Nanoscale Surface Creasing Induced by Post-polymerization Modification

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ABSTRACT Creasing in soft polymeric films is a result of substantial compressive stresses that trigger instability beyond a critical strain and have been directly related to failure mechanisms in different materials. However, it has been shown that programming these instabilities into soft materials can lead to new applications, such as particle sorting, deformable capillaries, and stimuli-responsive interfaces. In this work, we present a method for fabricating reproducible nanoscale surface instabilities using reactive microcontacting printing (μCP) on activated ester polymer brush layers of poly(pentafluorophenyl acrylate). The sizes and structures of the nanoscale creases can be modulated by varying the grafting density of the brush substrate and pressure applied during μCP. Stress is generated in the film under confinement due to the molecular weight increase of the side chains during post-polymerization modification, which results in substantial in-plane growth in the film and leads to the observed nanoscale creases.

KEYWORDS: nanoscale creasing - post-polymerization modification - polymer brushes

In soft polymeric materials, stresses beyond a critical strain can trigger deformations within the film, causing instabilities, which have been directly related to failure mechanisms in several materials ranging from rubber tires to insulating cables. For this reason, polymeric films that undergo buckling, wrinkling, or creasing have generally been avoided. However, in recent years, many groups have observed that programming these instabilities into soft materials can actually improve function in certain polymeric thin film devices, where controlled adhesion, cell patterning, and the fabrication of deformable capillaries for microfluidics all have been demonstrated. Having reproducible control over morphological features is, therefore, an attractive quality in designing materials for a wide variety of applications. In particular, creasing is an instability which results from a large compressive strain in a soft, elastic material. Many studies have shown excellent control of induced creasing through the use of external stimuli such as light, solvent, electric fields, temperature, and surface confinement; however, each of these methods results in structures with microscale features. Nanoscale creases have been reported; however, these systems are rare and require physical cross-linking as well as an external stimuli. Here, we present a system for fabricating controllable, reproducible nanoscale surface instabilities using a combination of polymer brushes and reactive microcontact printing.

Poly(pentafluorophenyl acrylate) (polyPFPA) is an activated ester polymer backbone that is highly reactive toward nucleophiles like primary amines, making it a prime candidate for post-polymerization modification (PPM). Our group has used this polymer backbone in combination with surface-initiated polymerization to decorate surfaces with a diverse collection of chemical functionalities that can be used in a variety of thin film applications. We have observed that performing PPM using a poly(dimethylsiloxane) (PDMS) stamp inked with amino-terminated polymers through microcontact printing (μCP) onto a reactive poly(PFPA) brush layer leads to structures with distinct creases throughout the film that resemble the structures of the sulci of the brain. Herein we report a highly reproducible method for generating surface creasing in which the nanoscale sizes and shapes of the creases can be controlled by...
changing the grafting density of the reactive ester brush layer and the amount of force applied to the PDMS stamp during printing. This dependence on the shape and size of the creases is also corroborated using computational simulations, which provides the ability to predict and design surface creasing of varied shapes and sizes.

RESULTS AND DISCUSSION

The poly(PFPA) brushes used in this study were synthesized through a photoinitiated free-radical polymerization from an asymmetric azo-based silane initiator, which was attached to silicon/silicon dioxide substrates through self-assembled monolayer (SAM) formation. In order to ensure a uniform grafting density throughout the substrate, the polymerization was carried out inside an inert atmosphere glovebox using a custom-built photoreactor to exclude oxygen. A hand-held UV lamp (350 nm, 4.15 W/cm²) was placed directly above the photoreactor, and the polymerization was carried out for a discrete period of time to generate lower grafting density (2 h, 0.363 chains/nm²) and higher grafting density (5 h, 2.58 chains/nm²) polymer brushes. The resulting PFPA brushes all have a smooth topography, with an average root mean squared (rms) roughness of 2.65 nm as measured by atomic force microscopy. The side chain chosen for PPM was a hydrophilic Jeffamine M-2070 (Huntsman Corp.), which is a 31:10 copolymer of poly(ethylene oxide) and poly(propylene oxide) with a molecular weight of 2000 g/mol, where the terminal hydroxyl group has been converted to an amine. The post-polymerization aminolysis reaction between the amino end group of the Jeffamine and the reactive ester of the poly(PFPA) backbone has been shown from previous experiments to be an extremely fast and efficient reaction with a pseudo-first-order rate constant of \( \sim 0.3 \text{ s}^{-1} \). For reactive \( \mu \text{CP} \) (Scheme 1), a 40 mM solution of Jeffamine M-2070 in toluene along with 80 mM of triethylamine was placed on the stamp and dried under a stream of nitrogen. The stamp was then placed onto a PFPA brush substrate and allowed to react for 90 s. Different pressures were applied to the stamp by placing a weight of known mass uniformly on top of the PDMS.

First, Table 1 and Figure 1A describes the typical result of a post-polymerization modification reaction on a polymer brush substrate when carried out in solution. The increase in molecular weight of the side chain (MW = 2000 g/mol) results in an increase in the overall thickness of the film. If one assumes that the grafting density of the polymer chains before and

<table>
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<tr>
<th>original PFPA brush thickness (nm)</th>
<th>pressure (Pa)</th>
<th>brush thickness after PPM (nm)</th>
<th>average QNM modulus (MPa)</th>
<th>static contact angle (deg)</th>
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<td>242.3</td>
<td>&lt;700 kPa</td>
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Figure 1. AFM topography images of PFPA films functionalized with Jeffamine M-2070: (A) from solution, (B) \( \mu \text{CP} \) with a pressure of 18.3 Pa, and (C) \( \mu \text{CP} \) with a pressure of 1.15 kPa.
M is the bulk density, and $F$ is the polymer brush thickness in the dry state, $M$ is the polymer brush thickness in the dry state, $M$ is the molecular weight. The subscript denotes the original (1) and Jefamine-functionalized (2) polymer brush. After PPM, the brush thickness increases from 61.3 nm ($L_1$) to 242.3 nm ($L_2$), with near-quantitative conversion, as evidenced from the decreases in the carbonyl (C═O) stretch at 1785 cm$^{-1}$ and the aromatic side chain at 1523 cm$^{-1}$ as well as the observance of several peaks attributed to the PEG side chain (1100 cm$^{-1}$) in the ATR-FTIR (Figure 2). The film morphology is smooth, with an rms roughness of 2.3 nm. However, Figure 1B,C shows the typical nanoscale creasing pattern observed when the PPM is performed using microcontact printing. These features are reproducible and consistent over multiple experiments (more than 5 with each pressure), where we observed the same average crease size and shape with each trial.

When a pressure of 18.3 Pa is applied on top of the brush using the PDMS stamp, the creases observed are small, with an average width of $107 \pm 10$ nm. When the printing pressure is increased to 1.15 kPa, the creasing size increases to a value of $203 \pm 24$ nm. To ensure the creasing is a result of the confined reaction of Jefamine with the poly(PFPA) brushes and not a result of toluene interacting/swelling the PDMS stamp, the stamp was inked using only toluene and placed in contact with a poly(PFPA) brush substrate. The morphology of the brush was smooth and resembled that of Figure 1A, indicating that the crease formation is a result of the post-polymerization modification with Jefamine. ATR-FTIR spectra of the films indicated a lack of full conversion, where the PFPA C═O stretch and the aromatic stretch of the pendant group are still present (Figure 2).

In order to obtain information about the modulus and adhesion of the film, PeakForce quantitative nanomechanical mapping (QNM) was performed on the substrates. PeakForce quantitative nanomechanical mapping is a scanning probe microscopy technique that allows for nanoscale property mapping of a substrate in real time. This is accomplished by oscillating the cantilever at a frequency below resonance and collecting a force curve at each surface contact. In addition to maintaining a constant peak force, mechanical information, such as the modulus and adhesion, can be extrapolated from these force curves at each pixel, resulting in a map of the mechanical properties like modulus and adhesion. Table 1 shows the average QNM modulus, which was obtained by averaging over the entire modulus map. The average modulus decreases steadily from 99.1 MPa for the poly(PFPA) brush to 15.1 MPa for the brushes functionalized with increasing pressure. As a comparison, the PPM in solution has a modulus lower than 0.7 MPa, which is the lower limit of measurement for the technique. Using cone and plate rheometry (amplitude sweep at constant angular frequency of 10 rad/s), we obtained a storage modulus of 818 Pa for a Jeamine-functionalized PFPA in solution, which matches well with the bottlebrush structure. The decrease in modulus with increasing $\mu$CP pressure, therefore, indicates a greater amount of Jefamine in the brush after PPM, which is indicative of a higher conversion (aminolysis) deeper into the brush layer. It is important to note that the mechanical information obtained from PeakForce QNM is not absolute but rather qualitative in the comparison of different mechanical properties between substrates. While the modulus measurements may change slightly with differences in calibration of the instrument and experimental setup, PeakForce QNM can serve as a useful tool for comparing a wide array of substrates if the experiments and calibration settings are performed consistently throughout experiments. PeakForce QNM aids in determining the mechanism of formation for appropriate models for the simulations as described below. The static contact angle of the substrates also follows a similar trend. Poly(PFPA) has a static contact angle of $96.2^\circ$, due to the hydrophobic nature of the pentfluoroester backbone. A printing pressure of 18.3 Pa yields a contact angle of $52.1^\circ$, with a decrease to 46.4 and $43.2^\circ$ for pressures of 124.3 Pa and 1.15 kPa, respectively. As a comparison, the brushes functionalized with Jefamine by PPM in solution are the most hydrophilic, with an average value of $32.6^\circ$. The steady decrease in contact angle also provides...
evidence for higher conversion with increasing \( \mu \text{CP} \) pressure. The film thickness for each process does not follow the same trend. While the PPM in solution yields a thickness increase of a factor of 4 (61.3 to 242.3 nm), the \( \mu \text{CP} \) with different pressures only increases the thickness by a factor of 2 for the 18.3 and 124.3 Pa and a factor of 2.5 for the 1.15 kPa samples.

The creases observed in Figure 3 were reproduced using computational simulations. In the models used, it was assumed that the effect of pressure due to the weight of the PDMS stamp correlated to the depth of Jeffamine penetration. With greater applied pressure and penetration depth, a larger extent of aminolysis and subsequent bottlebrush formation occurred. In the models, the top layer of the plate was defined as the depth of the film where Jeffamine had reacted with the poly(PFPA) brush, and the bottom layer contained the remaining unreacted poly(PFPA). Analytical and computational studies of a bilayer system have shown that the wavelength of creases is proportional to the thickness of the top layer.\(^{38,40–42} \)

As a result, a thin film on top of a soft material upon exposure to stress beyond a critical value forms small-sized creases, whereas a thick film can form large-sized creases. In our experiments, as observed in the low grafting density (0.363 chains/nm\(^2\)) cases, an increase in pressure leads to an increase in average crease size after post-polymerization modification. This trend suggests that a larger pressure results in more penetration of Jeffamine into the brush layer during post-polymerization modification, which results in the formation of a thicker top layer and creases with relatively large wavelengths. From Table 1, the thickness increases by a factor of 2 upon ceasing, which implies significant growth along the direction normal to the film. Figure 3A displays a simulation with small creases, which were formed under low-pressure conditions and correlate to the experimental data shown in Figure 18. Figure 3B has large-size creases simulated under a high pressure and correlate to Figure 1C. Here, the penetration depth of the Jeffamine into the film layer in the lower pressure simulation is considered to be smaller than the high-pressure simulation. From the experimental results, we can assume that the ratio of the penetration depth in the two models is equal to 2, which is reasonable from an analytical viewpoint since the wavelength of the buckled thin film on the substrate is linearly proportional to the thickness of the film.\(^{41} \)

Due to the complex nature of the system, it is difficult to develop an exact model for the surface functionalization. However, while simple in design, the proposed bilayer model results in simulations that mimic the experimental results, giving insight into the mechanism responsible for crease formation.

When the \( \mu \text{CP} \) with different pressures is performed on films of higher grafting density (2.58 chains/nm\(^2\)), the distinct creasing morphologies change drastically (Figure 4A–C). Using a printing pressure of 18.3 Pa, the creases have an average width of 417 ± 26 nm. Unlike the lower grafting density films, increasing the printing pressure to 124.3 Pa results in a decrease in crease size (350 ± 36 nm). The size of the features decreases even further when using a printing pressure of 1.15 kPa, where an average crease size of 243 ± 25 nm is observed. The modulus and adhesion maps are also shown in Figure 4D–F and Figure 4G–I, along with the average modulus and static contact angle measurements provided in Table 2. Unlike the lower grafting density brushes, an increase in printing pressure results in a steady increase in average modulus from 14.0 to 21.0 MPa for a pressure increase from 18.3 Pa to 1.15 kPa. The PPM in solution, however, still results in a modulus value less than 0.7 MPa. The increase in modulus observed for the film’s \( \mu \text{CP} \) with increasing printing pressure is likely due to the extremely dense packing of polymer chains on the substrate, which are more resistant to compression.\(^{43} \)

The static contact angle decreases only slightly with the increase in printing pressure, with an average value ranging from 55 to 53°. Also, an increase in film thickness for each substrate is observed with an increase in printing pressure, from an original value of 435.8 to 459.2, 515.1, and 736.6 nm for the 18.3 Pa, 124.3 Pa, and 1.15 kPa, respectively. Like the lower grafting density brushes described above, this value is still significantly less than the increase in film thickness that occurs when PPM is performed in solution (435.8 to 1410.0 nm).

For both the lower grafting density (0.363 chains/nm\(^2\)) and higher grafting density (2.58 chains/nm\(^2\)) brushes, the macromolecular monolayers are covalently linked to the substrate during the polymerization, which leads to a constant grafting density for the polymer layer before and after the PPM is performed. When the PDMS stamp inked with Jeffamine is placed into contact with the PFPA brush layer, the reactive species can penetrate, solvate, and react with the PFPA brush layer, which generates a large change in the molecular weight of the grafted polymer, leading to an increase in film thickness. In \( \mu \text{CP} \), the PDMS stamp confines or restricts growth normal to the surface, and therefore, the stress resulting in the film from PPM causes in-plane growth in the film, which leads to the
observed nanoscale creases. This creasing due to in-plane growth is similar to the phenomenon that occurs when a cross-linked gel is swollen in response to a favorable stimulus.1,9,24,27,30

In the lower grafting density films, the increasing size of the creases with increasing pressure is likely due to the increased penetration of the Jeffamine into the brush layer. This trend is also evident in the decreased modulus and static contact angle values for the films fabricated with increased pressure. With respect to the higher grafting density films, the crease size actually decreases with increasing pressure, likely due to less free volume available for in-plane deformation. This is also evident in the increasing modulus of the films, which are more resistant to compression.

It is important to note that the pressures applied to the PDMS stamps during printing are notably low. However, as evidenced by changes in thickness, contact angle, modulus, and adhesion, post-polymerization modification on each substrate does take place to yield films with different properties and morphologies. This trend indicates that the small and subtle pressures applied are sufficient to alter penetration and solvation of the brush undergoing PPM. We have exhausted every other variable (to the best of our ability) besides the amount of pressure applied to the PDMS stamp, and this consistently results in creases of different sizes.

Computational simulations for the high grafting density substrates are shown in Figure 5. For these substrates, although more penetration of Jeffamine into the brush is expected with larger pressures on top of the film, the changes in thickness are not remarkable, which indicates that the acting pressure causes

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<tr>
<td>435.8</td>
<td>PPM in solution</td>
<td>1410.0</td>
<td>&lt;700 kPa</td>
<td>33.4</td>
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Figure 4. AFM topographic (A–C), modulus (D–F), and adhesion (G–I) data for PFPA films functionalized with Jeffamine M-2070 by μCP. (A,D,G) 18.3 Pa, (B,E,H) 124.3 Pa, and (C,F,I) 1.15 kPa.
confinement in the direction perpendicular to the substrate, resulting in greater growth along the in-plane direction rather than the normal direction. In the FE models, the growth factor was adjusted to account for greater in-plane growth rather than growth normal to the surface. The growth ratio in each direction is based on the crease size ratio obtained from the experimental results. Greater in-plane growth results in the top layer having a lower thickness, which ultimately leads to smaller-sized creases. Although the total thickness change of the film is larger in the high-pressure case than in the low-pressure case, the thickness of the top layer due to post-polymerization modification is still relatively small. This may explain the inverse trend in crease size observed in the high grafting density substrates.

In Figure 5A, which correlates to the experimental morphology in Figure 4A under the lowest pressure, the growth normal to the surface is greater than that of in-plane growth, resulting in the formation of a thick film with large creases. Contrary to the low-pressure experiments, the influence of a greater pressure on the PDMS stamp leads to a change in the growth pattern from the direction normal to that of in-plane. These simulations are shown in Figure 5B,C and correlate to the experimental data in Figure 4B,C, respectively. This subtle change creates a film with smaller thickness changes, which produces smaller creases in the film. These simulations are in agreement with the experimental results and can further be corroborated in Figures S2 and S3, which display the crease size ratios and amplitude ratios for the simulations and experimental data.

CONCLUSION

Using µCP on poly(PFPA) brushes, we have introduced a method to both fabricate and control nanoscale creasing in ultrathin films using simple post-polymerization modification. The versatility of this method and ease of fabrication allows the generation of creases with controlled size simply by varying the pressure applied to the stamp during the printing process. This method was corroborated with simulations, which may allow for creased surfaces that can be easily manipulated for a desired application. Also, the reactive polymer used for PPM can be varied in terms of molecular weight and chemical functionality, which should open the door to a wide variety of applications in areas such as nanoparticle-directed assembly, thin films with increased surface area, sensors, and stimuli-responsive coatings.

Since the measurement of penetration depth and growth ratio in experiments is a challenging question, computational methods can help to further elucidate this process as well as quantify the crease morphologies. We are further investigating the subtle effects of pressure on the reactive printing process, as well as the influence of surface tension to further elucidate the mechanism of crease formation in these thin films.

MATERIALS AND METHODS

Materials. Silicon wafers (orientation (100), native oxide) were purchased from University Wafer. The PDMS stamps were made using a SYLGARD 184 silicone elastomer kit from Dow Corning. Solvents were purified using an MBraun purification system (MB-SPS). Jeffamine M-2070 was provided as a gift by Huntsman Chemical. All other chemicals were purchased from Sigma-Aldrich or TCI and were used as received.

Polymer Brush Synthesis. PFPA was synthesized following previously reported methods. It was further purified using a plug of neutral alumina with DCM as eluent to remove any residual acrylic acid. The AIBN-silane initiator was also prepared using previously reported methods and, after synthesis, stored immediately in an inert atmosphere glovebox. Silicon wafers were cut using a diamond scribe and cleaned by sonication in hexanes, isopropanol alcohol, acetone, and deionized water for 1 min each. The slides were then cleaned using argon plasma for 5 min (Harrick Plasma PDC-32G) and subsequently placed in a slide stainer and transferred to an inert atmosphere glovebox (Mbraun Labstar). A 10 mM solution of the AIBN-silane initiator was prepared in 20 mL of dry toluene in a scintillation vial. The vial was shaken vigorously to ensure full dissolution of the initiator and added to the slide stainer for 16 h. After 16 h, the initiator solution was removed and replaced with fresh toluene for storage until use. PFPA was degassed by bubbling argon through a needle at 0 °C and transferred to an inert atmosphere glovebox. An initiator substrate was sonicated in fresh toluene to remove any physisorbed material. The substrate was then dried under a stream of nitrogen and transferred back into the glovebox. The substrate was placed on a microscope slide (Fisherbrand precleaned microscope slides), and 300 μL of PFPA was added by pipet to the substrate. Another microscope slide was sandwiched on top of the substrate and clamped with four binder clips to ensure intimate contact. A hand-held UV lamp
D. Brooks et al. Multimode AFM, Scanasyst-AIR, substrates were collected using a PeakForce QNM (Bruker ethanol, and Scotch tape. was cut from the remaining PDMS and cleaned with acetone, placed in vial to equal the weight needed to obtain a certain triethylamine. The solution was inked onto the PDMS stamp Jeffamine M-2070 was prepared in toluene with 80 mM of the thinner substrate had a $M_w$ of 148 034 Da with a $\Delta F$ of 1.58. The molecular weight of the polymer from the thinner substrates was used to estimate the grafting density for both bushes since we were unable to isolate enough polymer from the longer polymerization time to get molecular weight information by GPC.

PDMS Stamp Fabrication. A 101 elastomer to curing agent mixture was made of the SYLGARD 184 silicone elastomer kit. The mixture was poured over a glass microscope slide in a Petri dish and cured for 2 h at 70 °C. After 2 h, the patterned stamp was cut from the remaining PDMS and cleaned with acetone, ethanol, and Scotch tape.

Creased Film Formation. Two milliliters of a 40 mM solution of Jeffamine M-2070 was prepared in toluene with 80 mM of triethyamine. The solution was inked onto the PDMS stamp using a cotton swab, and the solvent was evaporated under a stream of nitrogen. This was repeated several times in order to ensure a uniform coverage on the stamp. The stamp was then placed on the polymer brush substrate for 90 s. The substrate was then rinsed vigorously with toluene and dried under a stream of nitrogen. In order to obtain different pressures, the weight of the stamp and the weight added to the top of the stamps were varied. In the case of additional weight, sand was placed in vial to equal the weight needed to obtain a certain pressure.

Substrate Characterization. The wrinkled morphologies of the substrates were collected using a PeakForce QNM (Bruker Multimode AFM, Scanasyst-AIR, k = 0.4 M/N, resonant frequency ($f_0$) = 50–90 kHz). A 10 and 3 μm scan was taken for each substrate. The average number of creases for each substrate was calculated by measuring the distance from the end of a crease to the middle of a neighboring crease using Nanoscope Analysis Software (Bruker) and taking an average from over 30 different line profiles. The infrared spectra of the substrates were taken using a Nicolet model 6700 with a grazing angle attenuated total reflectance accessory at 256 scans with a 4 cm⁻¹ resolution. The thicknesses of the thinner polymer brushes were measured using a M-2000 spectroscopic ellipsometer (J.A. Woollam Co., Inc.) with a white light source at three angles of incidence (65, 70, and 72°) to the silicon wafer normal. The data were modeled using a Cauchy layer with an extinction coefficient of 0 and refractive index of 1.50 for the polymer brush layer. The thicker polymer brushes were measured using a Veeko Dektak 150 with a 3 mm radius stylus. Rheometry was performed using an Anton Paar modular compact rheometer (MCR 302), using an amplitude sweep at a constant angular frequency of 10 rad/s.

Computational Methods. To find the deformation field of a growing film in a bilayer model, decomposition of deformation gradient theory was carried out. Deformation gradient, $F$, is represented through the elastic tensor, $A$, which induces stress and a growth tensor, $G$, which causes volume change.

$$F = A \cdot G$$

Here, $F = \partial \sigma / \partial x$ and maps the initial configuration to the current configuration. Although both $G$ and $A$ tensors may be incompatible deformations, their multiplication, $F$, should be a compatible deformation. Generally, the basic concept is valid to both isotropic and anisotropic growth. Among other factors, the growth tensor typically depends on the stress state and deformation. For simplicity, it was assumed that the growth process has a known spatial distribution, insinuating that all of the information is independent of stress. The boundary value problem of the swollen gel is also equivalent to that of a hyperelastic solid. The growth of soft film can, therefore, be modeled by a hyperelastic material with a strain energy function $W(A)$, where the Cauchy stress, $\sigma$, is related to the strain energy function by

$$\sigma = A \cdot \frac{dW}{dA} \cdot p$$

where $p$ is the hydrostatic pressure and $I$ is a second-order unit vector. In the absence of any body force, the mechanical equilibrium imposes

$$\text{div} \ \sigma = 0$$

where “div” is the divergence operator in the current configuration. There are several proposed material behaviors for hyperelastic materials. Here, the Fung model was implemented and is given by

$$W = \chi (e^{Q} - 1)$$

where $\chi$ is a constant and $Q$ is a function of the three principal strain components.

To predict the morphologies after the onset of instability in the growing polymer brush, a computational model based on nonlinear finite element with anisotropic growth in bilayer film was carried out. In the computational model, a soft plate which mimics the polymer brush film is partitioned to the two layers; the top layer mimics the growing soft film with chemical reactions due to the polymerization process, and the bottom layer is considered as the relatively stiff substrate, as shown in Figure S1. Determination of the thickness in the bilayer model was based on experimental results and analytical predictions. The thickness ratio of the bilayers in the different models was determined based on the size of creases from the experimental results. For the growth ratio in the normal and in-plane directions, we considered different mechanisms for the low and high grafting density cases. The bottom surface of the substrate layer was fixed, and symmetry boundary conditions were employed along the sides of the soft plate. To maintain the accuracy and efficiency of the computational model, a soft plate with moderate dimensional sizes was chosen to produce the creasing patterns. Growth of the film is considered as the anisotropic growth, which allows growth to be controlled in normal and in-plane directions. The growth was simulated via thermal expansion; anisotropic growth was modeled by adjusting different thermal expansion coefficients in different directions. The outer surface of the film model was allowed to be in self-contact, and small structured mesh is distributed in the model. Dynamic-Explicit solver, which is suitable for large deformations and both nonlinear and quasi-static problems, was implemented to perform the morphological changes in the growing film. In the dynamic model, the inertial force acts as the perturbation to trigger instability. Deformation patterns after instability are not guaranteed to be exactly symmetric, even though the initial model is symmetric. Robustness studies concluded that as long as the mesh size is small enough, then the qualitative features of the model do not depend on mesh size. The created patterns of the model after growth and instability do not depend on the absolute values of the elastic moduli for the film and substrate; they only depend on the modulus ratios. Material properties of the film are considered to be growth-dependent since these properties show a decreasing trend as the reaction time goes on based on the experimental data (Figure S4).

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.5b04144.
Additional information on the methods used for the simulations (PDF)

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