

Electronic Supplementary Information on

Hierarchical Line-Defect Patterns in Wrinkled Surfaces

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Experimental

PDMS solution

15 The substrates were prepared with commercially available Sylgard 184 PDMS by Dow Corning Ltd, Midland, USA. A well-dispersed and degassed mixture of 20 g pre-polymer and 2 g curing agent was used for 1:10 ratio as well as 25 g pre-polymer with 1 g curing agent for 1:25 ratio.

Homogeneous samples

1:10 and 1:25 PDMS were cast each in a 10 cm x 10 cm Polystyrene (PS)-mold, set for 24 h at RT (48
20 h, respectively) and subsequently cured for 4 h at 80 °C. Stripes of 4.5 cm x 1 cm x 0.16 cm (resp. 0.17 cm) were cut out, ultrasonicated in Milli-Q H₂O for 10 min and dried with N₂.

1:25 Inclusion in 1:10 matrix

A 1:10 stripe from the homogeneous sample preparation was punched out in the size of 1 cm x 0.5 cm
right in the middle. The hole was filled with 1:25 PDMS solution just to level out with the surrounding
25 matrix and allowed to set for 48 h at RT. Afterwards another 1:10 layer of 0.1 cm thickness was cast

on top, set for 24 h at RT and then cured at 80 °C for 5 h. Eventually the stripe was ultrasonicated in Milli-Q H₂O for 10 min and dried with N₂.

Gradient inclusion in 1:10 matrix

1:10 PDMS was cast into a 14 cm diameter glass petri dish to fill it up for 2 mm. It was allowed to set
5 for 24 h. A 7 cm x 1 cm hole was punched out from the middle and filled with a slightly modified
gradient of Claussen et al.¹ with halved casting speed to reach a doubled layer thickness. After setting
at RT for 48 h another layer of 1:10 was cast on top of gradient and matrix with a height of 1 mm. It
was allowed to set for 24 h at RT followed by curing at 80 °C for 4 h. Afterwards the gradient with
surrounding matrix was cut out to give a sample of 11 cm overall length and 3 cm overall width, so 2
10 cm of protruding matrix on the long sides respectively 1 cm on the short sides. The sample was
ultrasonicated in Milli-Q H₂O for 10 min and dried with N₂.

Wrinkle generation

The stripes from the above described preparation were attached to a custom-made stretching device,
strained by 50 % and placed in a UV/Ozone (UVO)-cleaner (Novascan PSD-UV 8, Novascan
15 Technologies, Ames, USA) for 90 min. All samples were oxidized at their contact face with the glass
petri dish. This was to ensure a levelled interface of inclusion and matrix and for reproducibility. The
stress then was released instantaneously and wrinkles did form immediately. For the wrinkling process
all samples were oxidized at their bottom sides.

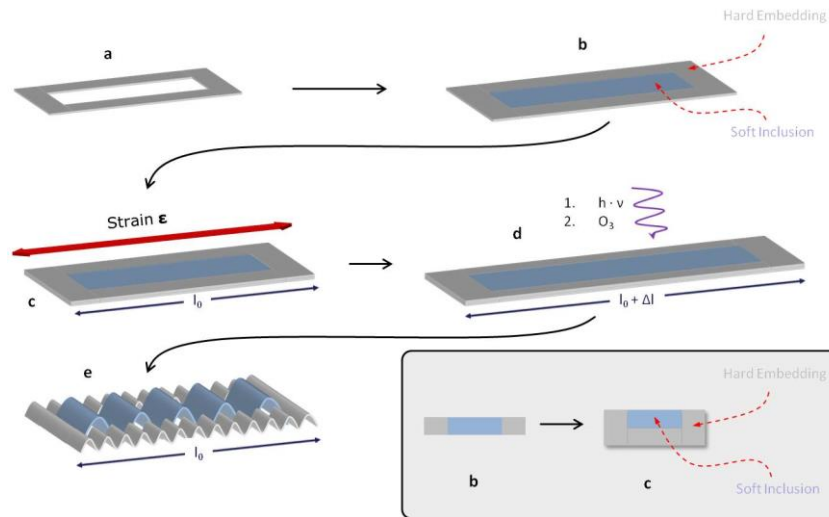


Figure S1: Heterogeneous sample preparation for a soft inclusion into a hard matrix. (a) RT-set, hard PDMS becomes punched out and filled with soft PDMS (b), followed by a cover layer over hard and soft (b \rightarrow c). The sample then is strained (c), UVO-oxidized (d) and strain-released (e) to form wrinkles.

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Characterization

Three different qualitative and quantitative methods were used for characterizing the formed morphologies as well as mechanical properties, namely reflected light microscopy, profilometry and Peak Force QNM.

10 *Optical microscopy*

Optical microscopy was performed with Axiovert 200, Carl Zeiss GmbH (Jena, Germany), equipped with a Plan-Apochromat 10x / 0.25 lens, a Axiomcam ERc 5s computer-controlled camera and AxioVision V. 4.8.2.0 (2010, Carl Zeiss MicroImaging GmbH, Jena, Germany) analysis software.

Profilometry

15 Measurements were done with a Dektak 150 Profilometer from Veeco (Plainview, USA) with following boundary conditions: stylus force = 1 mg for 1:10 and 0.05 mg for 1:25, a stylus radius of 2.5 μm (N-Lite sensor) and a scan length of 500 μm for each measurement.

Peak-Force QNM

Layer thickness and nanomechanical measurements were performed with a Dimension V Icon AFM (Bruker, Karlsruhe, Germany) with Peak-Force QNM software on a 20 μm x 20 μm area with 512 samples / line, Peak-Force set point = 0.15 V, driving amplitude = 150 V and tip radius = 5 nm.

Simulations

- 5 Wrinkling and branching property simulations were performed by solving a modified Swift-Hohenberg-Equation with initial surface noise.

Microscopy setup for *in-situ* analysis

In-situ measurements were accomplished with a custom-made stretching setup that allows control over strain and relaxation speed of the sample, respectively. It is schematically depicted in Figure S2. In order to ensure that a fixed section of the sample's surface may be observable throughout all the relaxation process, both ends of the clamping device were designed to move uniformly. This requires thoroughly focusing on the sample middle. An exemplary recorded video is also available within this ESI.

During the relaxation process the speed is set to 6.1 mm/min at an initial clamping length of 15 mm respectively 22.5 mm for the stretched state ($\epsilon = 50\%$). The samples were not strain released back to the initial length to avoid cracking of the film or bulging of the sample. For the latter also the focus would have been lost.

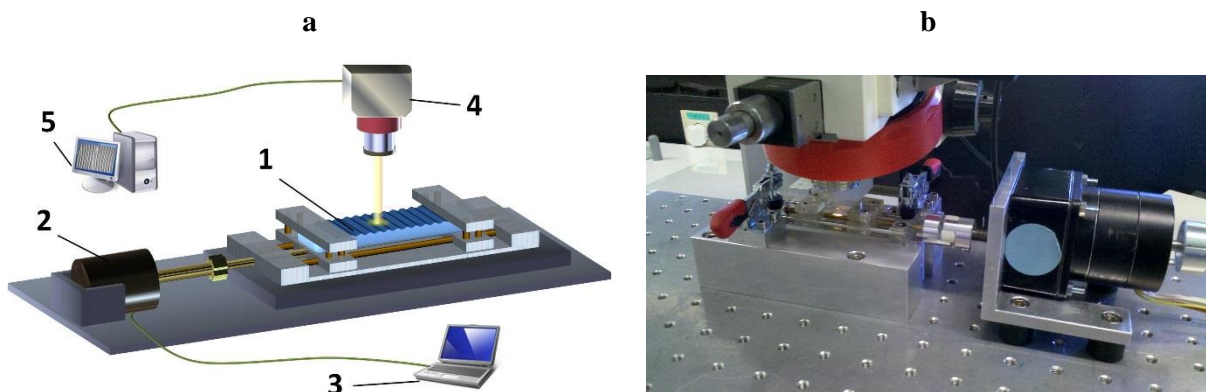


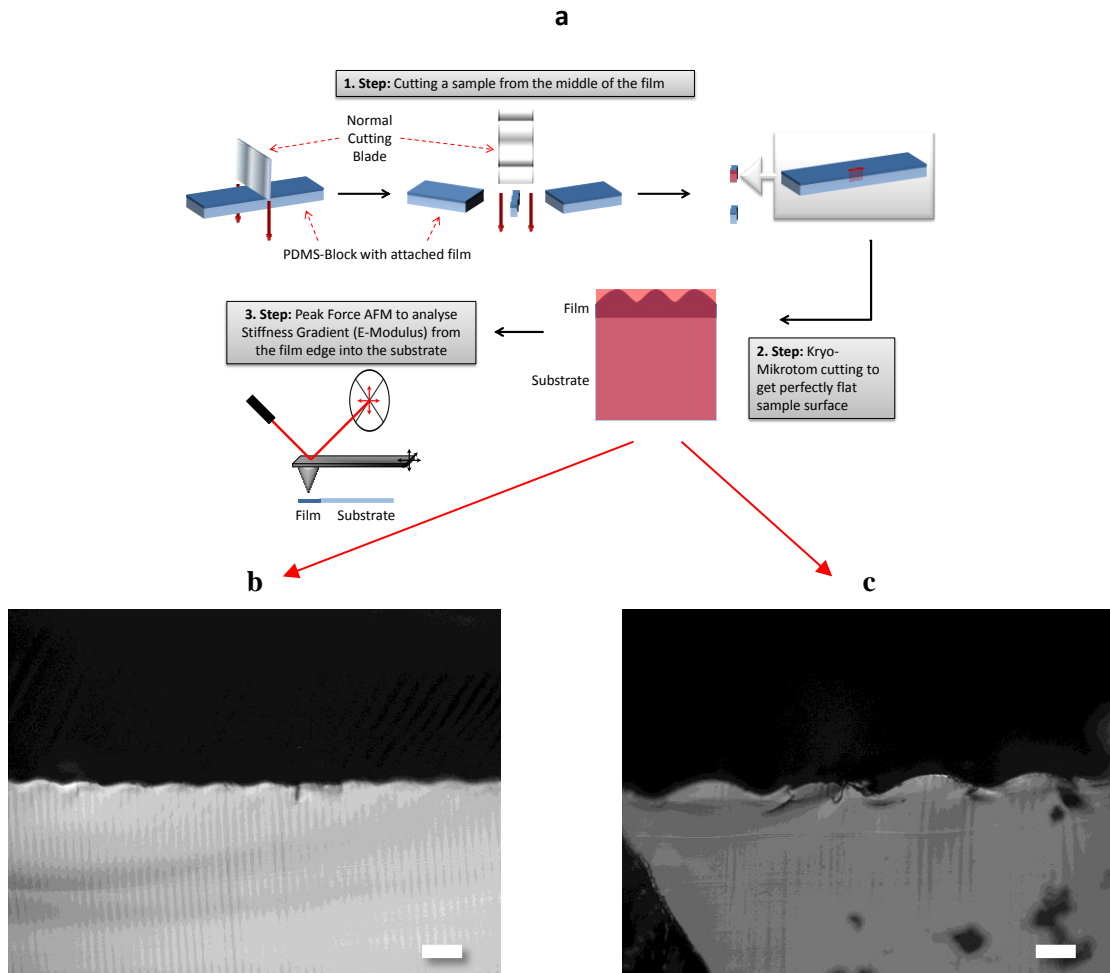
Figure S2: Reflected Light Microscopy setup for in-situ observations of the wrinkle formation schematically (a) and real (b). (1) custom-made stretching device with UVO-oxidized sample, (2) step-

motor to adjust the relaxation speed, (3) computer control for step-motor , (4) reflected light microscope with attached video camera, (5) computer control for microscope and camera

In most cases impurities on the PDMS surface were used to focus. Only in few cases it was possible without.

5 Peak Force QNM

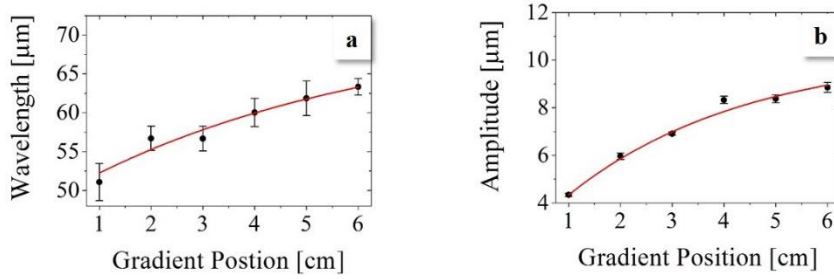
For Peak-Force the UVO-oxidized and wrinkled samples were prepared in the following way: In step 1 a cross profile at the layer edge was cut from the sample middle with a scalpel. For step 2 a cryo-mikrotome was used to smoothen surface (subsequent roughness: $\sim 5\text{nm}$). In the final step 3 the surface was analyzed with Peak-Force QNM and optical microscopy.



10 *Figure S3: (a) Preparation of a UVO-oxidized and wrinkled sample for Peak-Force QNM analysis. (b) and (c): optical microscopy images of the cross profiles from hard (b) and soft PDMS (c); scale bar length is $100\ \mu\text{m}$.*

Wrinkling with a lateral gradient

As for pure PDMS and the composite sample we also performed profilometry measurements to compare given Equations 1 – 4 with experimental data. The wrinkles show an exponential increase that can be explained by the process of gradient preparation where hard and soft PDMS tend to diffuse into each other. ¹ The results fit well to theoretical predictions, especially when compared to the samples with a neat soft inclusion. Figure S4 shows the results of wavelength and amplitude variation from the gradient's hard end (left, 1 cm) to its soft end (right, 6 cm). A slight increase of λ and A is recognizable that were fitted with exponential growth functions.



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Figure S4: Modification of λ (a) and A (b) along the gradient

Table S1: Comparison of theoretical values for λ with the gradient's hard left and soft end right, respectively; the applied strain is $\varepsilon = 20\%$.

Gradient Position	Theoretical λ /μm	λ on Gradient /μm	Deviation /%
1 cm	54.73	51.07 ± 2.40	- 6.69
6 cm	103.40	63.34 ± 1.07	- 38.74

Those slighter deviations can be explained with the different sizes of the samples, as the gradient has distinctly larger dimensions of 90 mm x 40 mm x 3 mm compared to 30 mm x 10 mm x 3 mm for the two-phase-system. It is also the reason, why only 20 % strain were applied: Strain and stress within the sample are connected over $= \frac{\varepsilon}{A}$, where A is larger in the gradient than in the composite (12 mm² respectively 2.7 mm²). A strain of 50 % would therefore have led to a rupture of the sample.

Double gradient along the soft-to-hard-crossover

In contrast to distinct interfaces as shown in the paper itself a few number of sample areas showed diffuse transition between both composite materials, where the transition spreads over several 100 μm . This is due to a partially tilted cut during the sample preparation. Soft and hard PDMS may flow underneath each other and create a blurred stiffness interface. It generates a second gradient, however
5 rectangular to the first and in a much shorter length scale. It features interesting effects, as within these regions the line-defect formation between hard and soft phase took place in a quantized manner, meaning defects did not occur randomly along the short gradient but in bands lateral to the wrinkling direction (Figure S5 a). We also employed numerical simulations on this behavior, where $q(y)$ was used to generate an imposed wavenumber (**Figure S5 c**) that increases linearly along the short
10 gradient. Simulations revealed a similar behavior in branching (**Figure S5 b**), which allowed only few, quantized wavelengths for different gradient slopes and heights. Thus, simulations performed for distinct jumps in the wavelength are in good agreement with the experimentally determined values with slight deviations in the branch positions and step widths.

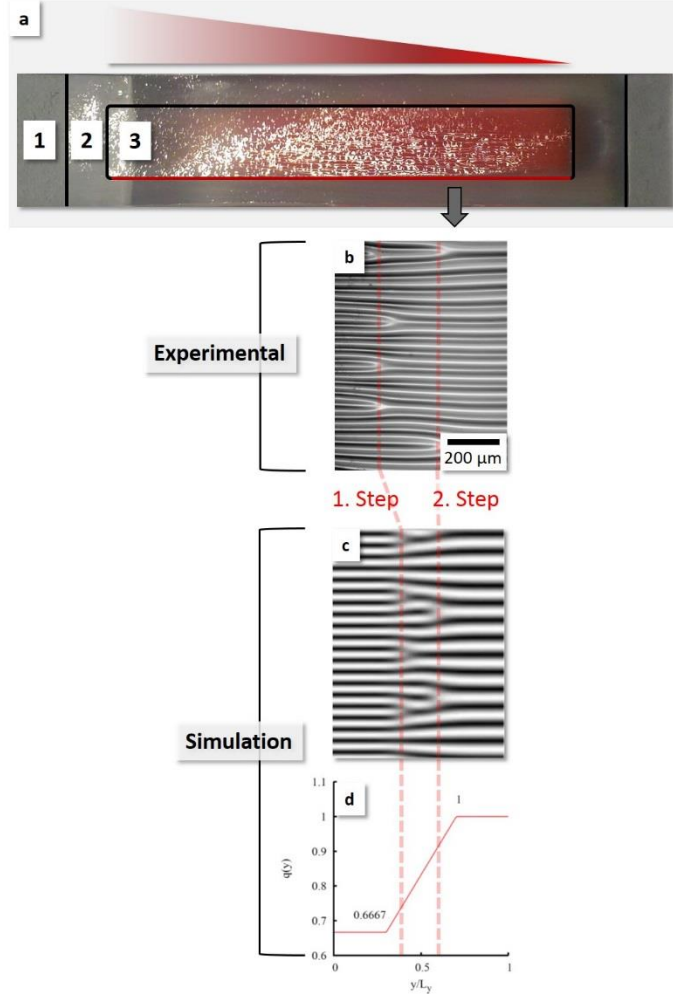


Figure S5: (a) Photo of the gradient sample; (1) shows the unwrinkled matrix, where the sample was clamped for stretching, (2) the wrinkled matrix and (3) the gradient with a stiffness decrease from left (translucent) to right (red dyed).

- 5 (b) Microscopy image of disordered branching over two steps, (c) numerical simulation (d) with a predetermined linear increase of $q(y)$ over a given gradient length L_y

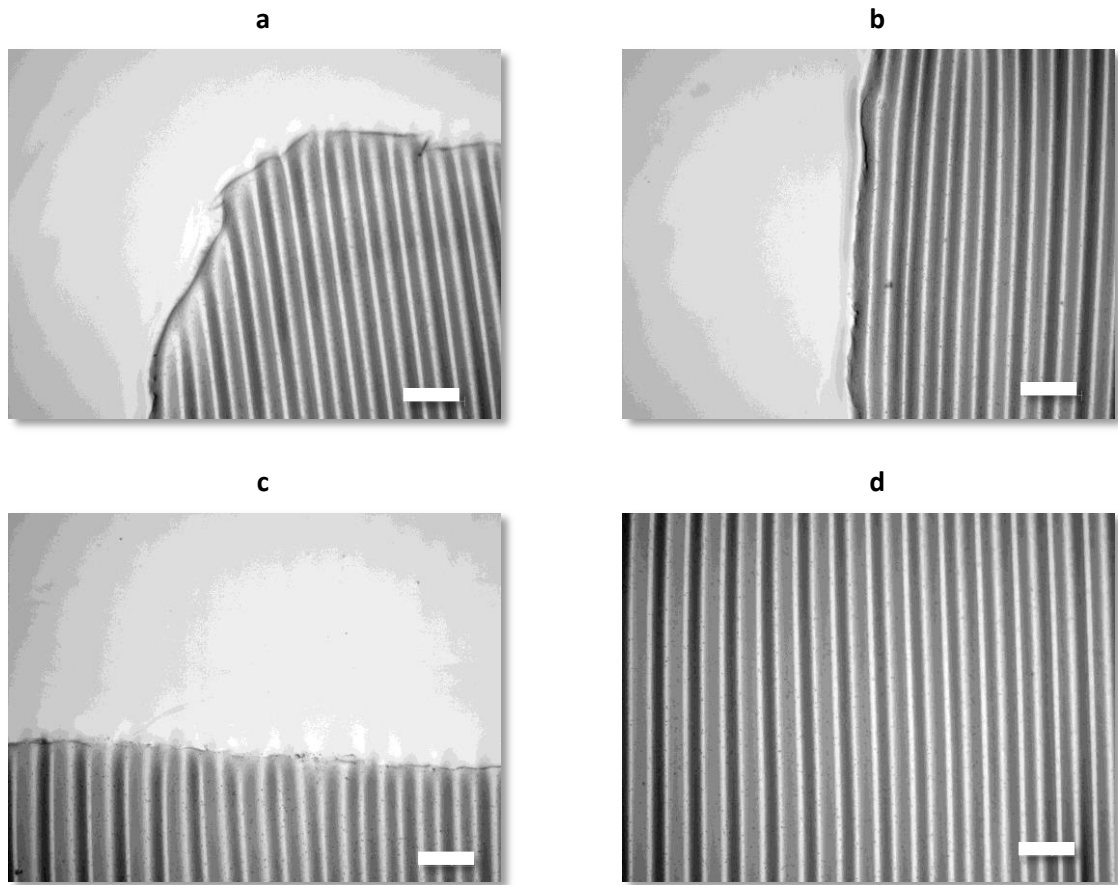
Specific wrinkling

A side aspect of heterogeneous substrates is the ability of specifically wrinkling just one of the

participating PDMS phases. According to $\varepsilon_c = \frac{\sigma_c}{\bar{E}_f} = \frac{1}{4} \left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{2/3}$ the Young's moduli of layer and

- 10 substrate influence the critical strain required for wrinkling. Providing that both hard and soft PDMS get oxidized equally and so \bar{E}_f is constant, their difference in \bar{E}_s can be measured directly. In this experiment the strain was set to $\varepsilon = 10\%$, with plain strain moduli of the soft substrate being \bar{E}_{ss} : 0.3

MPa and for the hard substrate \bar{E}_{hs} : 2.5 MPa. The film's modulus \bar{E}_f had to be determined in a subsequent measurement and was roughly estimated to 25 MPa. According to this a hard substrate starts to wrinkle not before $\varepsilon_c = 10.9\%$, while the soft one buckles already at a critical strain ε_c of 2.5%. We found the expected wrinkling behavior (**Figure S6**), with a well-defined crossover from the hard, unwrinkled to the soft and wrinkled PDMS. The surface corrugations at the boundary of soft and hard substrates induce a stress-field in the hard elastomer. Initial waves form close to the crossover, though they completely flatten out in a range of $\sim 50 \mu\text{m}$. The result is a chemically homogeneous surface, which is in parts mechanically modified.



10 *Figure S6: Wrinkled soft inclusion surrounded by an unwrinkled hard matrix; at the inclusion edge (a), the vertical and horizontal boundary lines (b and c) and inside the inclusion (d) with an average wavelength of $65 \mu\text{m}$ and an amplitude of $3 \mu\text{m}$; scale bar length is $100 \mu\text{m}$.*

References

1. K. U. Claussen, M. Tebbe, R. Giesa, A. Schweikart, A. Fery and H.-W. Schmidt, *RSC Advances*, 2012, **2**, 10185-10188.