

Quantifying Strain via Buckling Instabilities in Surface Modified Polymer Brushes

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KEYWORDS: polymer brush, postpolymerization modification, wrinkling

ABSTRACT A compressive strain applied to bilayer films (e.g. thin film adhered to a thick substrate) can lead to buckled or wrinkled morphologies, which has many important applications in stretchable electronics, anti-counterfeit technology, and high-precision micro and nano-metrology. A number of buckling-based metrology methods have been developed to quantify the residual stress and viscoelastic properties of polymer thin films. However, in some systems (e.g. solvent-induced swelling or thermal strain), the compressive strain is unknown or difficult to measure. We present a quantitative method of measuring the compressive strain of wrinkled polymer films and coatings with knowledge of the “skin” thickness, wrinkle wavelength, and wrinkle amplitude. The derived analytical expression is validated with a well-studied model

system, e.g., stiff, thin film (PS) bonded to a thick, compliant substrate (PDMS). After validation, we use our expression to quantify the applied swelling strain of previously reported wrinkled poly(styrene-alt-maleic anhydride) brush surfaces. Finally, the applied strain is used to rationalize the observed persistence length of aligned wrinkles created during AFM lithography and subsequent solvent exposure.

INTRODUCTION

Buckling instabilities lead to ubiquitous features in nature over a wide range of length scales (i.e. nanometers to kilometers). Common examples in everyday life are wrinkling in skin, imperfectly cured coatings, and thin rigid materials expanding while being bound to a compliant polymer film.¹⁻² In the buckling of thin films, the geometry is typically comprised of a thin, stiff coating (e.g. “skin” layer) adhered to a thick, compliant substrate. A compressive strain, arising from any one of a variety of stimuli, can lead to a buckled or wrinkled morphology having a characteristic wrinkle wavelength and amplitude.³ Significant efforts have focused on exploiting this approach to design surfaces for a wide range of applications in stretchable electronics,⁴⁻⁶ tunable optics,⁷⁻⁹ and anti-counterfeit technologies.¹⁰ In addition, these instabilities have been used as a metrology platform for characterizing mechanical properties of thin films.¹¹⁻¹³

Since the early work of buckled polymer surfaces by Whitesides and coworkers,¹⁴⁻¹⁶ there has been significant efforts to develop a comprehensive physical understanding of surface instability phenomena, particularly in thin polymer films. The mechanics of buckling or wrinkling relate the characteristic length scale of the instability (typically the wavelength) to the mechanical properties of the skin and substrate. Consequently, Stafford et al. have developed methods to quantify properties of both skin and substrate such as the elastic moduli,^{8, 17} residual stress,¹⁸ and

viscoelastic properties¹⁹ through detailed measurement of the wrinkle wavelength and amplitude. These approaches have proven useful in characterizing a number of polymer films and other materials.¹² However, in some systems, the applied strain is unknown or unmeasurable. For example, solvent-induced swelling of oxidized poly(dimethylsiloxane) (PDMS) leads to surface wrinkles due to differential swelling of the bilayer film.²⁰⁻²² Upon solvent-induced swelling, the top film preferentially swells perpendicular to the underlying substrate, resulting in an anisotropic compressive stress on the surface leading to the observed wrinkled morphologies. Similarly, Chan et al. demonstrated thermal wrinkling of a polyhydroxystyrene film sandwiched between a silicon substrate and aluminum thin film superstrate.¹¹ The difference in coefficients of thermal expansion between the layers results in a compressive stress at the polymer-superstrate interface when heated to elevated temperatures.¹⁹ Above a critical compressive stress, wrinkles develop on the superstrate surface. In both cases, the applied strain due to swelling or thermal contraction was unknown. Therefore, the ability to measure applied strain for systems where the strain is unknown may be integrated into buckling-based metrologies for investigating the mechanical properties of thin film systems. Moreover, knowledge of the applied strain may be useful to quantify other properties in buckled thin films (e.g. persistence lengths of aligned wrinkles).

Ultrathin polymer brush surfaces, in particular, are well-known for their unique physiochemical properties, however, measuring their chemomechanical properties is a significant challenge. For example, Huang et al. demonstrated thermal wrinkling of poly(2-hydroxyethyl methacrylate) (PHEMA) polymer brushes tethered to a PDMS substrate.²³ Heating the bilayer above the glass transition temperature of the brush and cooling it back to room temperature placed the film under compressive stress, inducing surface wrinkling. The critical temperature at

which wrinkles are observed can be related to the critical strain necessary to induce wrinkling; however, the strain in this thermal process was unknown.

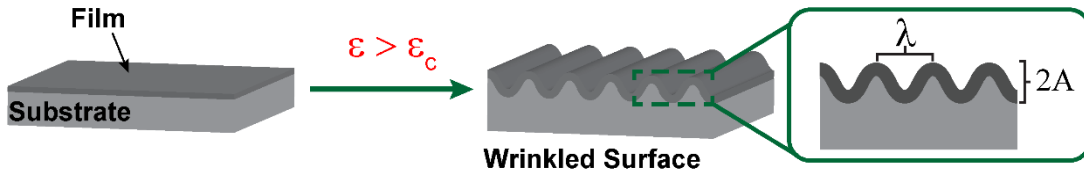
Recently, we reported a simple route to wrinkled poly(styrene-alt-maleic anhydride) (pSMA) brush surfaces via PPM techniques, where the wrinkle wavelength can be tuned using PPM reaction time and anhydride conversion.²⁴ PPM with a diamine modifier (cystamine) under poor solvent (aqueous) conditions limits crosslinking to the near surface region of the brush in a front-like process. This frontal modification reaction divides the brush into two distinct regions: a cystamine-modified “skin” thickness (h_1) and an unmodified thickness (h_2) that is covalently grafted to a rigid silicon support. Exposure to good solvent (acetonitrile) generates a compressive stress arising from strain compatibility between brush layers, one being tethered to the rigid silicon substrate. Above a critical swelling ratio of 1.8, the stress causes an out-of-plane deformation of the untethered surfaces resulting in the observed wrinkled morphologies. From this work, we were able to establish a linear relationship between wrinkle wavelength and anhydride conversion. Furthermore, we demonstrated that the wrinkled brush system conforms to the previously established linear scaling relationship for a rigid-on-soft multilayer construct,^{1,}
²⁴ $\lambda \sim (h_1 h_2)^{1/2} (E_{h_1} E_{h_2})^{1/6}$, where E_{h_1} and E_{h_2} are the Young’s moduli of the “skin” layer and unmodified layer, respectively.

Although we were able to quantify swelling ratios that result in the observed wrinkled morphologies, we lacked the ability to determine the applied swelling strain which led to the observed buckling instabilities. The measurement of applied swelling strain would be straightforward if we were able to determine the modulus of the “skin” and unmodified regions within the brush individually. However, modulus measurements remain a significant challenge in

polymer brush surfaces; thus, we derive an expression to deduce the compressive strain of wrinkled pSMA brushes by measuring cystamine-modified “skin” thickness, wrinkle wavelength, and wrinkle amplitude. First, we validate the derived expression using surface wrinkling of a prototypical model system, e.g., a thin polystyrene (PS) film mounted onto a PDMS substrate. Next, we utilize the derived expression to quantify applied strain of wrinkled pSMA brush surfaces. Finally, knowledge of the applied strain allows us to predict and ultimately validate the persistence lengths of aligned wrinkles created during AFM lithography and subsequent solvent exposure.

Results and Discussion

Calculating Compressive Strain of Wrinkled PS on PDMS



Scheme 1. Schematic illustration of wrinkles developed in a bilayer film (e.g. stiff, thin film bonded to a thick, compliant substrate). λ and A are the wrinkle wavelength and amplitude. The applied strain (ϵ) above the critical strain (ϵ_c) is unknown.

The derived expression to deduce the applied compressive strain is validated using the prototypical bilayer system (e.g. stiff, thin film bonded to a thick, compliant substrate) as shown in **Scheme 1**. Although, the wrinkled pSMA brush system represents a confined system, this bilayer model system is used as a first approximation to establish the following derivation. When a small uniaxial compressive strain, ϵ , above a critical strain, ϵ_c , is applied to the bilayer, the system wrinkles and the wrinkling wavelength λ can be expressed as²⁵⁻²⁶

$$\lambda = 2\pi h_1 \left(\frac{\bar{E}_1}{3\bar{E}_2} \right)^{1/3} \quad (1)$$

where h is the thickness, $\bar{E} = E/(1 - \nu^2)$ is the plane-strain modulus, E is the Young's modulus, and ν is Poisson's ratio. The subscripts 1 and 2 denote the PS film and the underlying PDMS substrate, respectively. Once a wrinkle wavelength is established, further strain is accommodated by increasing the amplitude, A ,

$$A^2 = h_1^2 \left(\frac{\varepsilon}{\varepsilon_c} - 1 \right) \quad (2)$$

The critical strain can be expressed as²⁷⁻²⁸

$$\varepsilon_c = \frac{1}{4} \left(\frac{3\bar{E}_2}{\bar{E}_1} \right)^{2/3} \quad (3)$$

Equation 1 and 3 can be combined to give

$$\varepsilon_c = \frac{\pi^2 h_1^2}{\lambda^2} \quad (4)$$

which can then be substituted into equation 2 to yield an expression relating the applied compressive strain, wrinkle wavelength, wrinkle amplitude, and skin thickness:

$$\varepsilon = \frac{\pi^2}{\lambda^2} (A^2 + h_1^2) \quad (5)$$

Equation 5 is nominally equivalent to the scaling relationship for the wrinkle amplitude derived previously,^{3, 12} with the additional detail of including the critical strain in the expression for a more complete derivation. The expression given in equation 5 will allow us to deduce the applied strain without any prior knowledge of the modulus ratio between the film and the substrate, as this ratio is encoded in the wavelength of wrinkling instability. We believe this is the first application of

equation 5 to deduce the system strain via measurements of the wrinkling amplitude and wavelength. This is critical in the polymer brush system, as the modulus of the modified skin layer and the underlying brush layer are difficult to assess in any quantitative fashion, so we believe this provides a significant contribution to the field when measuring chemomechanical properties.

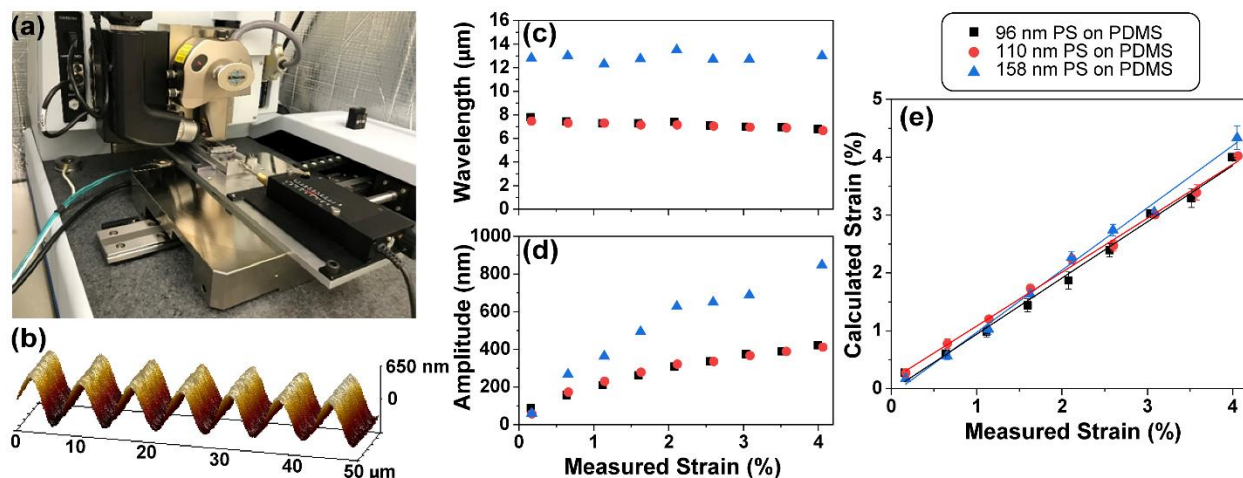


Figure 1. (a) Photograph of the strain stage mounted on a Bruker Dimension Icon AFM for conducting *in situ* AFM measurements while maintaining the applied strain. (b) AFM image of PS ($h_1 = 96$ nm) on PDMS wrinkled at 2.2 % compressional strain. (c) Wavelength and (d) amplitude as a function of applied strain for $h_1 = 96$ nm, 110 nm, and 158 nm on PDMS. (e) Calculated strain versus applied strain for $h_1 = 96$ nm, 110 nm, and 158 nm.

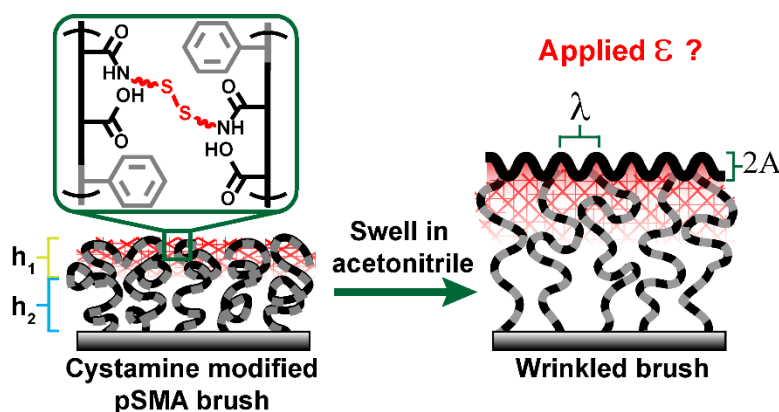
In this work, we utilize the wrinkling of poly(styrene) (PS) supported on a soft elastic substrate of poly(dimethylsiloxane) (PDMS) as a model system (**Scheme 1**) to validate equation 5. The PS on PDMS system was chosen since there has been significant work on this bilayer construct.^{18, 29-30} Furthermore, this bilayer film exhibits a reasonable critical strain given the modulus ratio (e.g. PDMS has an elastic modulus of ≈ 1 MPa and a Poisson's ratio of 0.5, and PS has a modulus of ≈ 3 GPa and a Poisson's ratio of 0.3).²⁹ The tackiness of PDMS also facilitates film transfer of PS, which makes this an attractive model system for wrinkling. The PDMS substrate was clamped onto a strain stage and pre-strained by elongating 5 %. The PS/PDMS bilayer was prepared by transferring a spin cast PS film from a silicon wafer to a pre-strained PDMS substrate using

aqueous immersion.^{8, 12, 30} Three PS films were prepared with thicknesses of 96 nm, 110 nm, and 158 nm and transferred to separate pre-strained PDMS substrates. After film transfer, the wrinkling instability was initiated by incrementally releasing the pre-strain on the PDMS, resulting in compression of the attached polymer film. To assess the wrinkle pattern, the strain stage was placed under an atomic force microscope (AFM) for *in situ* measurements of wavelength and amplitude (**Figure 1a**). For this study, a displacement increment for strain release of 0.25 mm was used, corresponding to a strain increment of $\approx 0.5\%$. A total of ten increments was employed for the *in situ* measurements.

Figure 1b shows a representative AFM micrograph for PS ($h_1 = 96$ nm) on PDMS at 2.1 % compressional strain. **Figure 1c** shows that wavelength remains relatively constant as a function of strain (by equation 1, λ is independent of ε) for various PS film thicknesses ($h_1 = 96, 110,$ and 158 nm) on PDMS. However, the amplitude can be seen to grow non-linearly with strain as expected ($A \sim \varepsilon^{1/2}$, equation 2), increasing to 411 nm, 422 nm, and 847 nm at 4 % strain for 96, 110 and 158 nm PS films, respectively, (**Figure 1d**). From these data, we utilized equation 5 to calculate the applied compressive strain and compared it to the measured strain for all three bilayer films. However, it is important to note that we must also account for the presence of a residual strain from spin coating PS into this calculation. Chung et al.¹⁸ quantified that approximately 0.8 % residual strain occurs when PS films were prepared via spin-coating. The residual strain arises from the fact that spin coating is inherently a non-equilibrium process and some amount of residual stress/strain is trapped in the film after spin coating.³¹⁻³² During the spin-coating process, the polymer film vitrifies and solidifies when the polymer solution reaches ambient temperature. During the solidification process, there is a large volume change that occurs, and this leads to the generation of tensile residual stress in the plane of the coating.

Therefore, we account for the 0.8 % residual strain that occurs when spin-coating PS films in our calculation of applied compressive strain. After accounting for 0.8 % residual strain in our analysis, we showed that the calculated strain versus measured strain are in excellent agreement (**Figure 1e**). The close agreement between calculated and measured strain data corroborates that equation 5 is a valid expression to quantify strain without knowledge of the Young's moduli of the skin layer or underlying substrate.

Calculating Compressive Strain of Wrinkled Polymer Brush Surfaces



Scheme 2. Wrinkled cystamine-modified pSMA brush surfaces, where h_1 and h_2 represent the cystamine-modified thickness and unmodified thickness layers, respectively. The applied strain to induce surface wrinkling is unknown.

After validation of equation 5, we next applied it to the wrinkled pSMA brush system where the applied compressive strain is unknown (**Scheme 2**). It should be noted that these calculations are based on wrinkling data we previously reported.²⁴ In brief, pSMA brushes with an initial thickness of 80 nm were postmodified with cystamine under aqueous conditions at discrete reaction times and various anhydride conversions. The cystamine-modified brush can be divided into two layers – the cystamine-modified crosslinked “skin” layer (h_1) and the unmodified layer (h_2). The thickness of the two layers were determined via time-of-flight secondary ion mass

spectroscopy (ToF-SIMS), as previously reported.²⁴ At each anhydride conversion (k), the morphology of the brush surface was imaged by AFM and, as shown in Figure 2a, the surface appeared relatively featureless. The anhydride conversion was calculated based on the difference in brush thickness before and after postmodification with cystamine.³³ Next, the brushes were exposed to good solvent conditions (acetonitrile) to generate an in-plane compressive stress arising from the mismatch between lateral and perpendicular swelling within the brush. Above a critical swelling ratio of 1.8, the stress causes an out-of-plane deformation of the untethered brush surface leading to the observed wrinkled morphologies shown in **Figure 2b**.

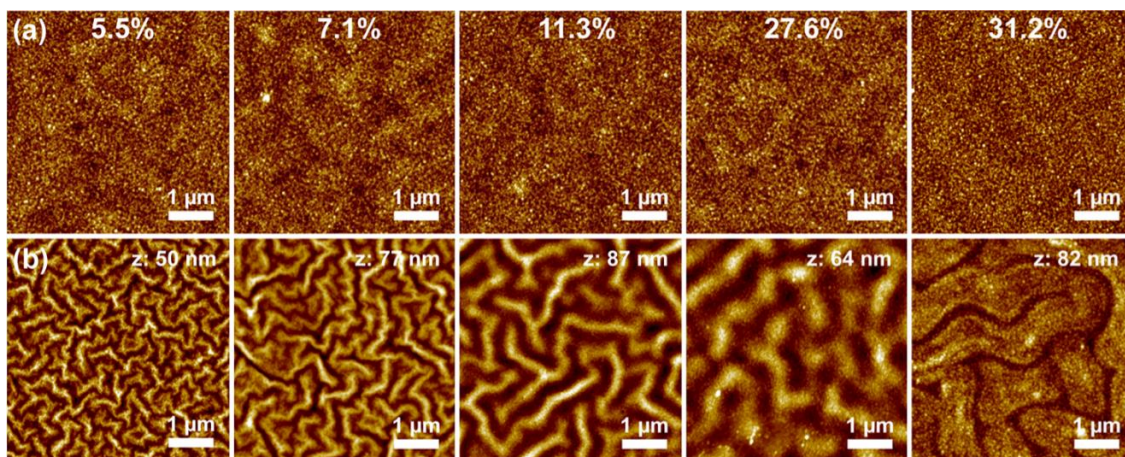


Figure 2. AFM images of (a) cystamine-modified brushes at discrete reaction times and anhydride conversions and (b) subsequent exposure to good solvent (acetonitrile) conditions. Reproduced with permission.²⁴

An empirical relationship we previously derived between anhydride conversion and brush thickness was used to determine the cystamine-modified skin thickness (h_1).²⁴ An example calculation is provided in the experimental section. The wavelength was calculated by taking the radial average of the AFM 2D fast Fourier transform power spectrum. The wrinkle amplitude was assessed from the RMS amplitude by taking a cross-section of the AFM image in Nanoscope Analysis software. An average of 20 cross-sections was taken to minimize error. The

values of wavelength, amplitude, and h_1 for each wrinkled pSMA brush scaffold were used to quantify strain of the wrinkled pSMA brushes according to equation 5. The strain values are shown in Table 1.

Table 1. Calculated values of applied strain based on cystamine-modified thickness (h_1), wrinkle wavelength (λ), and wrinkle amplitude (A).

Conversion (%)	h_1 (nm)	Wavelength (nm)	Amplitude (nm)	Calculated Strain (%)
5.5	7.16	315	3.36	0.62
7.1	9.18	411	5.60	0.68
11.3	15.9	480	6.45	1.26
27.6	37.3	968	6.51	1.51
31.2	39.2	1000	6.65	1.56

The strain values range from 0.62 % to 1.56 % for the wrinkled brush system. These values are representative of calculated strain above the critical strain. For the wrinkled pSMA brush system, we can only calculate strain after wrinkles are observed. However, from equation 3, the critical strain that leads to the wrinkled morphologies is inversely related to the skin's modulus, E_{h_1} .

Although we lack the ability to determine the modulus of the “skin” and unmodified “substrate” layers individually, we previously established a scaling relationship for a rigid-on-soft multilayer construct, where $\lambda \sim (h_1 h_2)^{1/2} (E_{h_1}/E_{h_2})^{1/6}$.²⁴ However, from the previous scaling relationship, we can calculate the modulus ratio, (E_{h_1}/E_{h_2}) , from the wrinkle wavelength thickness of the “skin” and unmodified layers, respectively. An increase in cystamine-modified thickness, h_1 , and an increase in wrinkle wavelength lead to an increase in the modulus ratio, E_{h_1}/E_{h_2} . For example, a cystamine-modified pSMA brush ($k = 5.5$ %) with $h_1 = 7.16$ nm, $h_2 = 74.2$ nm, and

$\lambda = 315$ nm results in a $(E_{h_1}/E_{h_2})^{1/6}$ value of 13.66. Increasing the conversion to 31.3 % with a $h_1 = 39.2$ nm, $h_2 = 52.2$ nm, and $\lambda = 1000$ nm results in a $(E_{h_1}/E_{h_2})^{1/6}$ value of 22.1. Thus, as the skin's modulus (E_{h_1}) increases with an increase in “skin” layer thickness (h_1), the critical strain for wrinkling to occur decreases (equation 3), and the calculated applied compressive strain above the critical strain increases. Although equation 5 allowed us to quantify the applied strain for the wrinkled pSMA brush surfaces, we corroborated the calculated strain values in Table 1 using another set of data described in the next section, specifically the relationship between applied strain and the persistence length of aligned wrinkled morphologies created by AFM lithography technique followed by subsequent solvent exposure.

Quantifying Persistence Lengths of Aligned Wrinkled pSMA Brushes

The ability to control the finer aspects of wrinkled morphologies beyond wrinkle wavelength and amplitude (e.g. wrinkle orientation and persistence lengths) is an important aspect for the design of novel materials with well-ordered and controlled topographies. For instance, if we can quantify applied strain for wrinkled bilayer systems, then we can make predictions about persistence lengths of aligned wrinkled morphologies for applications in microlens arrays,³⁴ diffraction gratings,^{14, 29} and open-channel microfluidics.³⁵

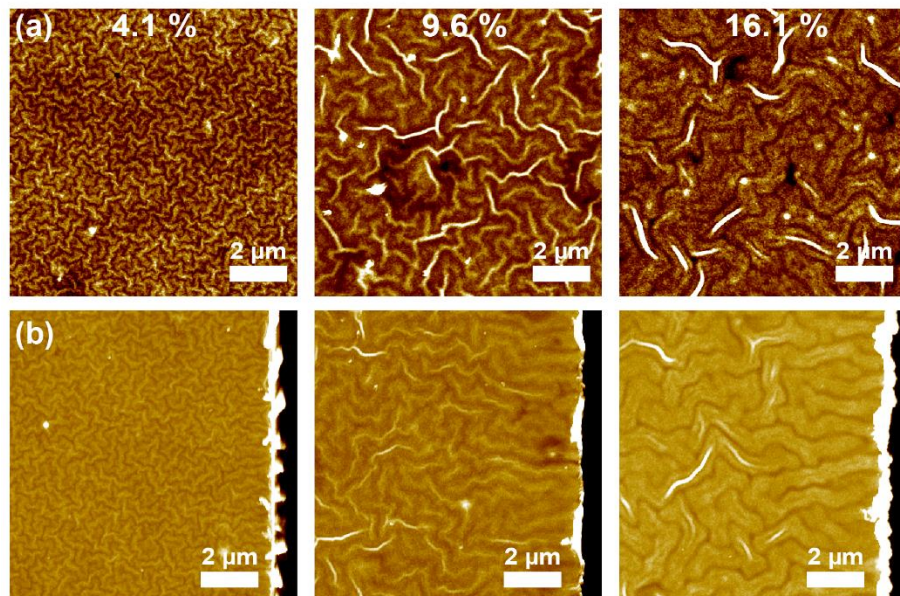


Figure 3. (a) AFM images of unpatterned cystamine-modified pSMA brush surfaces ($H_0 = 95$ nm) with 4.1 %, 9.6 %, and 16.1 % anhydride conversion. (b) Patterned pSMA brushes after swelling in acetonitrile

In this work, we exploit AFM lithography to pattern the pSMA brush surfaces to align the wrinkled morphologies. pSMA brushes with an initial thickness of 97 nm were modified with cystamine to afford brushes with 4.1 %, 9.6 % and 16.1 % anhydride conversion. **Figure 3** shows the AFM height images of the unpatterned and patterned cystamine-modified pSMA brushes after swelling. The unpatterned surfaces (Figure 3a) exhibited an equi-biaxial state of stress, where there is no preferred orientation of the wrinkles and thus show isotropic morphologies. When employing AFM lithography, the wrinkles aligned perpendicular to the boundary (Figure 3b). Near the boundary, the compressive stress in the direction perpendicular to the edge was released due to the discontinuity of the densely grafted polymer brush (stress-free boundary condition). Upon swelling in acetonitrile, the surface experiences stress parallel to the edge resulting in aligned wrinkles in the perpendicular direction.^{2, 8} Near the boundary the wrinkles persist over a finite distance until they become isotropic. The length over which the

wrinkle is aligned is referred to as the persistence length, ξ . The persistence length has been defined as:

$$\xi = \lambda \left(\frac{1}{2\Sigma^{1/2}} + 2 \left(\frac{1}{4(1-\nu_s^2)} \frac{E_f}{E_s} \right)^{1/3} \right) \quad (6)$$

where Σ is the strain applied to the rigid skin layer from swelling-induced osmotic stress. For the case of a bilayer film comprised of a thin rigid film on a viscoelastic substrate at sufficiently low strain, the persistence length can be simplified to the following scaling relationship,^{25, 36}

$$\xi = \frac{0.5\lambda}{\varepsilon^{1/2}} \quad (7)$$

where ξ is proportional to the wrinkle wavelength and applied compressive strain. Using this equation, we first calculated the strain of the pSMA wrinkled brushes in **Figure 3** using equation 5, then we calculated the ξ from equation 7 and compared the calculated ξ values to the measured ξ from equation 8 (Table 2).

Table 2. Calculated versus measured persistence length of patterned pSMA wrinkled brushes

Conversion (%)	h_1 (nm)	Wavelength (nm)	Amplitude (nm)	Calculated Strain (%) ^a	Calculated ξ (nm) ^b	Measured ξ (nm) ^c
4.1	6.48	270	2.12	0.63	1701	1683
9.6	15.13	450	2.54	1.14	2099	2136
16.1	25.38	705	3.67	1.31	3083	3008

^aCalculated from equation 5, ^bCalculated from equation 7, ^cCalculated from equation 8

The persistence lengths were measured following a previously reported procedure.³⁷⁻³⁹ In brief, persistence lengths were measured by drawing contour lengths (5 contours per image) using

ImageJ 1.51a³⁹ software. Tangent vectors were drawn along the lengths of the contour with an angle θ and a distance s between the tangents. The persistence length ξ was calculated according to the following equation:

$$\langle \cos(\theta(s)) \rangle = e^{-s/2\xi} \quad (8)$$

where $\langle \cos(\theta(s)) \rangle$ is the average cosine of the θ between the tangent vectors. The results were averaged to obtain the measured persistence values in Table 2. The measured persistence length showed excellent agreement with the calculated persistence length from equation 7. For example, a cystamine-modified pSMA brush (9.6 % anhydride conversion) after patterning yielded a measured persistence length of approximately 2136 nm. In comparison, a cystamine-modified brush (9.6 % anhydride conversion) with a wavelength of 450 nm and applied compressive strain of 1.14 % resulted in a calculated persistence length of 2099 nm. The close agreement between the calculated and measured persistent length corroborates the calculation strain values for the wrinkled pSMA brush surfaces, further validating equation 5. In addition, we can further corroborate the calculated strain values by plugging the measured persistence length values into equation 7 to calculate applied strain, which can be compared to the strain values from Table 1. For example, a wrinkled pSMA brush with wrinkle wavelength of 450 nm and a measured persistence length of approximately 2099 nm, results in a strain value of 1.11 % from equation 7. The calculated strain is in close agreement obtained from our data in Table 1; the strain is 1.26 % for a wrinkled pSMA brush with a wrinkle wavelength of 480 nm. Therefore, these data further support the derived equation 5, where applied strain can be calculated by measuring wrinkle wavelength, amplitude, and skin thickness. More importantly, the ability to quantify applied

strain of wrinkled films allow us to make predictions about persistence lengths of ordered wrinkled surfaces.

CONCLUSIONS

In summary, we have presented a new method for quantifying the compressive strain of buckled polymer thin films with knowledge of “skin” thickness, wrinkle wavelength, and wrinkle amplitude. The expression was validated using three spin-cast PS films (96 nm, 110 nm, and 158 nm) on PDMS substrates. Wrinkle wavelength and wrinkle amplitude were determined using *in situ* AFM experiments. After verification of our derived expression, compressive strain values of previously reported wrinkled poly(styrene-alt-maleic anhydride) (pSMA) brush surfaces were determined, where the strain values range from 0.62 % to 1.56 %. To further demonstrate the versatility of the analytical expression, persistence lengths of aligned wrinkled pSMA brushes created via AFM lithography were determined. The measured persistence length versus calculated persistence lengths were in good agreement, further validating the derived expression to determine compressive strain of buckled polymer films. This simple route to measure the compressive strain should provide a better fundamental understanding to determine the mechanical properties of polymer thin films.

EXPERIMENTAL SECTION

General. Certain commercial materials and equipment are identified to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Materials. Maleic anhydride (MA), acetonitrile, cystamine dihydrochloride, triethylamine, were purchased from Sigma-Aldrich and were used as received. Styrene (Sty) was purchased from Sigma-Aldrich and was purified by passing through an alumina column to remove inhibitor before use. Silicon wafers (orientation <100>, native oxide) were purchased from University Wafer. The silicon wafers were cleaned prior to use in a plasma cleaner from Harrick Plasma.

Instrumentation and Characterization. Atomic force microscopy (AFM) was performed using a Bruker Dimension Icon instrument. AFM height images were collected in tapping mode (in air) to obtain thin film morphology/topography. The polymer brush samples were imaged using RTESPA-300 probes (Bruker) with a spring constant of 40 N/m. The AFM height images were analyzed using the SPIP software. The wrinkle wavelengths were obtained from the radial averaged cross-section of fast Fourier transform (FFT) of the height image. The wrinkle amplitudes were calculated from the spectral RMS amplitude values by taking a line section of the image using Nanoscope Analysis software. Specifically, an average of 20 line sections was utilized to minimize error in the measurement. AFM lithography was performed on the same instrument with Aspire CT300-10 probes with spring constant of 40 N/m in contact mode (in air). The persistence lengths were measured using a previously reported procedure.³⁷⁻³⁹ In brief, persistence lengths were measured using by drawing contour lengths using the “freehand line tool” ImageJ 1.51a software. The contour lengths were smoothed using the weighted average of five contiguous coordinates. Ten contours were drawn for each image. Tangent vectors were drawn separated by a distance s along the contour length. The angle (Θ) between the tangent vectors was measured and persistence length ξ was calculated according to:

$$\langle \cos(\theta(s)) \rangle = e^{-s/2\xi}$$

where $\langle \cos(\theta(s)) \rangle$ is the average cosine of the θ between the tangent vectors.

Surface-Initiated Polymerization of pSMA Brush. An azo-based trichlorosilane initiator was used and it was synthesized following literature procedures.⁴⁰⁻⁴¹ Silicon substrates were cleaned and functionalized with the azo-based initiator following the procedures reported in the previous chapter. An oxygen free solution containing styrene (1.0 mL, 0.91 g, 8.7 mmol), maleic anhydride (1.0 g, 10.2 mol) and anhydrous acetonitrile (10.0 mL) was prepared and was transferred into a test tube that contains an initiator modified silicon substrate under nitrogen protection. The test tube was heated at 95 °C for various times to obtain polymer brushes of different thickness. After heating, the pSMA substrate was thoroughly rinsed with acetonitrile and dried under a flow of nitrogen.

PPM of pSMA Brush with Cystamine Dihydrochloride under Aqueous Conditions.

Cystamine dihydrochloride (40 mg, 0.18 mmol) and triethylamine (40 μ L, 29 mg, 0.29 mmol) were dissolved in 4.0 mL of DI water. A substrate with pSMA brush on the surface was placed in the cystamine solution at discrete reaction times (from 30 s to 3 h). After PPM, the polymer brush substrate was thoroughly rinsed with DI water and dried with a flow of nitrogen.

Calculation of Brush Thickness Parameters. From previous work,²⁴ cystamine postmodification of a pSMA brush to near-quantitative conversion (k) results in a 66% increase in thickness ($H_0 = 77.9$ nm, $H_f = 129.8$ nm, or $1.66H_0$). Assuming the postmodification reactions occurs in a front-like process, the brush is divided into two distinct regimes: a cystamine-modified “skin” layer (h_1) and an unmodified brush layer (h_2).²⁴ Using this model, we previously established the following relationships, where the cystamine-modified skin thickness layer is $h_1 = (1.66H_0)k$, the unmodified thickness layer is $h_2 = H_0(1 - k)$, and the final total brush thickness

is $H_f = h_1 + h_2$. Utilizing these relationships, a pSMA brush ($H_0 = 84.5$) with anhydride conversion of 9.9% results in predicted values for $h_1 = 13.8$ nm, $h_2 = 76.1$ nm and $H_f = 89.9$ nm.

Sample Preparation for Wrinkling. PDMS was prepared mixing Sylgard 184 at a ratio of 20:1 by mass of base to crosslinker, casting on to a large glass plate, allowing the PDMS pre-polymer to flow and level overnight at room temperature, and final curing at 75 °C for 2 h in a convection oven. Then, 25 mm × 75 mm coupons were cut out and clamped onto a custom-built strain-stage.³⁰ A 5 % pre-strain (50 mm to 52.5 mm) was applied to the PDMS coupon by elongation.

Separately, a silicon wafer (silicon 100, University Wafers) was cleaned in an ultraviolet light-ozone chamber for 20 min to render the surface hydrophilic. Poly(4-styrene sulfonate) sodium salt (PSS) (Aldrich, $M_w \approx 200 \times 10^3$ g mol⁻¹, where M_w is the mass-average molecular mass) was spin coated onto the wafer from deionized water, followed by spin coating of atactic PS (Polymer Source, $M_w = 654.4 \times 10^3$ g mol⁻¹, $\bar{D} = 1.09$) from toluene. The PSS layer was used as a sacrificial layer to facilitate expedient film transfer. The thickness of the initial PSS layer and the total film thickness (PSS+PS) was measured by spectral reflectometry (Filmetrics F20), and the PS thickness was taken to be the difference between the two measured values. The spin-coated wafer was then diced to form clean, fresh edges, and gently placed onto the pre-stressed PDMS before immersing the entire strain stage in water, releasing the film from the silicon wafer and thus transferring it to PDMS.

ASSOCIATED CONTENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

C.M.R. acknowledges support from the NSF Graduate Research Fellowship Program (DGE-1445151) and traineeship support from the NSF NRT program “Interface” (DGE-1449999).

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