From wrinkly elastomers to Janus particles to Janus fibres

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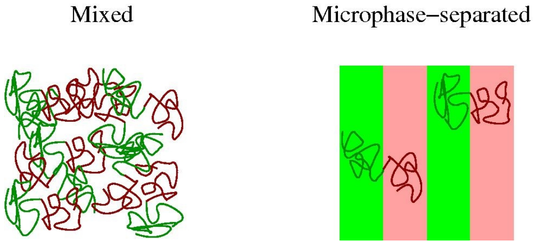
P. Patrício (ISEL and CFTC-UL)

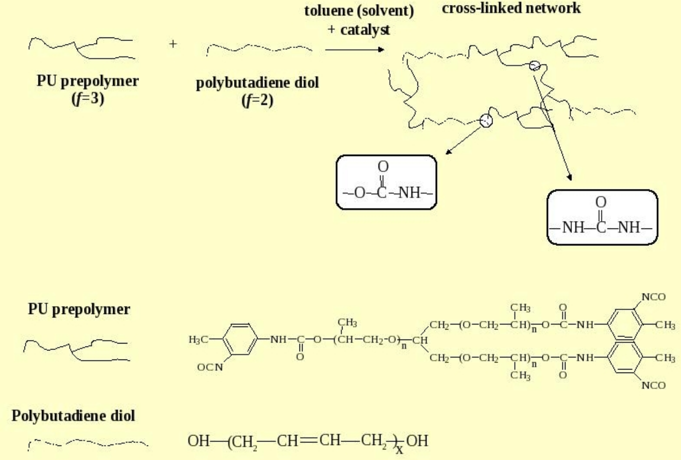
Introduction

- Next-generation micromechanical systems require adaptive surfaces with tailored properties.
- The micropatterning of soft materials should be simple and low-cost.
- Ideally use a single compound – a polymer:
  - Mechanically compliant;
  - Easily and cheaply prepared by standard laboratory procedures.
- Copolymers are particularly interesting. Their equilibrium structure may be mixed or microphase separated, with different properties.



Urethane-urea polymers

- Block copolymers containing 'stiff' and 'soft' groups:

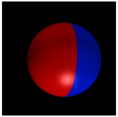


- If one or more of the blocks is multifunctional ($f > 2$), chains can be cross-linked and an elastomer is obtained.

Why Janus?

- Janus is the Roman god of gates, doors and passages. He is often depicted as having two faces.

- Janus objects likewise possess two sides with distinct compositions or textures.

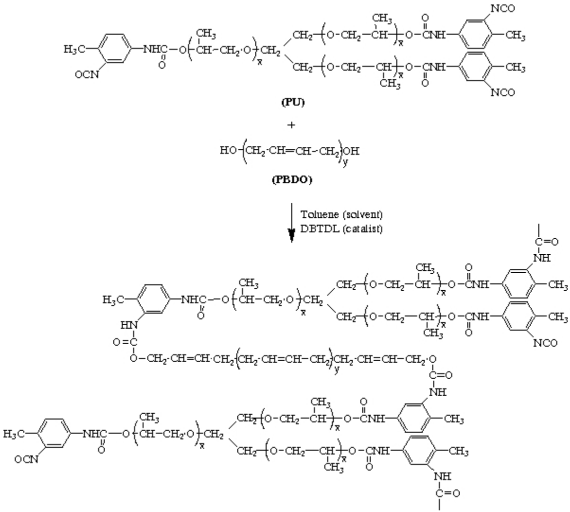


- Potential applications of Janus particles include:
  - Optical biosensors;
  - Electronic paper;
  - Anisotropic building blocks for supra-assemblies;
  - Functional surfactants.

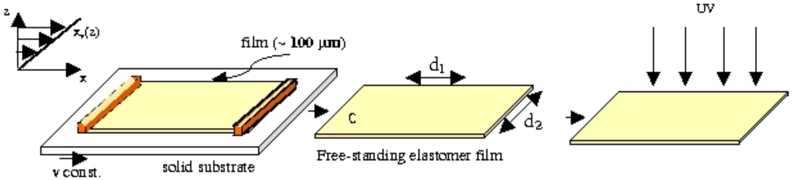
What we did

- We have fabricated and studied urethane/urea elastomer Janus films, spheres and fibres by inducing textures.
- Low-cost and low-tech methods, using easily evailable chemicals.
- Textures induced through strains, either applied or due to swelling.
- Textures have well-defined wavelengths, from below microns to mm, which can be easily tuned.
- We used a simple model to interpret results.
- Summary of studies performed:
  - Measured mechanical properties: stress-strain curves, Young's moduli
  - Polarised optical microscopy (POM)
  - Small-angle light scattering (SALS)
  - Atomic force microscopy (AFM)
  - Scanning electron microscopy (SEM)
  - Continuum mechanics modelling: analytics, bit of ABAQUS.

Synthesis of PU/PBDO 60:40 urethane/urea films

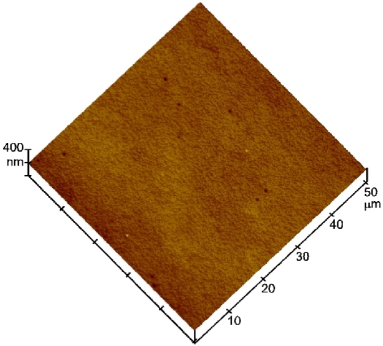


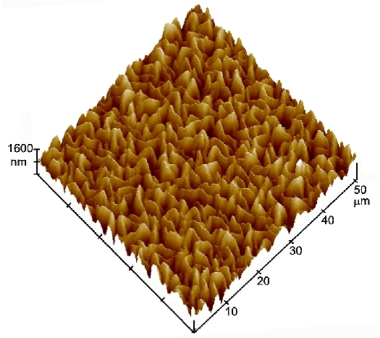
Shear-casting and UV irradiation of films



- Cast and sheared on glass plate, at room temperature, $v = 5$ mm/s.
- Films are mechanically anisotropic as a result of shearing.
- Cast elastomer cured in oven ($70 - 80^{\circ}$C) for 3.5 hours, then in air for 72 hours.
- UV-irradiated ($\lambda = 254$ nm) for 4 days.

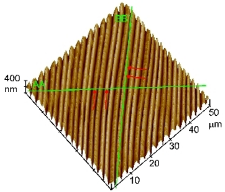
Film swelling in toluene without deformation (AFM)

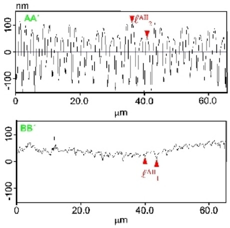


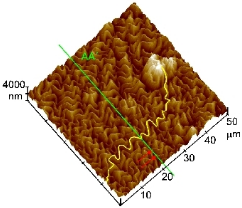


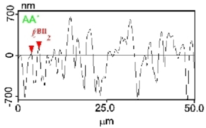
Dramatic increase in roughness

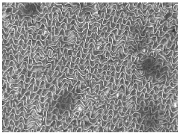
Film swelling in toluene after uniaxial deformation (AFM, POM, SALS)

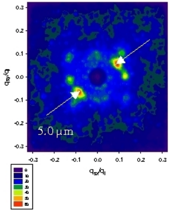




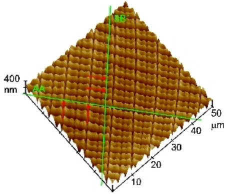


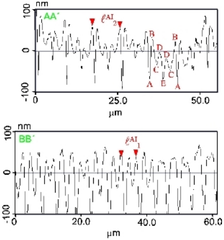


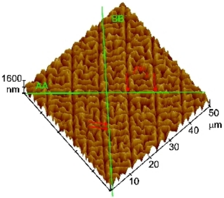


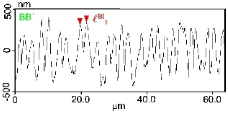


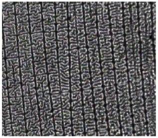
Film swelling in toluene after deformations at right angles (AFM, POM, SALS)

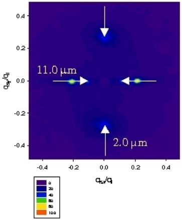




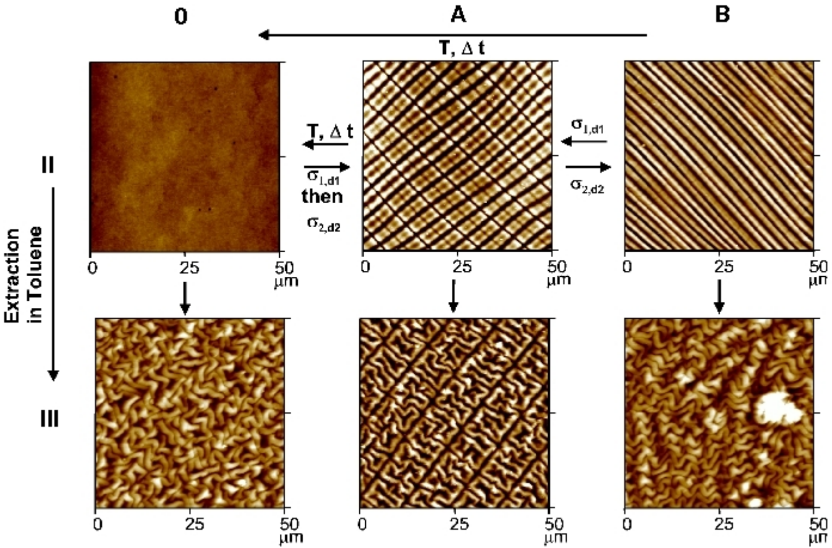






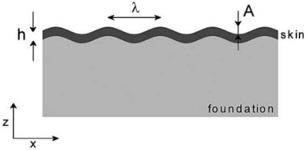


Summary of results for films (AFM)



Theoretical model of wrinkling: physical picture

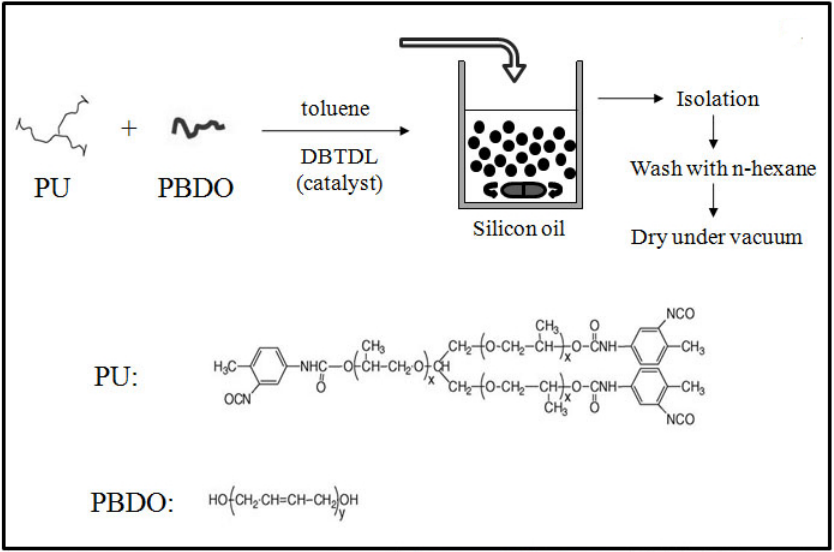
- Each film consists of a soft bulk and a (partial) stiff skin.



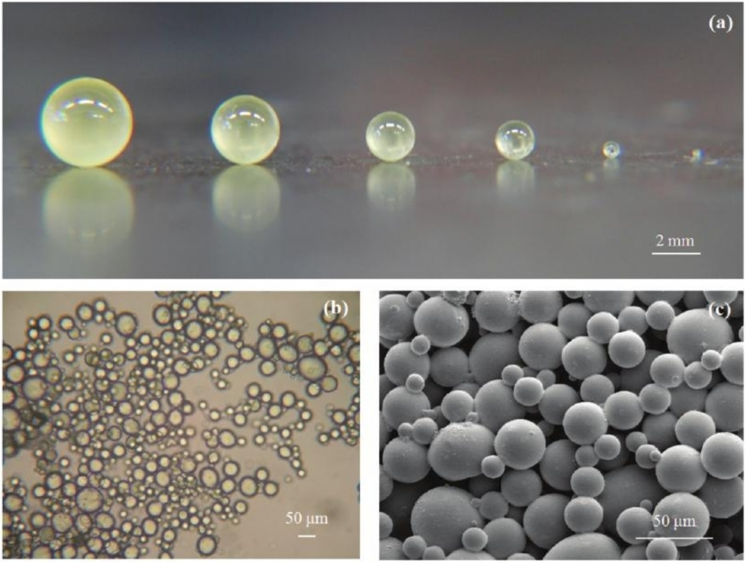
$$\lambda \sim h \left(\frac{E_{ss}}{E_{sc}} \right)^{1/3}$$

- When the film is stretched or swollen in toluene, both bulk and skin deform by the same amount. The surface remains smooth.
- BUT when stress is removed or toluene is extracted, the soft bulk will contract more than the stiff skin $\Rightarrow$ bending instability of skin.
- Wrinkle wavelength λ determined by competition between:
  - Bending stiffness of thin stiff skin (penalises short wavelengths); and
  - Bulk elastic energy of soft bulk deformation (penalises long wavelengths).

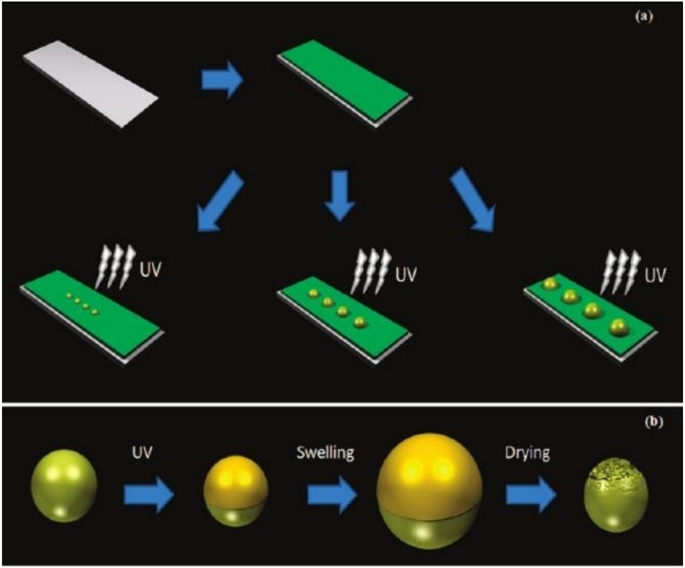
Synthesis of PU/PBDO 60:40 urethane/urea spheres



Making spheres of different sizes: vary stirring speed



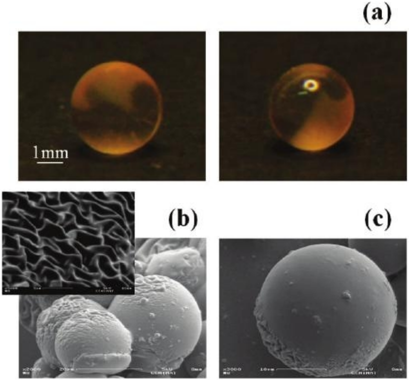
Irradiation and swelling of spheres: Janus particles



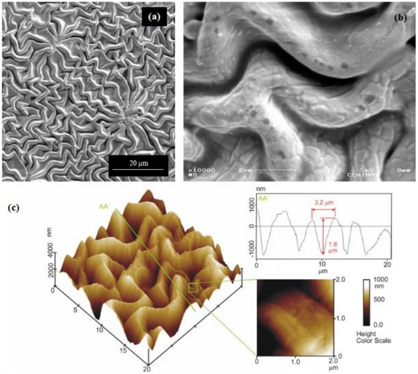
Swelling can be dramatic. . .

Janus particles: optical, SEM (left); SEM, AFM (right)

"Cloudy" and "shiny" hemispheres

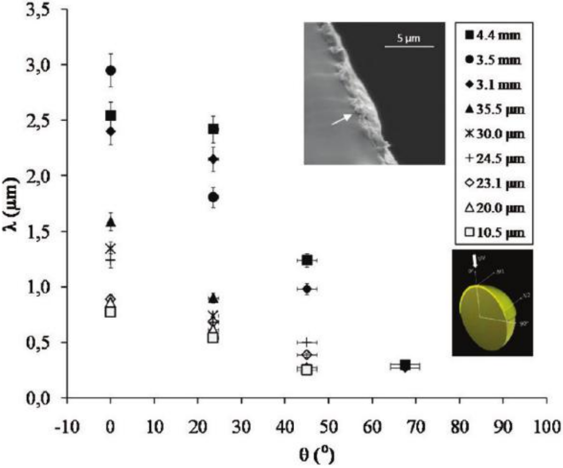


"Parasols" .and "fine structures"



Janus particles: wrinkle wavelength *vs* skin thickness

Irradiation depth varies with polar angle ⇒ variable wrinkle wavelength



Earlier models for flat and curved substrates

- Planar substrate (Bowden *et al.*):

$$\lambda \sim h \left(\frac{E_{ss}}{E_{sc}} \right)^{1/3}$$

- Spherical substrate (Cao *et al.*):

$$\frac{\lambda}{R} \sim \left(\frac{R}{h} \right)^{-0.8} \qquad (R/h < 50)$$

- Cylindrical substrate with external pressure (Yin *et al.*):

$$\frac{\lambda}{R} \sim \left(\frac{R}{h} \right)^{-3/4} \left(\frac{E_{ss}}{E_{sc}} \right)^{1/4}$$

Our model (for a cylinder)

- Elastic energy of shrunken soft core:

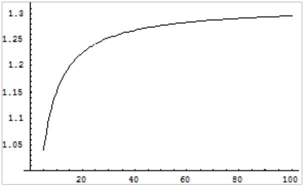
$$F_{sc} = \frac{E_{sc}}{2(1+\nu_{sc})} \int \left[\left(u_r^2 + \left(\frac{u}{r}\right)^2 + \frac{u_\theta^2}{2r^2} \right) + \frac{\nu_{sc}}{1-2\nu_{sc}} \left(u_r + \frac{u}{r} \right)^2 \right] dV$$

- Elastic energy of stiff skin (bend only):

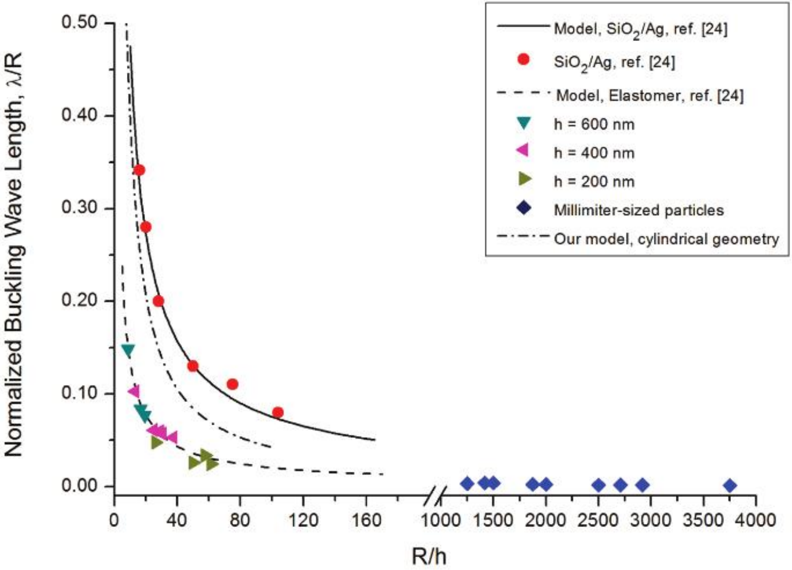
$$F_{ss} = \frac{E_{ss} h^3}{24(1-\nu_{ss}^2)} \int (k - k_0)^2 dA$$

- Minimise $F = F_{sc} + F_{ss}$.
- Wavelength decreases very smoothly with R, recover planar limit and

$$\frac{\lambda}{R} \sim \left(\frac{R}{h}\right)^{-3/4} \qquad (R/h < 50)$$

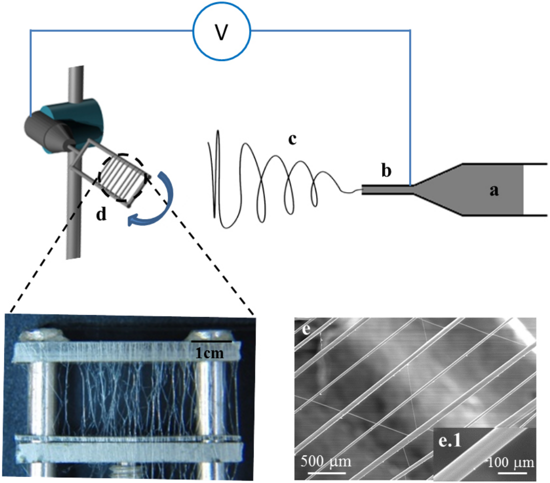


Comparison with experiments (spheres and cylinders)



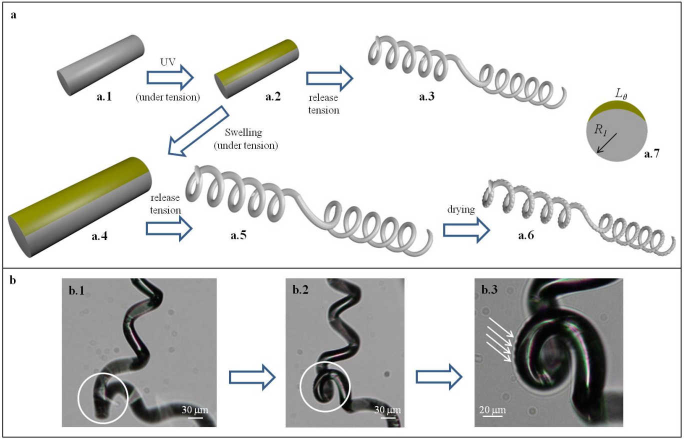
How to make fibres: electrospinning

Fibres are electrospun into non-woven mats



Irradiation and swelling: Janus fibres

- Fibres are UV-irradiated and swollen in toluene under tension, then allowed to relax and dry.



- As fibres dry, they first curl, then wrinkle.

Theoretical model of curling and wrinkling

- Both curling and wrinkling are be determined by interplay of bending stiffness of skin and bulk elastic energy of core.
- Total elastic energies (ϵ_z is skin-core size mismatch):

$$\begin{aligned} F_{nw} &\sim \epsilon_z^2 && \text{(non-wrinkled state)} \\ F_w &\sim \epsilon_z && \text{(wrinkled state)} \end{aligned}$$

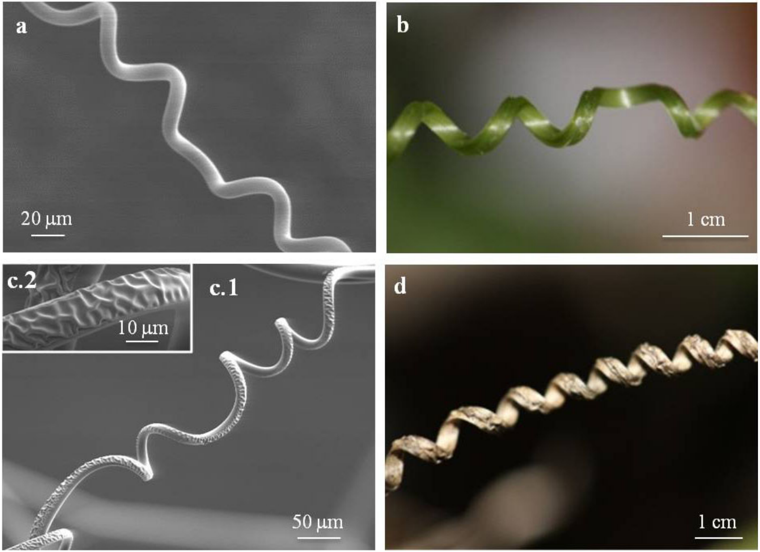
- As fibre dries, size mismatch ϵ_z increases and fibre curls:

$$c_{nw} \simeq \frac{\epsilon_z}{R} \frac{E_{ss} h L_\theta R^2}{(E_{sc} I_{sc} + E_{ss} h L_\theta R^2)}$$

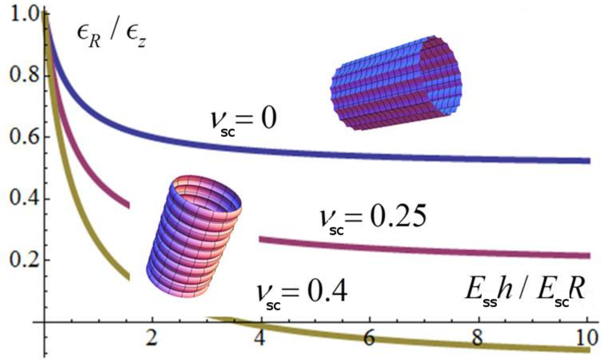
- At some critical mismatch $\epsilon_z^c \sim (E_{sc}/E_{ss})^{2/3}$, it becomes energetically cheaper to stop curling and wrinkle instead:

$$\begin{aligned} c_w &\simeq \frac{h L_\theta}{R^3} \left(\frac{E_{ss}}{E_{sc}} \right)^{1/3} \\ \lambda &= h \left(\frac{E_{ss}}{E_{sc}} \right)^{1/3} \end{aligned}$$

Janus fibres mimic young and old plant tendrils

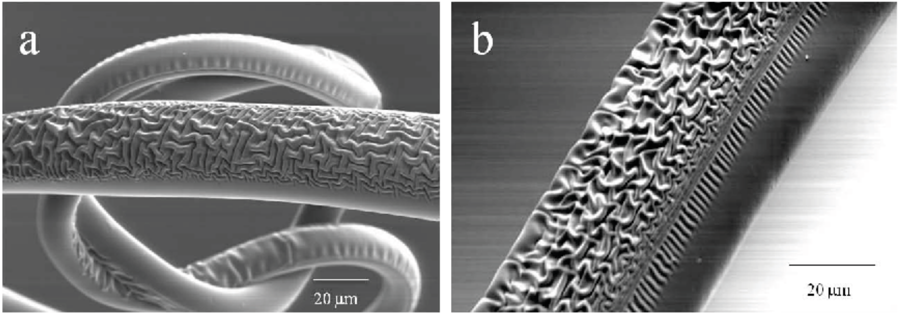


Which way does a fibre wrinkle – polar or longitudinal?



- $\epsilon_r/\epsilon_z \geq 1$: preferentially polar wrinkling.
- $\epsilon_r/\epsilon_z < 1$: polar wrinkling in stiffer, thicker skin, longitudinal in thinner, softer one. Effect is more pronounced the more incompressible the fibre core: for $\nu_{sc} > \nu_{sc}^* = 0.34$ wrinkling is always polar, provided $\rho = E_{ss}h/E_{sc}R$ exceeds a critical threshold that is a decreasing function of ν_{sc}.

Which way does a fibre *actually* wrinkle?



Summary and Outlook

- We have devised a very simple method to fabricate Janus films, Janus particles and Janus fibres from a single elastomeric material.
- Particles and fibres with diameters ranging from tenths of a μm to a few mm can be fabricated.
- Synthesis and preparation are straightforward and use current chemicals and techniques.
- The wrinkle wavelengths are controllable by varying particle or fibre diameter, surface layer thickness and degree of swelling.
- The wavelength dependence on radius and material properties is well described by a model of a stiff film on a soft curved substrate.
- The same model describes the crossover between curling and wrinkling regimes in drying Janus fibres, as well as wrinkle orientation.

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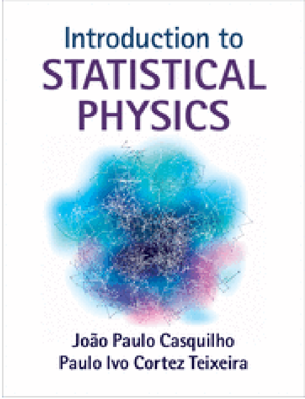
Shameless publicity plug



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