# Structuring Nanocellulose Films for Mechanical Measurements & New Applications

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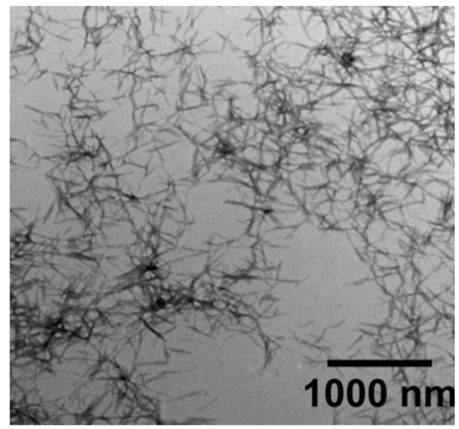
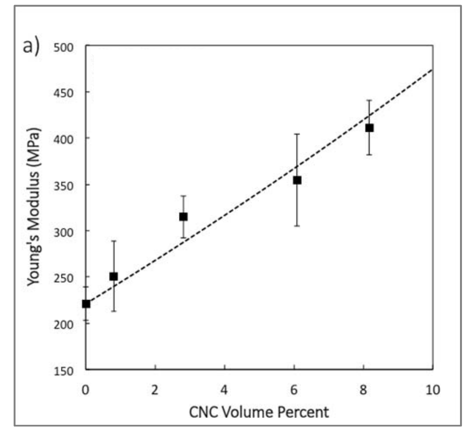
# Nano Advantage of CNCs?

- Large **aspect ratio** and high surface-area-to-volume ratio (surface area 250 $m^2/g$)
  - ✓ A little goes a long way!

- Ideal **reinforcing** component in nanocomposites
  - ✓ Strong but flexible (specific modulus > steel & Kevlar)

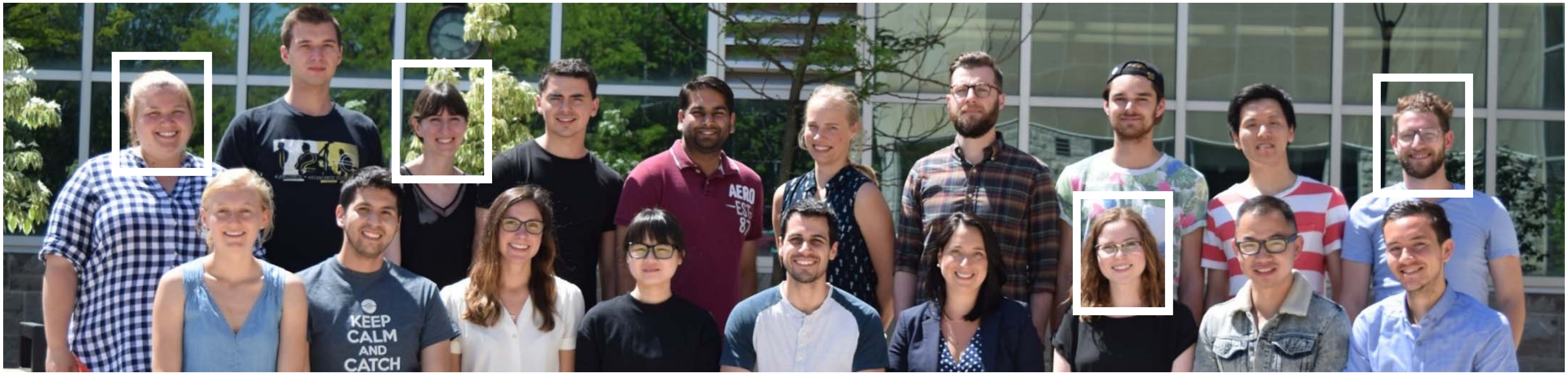
- Ideal **stabilizing** agent in foams, gels, and emulsions (edible?)
  - ✓ Intermediate hydrophilicity



# Purpose

Precise knowledge of CNC mechanical properties alone and in nanocomposites is crucial for development of suitable applications

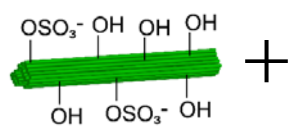


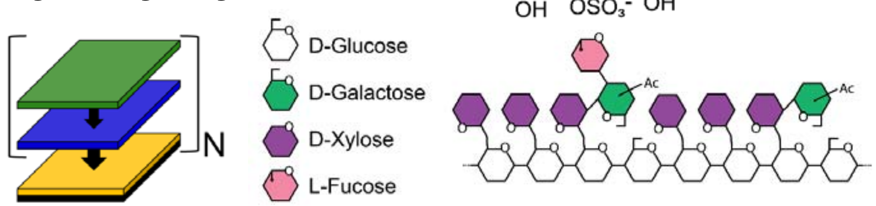

- ***Packaging, coatings, hydrogels, medical materials (sensors, drug delivery, tissue engineering)***
- ***Biomimetic model systems (plant cell wall)***

# Outline

1. Compare mechanically and thermally-induced buckling methods
2. Structured nanocomposite examples:

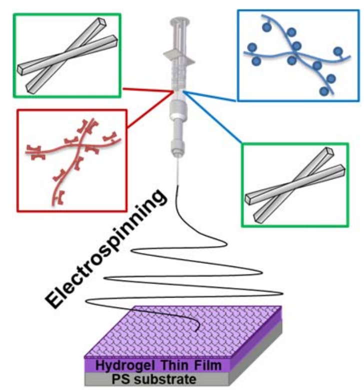
**Xyloglucan-CNC layer-by-layer films**



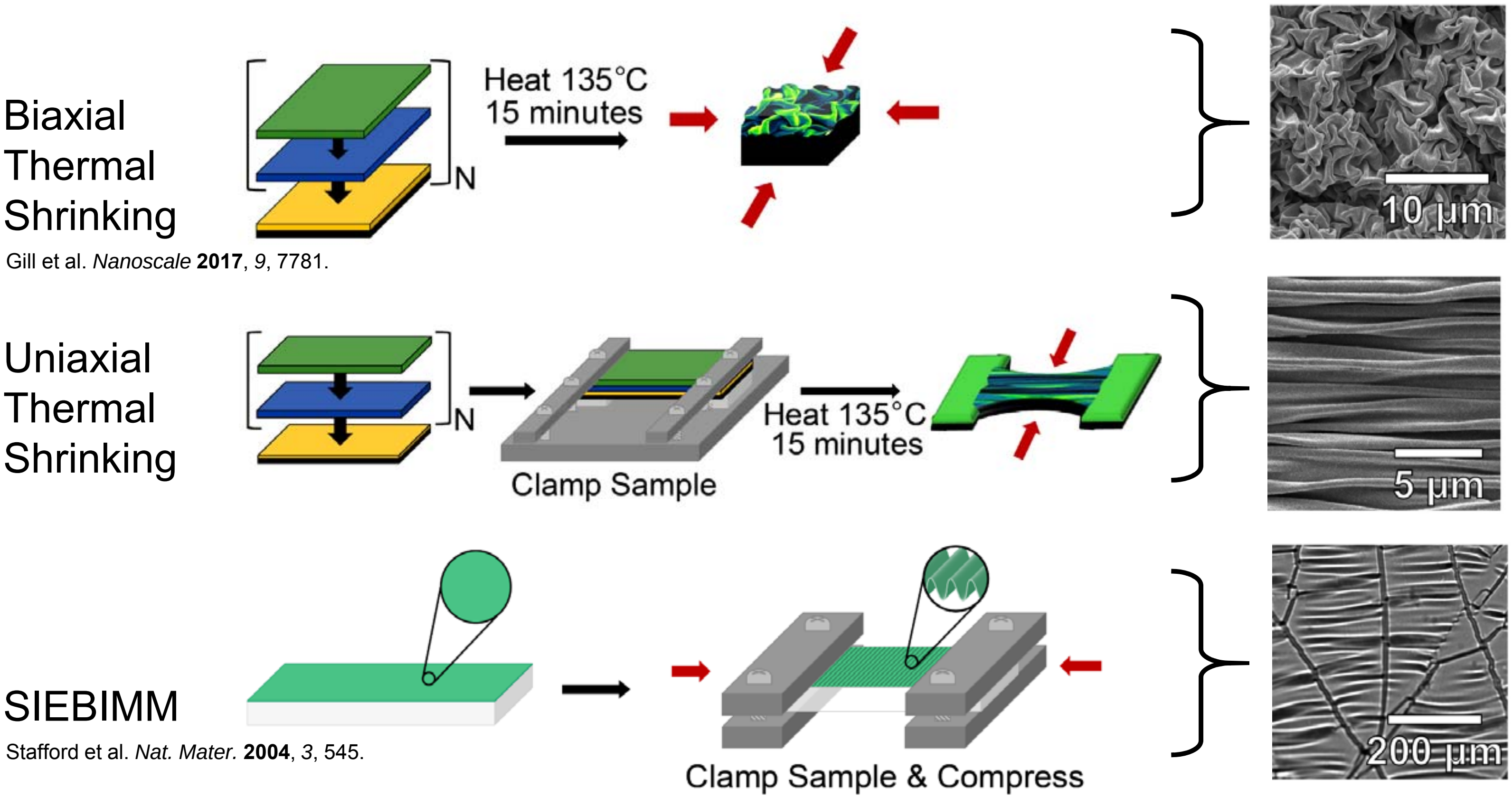




**Polyvinyl alcohol-CNC coatings**


**Injectable POEGMA-CNC hydrogels & electrospun mats**



# Buckling Mechanical Methods




Gill et al. *Nanoscale* **2017**, *9*, 7781.

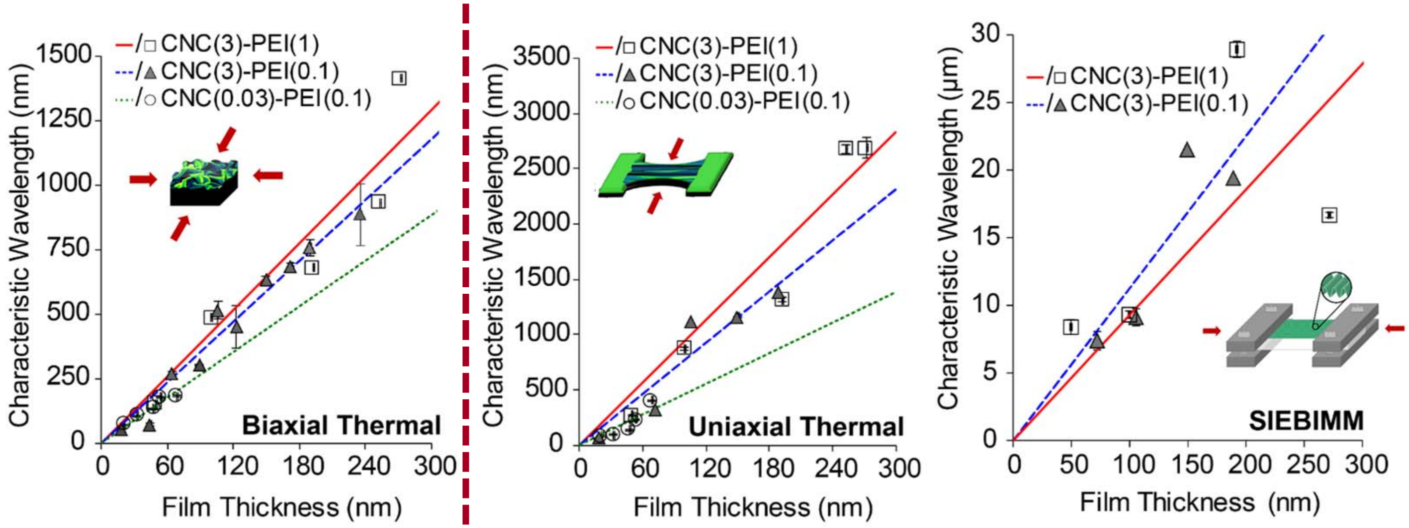
Stafford et al. *Nat. Mater.* **2004**, *3*, 545.

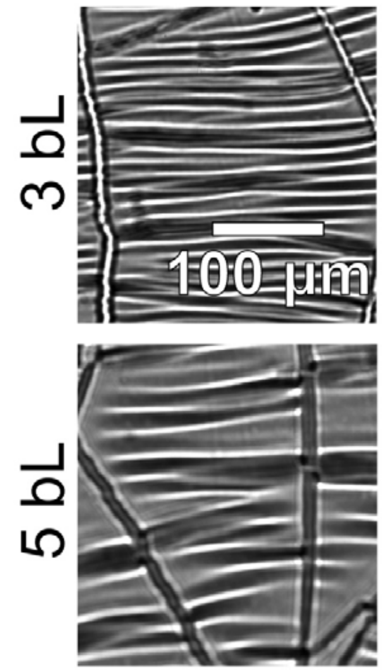
***Do all methods give the same elastic modulus?***

***Which method is most accurate?***

# Direct Comparison of Moduli

**Most robust, easiest, lowest sensitivity (-SEM)**

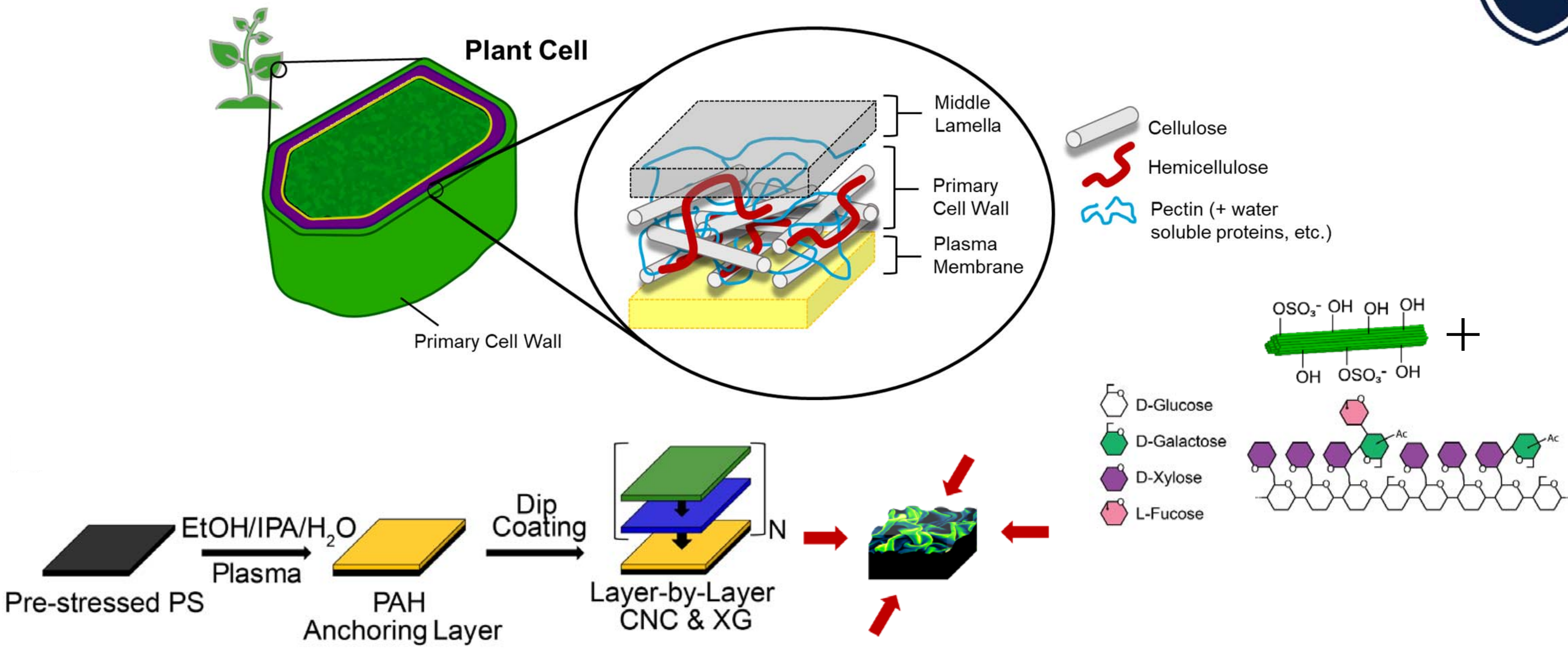



| Film Composition | Elastic Moduli (GPa) Biaxial Thermal | Uniaxial Thermal | SIEBIMM |
|---|---|---|---|
| CNC(0.03)-PEI(0.1) | 21 ± 2 | 15 ± 3 | - |
| CNC(3)-PEI(0.1) | 35 ± 3 | 33 ± 5 | 40 ± 13 |
| CNC(3)-PEI(1) | 37 ± 5 | 44 ± 5 | 20 ± 20 |

- Stimpson et al. In revision for *ACS Adv. Mater. Interfaces* **2021.**
- Stimpson et al. Submitted to *Micromachines.* **2021.**

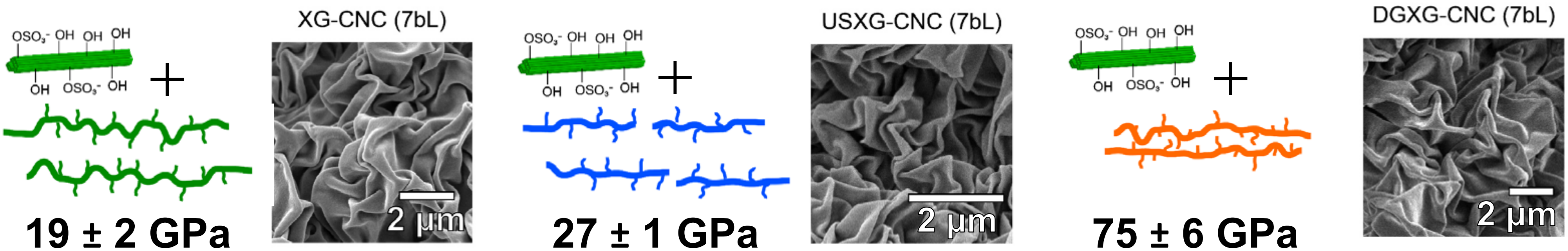
# Xyloglucan-CNC Thin Films



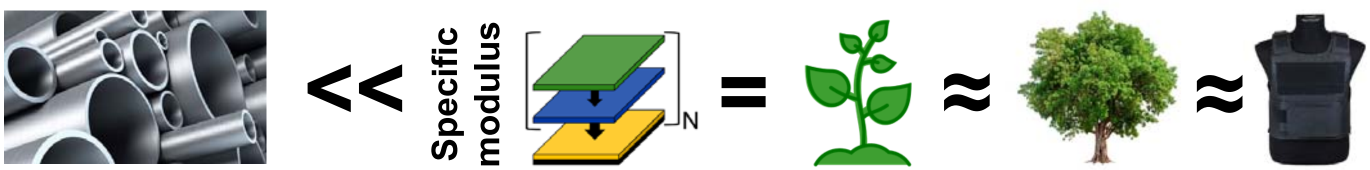

- Stimpson et al. *Biomacromolecules* **2020**, *21,* 3898.
- Talantikite et al. *Biomacromolecules* **2021**, *22*, 743.

# Structuring of XG-CNC Thin Films

**Control xyloglucan** | **Low MW xyloglucan** | **Degalatosylated xyloglucan**



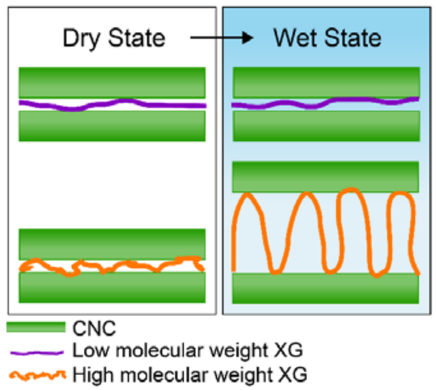

- ***Promoting closer/more cellulose-XG interactions increases film dry moduli.***
- ***D-galactose residues are "optimized" in nature to provide flexibility.***



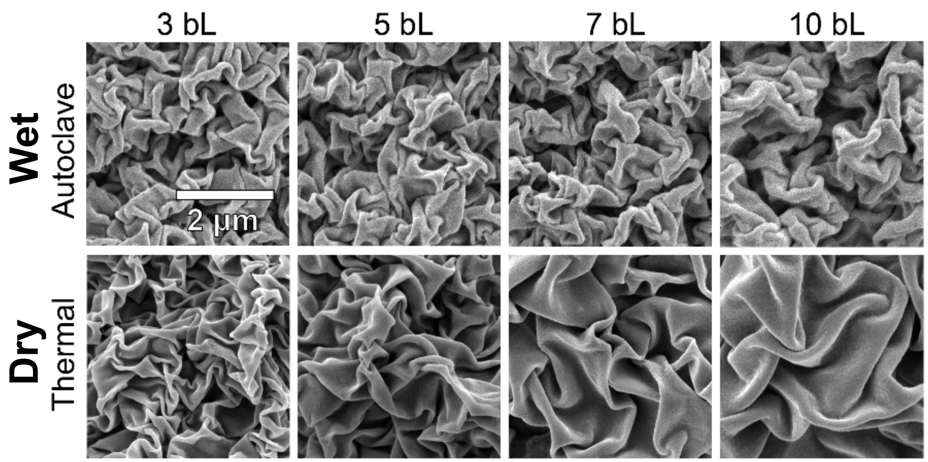


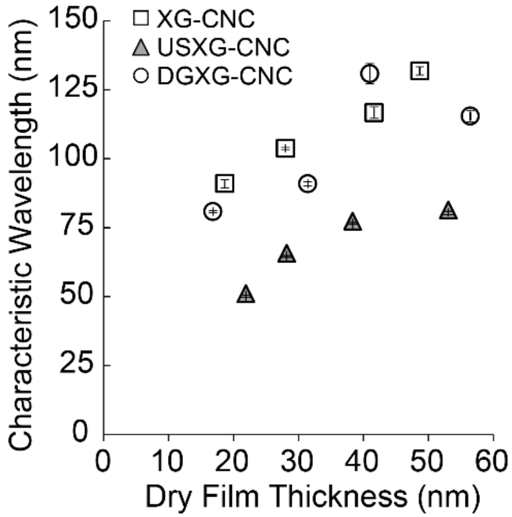
- Stimpson et al. *Biomacromolecules* **2020**, *21*, 3898.
- Talantikite et al. *Biomacromolecules* **2021**, *22*, 743.

# XG-CNC Modulus Dry vs. Wet




Villares et al. *Carbohydr. Polym.* **2017**, *157*, 1105.




- ***Smaller wrinkles ≈ 60% softer (all similar).***
  - ***Low MW XG swells least and is stiffest.***
  - ***Cell wall is more elastic when hydrated.***
- ***Autoclave shrinking is helpful for materials that must remain wet (e.g. hydrogels).***

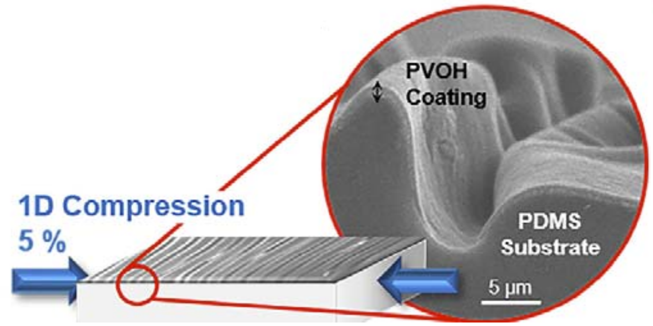
- Stimpson et al. *Biomacromolecules* **2020**, *21*, 3898.
- Talantikite et al. *Biomacromolecules* **2021**, *22*, 743.

# Polyvinyl Alcohol-CNC Coatings

- Coatings are thicker than thin films → buckling mechanics still work

  Niinivaara et al. JCIS **2020**, *582*, 2227.

- CNCs act as nucleating agents = increased PVOH crystallinity
  - 100% PVOH: 22% crystallinity
  - 90% PVOH – 10% CNC: 38% crystallinity




- ***Good CNC dispersibility.***
- ***Rigid percolated network of CNCs enhanced by matrix crystallinity.***
- ***Functional coatings.***

**SIEBIMM Young's modulus**

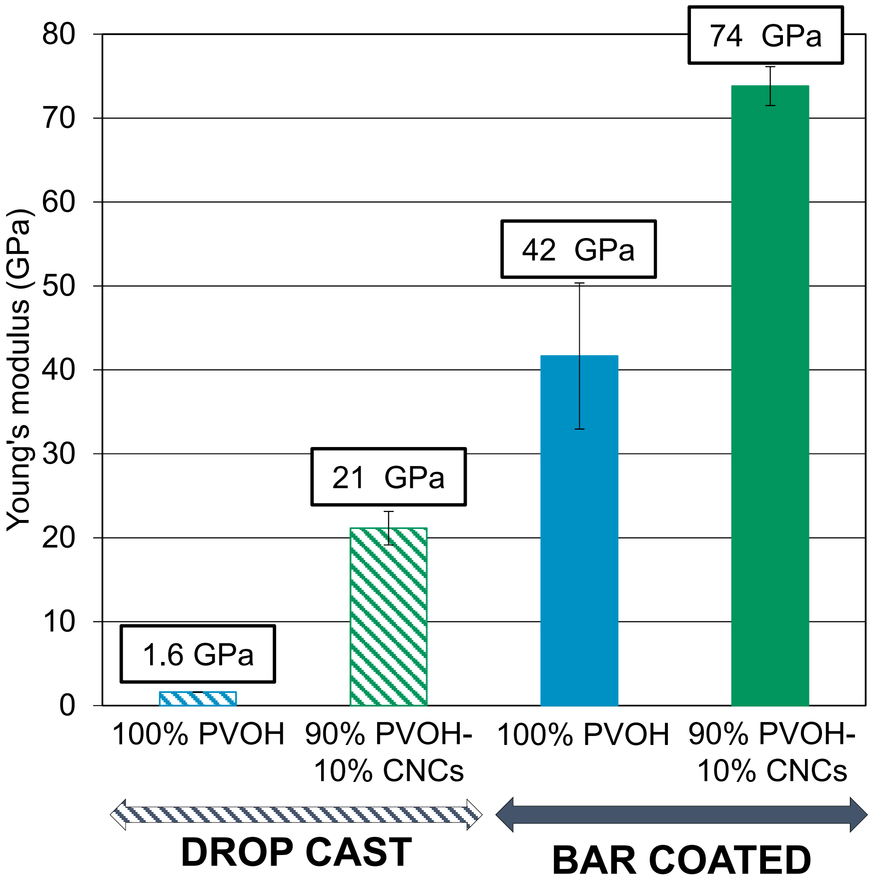
Neat PVOH Coating: **1.6 ± 0.1 GPa**

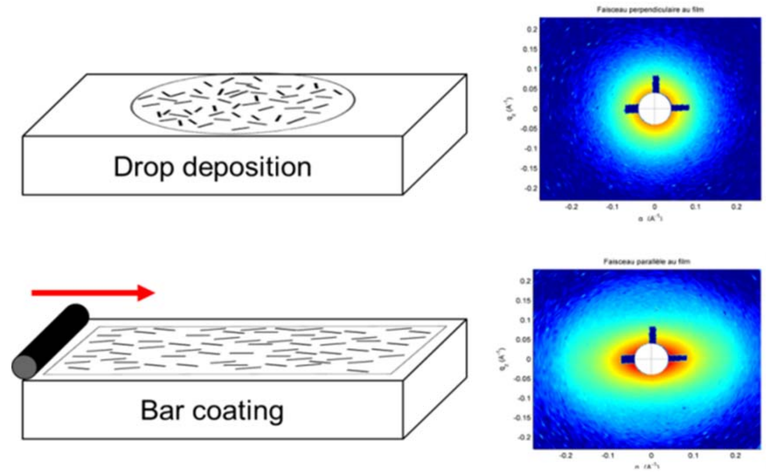
13x improvement →

90% PVOH – 10% CNCs Coating: **21 ± 2 GPa**

Niinivaara et al. Submitted to *ACS Applied Nano Materials* **2021**.

# Coating Method Affects Modulus



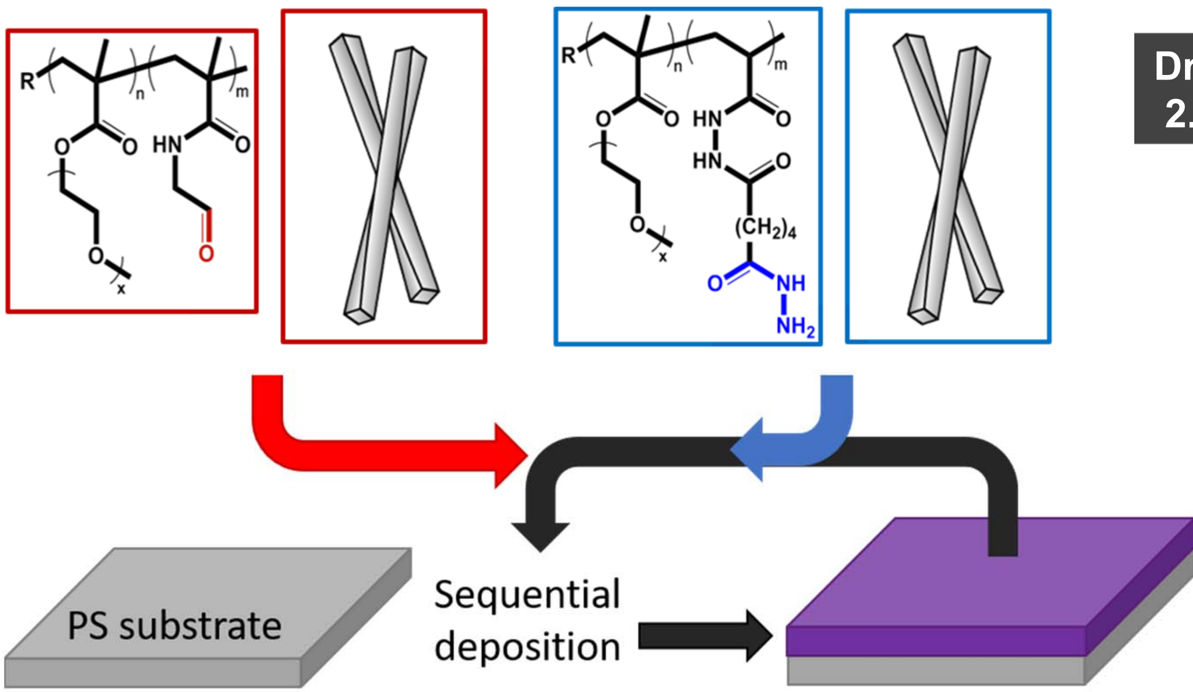

Sénéchal et al. (2010) 6th International ECNP Conference on Nano-structured Polymers & Nanocomposites; Madrid, Spain; Poster #125.

***Aligned CNCs in bar coated coatings have the highest modulus.***

Niinivaara et al. Submitted to *ACS Applied Nano Materials* **2021**.

# Structured Hydrogel Films & Mats

Thermal shrinking to tailor surface area and morphology for biosensing, bioseparations, tissue culture, and wound healing



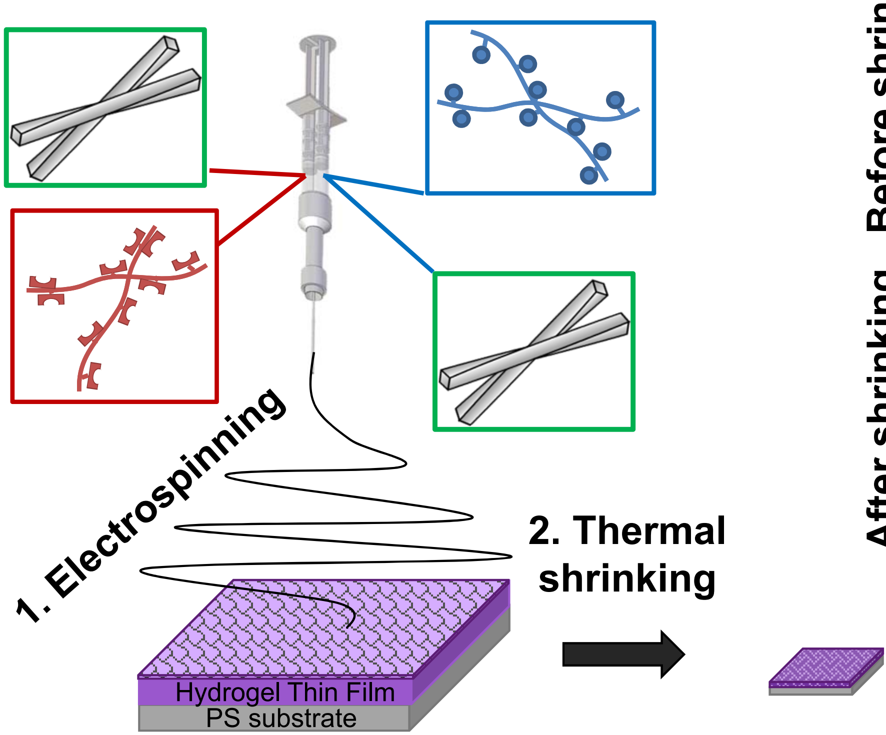

**Dry modulus: 2.5 – 18 GPa**

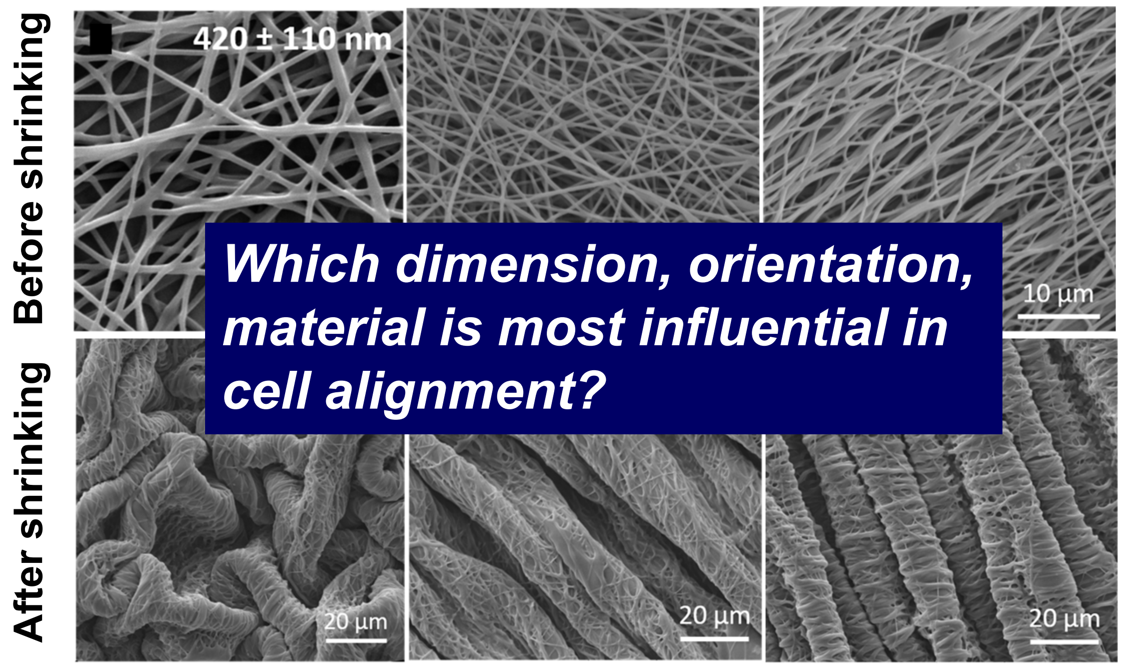
De France et al. *ACS Appl. Mater. Interfaces* **2019**, 11, 6325

# Tuning Hydrogel Morphology in 2.5D

De France et al. *ACS Appl. Mater. Interfaces* **2019**, 11, 6325

# Structured Electrospun Hydrogels

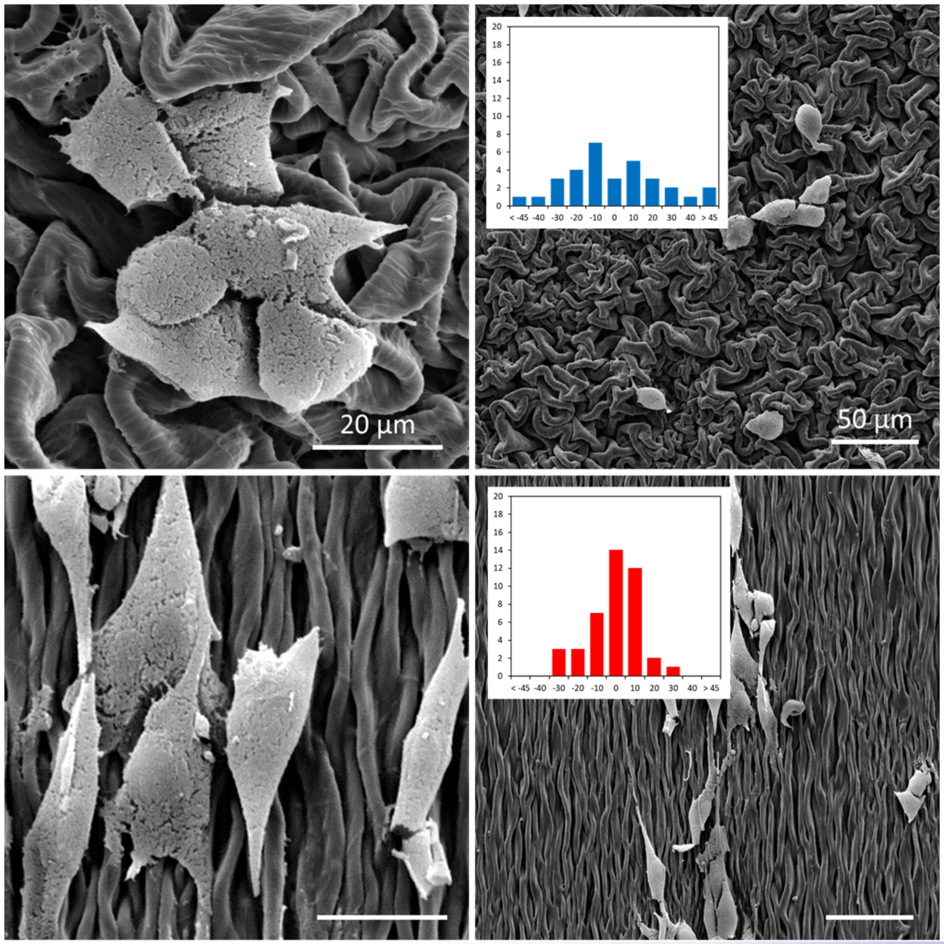


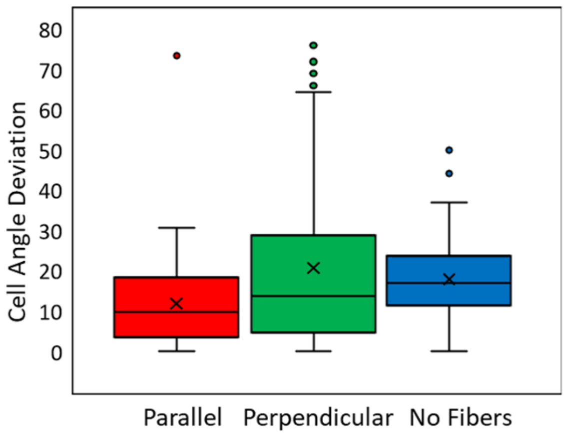

***Which dimension, orientation, material is most influential in cell alignment?***

De France et al. *Acta Biomaterialia* **2021**, ASAP.

# Directional Cell Scaffolding




- “Cell orientation angle” is with respect to average (predominant) cell direction in a given SEM
- “Cell angle deviation” is with respect to wrinkle direction (this can only be done for uniaxial)



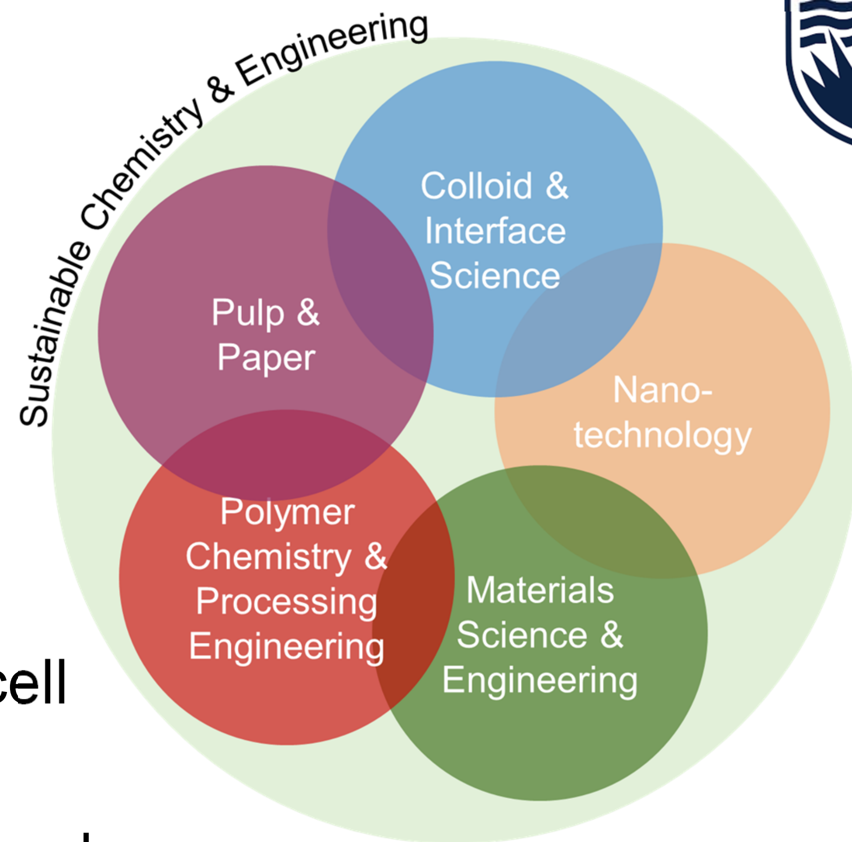

***Cells primarily follow wrinkles.***

***Parallel fibers help alignment while ⊥ fibers hinder it.***

De France et al. *Acta Biomaterialia* **2021**, ASAP.

# Conclusions

1. Buckling/structuring methods can overcome limitations of other mechanical measurement methods
2. Biaxial (unconstrained) thermal shrinking is the most robust and straightforward
3. CNC-XG thin films mimic the plant cell wall well & suggest “design rules”
4. Coatings and hydrogels can be tailored through processing and structuring



# Thank You!

- Students & Collaborators

  Taylor C. Stimpson, Kevin J. De France,
  Elina Niinivaara, Johanna Desmaisons

- Prof. Julien Bras (Univ. Grenoble Alpes)
- Prof. Bernard Cathala (INRA)
- Prof. Todd Hoare (McMaster)
- Prof. Jose Moran-Mirabal (McMaster)

- TAPPI staff, leadership and conference organizers

**Questions? emily.cranston@ubc.ca**

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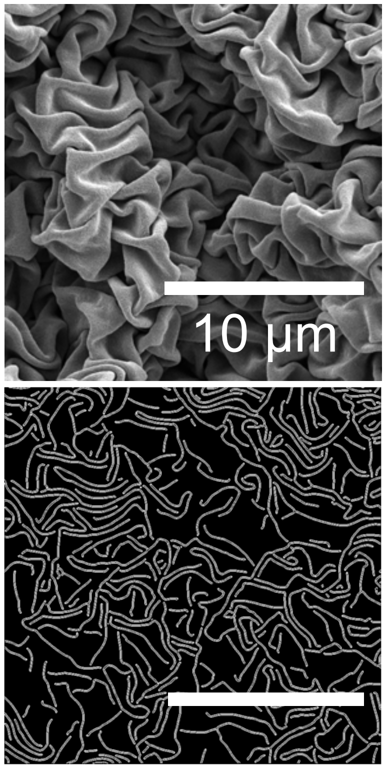
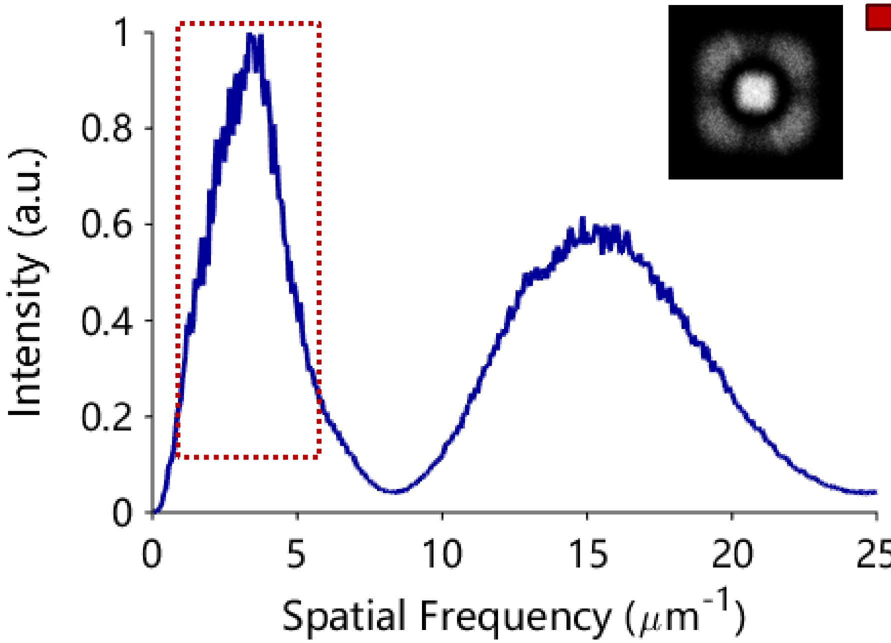
# Measuring Thin-Film Mechanical Properties: Fourier Analysis

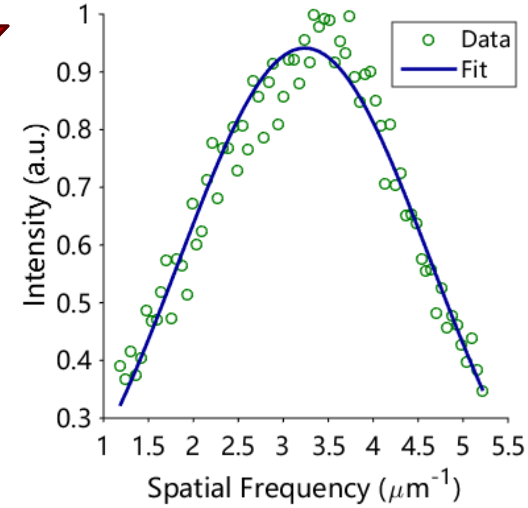



How do we extract wrinkle size?




**Fast Fourier Transform (FFT)**
(of binary image)

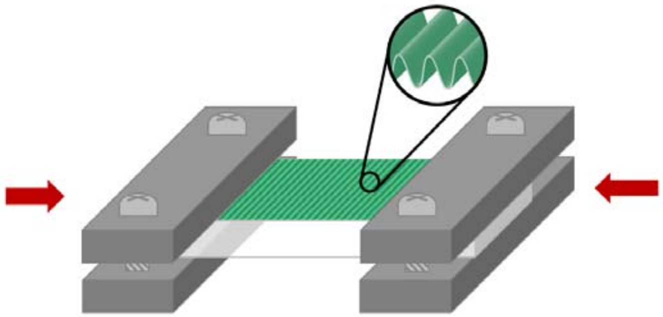
**Gaussian Curve Fit**
(of characteristic peak)

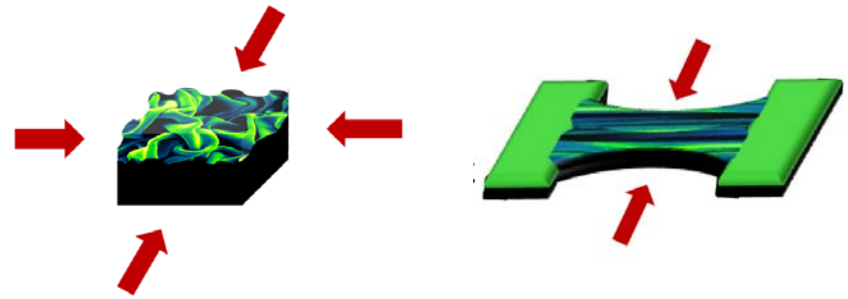



**Reciprocal of mean (peak) taken as wrinkle wavelength**

Stimpson et al. *Submitted to Micromachines.* **2021.**

# Direct Comparison of Moduli from Buckling Methods





$$\boldsymbol{E_f} = 3E_S \frac{(1-\nu_f^2)}{(1-\nu_S^2)} \left(\frac{\lambda}{2\pi h}\right)^3$$

$$\boldsymbol{E_f} = 3E_S \frac{(1-\nu_f^2)}{(1-\nu_S^2)} \left(\frac{a\lambda}{2\pi h}\right)^{\frac{3}{2}}$$

Obtain wrinkle wavelength ($\lambda$) and film thickness ($h$) experimentally

Stafford et al. *Nat. Mater.* **2004**, *3*, 545.
Gill et al. *Nanoscale* **2017**, *9*, 7781.