Fracture-Induced Alignment of Surface Wrinkles

Charles J. Rand
Renee Sweeney
Mary Morrissey
Lauren Hazel
Alfred Crosby, University of Massachusetts - Amherst
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Charles J. Rand, Renee Sweeney, Mary Morrissey, Lauren Hazel and Alfred J. Crosby*

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We introduce a simple process for creating materials that produce osmotically-driven surface wrinkles with long-range alignment, sans lithographically-defined topography and selective oxidation. Mechanically-induced surface defects create stress discontinuities that convert the global biaxial stress state to local uniaxial stresses, producing aligned wrinkles across the surface.

Wrinkled or buckled surfaces with well-defined wavelengths can be created by a variety of methods, which typically rely upon the deposition or attachment of a thin rigid film on an elastomeric substrate and subsequent compression of the film/elastomer composite beyond a critical strain. Mechanical compression, thermal mismatch strains, and differential swelling all have been demonstrated as viable routes for strain-induced wrinkling. In the case of differential swelling, the film resists the swelling of the underlying elastomer, leading to the development of a compressive stress near the film/elastomer interface. Experimentally, the general phenomena of swelling-induced wrinkling was first seen by Southern and Thomas, who evaluated the swelling of a laterally-confined rubber block with an attached film, which is especially attractive for the scaleable fabrication of ‘smart’ or responsive coatings.

Under ideal conditions, surface wrinkling from equi-biaxial stresses, such as swelling or thermal stresses, results in a herringbone pattern as described by Chen and Hutchinson. Although herringbone patterns are sufficient or convenient for the topographic control of certain surface properties, such as adhesion, many potential applications of wrinkled surfaces will require the long-range control of non-herringbone wrinkled arrangements. Previous research has largely relied upon lithographic methods to locally alter the equi-biaxial stress state, thus altering the wrinkling morphology. For example, Bowden and co-workers used a topographically-patterned elastomer to align wrinkles local to the topographic edges. Chan and Crosby demonstrated the use of lithographically-patterned constraining films, in absence of topographical changes, to produce aligned wrinkled surfaces for osmotically-driven wrinkles. In both of these methods, the applied equi-biaxial stress on the rigid upper layer changes locally to a primary compression parallel to an edge discontinuity, resulting in the alignment of wrinkles. Although both methods are powerful, they ultimately rely upon top-down processing methods, which can be potentially limiting for laterally extensive applications. In this report, we similarly use stress discontinuities to locally alter the equi-biaxial structures of osmotically-driven wrinkles, but our process does not rely upon lithographic processing. Instead, a simple process of fracturing the upper layer through the use of controlled uniaxial strain is used. This process not only leads to local rearrangement, but demonstrated long-range order across samples with lateral dimensions on the order of centimetres. The combination of osmotically-driven surface wrinkles and non-lithographic routes to long-range alignment makes this process especially attractive for numerous applications.

To create wrinkled surfaces, we used a crosslinked polydimethyl siloxane (PDMS) as the elastomeric substrate. The upper rigid layer was created by exposing the elastomeric substrate to ultraviolet light in the presence of ozone (UVO). This UVO process converts the surface of the PDMS into a silica-like layer (SiOx). The samples were then immersed in ethanol which swells PDMS. The rigid SiOx layer restricts the swelling of the upper portion of the PDMS, while the lower portion is allowed to expand. Upon exceeding a critical osmotic stress which develops a compressive stress at the SiOx/PDMS interface, the surface wrinkles. This stress (σc) for buckling a thin film on elastic substrate is:

\[ \sigma_c = \frac{E_f}{4(1 - \nu_f^2)} \left( \frac{3E_s(1 - \nu_s^2)}{E_f(1 - \nu_f^2)} \right)^{2/3} \]

where \( E_f \) and \( E_s \) are the elastic modulus of the film and the substrate, and \( \nu_f \) and \( \nu_s \) are the Poisson’s ratio of the film and substrate, respectively. Fig. 1(a) shows the wrinkling of a defect-free pattern-free surface using this method. In this situation, wrinkle direction is random on the surface, showing no noticeable order.

To align the surface wrinkles, we apply uniaxial strain to the substrate, after SiOx formation, to provide discrete fracture lines in the SiOx layer. After release of the uniaxial strain, subsequent swelling

![Fig. 1](image-url) (a) Random wrinkling prior to fracture process, characteristic of biaxial wrinkling of a pattern free surface. (b) Wrinkling of a surface with uni-axially created fractures. (c) Wrinkle alignment process.
of the samples provides aligned wrinkles perpendicular to the fracture direction. An example of these aligned wrinkles is shown in Fig. 1(b) and the alignment process is summarized in Fig. 1(c).

To evaluate wrinkle alignment using a fracture process, we varied the UVO exposure time and applied uniaxial strain. The UVO exposure time determines the conversion of the upper most layer to SiO$_x$, changing the thickness ($h$) and modulus of this rigid upper layer ($E_t$). Both $h$ and $E_t$ control the wavelength ($\lambda$) of the surface wrinkles:\(^\dagger\)

$$\lambda = 2\pi h \left(\frac{1}{4(1 - \nu^2)} \frac{E_t}{E_s}\right)^{1/3}$$  \hspace{1cm} (2)

where $E_s$ is the elastic modulus of the PDMS substrate and $\nu$ is the Poisson’s ratio of the SiO$_x$ layer. For our material, similar to Chan and Crosby,\(^\ddagger\) we use a multilayer model for $h$ and $E_t$ to properly relate $\lambda$ to the material’s properties (Fig. 2(a)).

The other variable, applied strain, controls the fracture process by dictating the average spacing between fracture lines $\langle L \rangle$:

$$\langle L \rangle = \Sigma c e^{-k}$$  \hspace{1cm} (3)

\(^\dagger\)where $c$ is a constant, $k$ is an empirically determined exponent, and $\epsilon$ is the applied uniaxial strain. The fracture spacing versus the applied strain is shown in Fig. 2(b) for various UVO times. Heinrich and co-workers indicate that $\epsilon$ changes at a critical strain ($\epsilon_c$) and critical fracture spacing ($L_c$).\(^\ddagger\) Below $\epsilon_c$, $\epsilon$ is equal to the Weibull exponent of the strength distribution of the film.\(^\ddagger\) Fracture spacing versus strain is plotted in Fig. 2(b). At low strains the spacing is difficult to control uniformly, as noted in the error bars, but the spacings become more homogenous at higher strains.

For a wrinkled surface created using biaxial stresses, the length over which a wrinkle is ordered or aligned is referred to as the persistence length ($\zeta$). The persistence length is:

$$\zeta = \lambda \left(\frac{1}{2\Sigma^{1/2}} + 2 \left(\frac{1}{4(1 - \nu^2)} \frac{E_t}{E_s}\right)^{1/3}\right)$$  \hspace{1cm} (4)

\(^\ddagger\)where $\Sigma$ is not the strain applied prior to swelling, but rather the strain applied to the rigid upper layer from the osmotic stress developed from swelling. It should be noted that persistence length scales directly with wrinkle periodicity and hence increasing the wrinkle periodicity by increasing UVO exposure time thus increases $\zeta$ (Fig. 2(a)). The persistence length as a function of UVO exposure time is shown in Fig. 2(a).

Similar to previous work on wrinkle patterning,\(^\ddagger\) in our process the stress discontinuity at the fracture causes the primary compressive stress to develop parallel to the fracture line. Therefore, upon exceeding a critical stress, surface wrinkles align perpendicular to a fracture line. This alignment persists for distances up to $\zeta$ away from the defect. Accordingly, if the average spacing between defects is smaller than $\zeta$, the wrinkles align across the entire surface. It should be noted that homogenous fracture spacing is not required for alignment as long as the fracture spacing is less than the persistence length of the wrinkles.

A phase map confirming the balance of oxidation time and fracture strain, i.e. persistence length and fracture spacing, is shown in Fig. 3. For all samples, a finite conversion of the upper layer to SiO$_x$ must be achieved in order to fracture the SiO$_x$ surface layer prior to fracturing the entire PDMS sample. At low UVO times (as seen in the 15 minute UVO sample), the conversion of the silica-like layer is not sufficient to provide fractures when subjected to strains of up to 50%. For longer UVO times, a critical processing strain can produce fracture lines, but systematic alignment of the surface wrinkles requires the applied strain to produce fracture line spacings less than $\zeta$. This condition is satisfied for UVO times and strains in region II; whereas fracture lines in region I only produce local alignment. Although alignment in region II is achieved on average, some regions

![Fig. 2](image-url)  \hspace{1cm} (a) Wrinkle periodicity ($\lambda$) (open symbols) and persistence length ($\zeta$) (closed symbols) versus ultraviolet light/ozone exposure time (● – 0% strain, □ – 10% strain, △ – 25% strain, and ○ – 50% strain). (b) Fracture spacing versus applied uniaxial strain (■ – 30 min UVO exposure, ▲ – 45 min UVO exposure, ● – 60 min UVO exposure).

![Fig. 3](image-url)  \hspace{1cm} (a) Phase map of wrinkle alignment. (b) Wrinkle shift and defect buckling.
are observed where local fracture spacing is greater than \( \xi \). One example of this condition is in the sample exposed to 30 minutes of UVO followed by a 25% strain, the fracture spacing is much larger than \( \xi \) (\( \sim 77 \, \mu m \)), and hence biaxial strain causes the herringbone structure in the wider sections.

While smaller fracture spacings can be achieved at higher strains, it appears that these strains are not necessary to produce surfaces with aligned wrinkles, and perhaps may lead to misaligned regions, as shown in Fig. 3(b). In this high-strain, high-UVO time region, alignment of the surface wrinkles across the fracture line is shifted as fracture spacing decreases.

We believe that the fracture depth is increased in this regime, but this result has not been experimentally verified. Similar to work on stress transfer in the delamination test of thin films, an increased depth of the fracture line would minimize stress transfer between wrinkling regions. For shallow edge discontinuities, sufficient stress transfer leads to correlated wrinkling patterns across the defect. The details of this effect will be reported in a subsequent publication, and we report the observation here as a known limit in our wrinkle alignment process.

In summary, we have shown a simple method to align osmotically-driven surface wrinkles over large length scales without the use of lithography. For this method, no template is required to orient the wrinkles. Uniaxial tension is used to define fracture lines with average spacings smaller than the persistence length. This process applies to elastic systems coated with a thin rigid material that undergoes fracture in uniaxial tension and wrinkles upon equi-biaxial compression above a critical stress. For equi-biaxial stresses induced by swelling, cross-linkable swelling agents can be used to “lock in” the wrinkle structures. Such structures can be used as smart frictional and adhesive surfaces, micro-fluidic devices, and other advanced applications as discussed in recent publications.

**Experimental**

Dow Corning’s Sylgard® 184 was used for the PDMS substrate. The crosslinked PDMS films were prepared by mixing 1 part crosslinker with 10 parts prepolymer. The uncured mixture was poured into a circular mold with a diameter of 50 mm and a depth of 1 mm. The samples were then cured at 70 °C for 2 hours. The cured samples were cut with a dog-bone-shaped template to control the uniaxial strain distribution. The dog-bone samples were subjected to 15, 30, 45 or 60 minutes of ultraviolet/ozone exposure using Geljet’s UV/Ozone cleaner (model number 342). After UVO exposure, the samples were subjected to uniaxial extension in a custom-built strain stage. Upon removal from the strain stage, the samples were immersed in ethanol to wrinkle the surface. Wrinkles were observed while submerged in alcohol. While the longevity of the wrinkle structure has yet to be explored, these structures have remained the same for 6 months while immersed in ethanol. \( \lambda \), \( \xi \), and \( L \) were all quantified using ImageJ software.

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**Notes and references**