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Luca Lanotte, Ming Yu, Françoise Boissel, Cécile Le Floch-Fouéré, Ludovic Pauchard, et al.. Crack patterns in binary mixes of dairy colloids: The impact of protein properties.. Workshops – CECAM, Oct 2019, Lausanne, Switzerland. hal-02737430

HAL Id: hal-02737430

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Submitted on 2 Jun 2020

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Crack patterns in binary mixes of dairy colloids: *The impact of protein properties*

L. Lanotte, M. Yu, F. Boissel, C. Le Floch-Fouéré, R. Jeantet, L. Pauchard

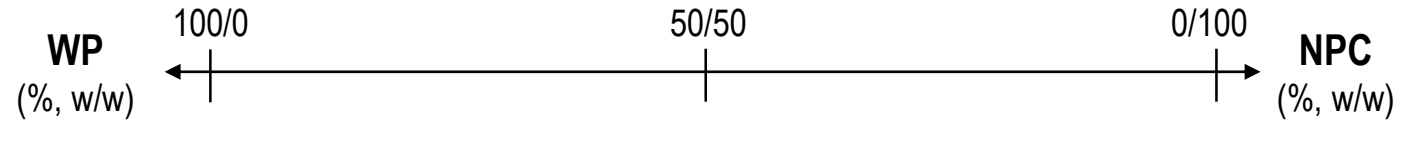


Rennes (France)



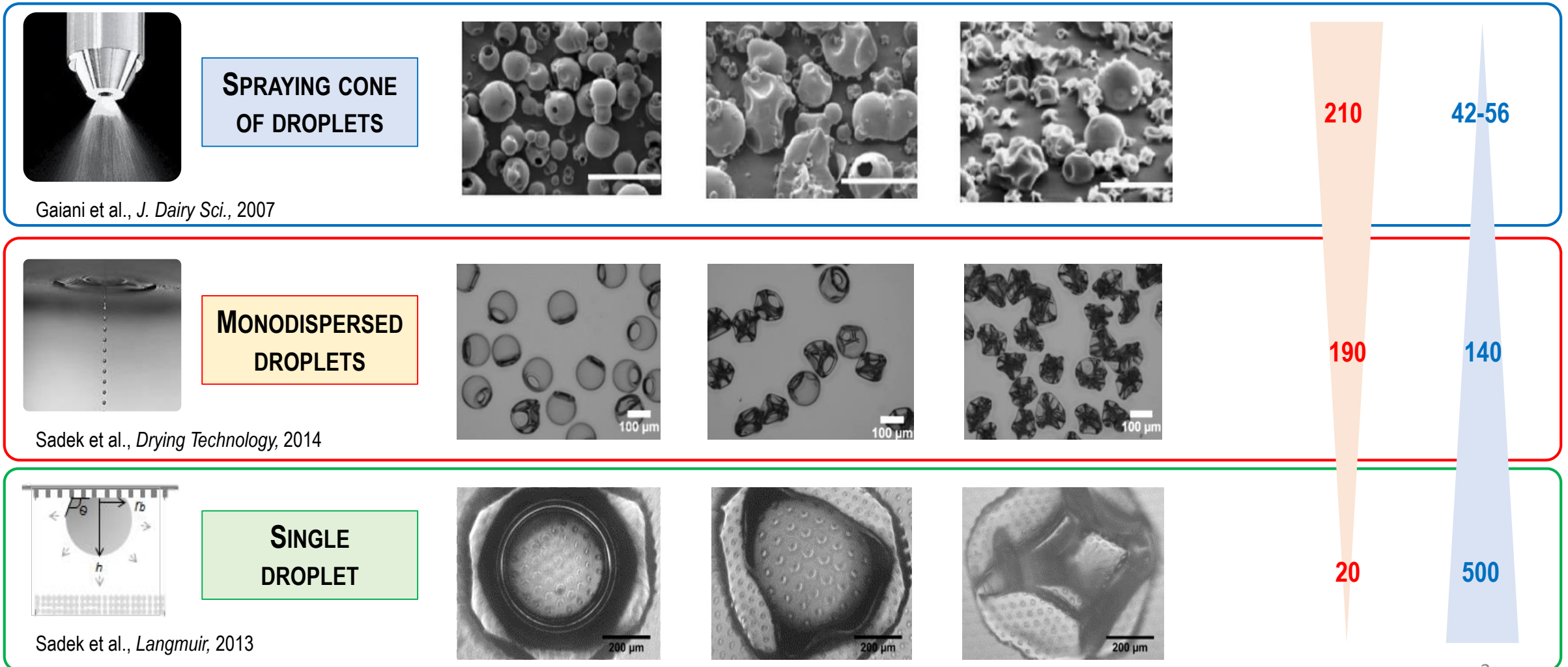
Paris Sud (France)

Drying of dairy proteins by multiscale approach



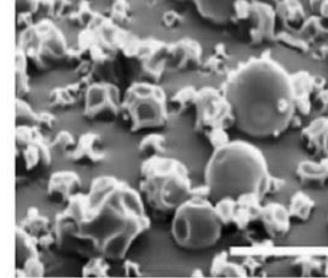
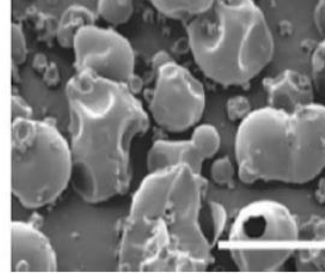
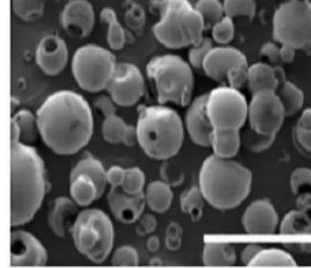
Drying Temp
(°C)

Particle Sizes
(µm)



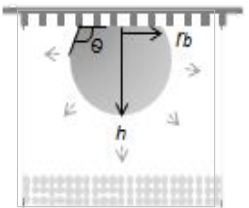
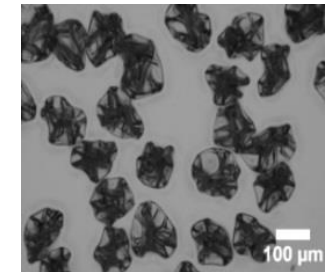
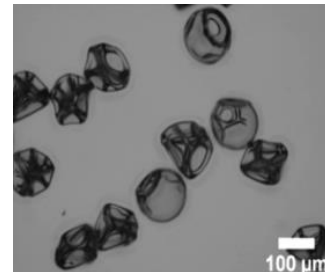
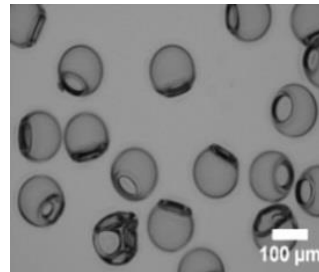
SPRAYING CONE OF DROPLETS

Gaiani et al., *J. Dairy Sci.*, 2007



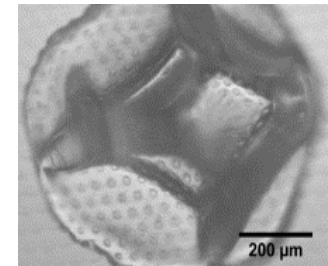
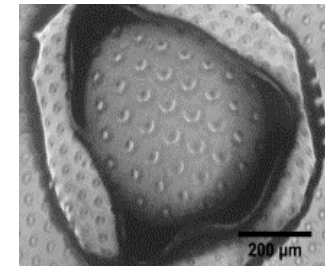
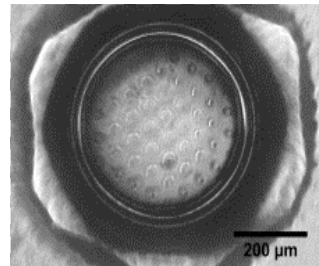
MONODISPERSED DROPLETS

Sadek et al., *Drying Technology*, 2014

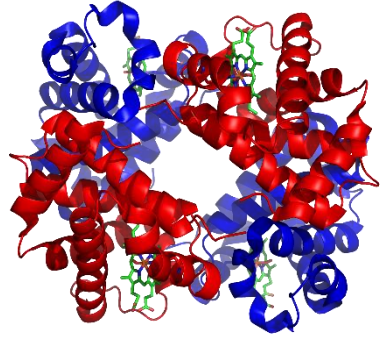


SINGLE DROPLET

Sadek et al., *Langmuir*, 2013



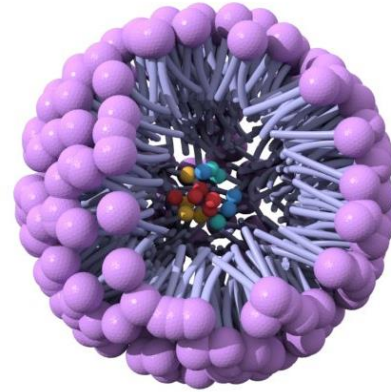
Whey proteins and casein micelles: a complex colloidal mix



Whey Proteins (WP)

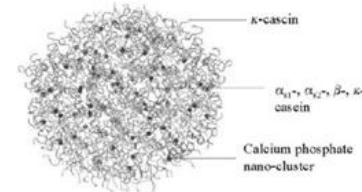
- Small size (average diameter ≈ 10 nm)
- **Rigid, globular structure**

Yohko, 2012.

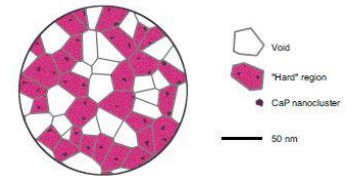


Native Phosphocaseinates (NPC)

- Average diameter $\approx 100-300$ nm
- **Sponge-like micellar structure**



Holt and Horne, 1996.



Bouchoux, 2010.

DIFFERENT SIZE, CHARGE AND MECHANICAL PROPERTIES

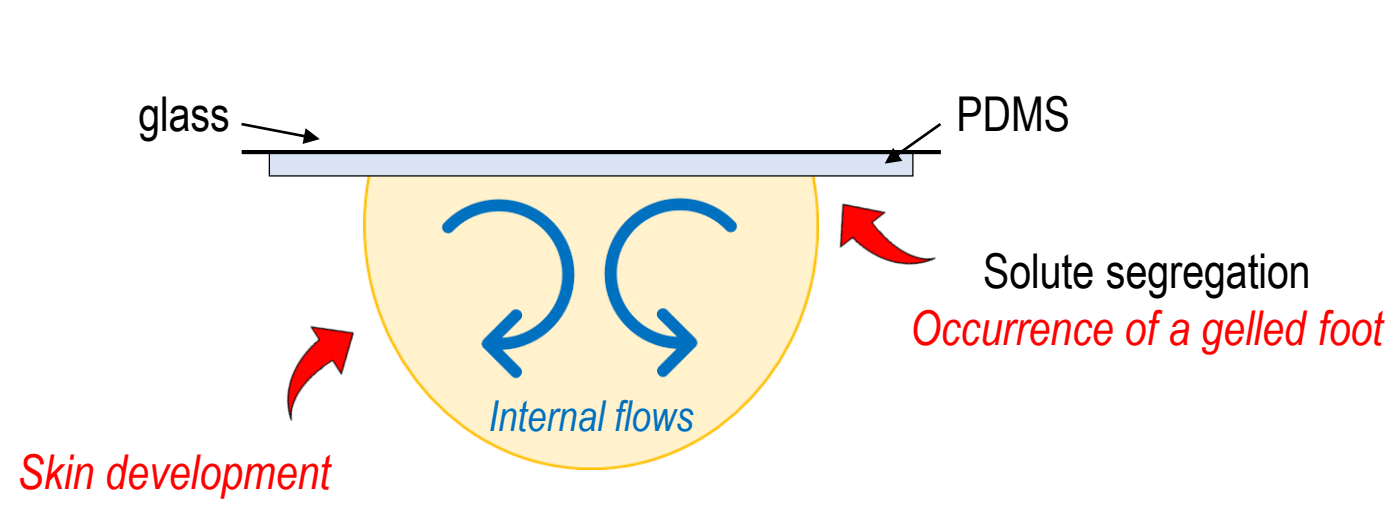
Study of the evaporation in a binary colloidal solution



Open questions

1 **INTERNAL FLOWS DRIVING THE EVAPORATION IN WP/NPC MIXES**

IMPACT OF THE MOLECULAR PROPERTIES ON THE FINAL SHAPE

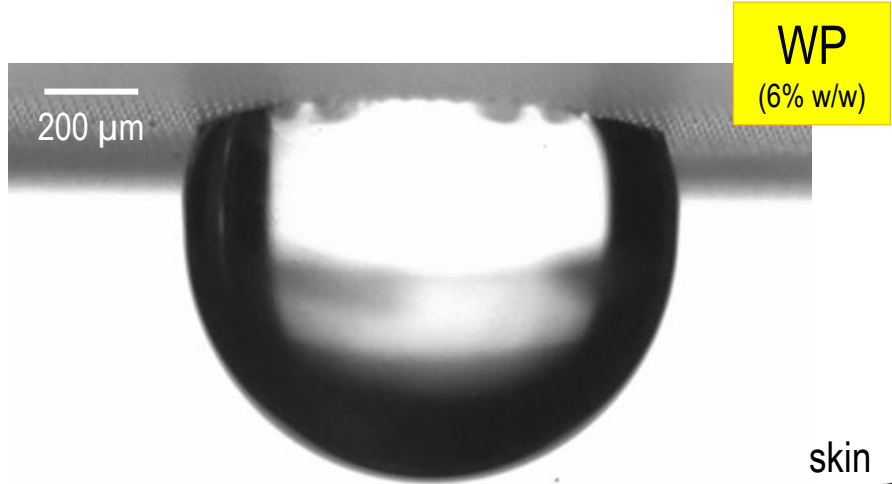


2 **CHARACTERIZATION OF THE SOL-GEL TRANSITION**
(skin formation, external segregation)

3 **MORPHOLOGY OF THE DRY PARTICLES**
(skin deformation, delamination)



Characterization of the sol-gel transition in WP/NPC mixes



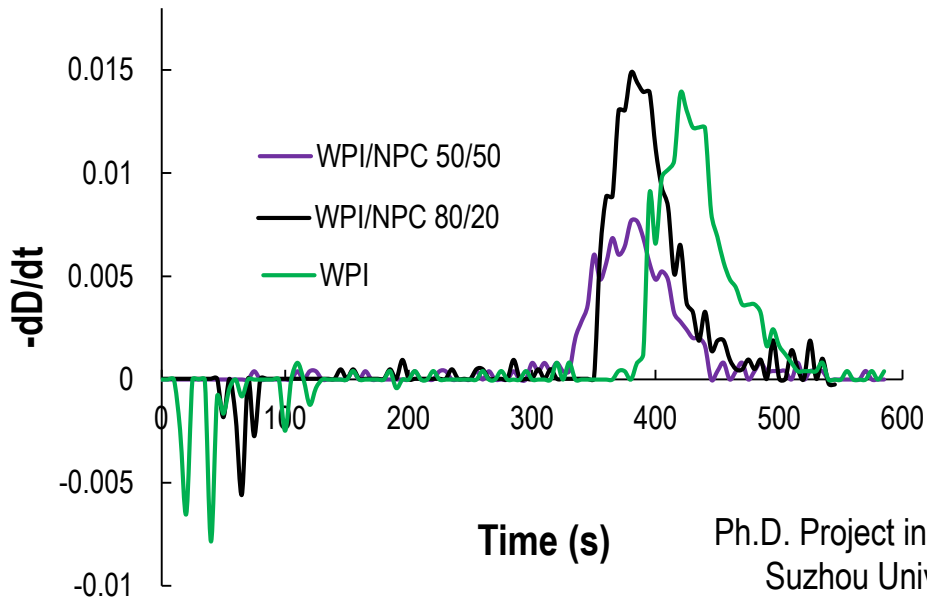
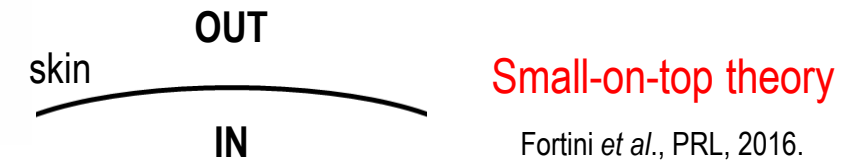
BORDER DELAMINATION

SKIN FORMATION

Evaluation of Calcium (Ca) % by SEM

Occurrence and intensity

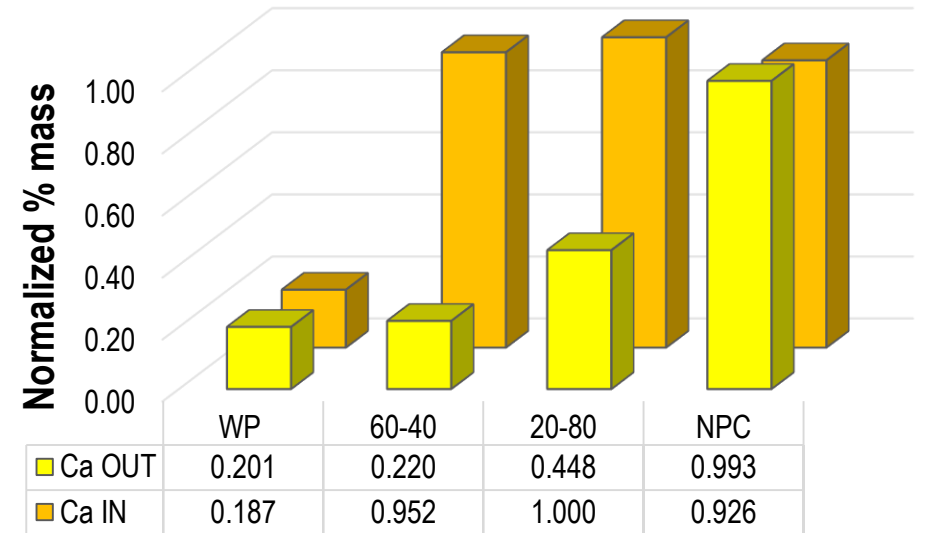
- Resistance to internal stress
- Increase of micelles → energy storage



Yu *et al.*, JCIS, in preparation.

Ph.D. Project in collaboration with
Suzhou University (China)

Prof. X.D. Chen



Lanotte *et al.*, Colloids and Surfaces A, 2018.

Evaluation of the mechanical behavior by crack formation

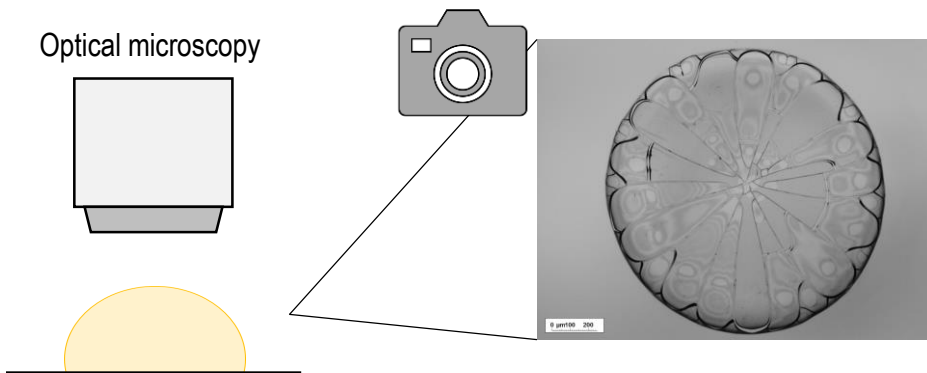
Online observation of drying WP/NPC droplets

SAMPLES

- Overall concentration =10% w/w
- Different WP/NPC ratio
(100/0, 90/10, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100)

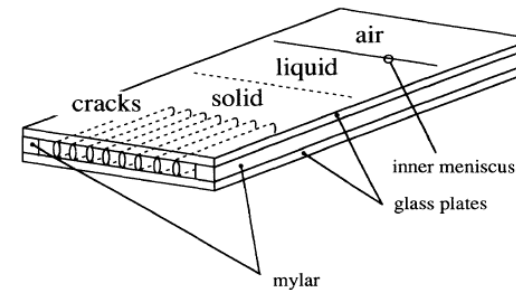
Sessile droplet

- Average droplet volume $\approx 0.5 \mu\text{l}$
- Glass coverslips
- Controlled environmental conditions
(temperature, $T=25^\circ\text{C}$; relative humidity, $RH=40\%$)

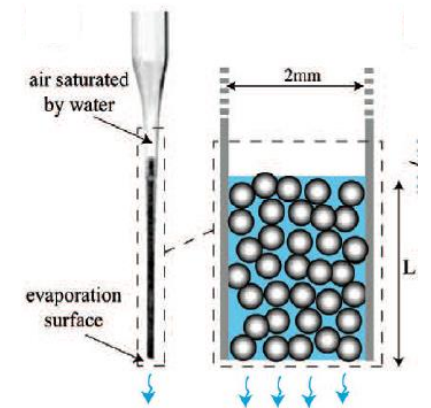


Hele-Shaw Cell – Pipette

- Temperature, $T=25-30^\circ\text{C}$
- Relative humidity, $RH=40\%$



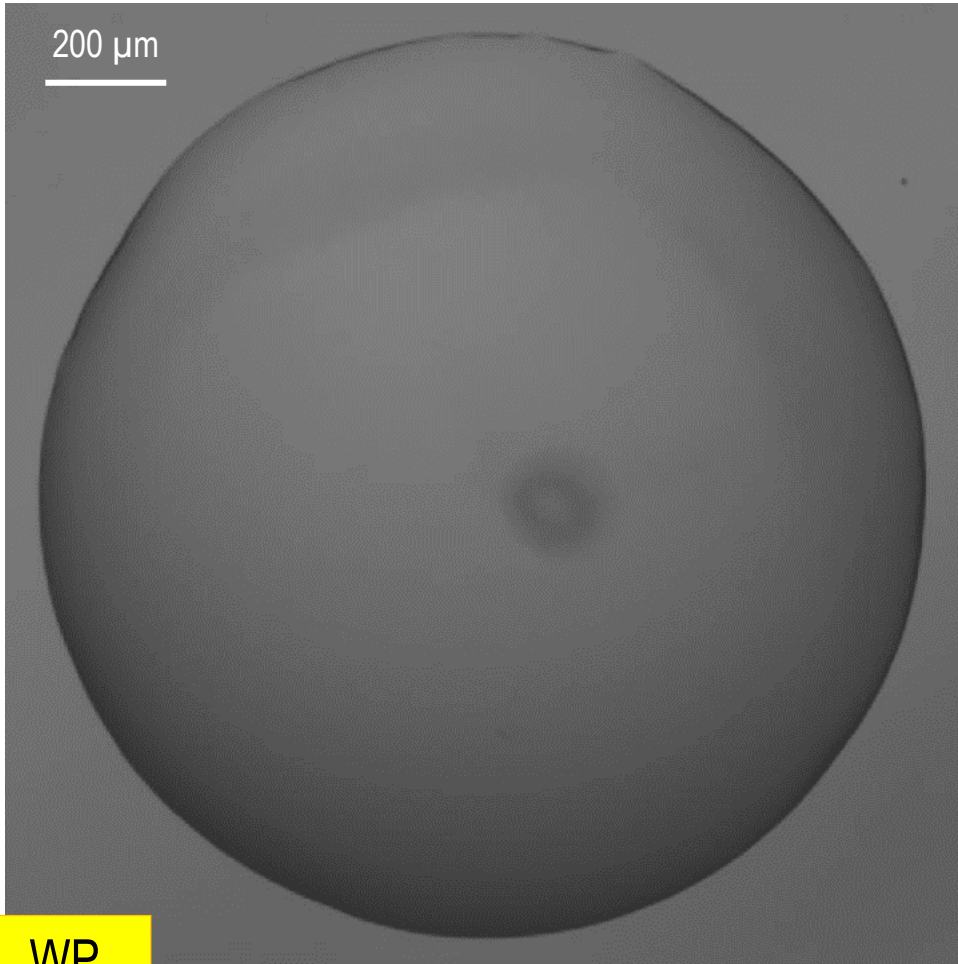
Allain and Limat, PRL, 1995.



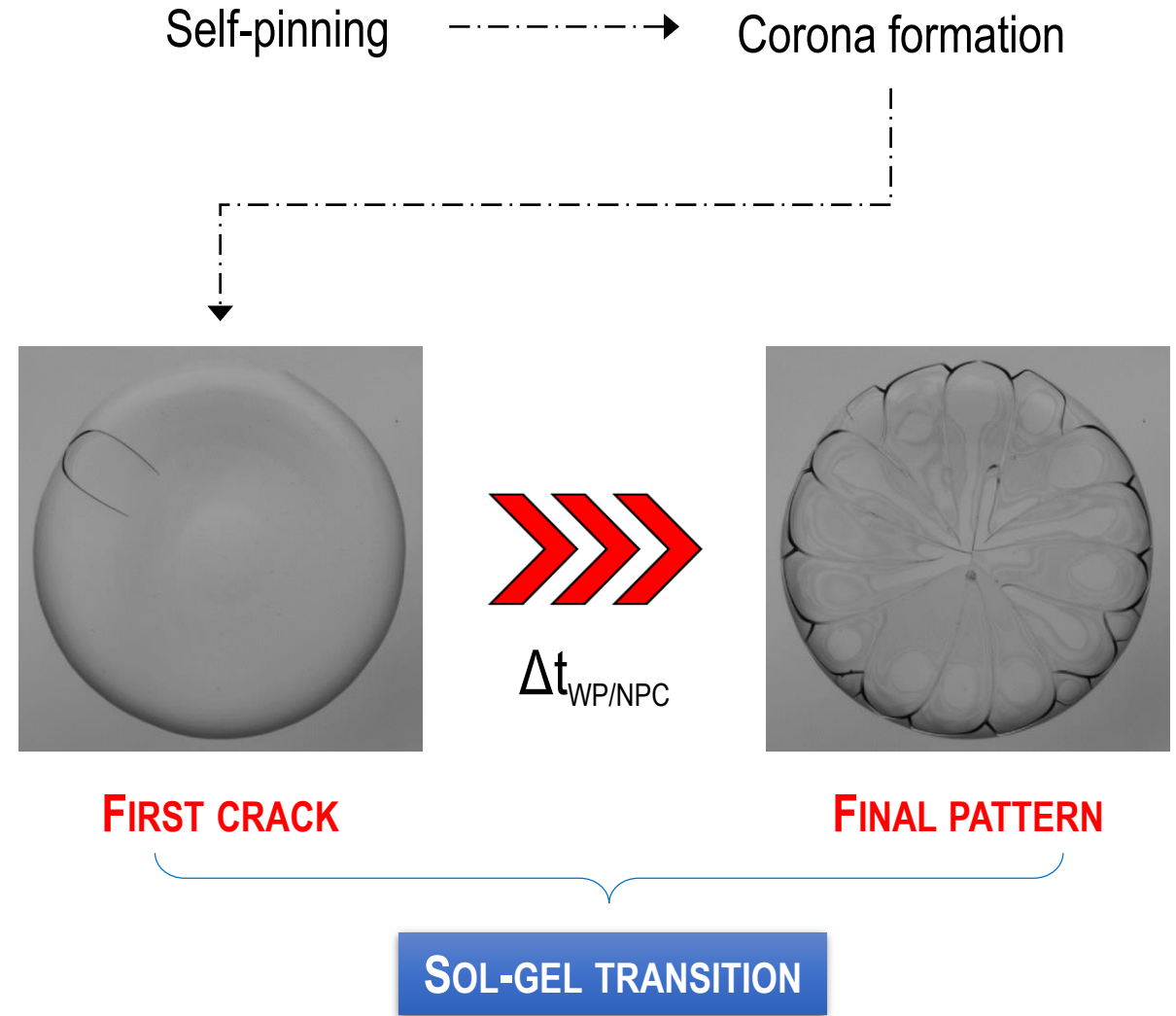
Sibrant and Pauchard, EPL, 2016.

Shape evolution with time

Morphology and mechanical properties

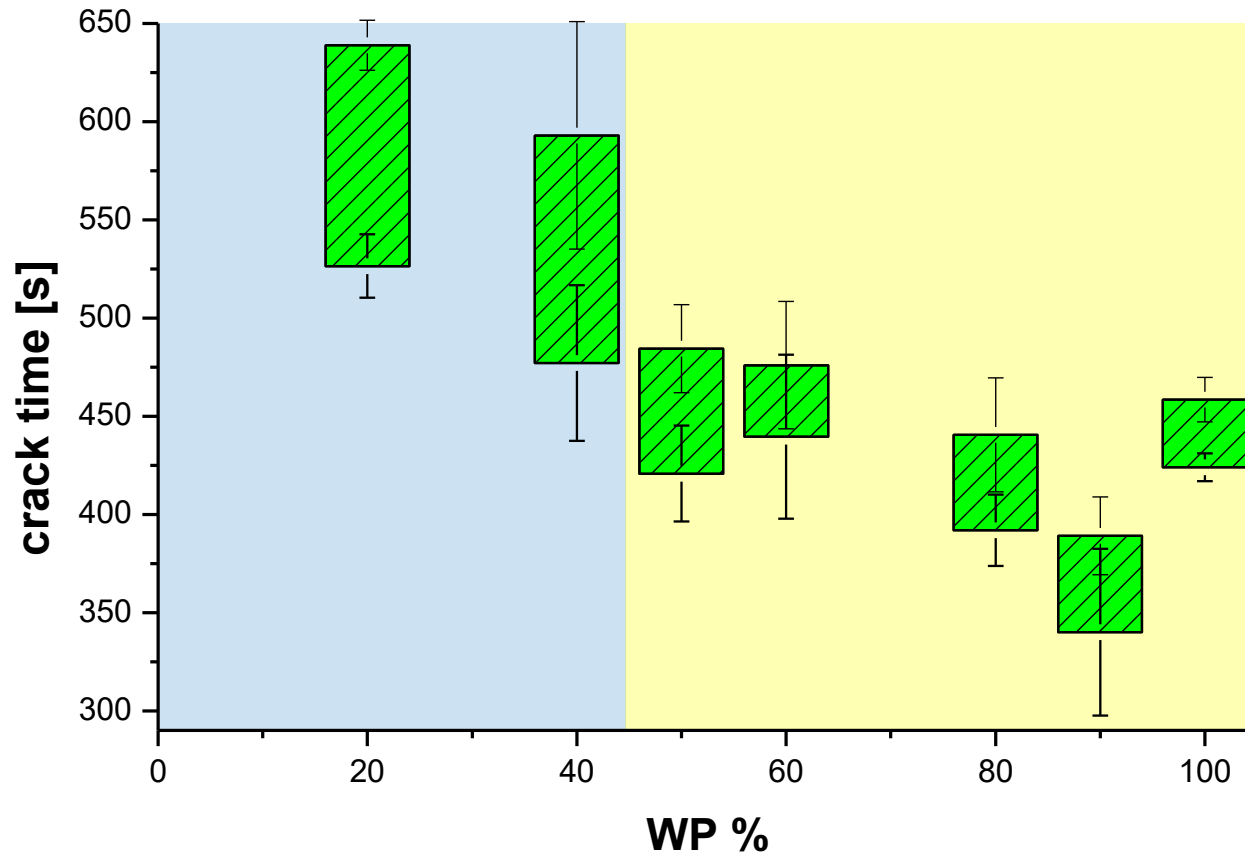


WP
(10% w/w)



The sol-gel transition

Crack formation and development



The rectangles represent the average duration of the final sol-gel transition. Thus, the minimum of the rectangles corresponds to the first crack time

WP-rich samples

- ☐ Delayed sol-gel transition in pure WP

High rigidity of whey proteins

Water retention due to NPC presence

- ☐ Almost comparable duration for the mixes

Probable WP deposition at borders and interface

(link with the small-on-top theory?)

NPC-rich samples

- ☐ No crack formation in pure NPC

Micelle high deformability – stress storage/release

- ☐ Earlier sol-gel transition with WPI increase, but similar duration

WPI-NPC interaction (any WP molecule trapped into NPC micelles?)

Impact of WPI percentage on crack structure

Qualitative overview

NPC

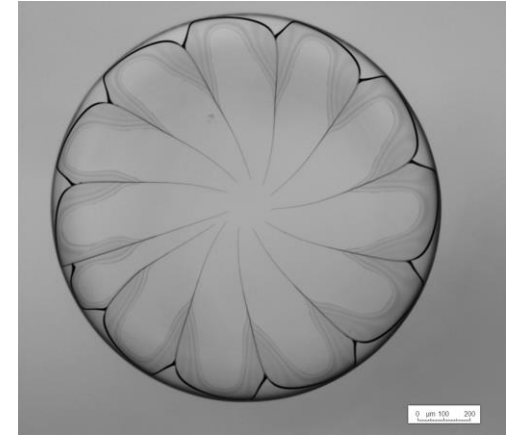


Addition of NPC in WP samples

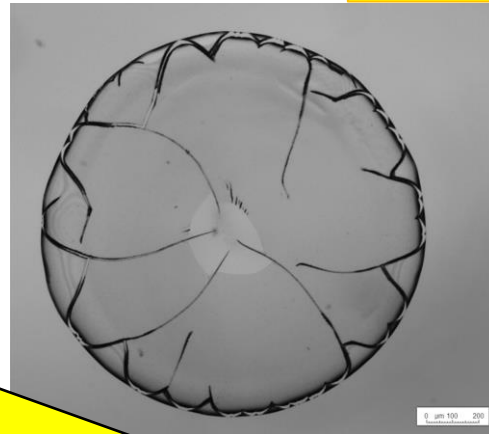
- Enhanced brittle character
- Stress released even by ortho-radial cracks

1

WP



20/80



50/50



80/20



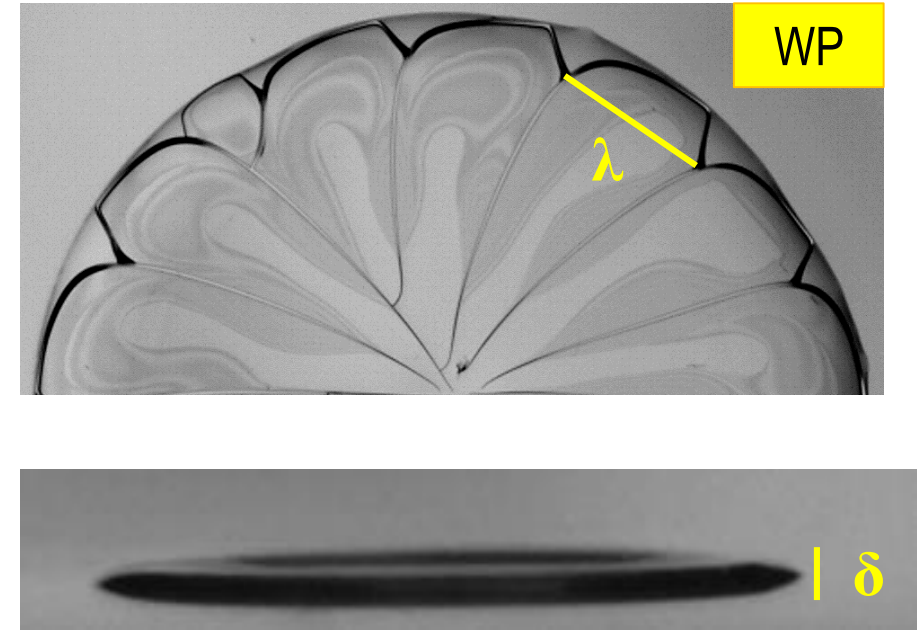
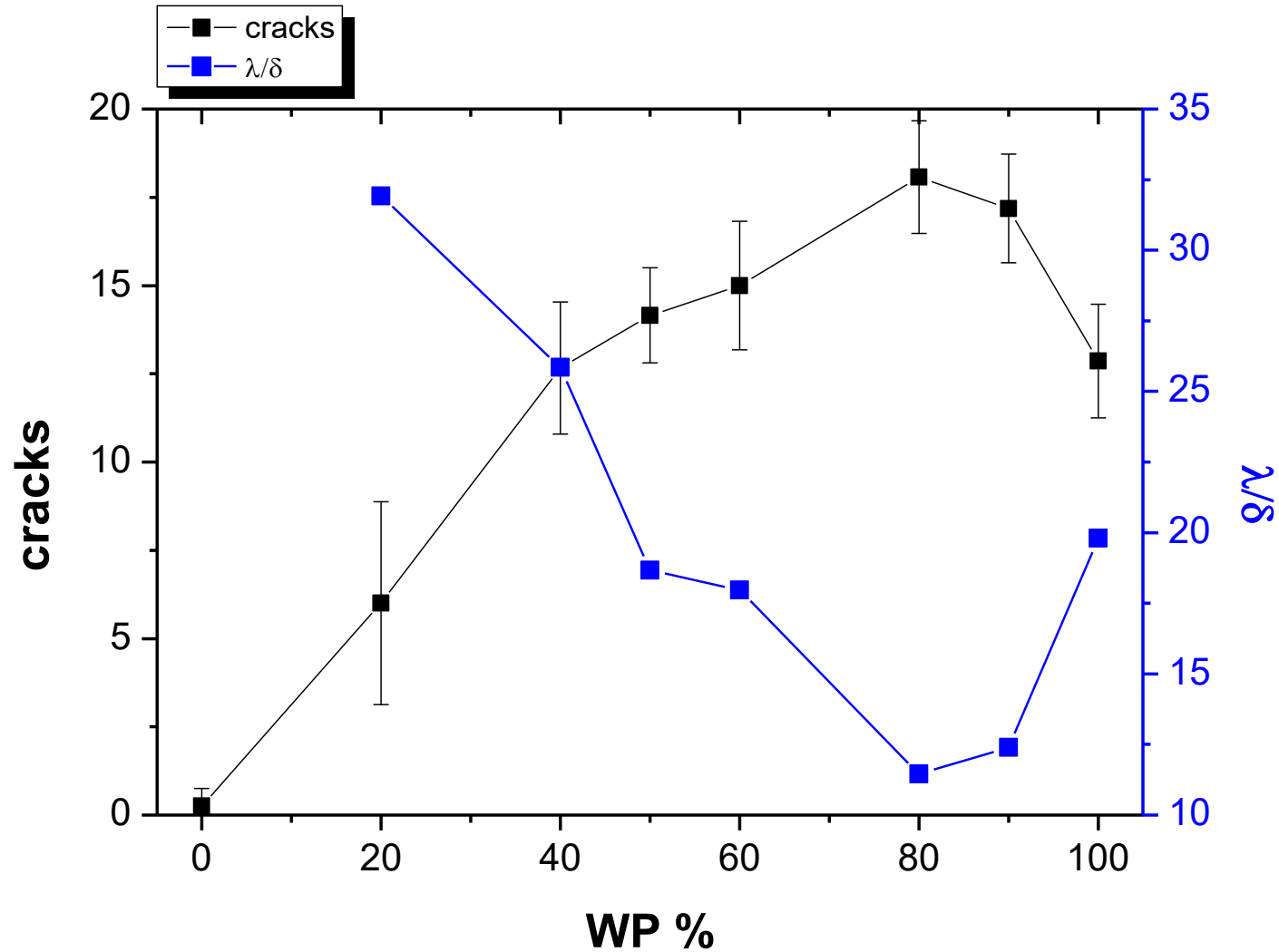
Increase of NPC%

- Crack decrease and loss of geometry
- Increase of material ductility

2

Impact of WPI percentage on radial crack formation

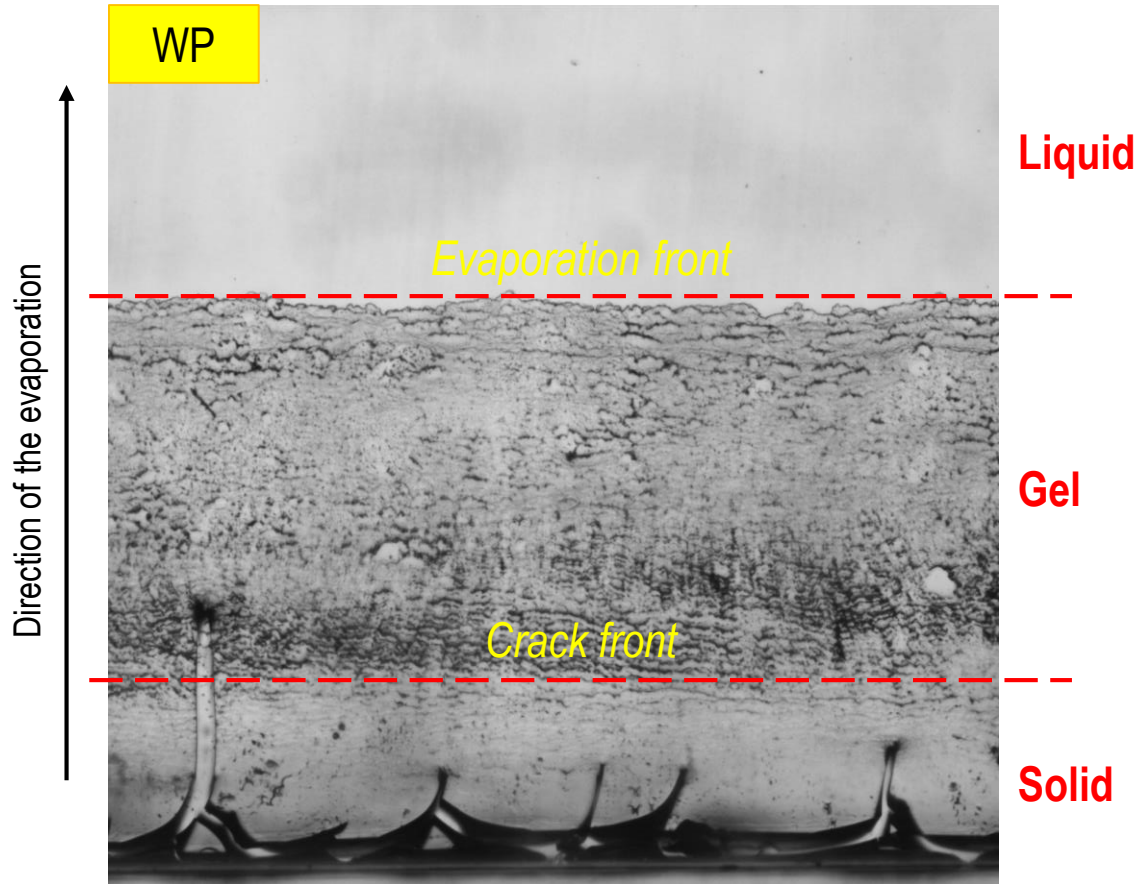
Colloidal mechanical properties



**THE PRESENCE OF A LOW AMOUNT OF
CASEIN MICELLES
STRONGLY FOSTERS THE CRACK FORMATION**

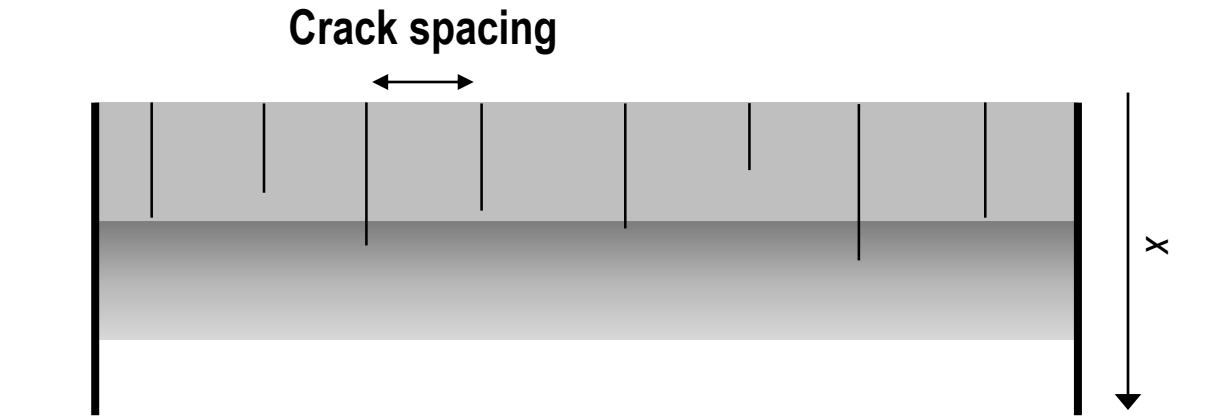
Evaporation in Hele-Shaw cells

Mono-directional drying process



Allain and Limat, PRL, 1995.

Dufresne et al., PRL, 2003.



FIRST CRACK

$$\text{stress} = K_{IC} / \sqrt{\pi a}$$

Particle size and structure inhomogeneity (porosity)

CRACK SPACING

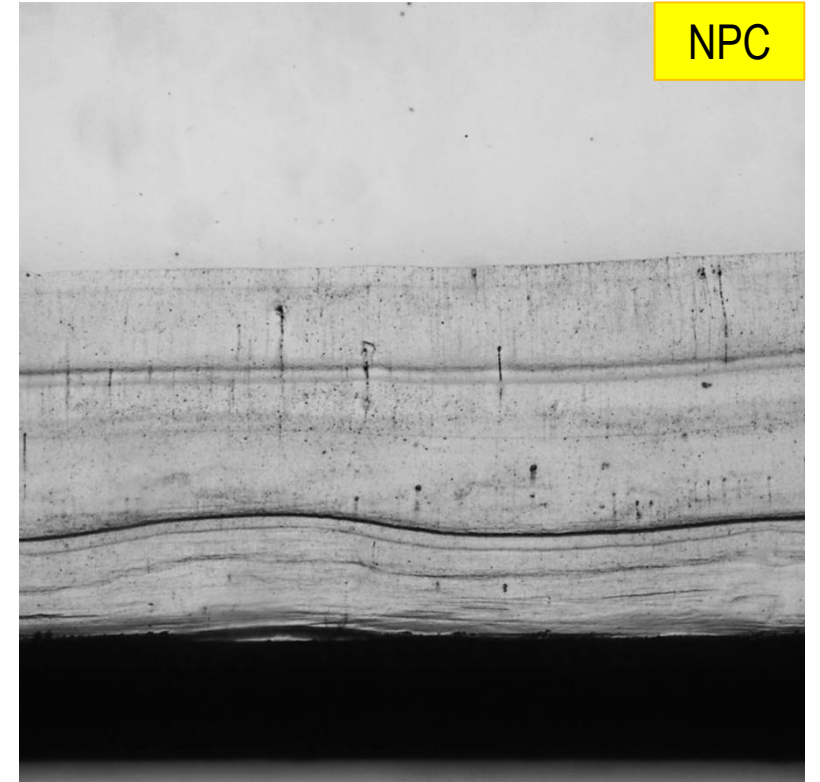
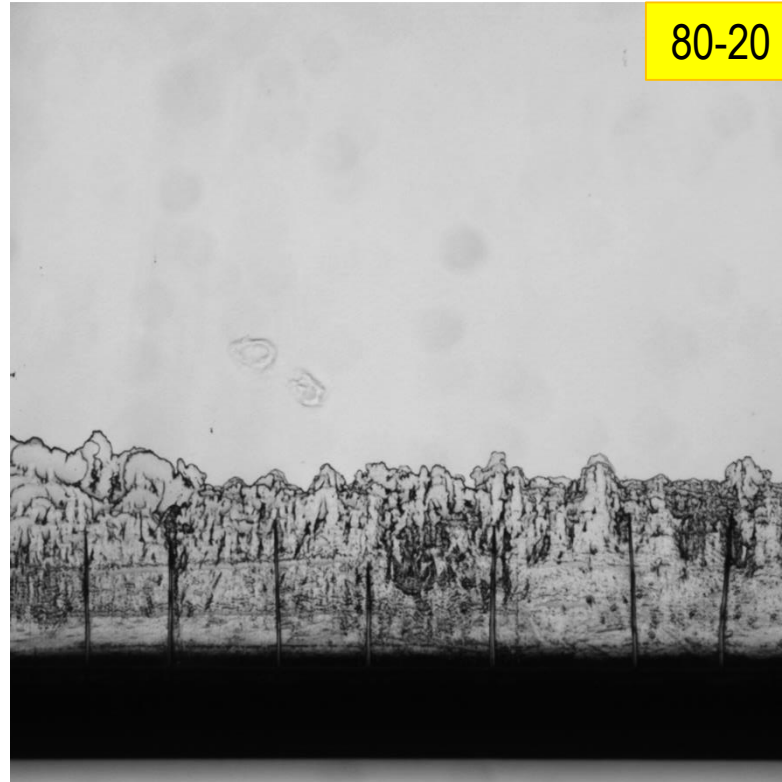
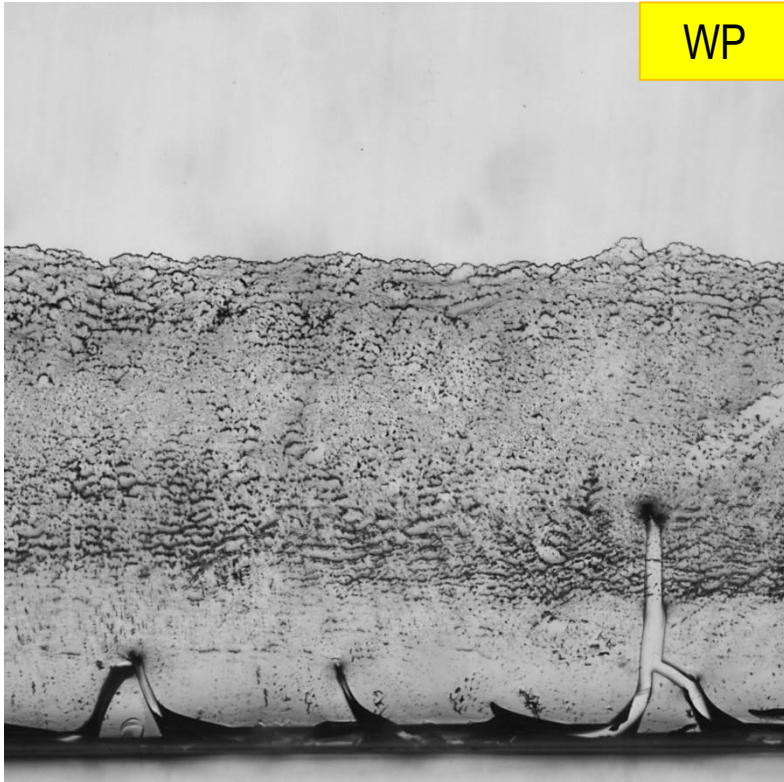
$$\sigma_{xx} = \tilde{E} \left[\left(\frac{\partial u}{\partial x} \right) + C \right]$$

Stress balance
 ↓ crack relaxation ↑ water evaporation

Mechanical properties and structure of the material

Drying-induced parallel crack formation

Qualitative observation



WP samples

The high rigidity of the material affects the formation of the pattern of parallel cracks



$90 < WP\% < 50$

The number of cracks increases with the diminution of WP%

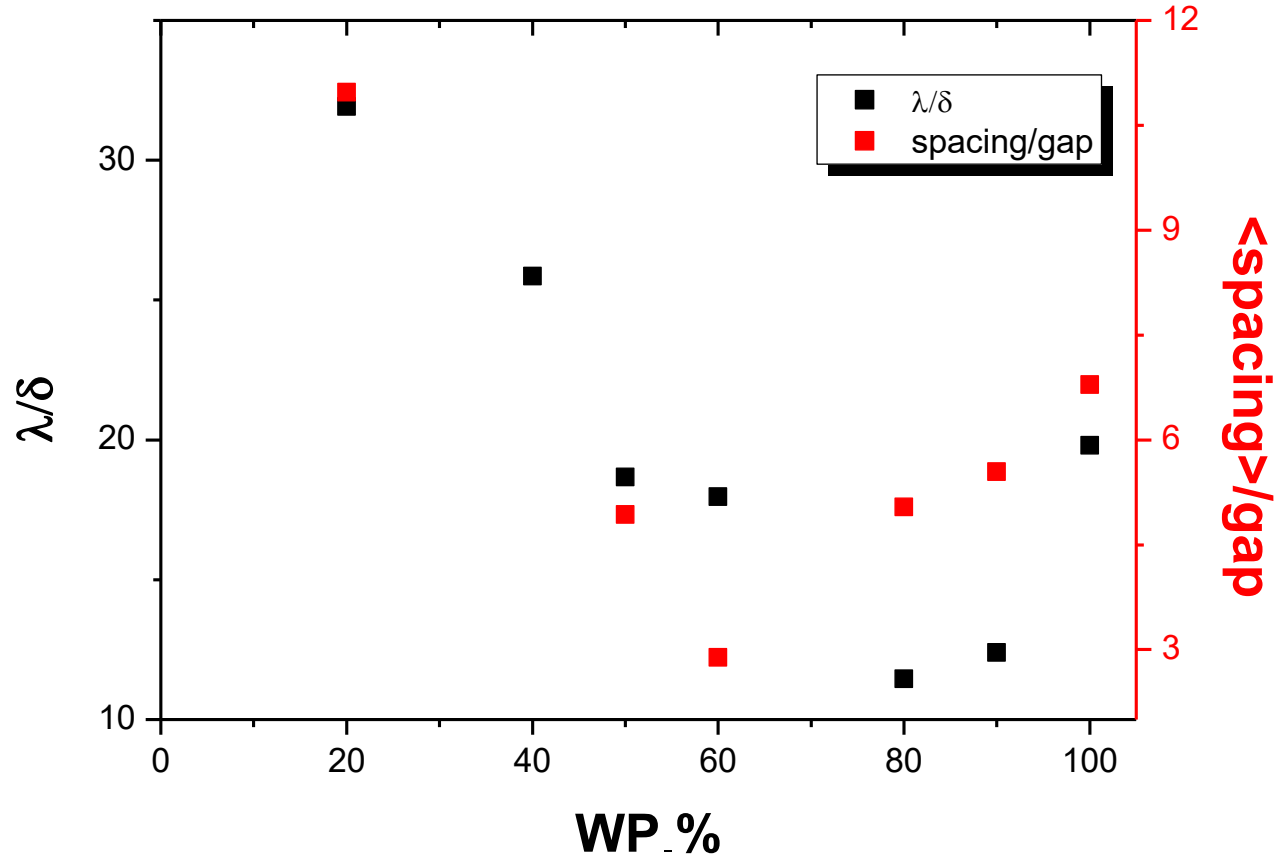


$50 < WP\% < 0$

Few irregular cracks or complete absence of fractures in case of NPC samples

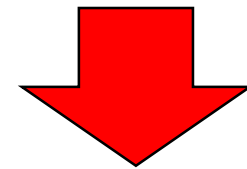
Drying-induced parallel crack formation

Comparison with crack formation in sessile droplets



Good qualitative agreement between the two approaches

Slight shift of the minimum



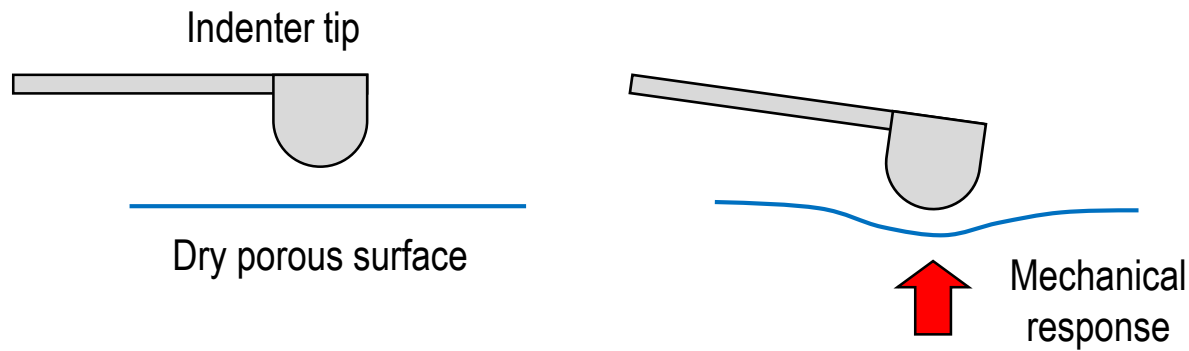
Need of more experimental tests or geometry effect on crack occurrence?

Conclusions and next steps..

- ❑ Corona development (solute segregation) and sample composition (WP/NPC)
 - Combination of optical microscopy (bright field, fluorescence) and profile visualization*

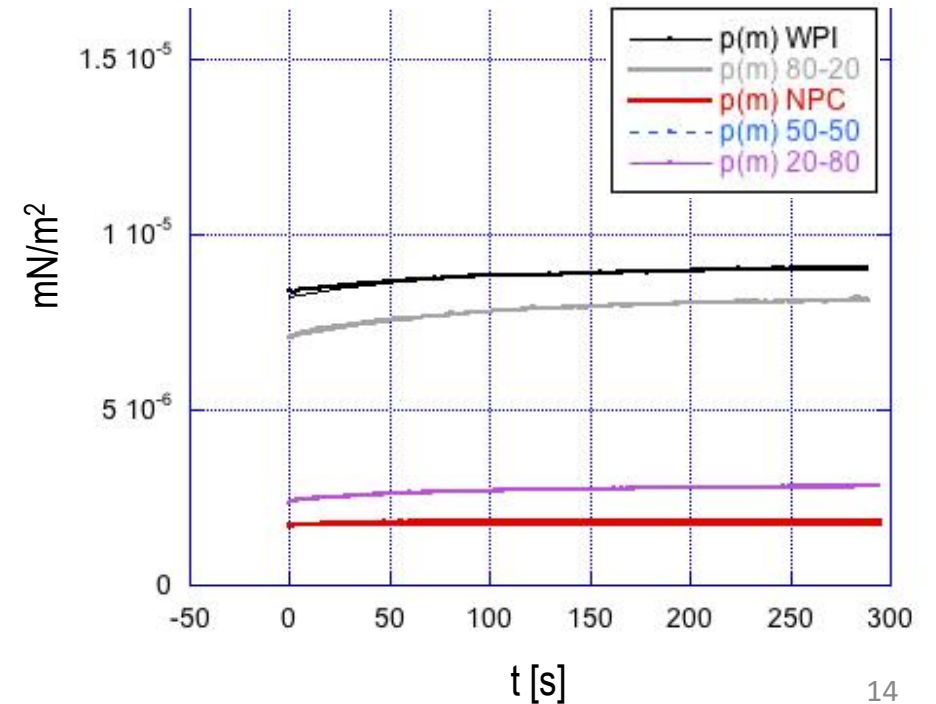
- ❑ Impact of WP/NPC ratio on the sol-gel transition mechanisms (first crack formation, duration)
- ❑ Stress release highlighted by crack formation

Interfacial rheology and indentation tests to evaluate the mechanical properties of the skin during and after the drying process



Two categories of samples depending on WP%

Colloidal deposition at the air-liquid interface



A grayscale microscopic image of plant cells, showing large, rounded cells with prominent cell walls and internal structures like chloroplasts. The cells are arranged in a somewhat regular pattern, with some showing clear circular structures.

Thank you for your attention