Engineering Biomimetic Materials by Harnessing Mechanical Instability of High-Aspect-Ratio Polymer Pillar Arrays

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Various Instabilities in Soft Materials

Dewetting
Herminghaus et al.

Wrinkling
Lin, et al

Spinodal instability
Steiner, et al.

Clustering
Zhang, et al.

E-induced
Chu, et al.

Creasing
Tanaka, et al.

Capillary instability
Alvine, et al.

Rayleigh-Plateau instability
Utada, Weitz
Bottom-up Complex Patterns in Nature

Phyllotactic growth of plants

Sea shells

Structural colors

Instabilities, packing constraints, and simple geometries drive the formation of delicate, detailed, and beautiful patterns

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Harnessing Instabilities to Create Ordered Structures

- **Wrinkling of bilayer films**
- **Buckling of hydrogel films with crosslinking gradient**
- **Pattern transformation**

Dry

Swollen

Glassy (Dry)

Elastic solid

Viscoelastic liquid-like

Dry

Swell

W

P

D

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Pillar Structures in Nature

Lotus leaves

Red blood cells

Circulating tumor cell

Intestinal microvilli

Gecko toe pads

Autumn et al., *Nature*, 2000

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Burdock Seeds

Harnessing Mechanical Instability of High-Aspect-Ratio Polymer Pillar Arrays

**Advantages**

- Mechanically compliant
- Large surface area
- True surface topography

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Fabrication of High-Aspect-Ratio Polymer Pillars Arrays

**Replica molding**

PDMS precursor

PDMS replica

Liquid precursor

Polymer Nanopillars

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**Nanoimprint Lithography**

Capillary force lithography (CFL)

Y. Zhang, et al. Langmuir, 2006; Small 2010;
High-Aspect-ratio (HAR) Micropillar Arrays

However,

polymer pillars are susceptible to surface forces

- Adhesive force
- Capillary force

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Stability of Polymer Pillars In Air

Adhesion Energy vs. Bending Energy

PDMS, E=1.7 MPa

PU, E=183 MPa

Ground collapse

Lateral collapse

\[ E_b^* = \frac{11^{\frac{3}{5}}}{2^{\frac{2}{5}}} \frac{3^{\frac{1}{5}}}{4^{\frac{3}{5}}} (1-v^2)^{\frac{4}{5}} \frac{1}{h^2 W} \frac{(\pi d)^2}{5} \]

\[ E_L^* = \frac{5.32 \times h^3 \gamma_s (1-v^2)^{\frac{1}{4}}}{d^2 w^2} \]


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### Highly Stable HAR Epoxy Pillar Arrays: $E = 3\text{GPa} > E_{\text{crit}}$

<table>
<thead>
<tr>
<th>Shape</th>
<th>Conical</th>
<th>Cylindrical</th>
<th>Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>$7 \mu m$</td>
<td>$9 \mu m$</td>
<td>$9 \mu m$</td>
</tr>
<tr>
<td>$d$</td>
<td>$300-680 \text{nm}$</td>
<td>$500 \text{nm}$</td>
<td>$1 \mu m$</td>
</tr>
<tr>
<td>$w$</td>
<td>$1.32 \mu m$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Si Master

PDMS Membrane

Epoxy Nanopillars


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(Non)wettability on Nanoggrass

Krupenkin et al. \textit{Langmuir} 2004, 20, 3824

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Dry Adhesion in Gecko Toe Pads


6 million setae per gecko
100-1000 spatulae per seta (10^9 per gecko)

Contribution of van der Waals Force

$$200 \, \mu N \times 14400 \times 100 \times 4 = 1150 \, N \, or \, 115 \, kg$$

Single seta force
Setal Density Pad # of
Area Feet

Need only 0.04% of maximal force to hold body weight
Directional Tilt of Fibrils (Setae) Plays a Crucial Role in Rapid Switching bet Attached and Detached States


- Shearing along the backward (releasing) direction opens the cracks leading to low adhesion and friction;
- Shearing along the forward (gripping) direction gives rise to high adhesion and friction

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Fabrication of Slanted Pillars


Anisotropic adhesion and wetting

Hierarchical Slanted hairs


transport of a large-area LCD glass

The glass is 0.9 mm thick, 47.5 x 37.5 cm² in area, and 470 g in weight.

• Increases compliance of the fibrillar structures
  → Better contact between substrate and nanohairs

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Stability of Microstructures During Solvent Drying

Two scenarios of pattern collapse

(a) Capillary force

(b) Plasticization

Capillary Forces on HAR Microstructures

### Laplace pressure

\[ P_1 - P_2 = \frac{\gamma}{R} \]


Stoykovich et al., *Adv. Mater.*, 2003

### Buckling

\[ F = 2\pi r \gamma \cos \theta \]

Cohen et al., *PNAS*, 2003

### Coalescence

Bico et al., *Nature*, 2004

Py et al., *EPL*, 2005

### Capillary meniscus interaction force due to deformation of flat liquid surface

Chandra et al., *Langmuir*, 2009
Replica Molding of PHEMA based Hydrogel Micropillar Arrays


HEMA
Glassy in air
Swellable in water

MMA
Co-monomer

NIPA
Co-monomer
Temp. sensitive

EGDMA
Monomer or crosslinker
PHEMA-co-PMMA Hydrogel Pillar Arrays
Manipulating Collapse Behaviors after Drying from Water

Chandra et al., ACS Appl. Mater. Interface, 2009, 1 (8), 1698
Collapsed Micropillar Arrays As Ultrathin Whitening Layers

Uncoated paper: whiteness ~ 65; thickness ~ 150 μm

CIE lightness index (diffuse reflectance):
0 = black; 100 = perfect white


Vakusic et al., *Science*, 2007
- Whiteness of 60
- Brightness of 65,
- Filaments diameters, ~200-250 nm,
- Scale thickness of 5 μm
Applications of High-Aspect-Ration (HAR) Pillars

**Color Display**

**Wetting**
Krupenkin et al., *Langmuir*, 2004

**Cellular Sensing**
Jones et al.

**Gecko-inspired Adhesives**
Autumn, Fearing, et al.
http://robotics.eecs.berkeley.edu/~ronf/Gecko/interface08.html
What Else Can We Do with Pillars?

Entrapping particles


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Ying Zhang
Summary

• High-aspect-ratio (HAR) pillars offer an interesting example to study and harness mechanical instability

• Fabrication of various pillar arrays and study of their deformation and clustering in air and after drying from water

• Exemplary applications of instability of HAR pillars
  • Dry adhesion & non-wetting
  • Ultrathin whiteness
  • Cell sensing

• Future prospects of HAR pillars
  • Making them responsive, hybrid
  • As templates to assist assembly (epitaxial, phyllotactic...)
  • Exploiting applications in energy harvesting and storage, architecture, biotechnology...