larger than \(\sigma_r\) as \(r/a\) approaches 1, while at small values of \(r/a\) the two stresses are nearly equal. This ranking is reflected in the observation that the dominant buckling mode near the edge

\[
\frac{\sigma_c}{p_0} = \frac{1 - 2\nu}{3} \left( \frac{a^2}{r^2} \right) \left[ 1 - \left( 1 - r^2/a^2 \right)^{3/2} \right] - 2\nu \left( 1 - r^2/a^2 \right)^{1/2}
\]

(5)

The maximum of each curve was assumed to be 1.05*\(\sigma_r\).
indicates a bias towards the circumferential stress component, while the isotropic dimples near the center suggest an equibiaxial stress state.

A convolution of the stress distribution for a uniform swelling concentration near a rigid plate and the diffusion-controlled concentration gradient results in the stress profiles shown in Fig. 4c. However, these profiles alone are not indicative of the effect of plate size on the resulting buckle initiation location, as every plate will pass through each of these stress states at some point in time. Therefore, we must examine more closely the stress distribution at the specific time when the critical buckling stress is first attained. Plate size plays a role in determining the magnitude of the developing and final stress profiles: the stress-reducing effect of the plate edge is felt more strongly in small plates than in large ones, resulting in a diminished \( p_0 \) in smaller plates. As a result, \( \sigma_r \)—which is a constant for a given material system—is reached quickly for large plates, first occurring near the edge while the solvent concentration gradient still dominates the stress profile (Fig. 4c, dotted line). Conversely, small plates allow the solvent to almost totally diffuse until no appreciable concentration gradient remains before \( \sigma_r \) is reached (Fig. 4c, solid line). By multiplying the stress curves in Fig. 4c by \( p_0/\sigma_r \), with \( p_0 \) dependent upon the plate size, we can generate a more accurate comparison of the stress states at the point of buckle initiation as a function of plate size (Fig. 4d).

Although elementary, this convolution provides an explanation for the observed radial shift in location for buckle initiation. Furthermore, the stress distributions are consistent with the morphology of the wrinkles at wrinkle initiation. For larger oxide plates, buckling initiates near the plates’ edge, where stresses in the \( \theta \)-direction dominate. This local dominance is similar to a uniaxial stress condition, under which unidirectional surface wrinkles develop as observed in our experiments. For smaller oxide plates, buckling initiates in the plates’ center, where the in-plane stresses are equibiaxial. This equibiaxial condition is consistent with the hexagonal array of dimples observed in Fig. 3c.

Although the hexagonal arrangement of dimples is consistent with an equibiaxial stress condition, it differs greatly from the herringbone morphology that is commonly observed under equibiaxial loading from thermal processing, swelling, or mechanical procedures. The difference presents the question of whether the dimple array is a kinetic or equilibrium structure. In their consideration of the predicted equilibrium morphology of materials wrinkled by thermal expansion mismatch Chen and Hutchinson\(^5,\)\(^22\) calculated the energy of both the herringbone morphology and of a family of periodic solutions predicted by linearized stability analysis, as a function of applied stress. They demonstrated that for stresses far exceeding the materials-defined critical stress (eqn (1)), the herringbone morphology was the most energetically favorable. For stresses approaching the critical stress for buckling, the morphology of lowest energy is not well defined due to the singularity at the critical stress. The linearized stability analysis considered by Chen and Hutchinson predicted solutions of orthogonal waves whose wavenumbers satisfy eqn (2). The family of solutions described by this condition ranges from 1-dimensional buckles for \( k_1 = 0 \), to a symmetric checkerboard pattern when \( k_1 = k_2 \). Within this solution set also lies the case where \( k_1 = \sqrt{3} k_2 \) which describes a pattern whose peaks form a hexagonal array. Therefore, our observed hexagonal array of dimples may be an equilibrium structure seen as the osmotically-induced stress state passes through the critical point.

Buckling-based dimple formation has been recently predicted using finite element numerical modeling by Cao et al.\(^7\) for a buckling spherical surface, particularly at low stresses. Their model predicted an array of hexagonally arranged dimples on the surface of spheres which were sufficiently small and subjected to stresses only slightly greater than the critical buckling stress for their materials. Additionally, Kücken and Newell\(^26\) suggested in their theoretical analysis of fingerprint formation that a hexagonal pattern may arise at the onset of buckling for an equibiaxial stress state. Their analysis is particularly relevant to the results presented here, as the compressive stress results from the expansion of a subsurface basal cell layer.

To test this hypothesis, we experimentally investigated the behavior of buckled plates when the system remains near \( \sigma_1/\sigma_r = 1 \). To attain these conditions, we lowered the driving force of the solvent vapor to swell the PDMS by diluting the liquid pyridine with glycerol, a non-volatile cosolvent. This cosolvent lowers the pyridine’s partial pressure and reduces its vapor concentration in the sealed atmosphere. Samples were left to equilibrate in the vapor for at least 24 hours, after which evolution of the buckled surface structure was no longer observed. Fig. 5a shows plates with \( a = 1.24 \) mm where the concentration of pyridine in the solvent reservoir was varied from 80% to 95% by volume. No buckling was observed for pyridine concentrations below 80%. At 80% pyridine, an array of dimples is formed, but the swelling stress remains low enough that no coalescence is observed, even at long times. As the solvent concentration in the atmosphere increases, the imparted swelling stress becomes larger and results in coalescence near the center as well as extending the radius of the region in which buckling is observed. A similar trend is seen with respect to increasing plate dimension at a constant solvent concentration of 80% (Fig. 5b), thus confirming an earlier statement that \( p_0 \) increases with larger plates.

**Conclusions**

We have demonstrated the formation of a hexagonally-packed array of concave dimples as a consequence of the buckling of millimetre-scale circular oxidized plates of a PDMS surface, through swelling by absorption of solvent vapor into the PDMS. This morphology arises when the applied osmotic stress is just slightly above the critical buckling stress—observed here at early buckling times or by lowering the vapor pressure of the solvent atmosphere. In addition, an equibiaxial stress state is necessary for the formation of the dimples. We proposed a model for the development of stress as a function of position within the plate, which describes a range of plate widths, material diffusion coefficients, and timescales. As the stress is allowed to increase far above the critical buckling stress, these dimples coalesce to form higher-order buckling morphologies. This method of buckle formation may be useful in studying the order and arrangement of both long- and short-term buckled structures at multiple length scales, toward greater control of these structures for applications requiring low-cost, high-throughput fabrication of microstructured surfaces.
Experimental

Materials

PDMS oligomer (Dow-Corning Sylgard 184) was mixed with its crosslinking agent in a 10:1 weight ratio and degassed under vacuum. Then, 0.5 mL of the degassed mixture was dispensed onto a 1 inch square glass slide and cured at 70°C for at least 2 hours. Once cooled, the sample was oxidized for 30 minutes using a Jelight 342 UVO system. Stencil masks were placed on the samples to produce selectively oxidized circular regions with radius \( a \), ranging from 0.83 mm to 8.6 mm. Pyridine was used as the primary swelling solvent, with some experiments employing a glycerol cosolvent to control the resultant vapor pressure. Fig. 1c shows a schematic of the sample preparation and exposure to solvent vapor.

Buckling process

The oxidized samples were placed on a circular glass pedestal inside a cylindrical glass chamber, which was then covered by a watch glass, using vacuum grease to seal the chamber. Immediately prior to sealing, 1 mL of solvent was dispensed via syringe into the moat surrounding the pedestal, taking care to keep the sample itself from contacting the liquid solvent.

Characterization

The entire apparatus was placed on a Zeiss Axiovert inverted microscope equipped with an XY-controllable stage in order to record optical micrographs of the buckling process. Using a customized LABview program, images were recorded at intervals of 30 seconds at up to 6 different locations on the
sample. For experiments using glycerol-diluted pyridine in the solvent reservoir, only final images were taken, after absorption of the solvent had stopped (at least 24 hours).

To obtain surface profiles using optical profilometry, the samples were first exposed to a vapor atmosphere arising from an 80%/20% pyridine/glycerol solution for 24 hours. A mold of the surface was made using Norland 60 UV-curable adhesive; upon removal from the sealed chamber, the samples were quickly covered with the uncured adhesive to prevent solvent evaporation and cured for 1 additional minute. The molded surfaces were then characterized by a Zygo 6000 3D optical profilometer, using a 25x objective. The raw surface profile data was inverted to recover the profile of the original buckled surface.

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