Infrared Radiation-Assisted Evaporative Lithography of Colloidal Films

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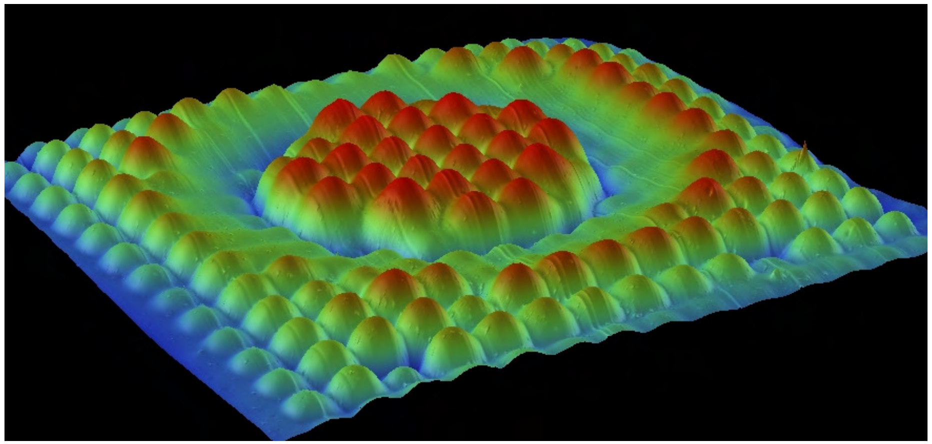
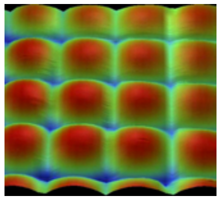
Akzo Nobel, UK





McBain Symposium
December 8, 2010

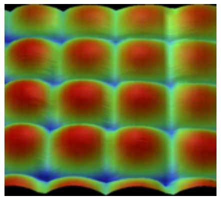
www.surrey.ac.uk

A Fateful Meeting….

1999

ACS National Meeting

New Orleans



Wrongly-Assumed Nationalities….

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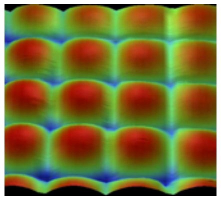


Alex Routh in Princeton

Me in the UK

Routh & Russel's Original Idea

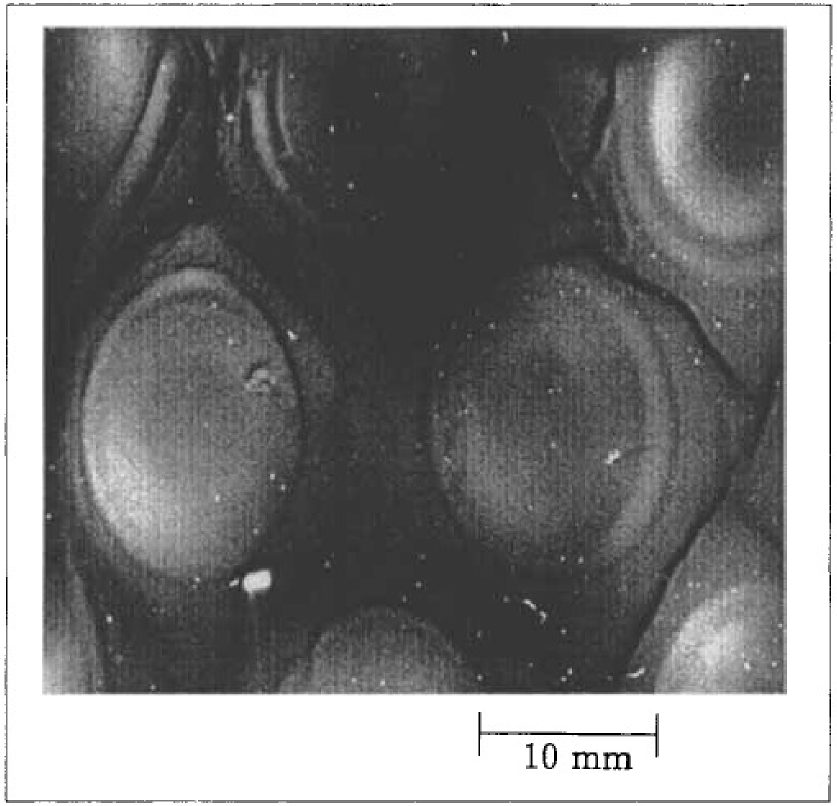


Figure 13. Film with selective evaporation in circular regions.

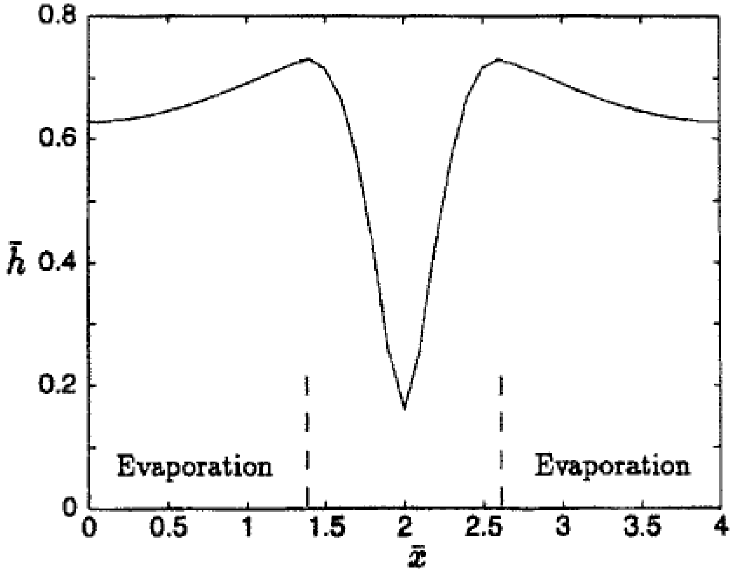
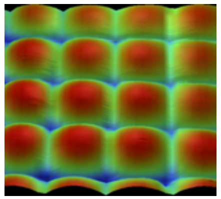


Figure 15. Final film profile with evaporation for $0 \leq \bar{x} \leq 1.4$ and $2.6 \leq \bar{x} \leq 4$.

Pitch of 16 mm



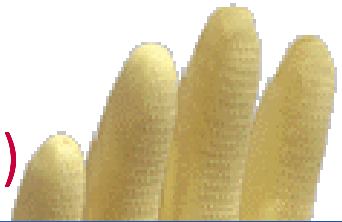
A.F. Routh & W.B. Russel, *AIChE J.* (1999) ***44,*** 2088-2098

Need for Textured Coatings

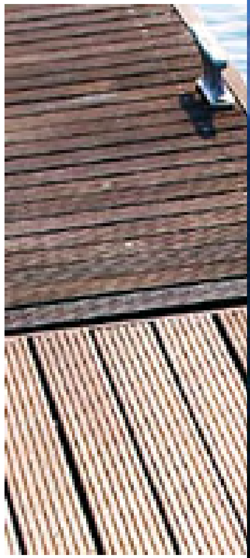
Aesthetic effects or identification (*e.g*. logos)

Introduce partial opacity (light diffusers)

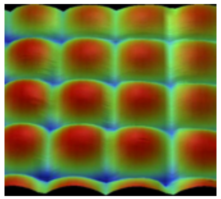
Increased grip (*e.g*. on handles, floors or gloves)



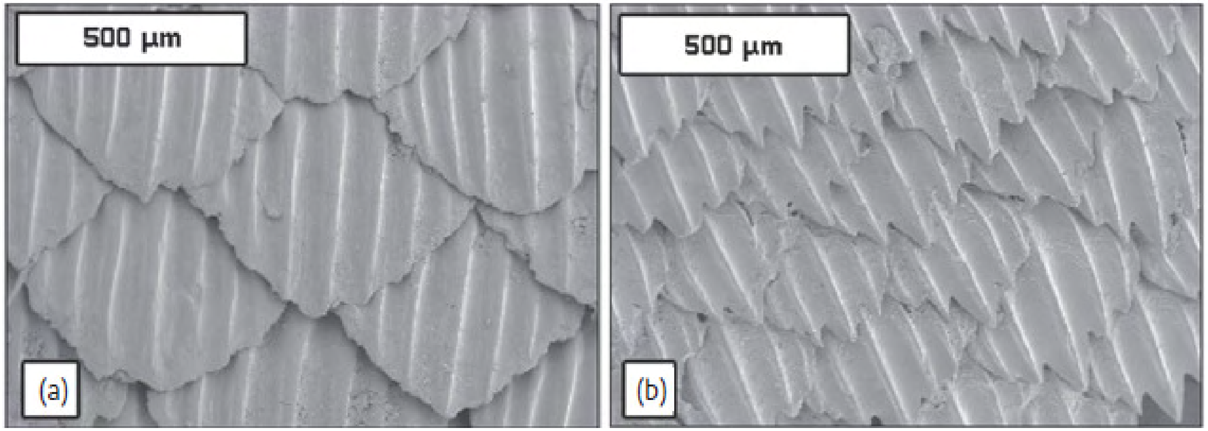
Riblets for drag reduction



Anti-fouling

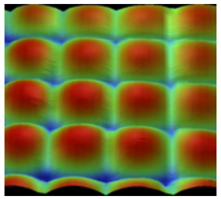


Inspiration from Nature



Placoid scales on Spinner shark (left) and Galapagos shark (right)

- No fouling from algae
- Reduced hydrodynamic drag
- Pitch of 100 m and length of 0.5 mm

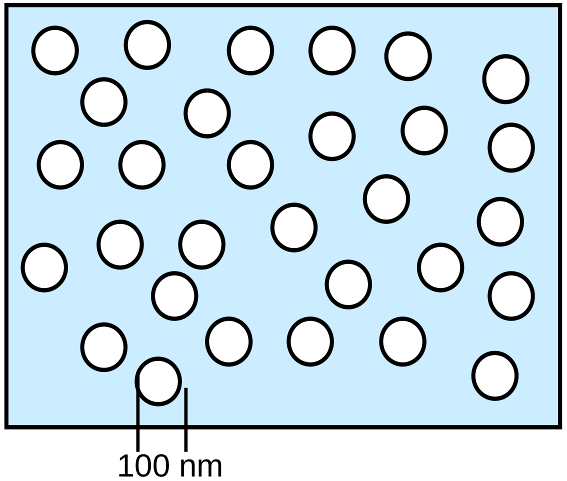


V.A. Bers and M. Wahl, *Biofouling* (2004) **20** (1), 43.

M.L. Carman *et al.*, *Biofouling* (2006) **22** (1), 11.

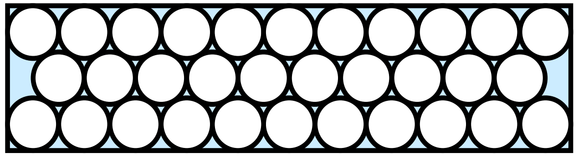
Latex Film Formation

Colloidal polymer-in-water dispersion



Water loss

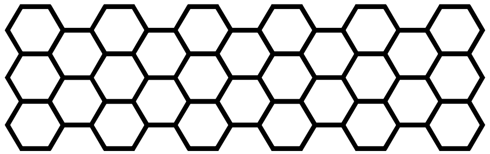
Close-packing of particles



T > Minimum Film Formation Temperature

Deformation of particles

Optical Clarity



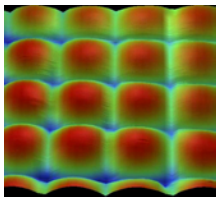
Dodecahedral structure (honey-comb)

Interdiffusion and coalescence

$T > T_g$

Surface tension leads to film flattening!

Smooth Film



The "Film Formation Dilemma"

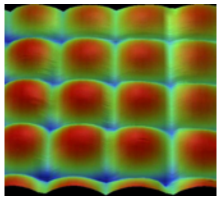
Hard latex (T_g polymer > RT)

- Subject to cracking
- One solution: plasticizers
- **Problem:** releases VOCs
- Another solution: heating/ sintering in oven
- **Problem:** high energy use

Soft Latex (T_g polymer < RT)

- Good film formation
- So... coating
- Po... e/dirt pick-up

How can we obtain a hard latex coating?

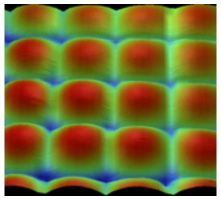


www.mustknowhow.com

The Research Problem

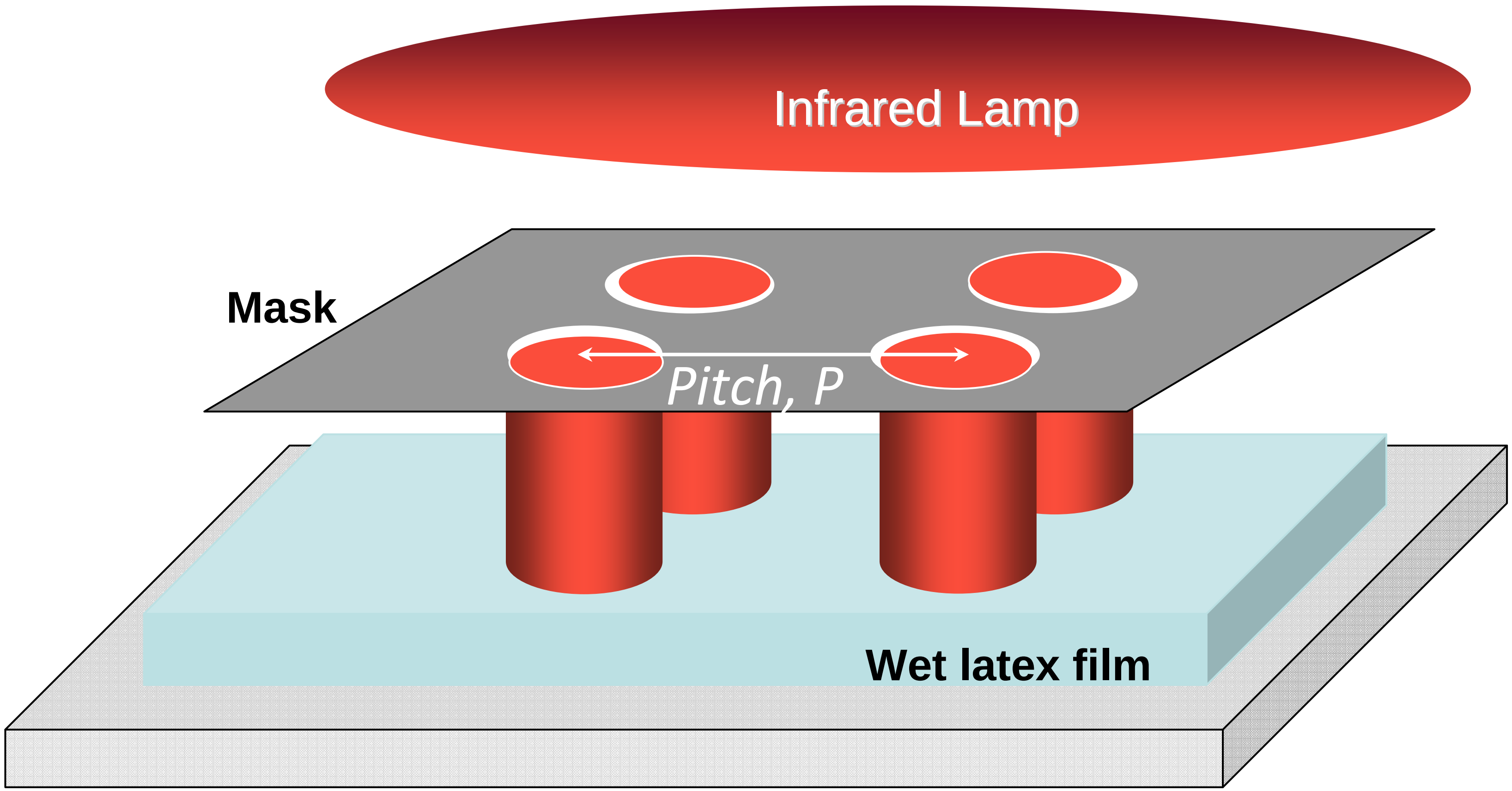
How do you make textured coatings that are:

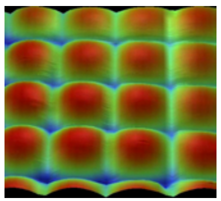
- Waterborne (environmentally-friendly)?
- Hard and scratch-resistant?
- Controllable over a range of length scales?
- *<u>Easy</u>* to make in a one-step process without chemical crosslinkers?



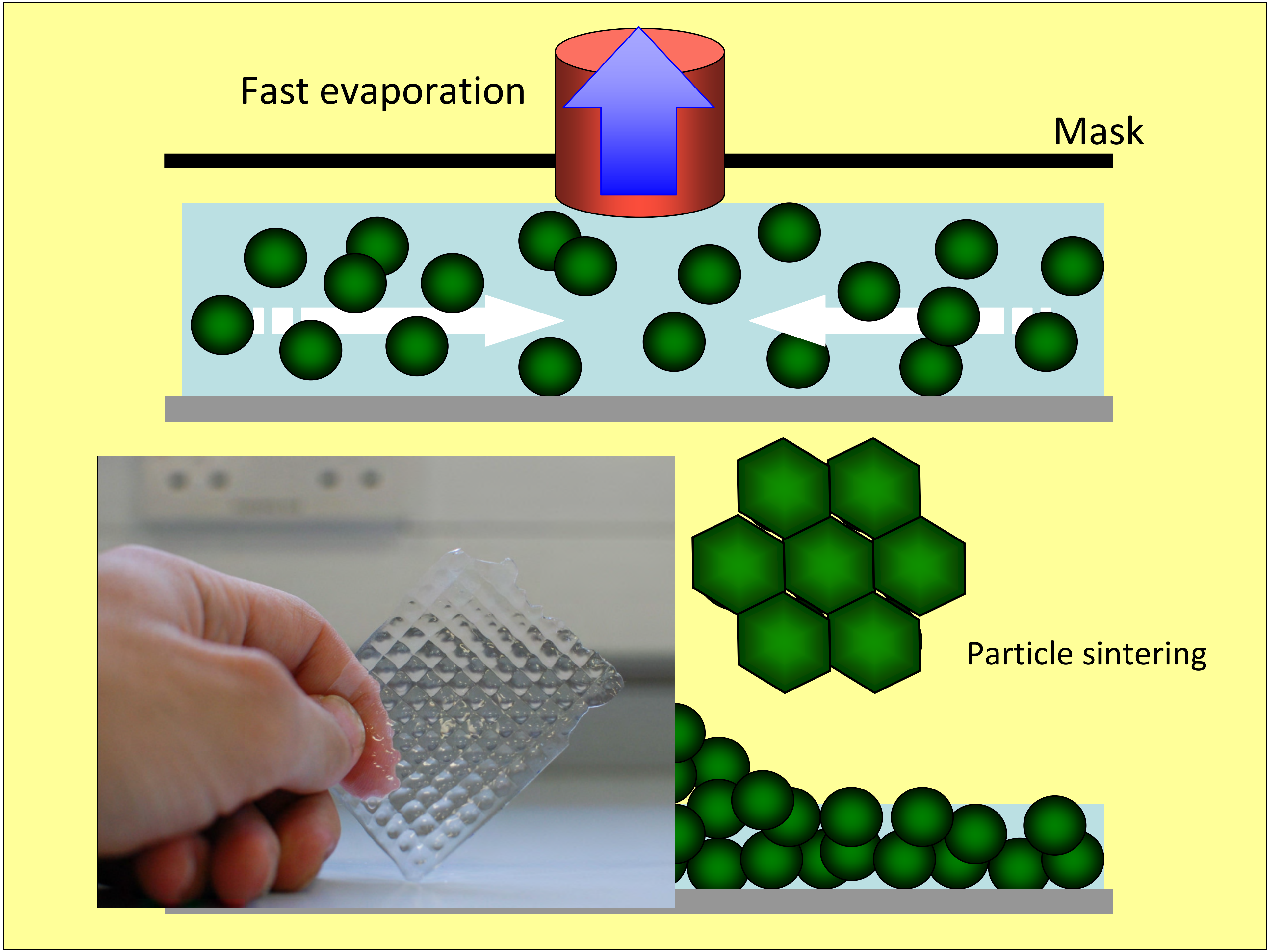
The Answer:

"Infrared-Assisted Evaporative Lithography"

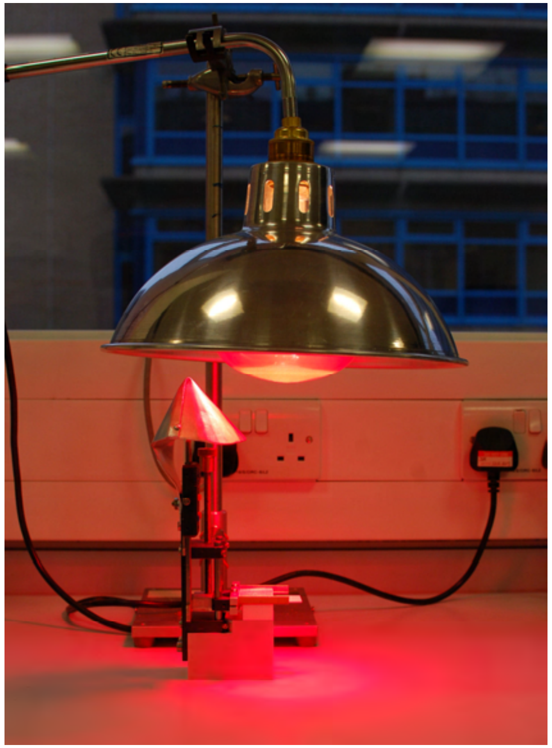


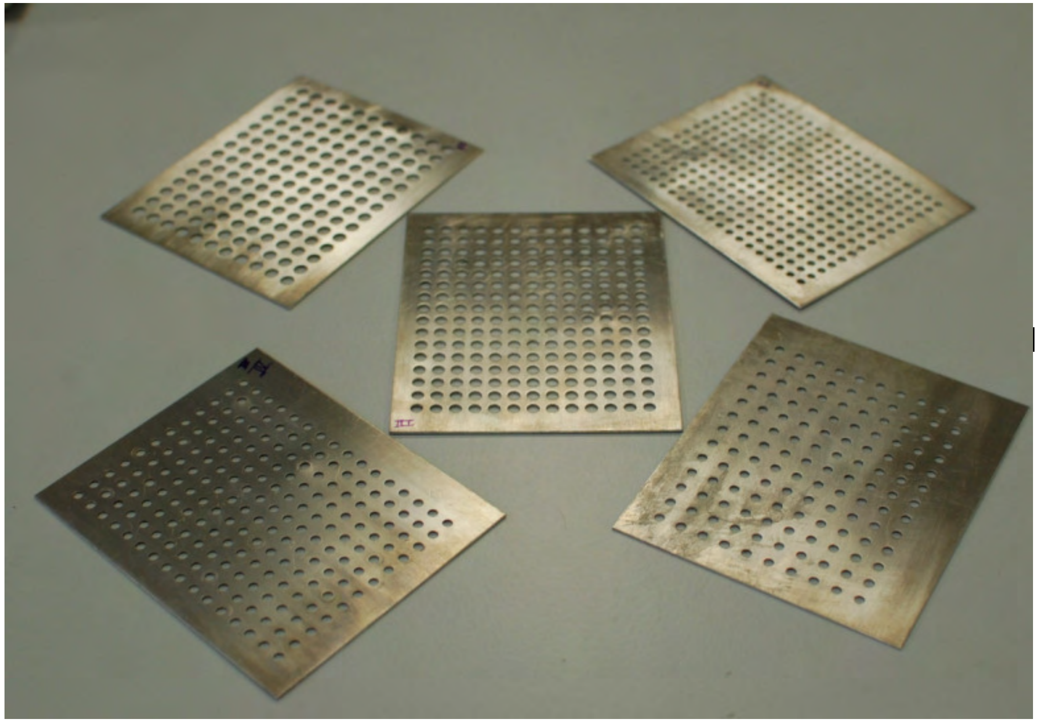


J. L. Keddie and A. Georgiadis, "A Method of Making a Patterned Latex Film and a Patterned Latex Film", world patent application submitted in October 2010


Fast evaporation
Mask
Particle sintering

Experimental Set-Up

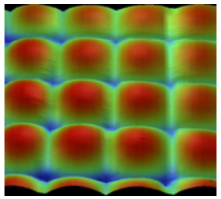




bstrate

250W IR Reflective Lamp

Maximum emission: 1.3 m

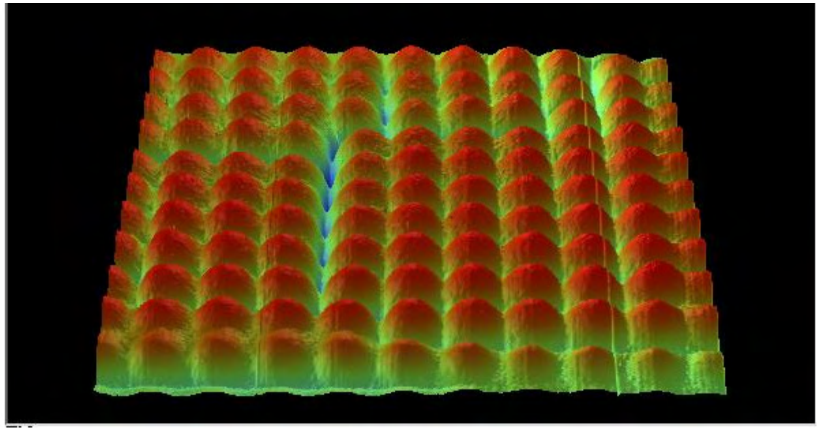


J. L. Keddie and A. Georgiadis, "A Method of Making a Patterned Latex Film and a Patterned Latex Film", British patent application submitted in October 2009

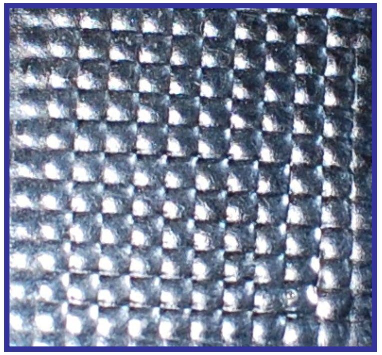
Example of a Textured Coating

Experimental Parameters

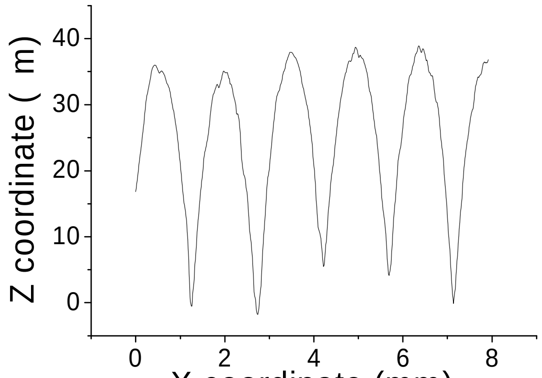
Hole diameter, d_h: 1 mm
Pitch, P : 1.5 mm
Wet film thickness, h_i= 330 m
Polymer T_g = 38 °C



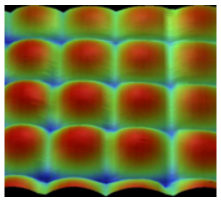
3-D profilometry (1.5 cm x 1.5 cm)



(1.5 cm x 1.5 cm)



2-D profile



J. L. Keddie and A. Georgiadis, "A Method of Making a Patterned Latex Film and a Patterned Latex Film", World patent application submitted in October 2010

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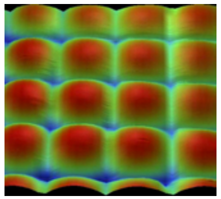
Radiative Heating

Radiative heating is energy efficient:

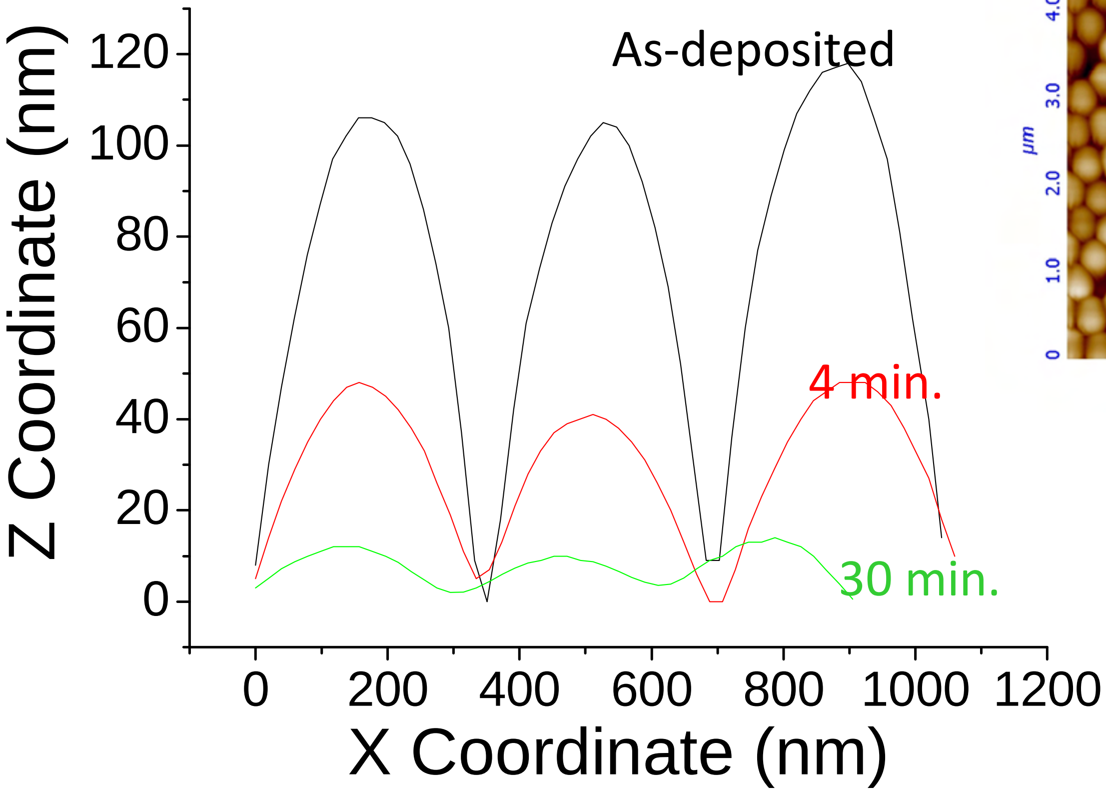
- Heats directly and locally *whereas* convective heating in an oven requires heat transfer from air
- Ideal for use with shadow masks
- Can heat water to its boiling point!
- Industrial-scale IR lamps are commercially available

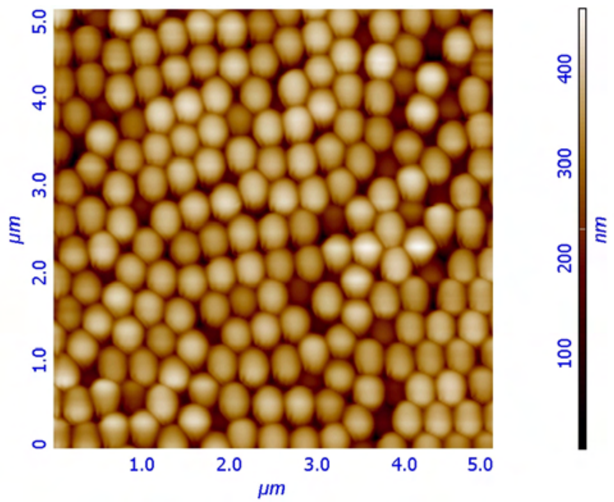


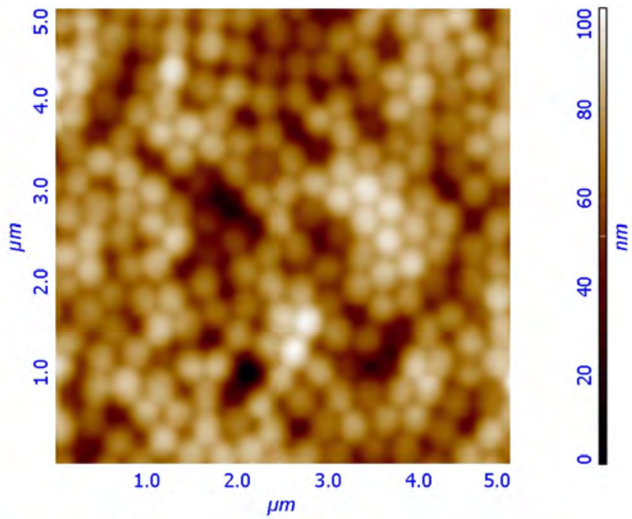
World patent application: "A method of making a hard latex and a hard latex." 2 Sept. 2010: WO 2010/097592

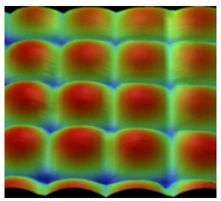
Nanoscale: Infrared Sintering

P(BuA-MMA) T_g = 38 °C



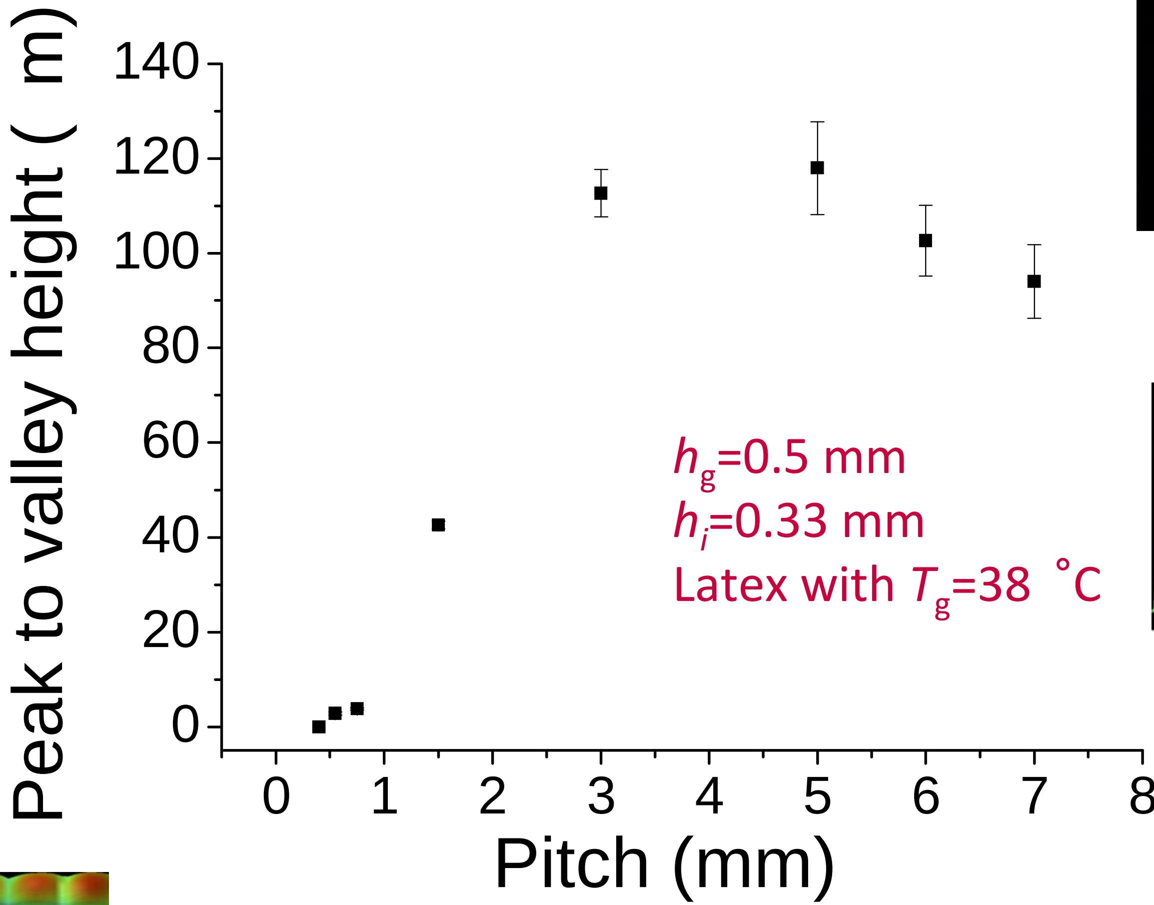


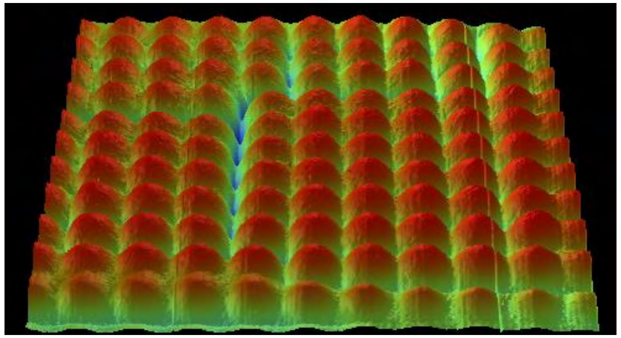




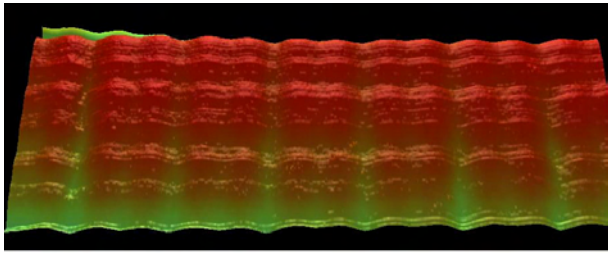
World patent application: "A method of making a hard latex and a hard latex." 2 Sept. 2010: WO 2010/097592

Influence of Pitch

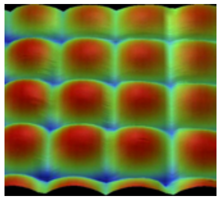




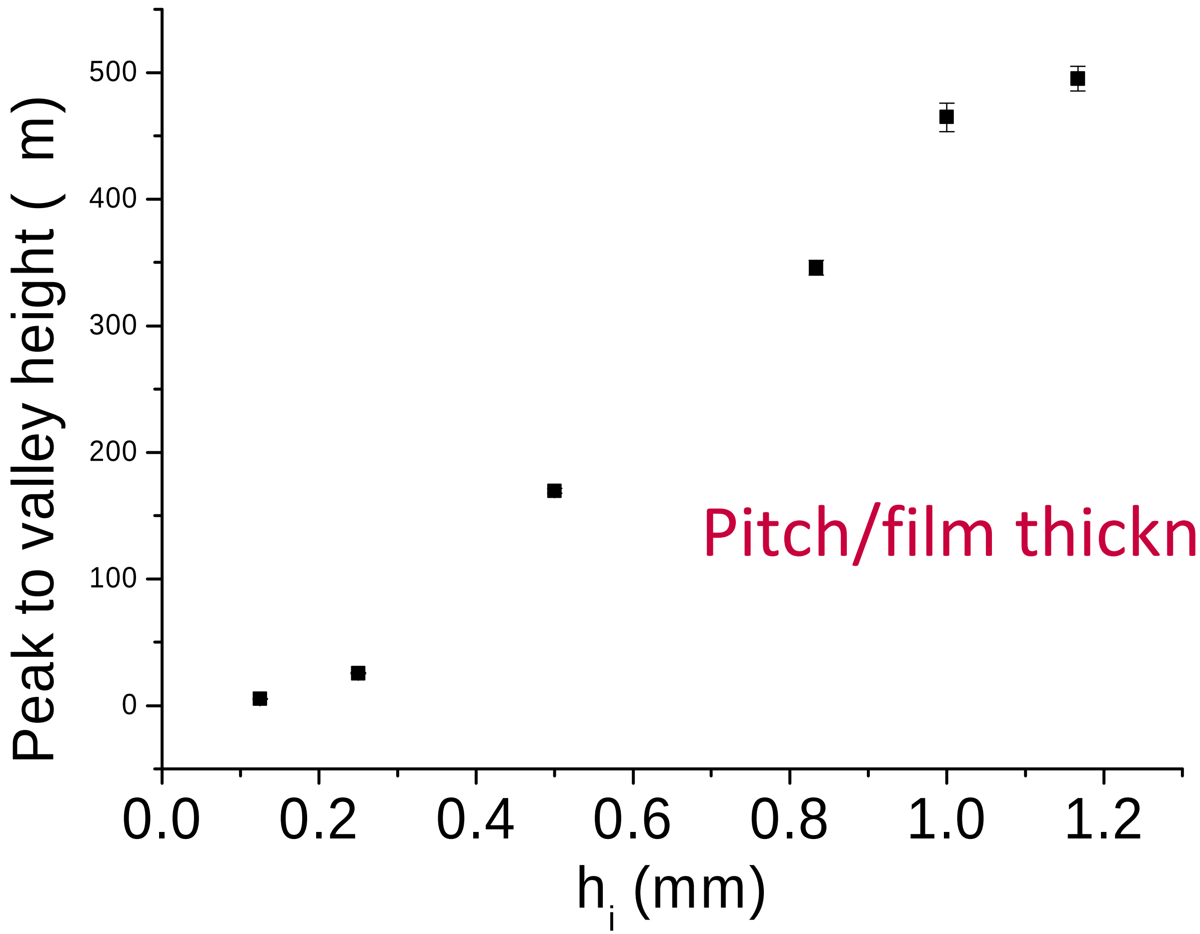
P = 1.5 mm



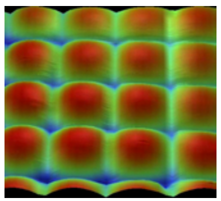
P = 750 m



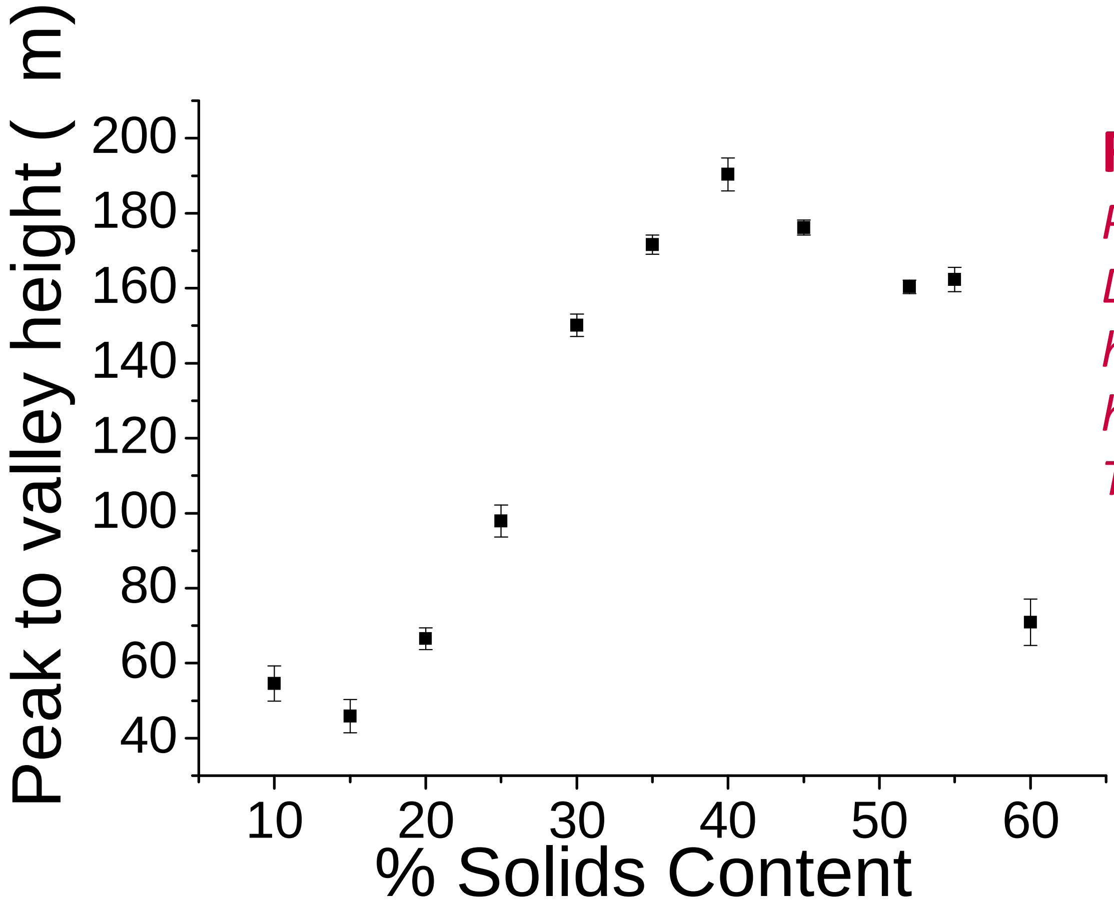
Influence of Film Thickness, h_i



Pitch/film thickness = 6



Influence of Solids Content



Fixed Parameters

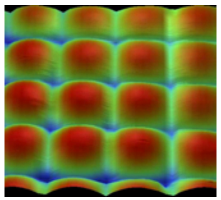
P = 3 mm

D_h = 2 mm

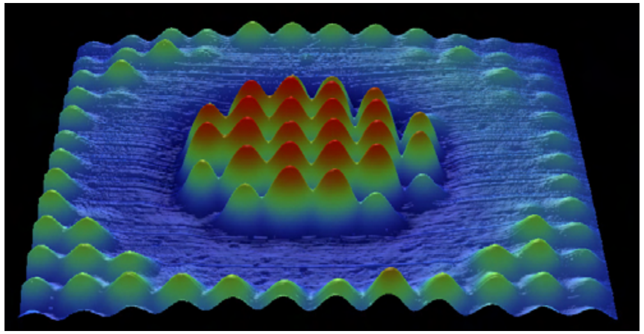
h_i = 0.47 mm

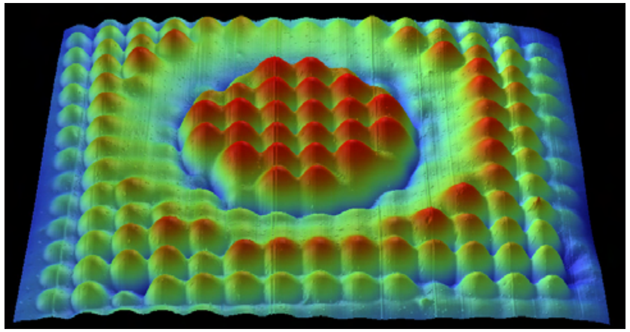
h_g = 0.7 mm

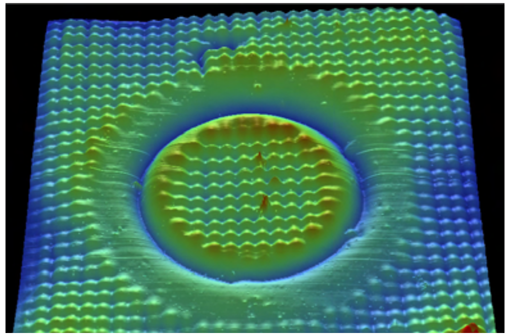
T_g=38 °C

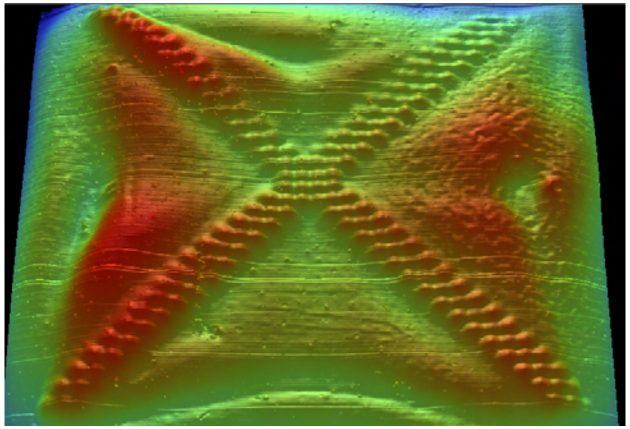


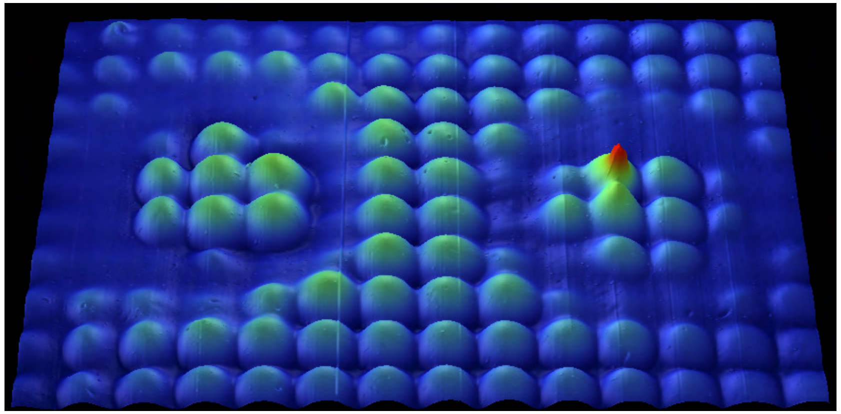
Other Types of Textured Coatings



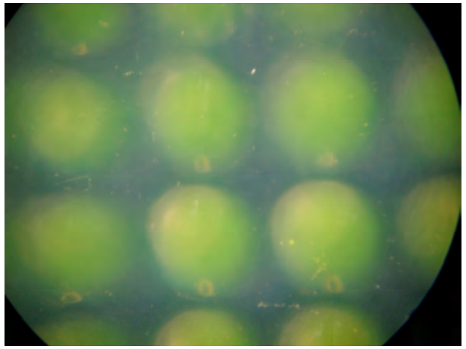




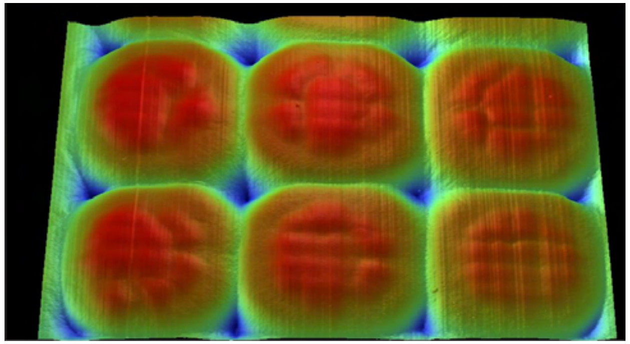




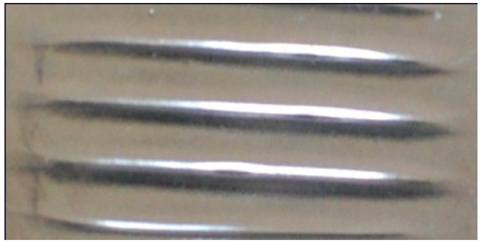
Other Types of Textured Coatings



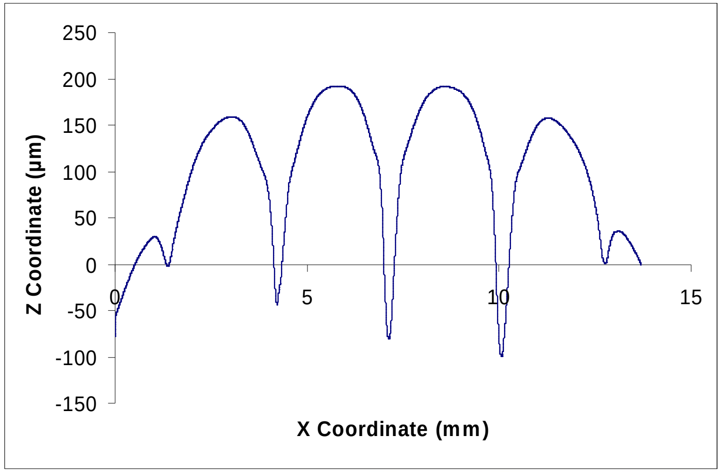
Coloured patterns (using fluorescent dyes)

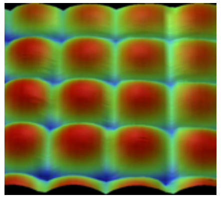


Patterns with two length scales of surface features: long and short

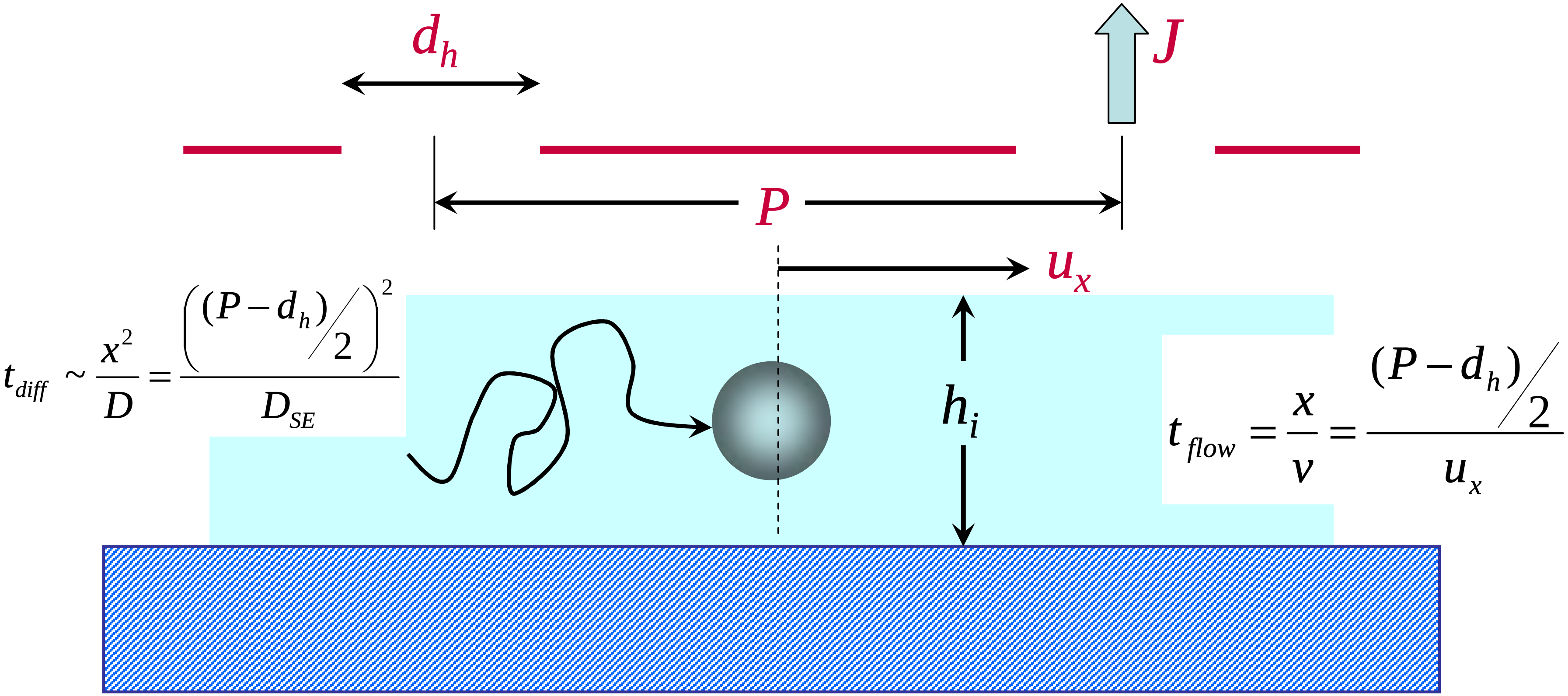


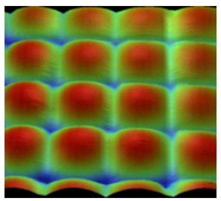
Ridged patterns





Model of Evaporative Lithography





D. J. Harris *et al.*, *Phys. Rev. Lett.* (2007) vol. 98, 148301

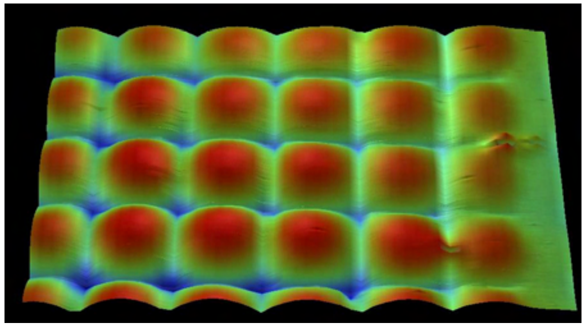
Significance of the Peclet Number, *Pe*

$$Pe = \frac{t_{diff}}{t_{flow}}$$

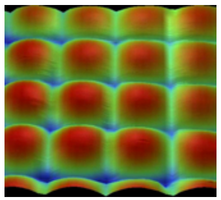
- If *Pe* >1: Diffusion is slow relative to evaporative flow → patterned film
- If *Pe* < 1: Diffusion is fast relative to evaporative flow → smooth surface

Pe = 630: flow wins!

P = 3 mm
d_h = 2 mm
h_g = 500 m
h_i = 330 m



P-V height: 102 m

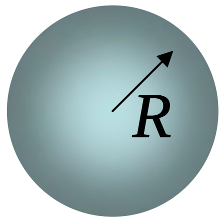


Control Parameter: Peclet Number, *Pe*

Comparison of times for diffusion and convective flow:

$$Pe = \frac{t_{diff}}{t_{flow}} = \frac{(P - d_h)u_x}{2D_{SE}}$$

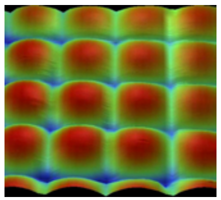
$$D_{SE} = \frac{kT}{6 \quad R}$$



Convective flow: $u_x = \frac{Jd_h}{2 \quad h_i}$

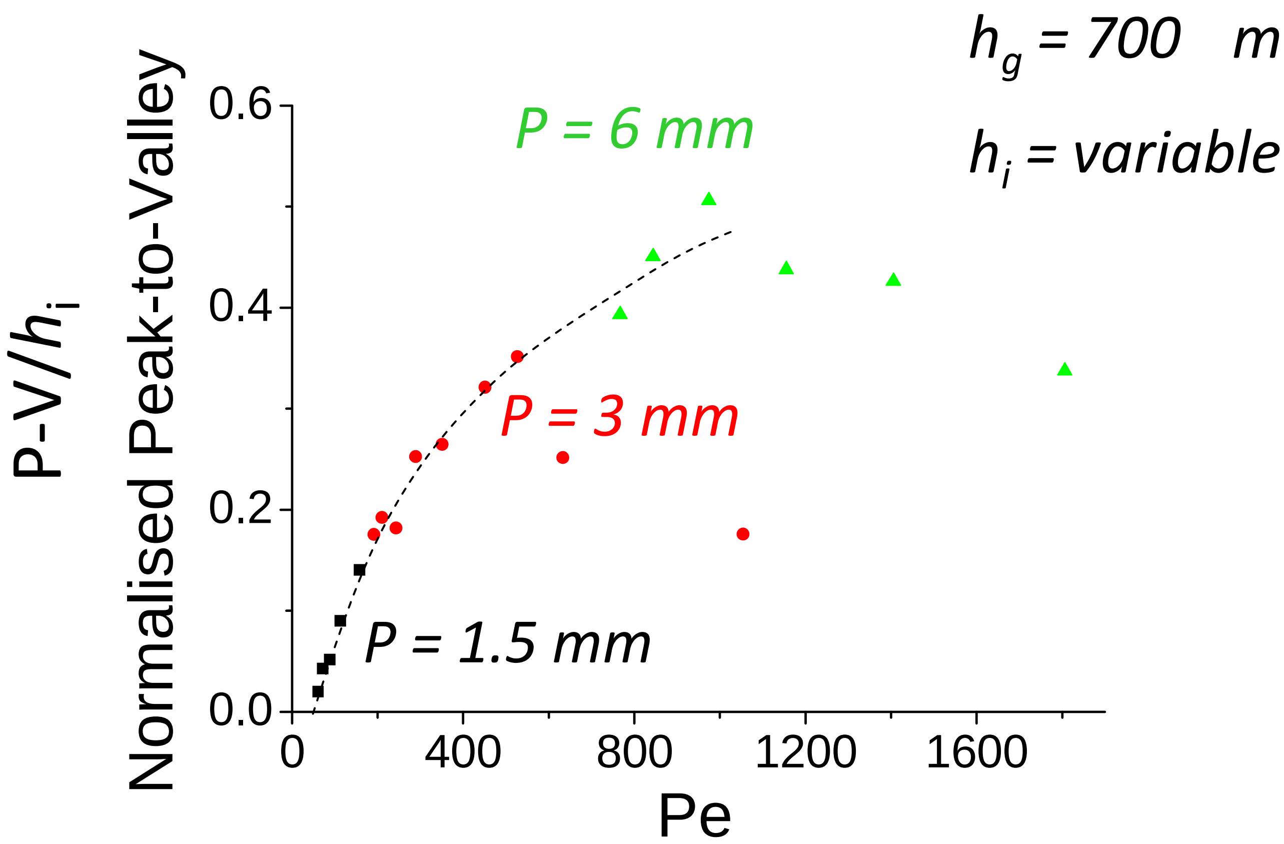
Substituting: $Pe = \frac{t_{diff}}{t_{flow}} = \frac{Jd_h(P - d_h)}{4 \quad D_{SE} h_i}$

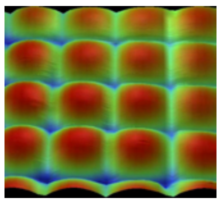
As *Pe* ∝ *P*, there is a minimum *P* that defines the minimum texture length scale that is possible.



D. J. Harris, *Phys. Rev.Lett.* (2007) vol. 98, 148301

Dependence of Structure on *Pe*





Computational Modelling

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Film height, *h*, evolution

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial x}\left(h^3 \frac{\partial^3 h}{\partial x^3} \right) - \dot{E}$$

E is evaporation rate (a velocity)

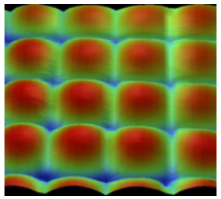
Vertically-averaged lateral velocity:

$$\overline{u_x} = h^2 \frac{\partial^3 h}{\partial x^3}$$

Solids fraction, , evolution

$$\frac{\partial (h \quad)}{\partial t} + \frac{\partial \left(h \quad \overline{u_x} \right)}{\partial x} = \frac{\partial}{\partial x}\left(h \frac{\partial \quad}{\partial x} \right) \times \frac{1}{Pe}$$

$$Pe = \frac{h_i \dot{E}}{D_{SE}}$$



A.F. Routh & W.B. Russel, *AIChE J.* (1999) ***44***, 2088-2098

Boundary Conditions

At fluid-solid boundary

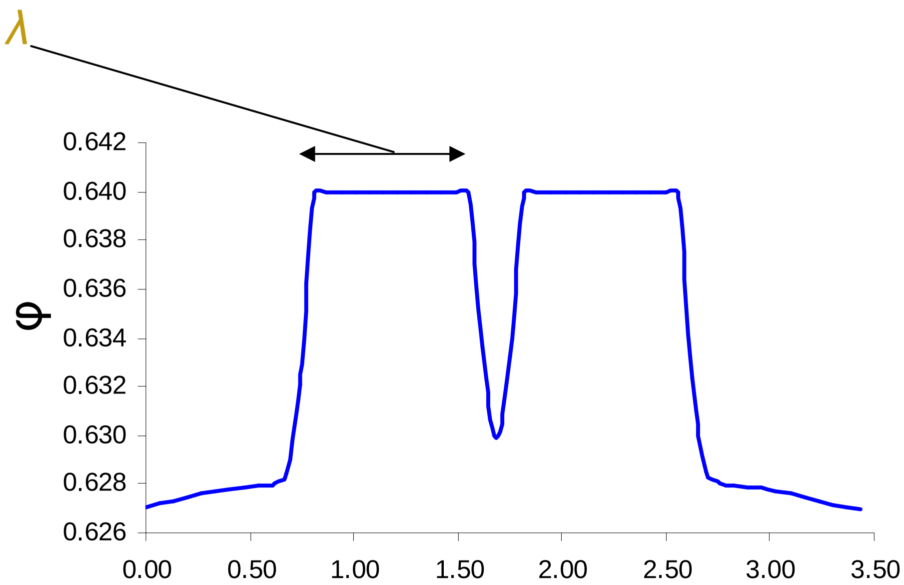
$$\overline{u_x(i)} = \frac{\quad}{h(i)} - \left(\ _f - \ (i-1)\right)\frac{\partial(x1)}{\partial t}$$

Forced by changing third derivative

At film edge

$$\frac{\partial h}{\partial x} = 0$$

Forced by 2 elements on outside set to first element

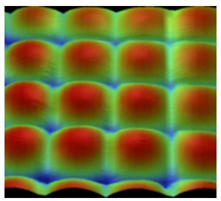


Conservation of particles:

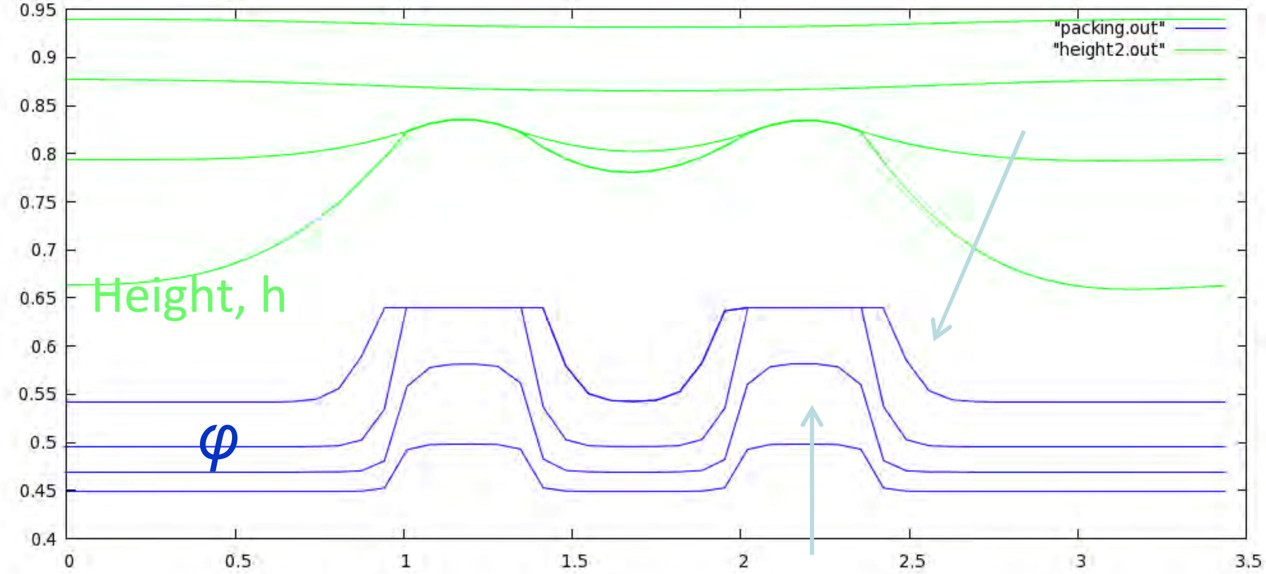
$$\sum_{i=1}^{n} h_i \ _i = \text{constant}$$

Capillary length, L:

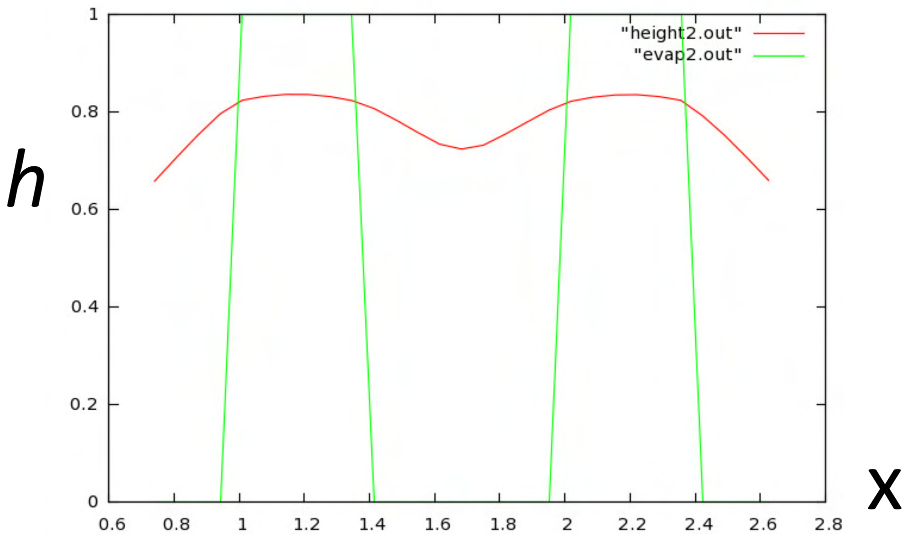
$$L = h_i \left(\frac{\quad}{3 \ _0 \dot{E}} \right)^{1/4}$$



Simulation Results

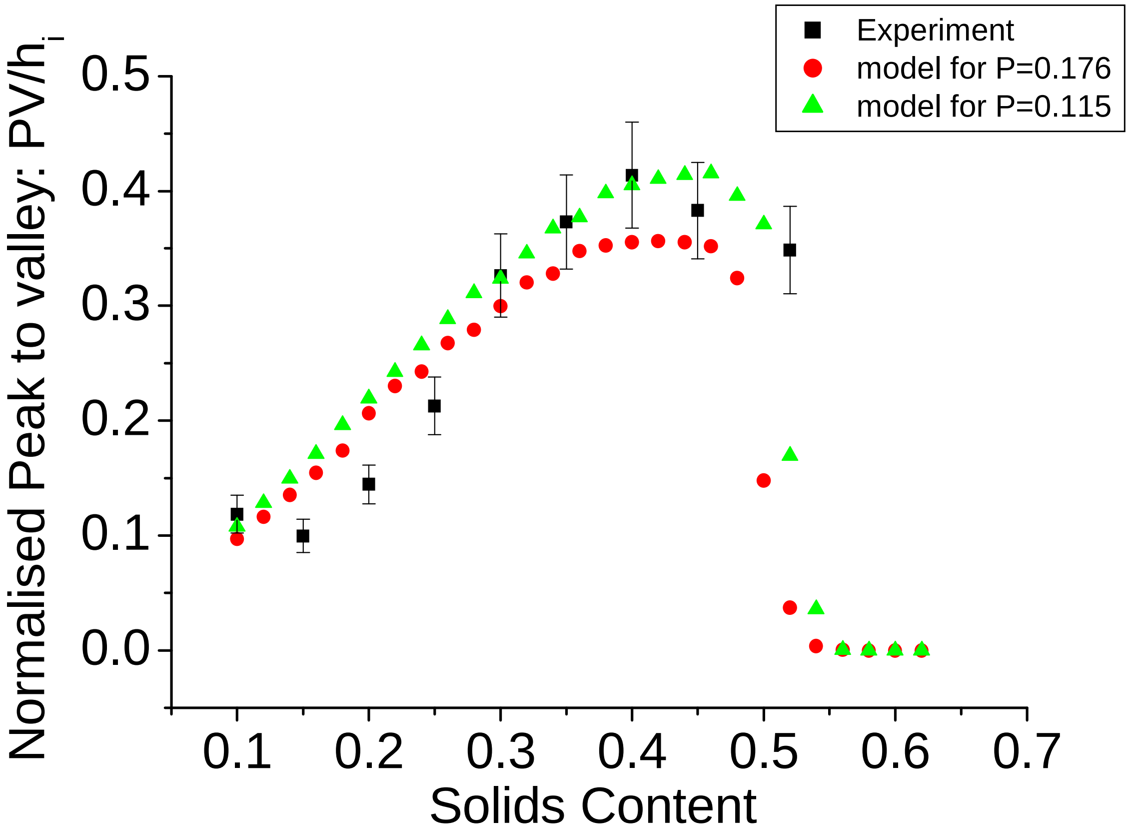


Over time, the height decreases while the packing fraction increases to a maximum of 0.64 (rcp).



Peak-to-valley height is taken as the highest point in the evaporating region to the lowest point in the masked region.

Some Initial Results from the Modelling



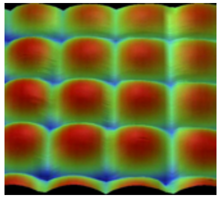
P=3 mm

d_h=2 mm

h_g= 0.7 mm

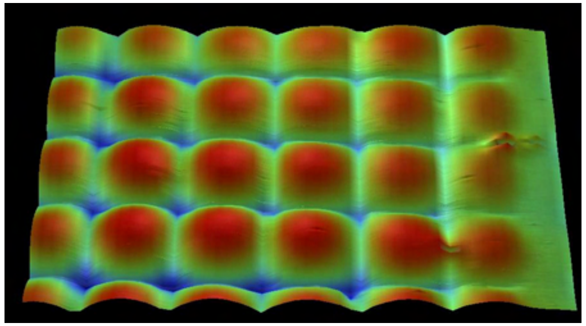
h_i=0.47 mm

T_g=38 °C



Advantages of IR-Assisted Evaporative Lithography

- Applicable to waterborne polymers → No VOCs
- Variety of substrates and variety of patterns are possible – with control over topography
- Hard coatings (T_g > 40 °C) can be made, resolving the film formation dilemma
- Low energy, one-step process
- Potential for scale-up
- No crosslinking chemistry



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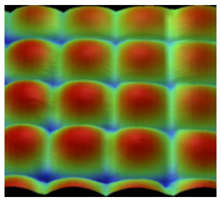
South East Physics Network (SEPNet) Summary Bursary

EPSRC

Pioneering research and skills

AkzoNobel

Tomorrow's Answers Today



Our research truly is as much fun as ….