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

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STLO — Rennes (France)

FAST — Paris Sud (France)

CECAM Workshop (Lausanne, Switzerland), October 30th - November 1st, 2019

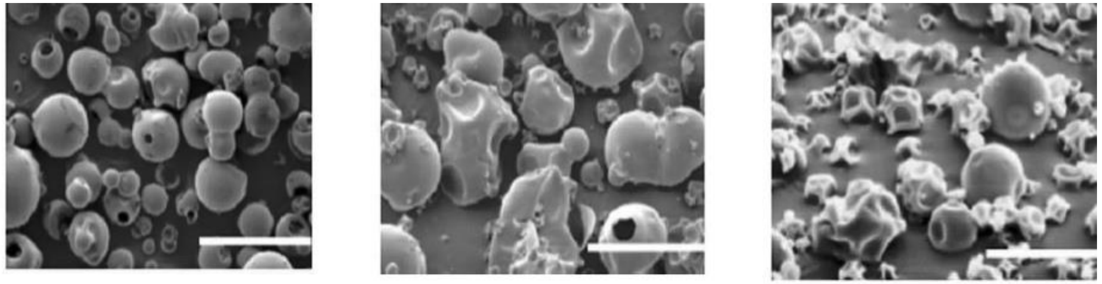
Drying of dairy proteins by multiscale approach

INRA SCIENCE & IMPACT

WP (%, w/w) — 100/0 — 50/50 — 0/100 — **NPC** (%, w/w)

Drying Temp (°C) | **Particle Sizes** (µm)

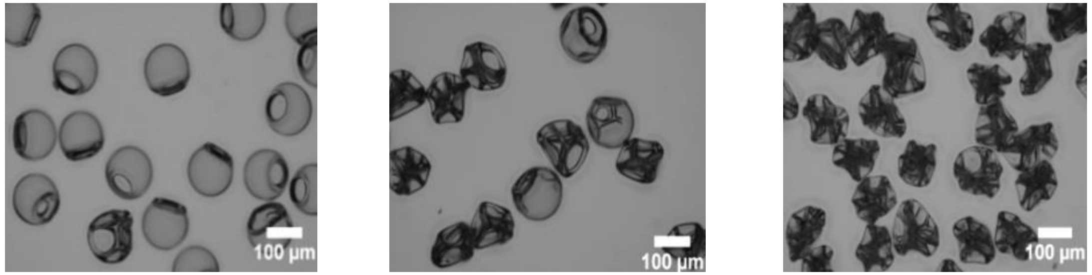
SPRAYING CONE OF DROPLETS



Drying Temp: 210 — Particle Sizes: 42-56

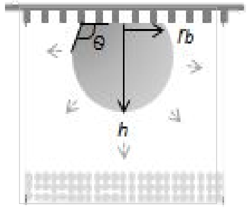
Gaiani et al., *J. Dairy Sci.*, 2007

MONODISPERSED DROPLETS

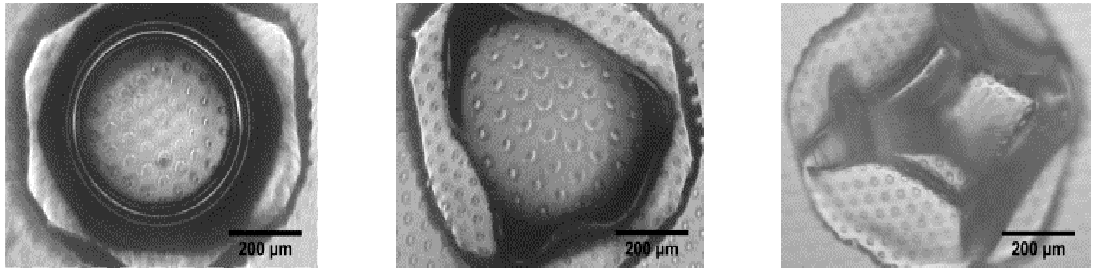


Drying Temp: 190 — Particle Sizes: 140

Sadek et al., *Drying Technology*, 2014



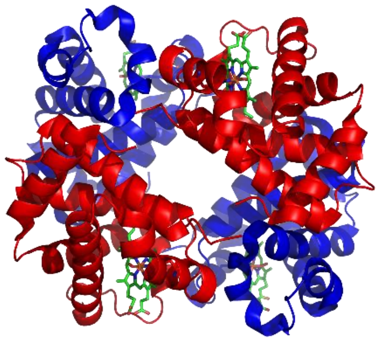
SINGLE DROPLET



Drying Temp: 20 — Particle Sizes: 500

Sadek et al., *Langmuir*, 2013

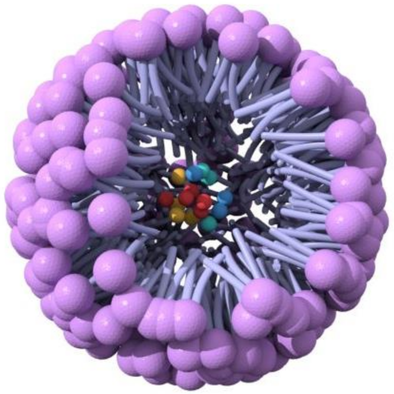
Whey proteins and casein micelles: a complex colloidal mix



Whey Proteins (WP)

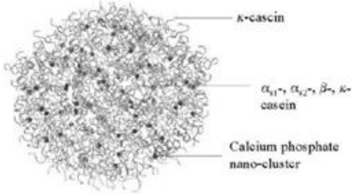
- Small size (average diameter ≈10 nm)
- **Rigid, globular structure**

Yohko, 2012.

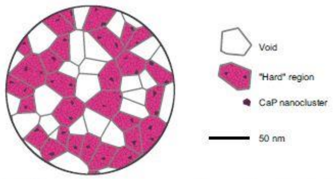


Native Phosphocaseinates (NPC)

- Average diameter ≈100-300 nm
- **Sponge-like micellar structure**



Holt and Horne, 1996.



Bouchoux, 2010.

DIFFERENT SIZE, CHARGE AND MECHANICAL PROPERTIES

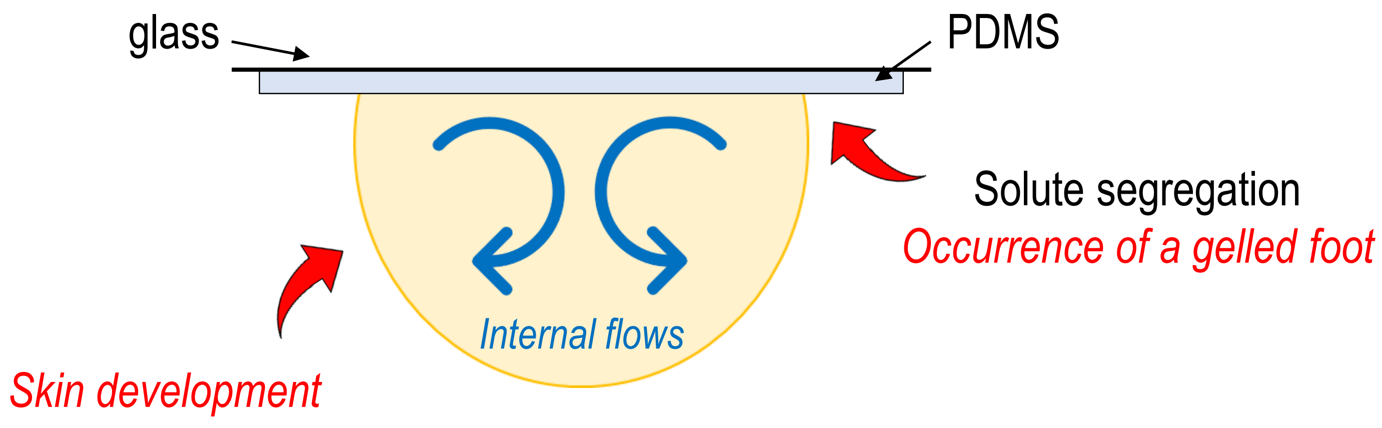
Study of the evaporation in a binary colloidal solution

Open questions

1

INTERNAL FLOWS DRIVING THE EVAPORATION IN WP/NPC MIXES

IMPACT OF THE MOLECULAR PROPERTIES ON THE FINAL SHAPE



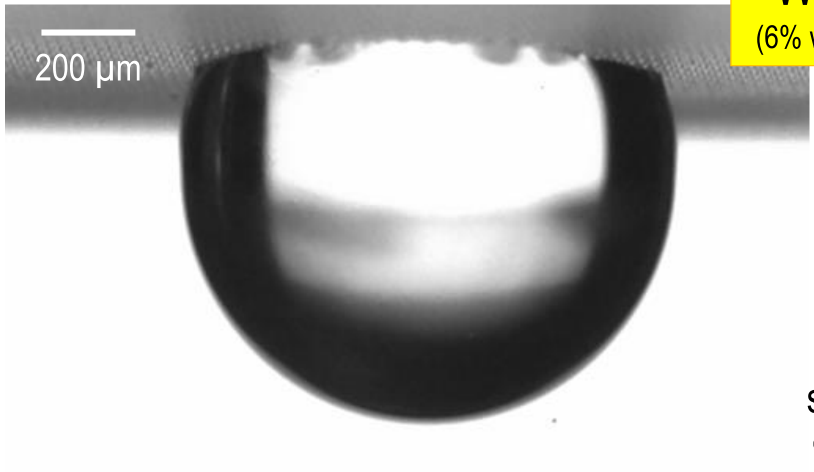
2

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

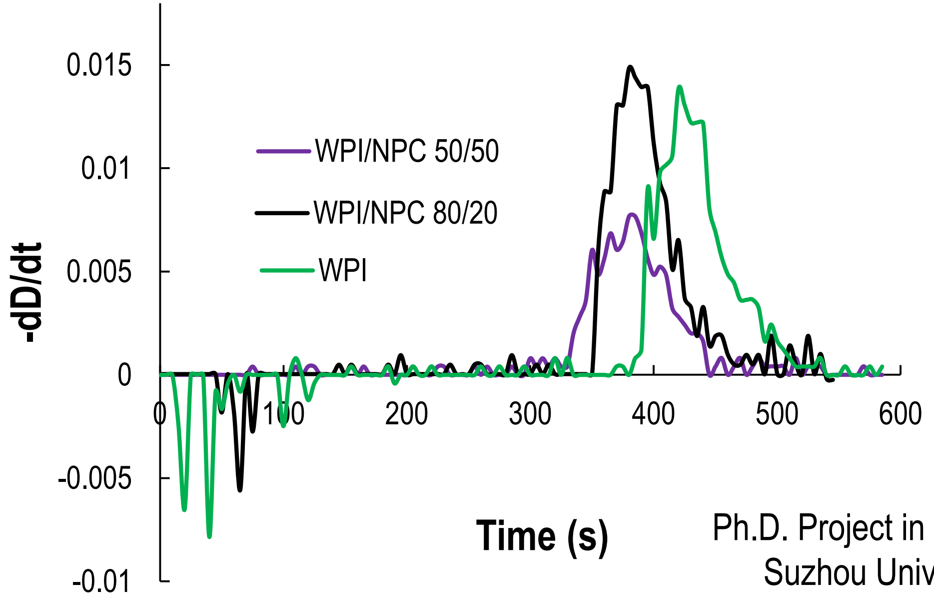


WP
(6% w/w)

Border delamination

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

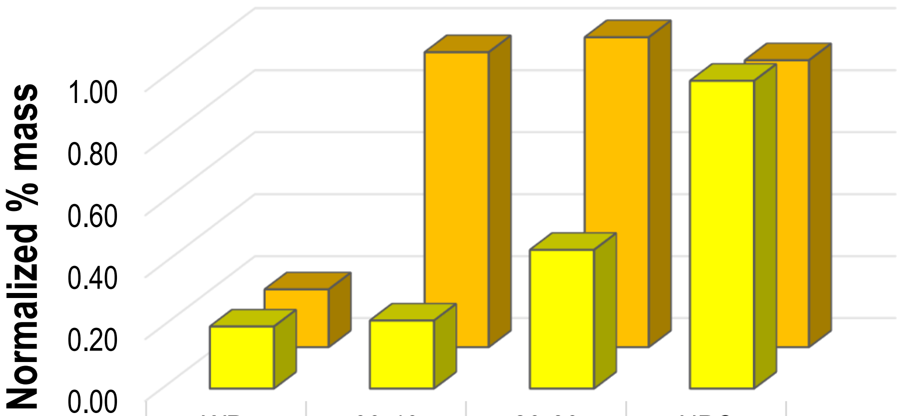
Skin formation

Evaluation of Calcium (Ca) % by SEM

OUT
skin
IN

Small-on-top theory

Fortini *et al.*, PRL, 2016.



	WP	60-40	20-80	NPC
Ca OUT	0.201	0.220	0.448	0.993
Ca IN	0.187	0.952	1.000	0.926

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

Evaluation of the mechanical behavior by crack formation

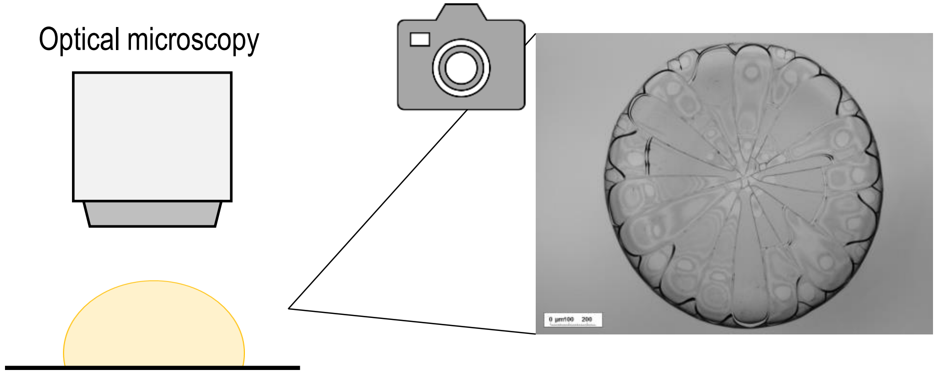
Online observation of drying WP/NPC droplets

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)

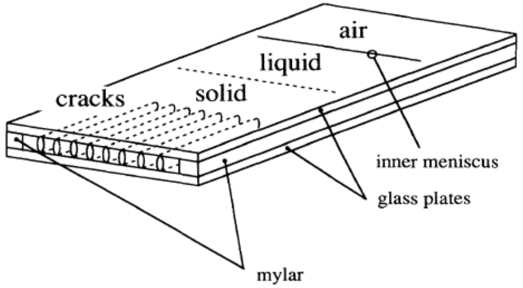
Sessile droplet

- *Average droplet volume ≈0.5 µl*
- *Glass coverslips*
- *Controlled environmental conditions (temperature, T=25°C; relative humidity, RH=40%)*

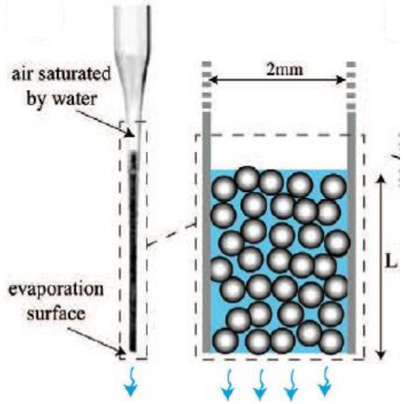


Hele-Shaw Cell – Pipette

- *Temperature, T=25-30°C*
- *Relative humidity, RH=40%*



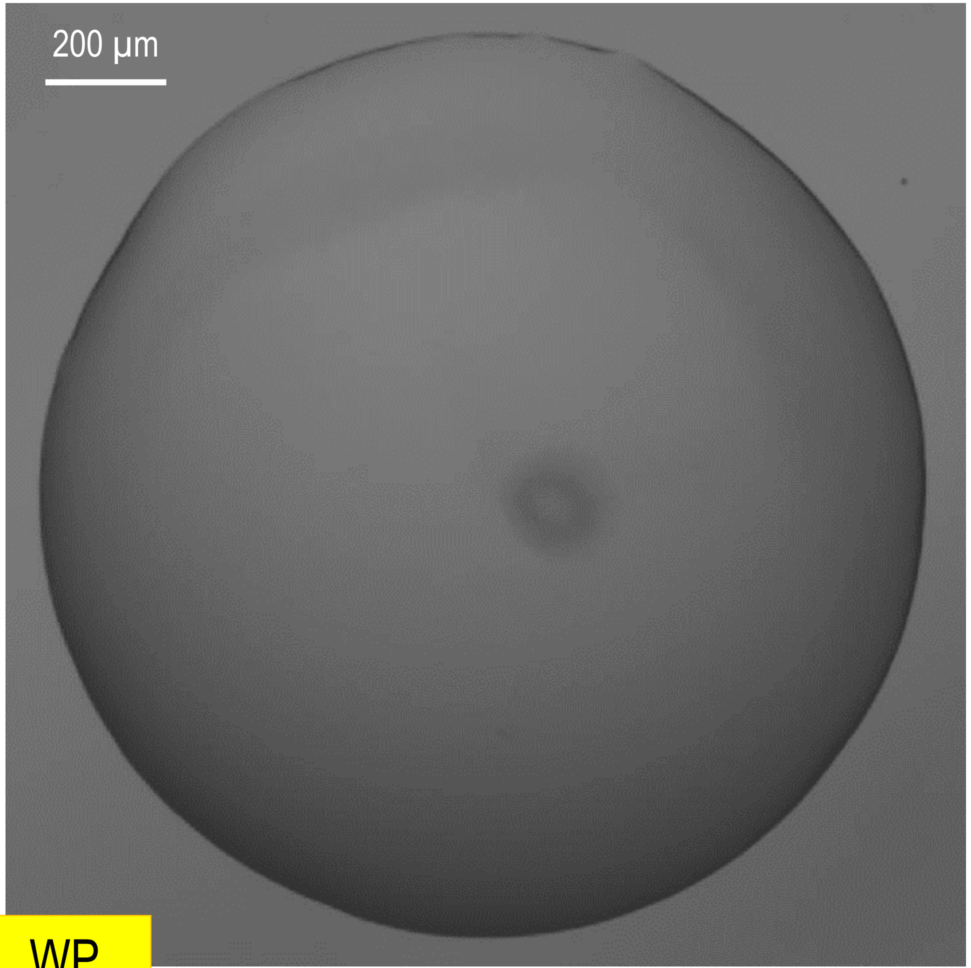
Allain and Limat, PRL, 1995.



Sibrant and Pauchard, EPL, 2016.

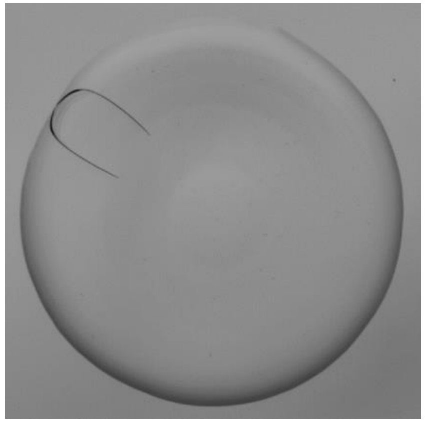
Shape evolution with time

Morphology and mechanical properties

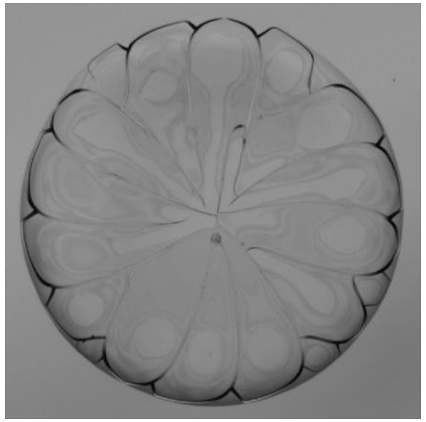


WP
(10% w/w)

Self-pinning → Corona formation



$\Delta t_{WP/NPC}$



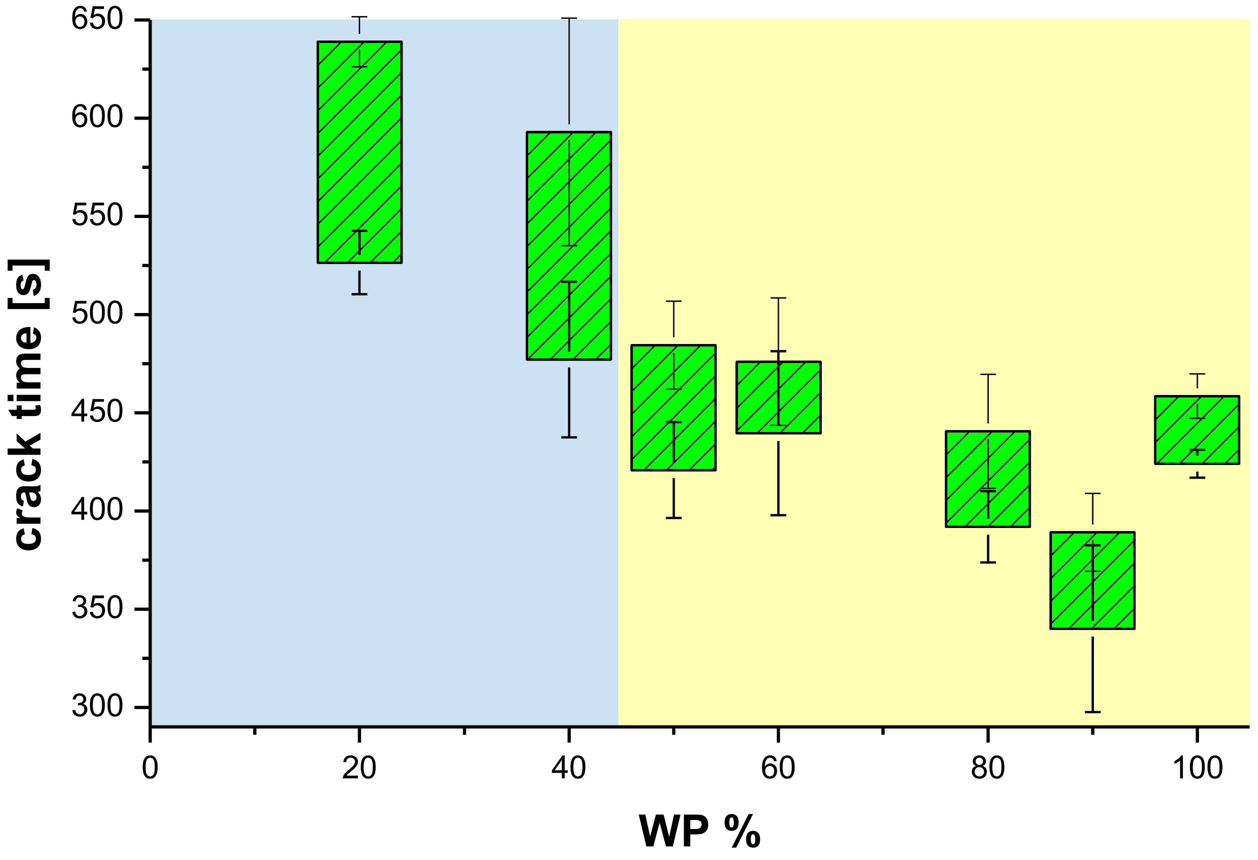
FIRST CRACK

FINAL PATTERN

SOL-GEL TRANSITION

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

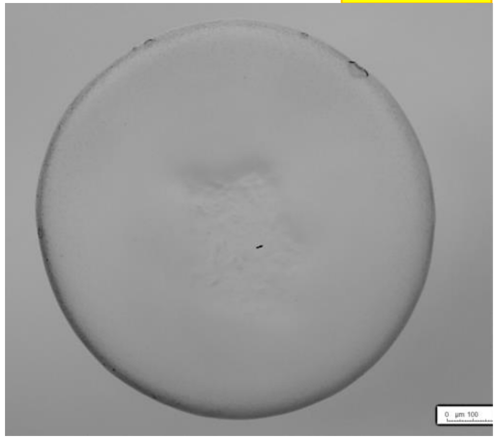
- ❑ No crack formation in pure NPC
  Micelle high deformability – stress storage/release

- ❑ 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

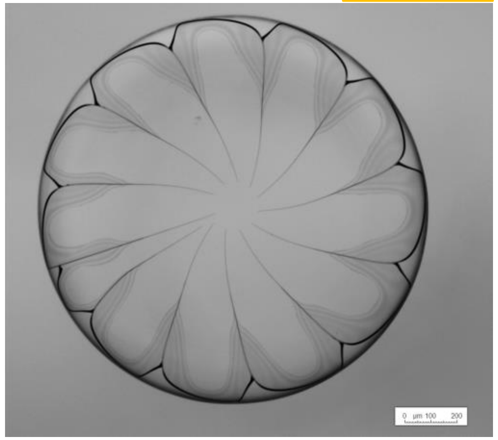
NPC



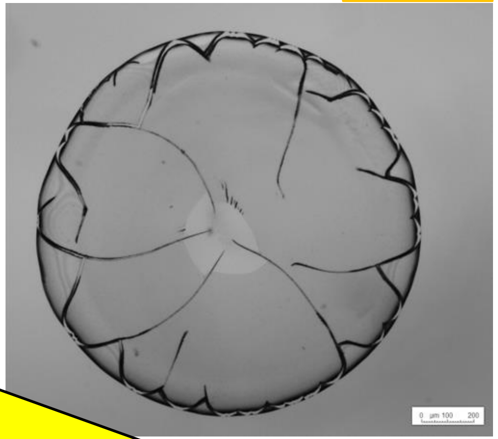
Addition of NPC in WP samples (1)

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

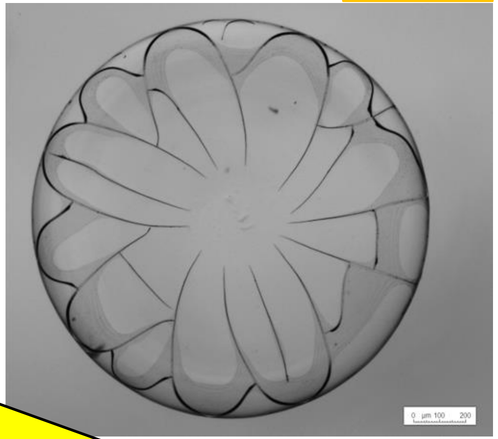
WP



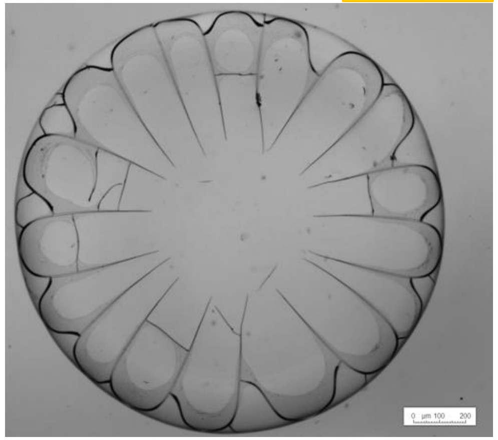
20/80



50/50



80/20

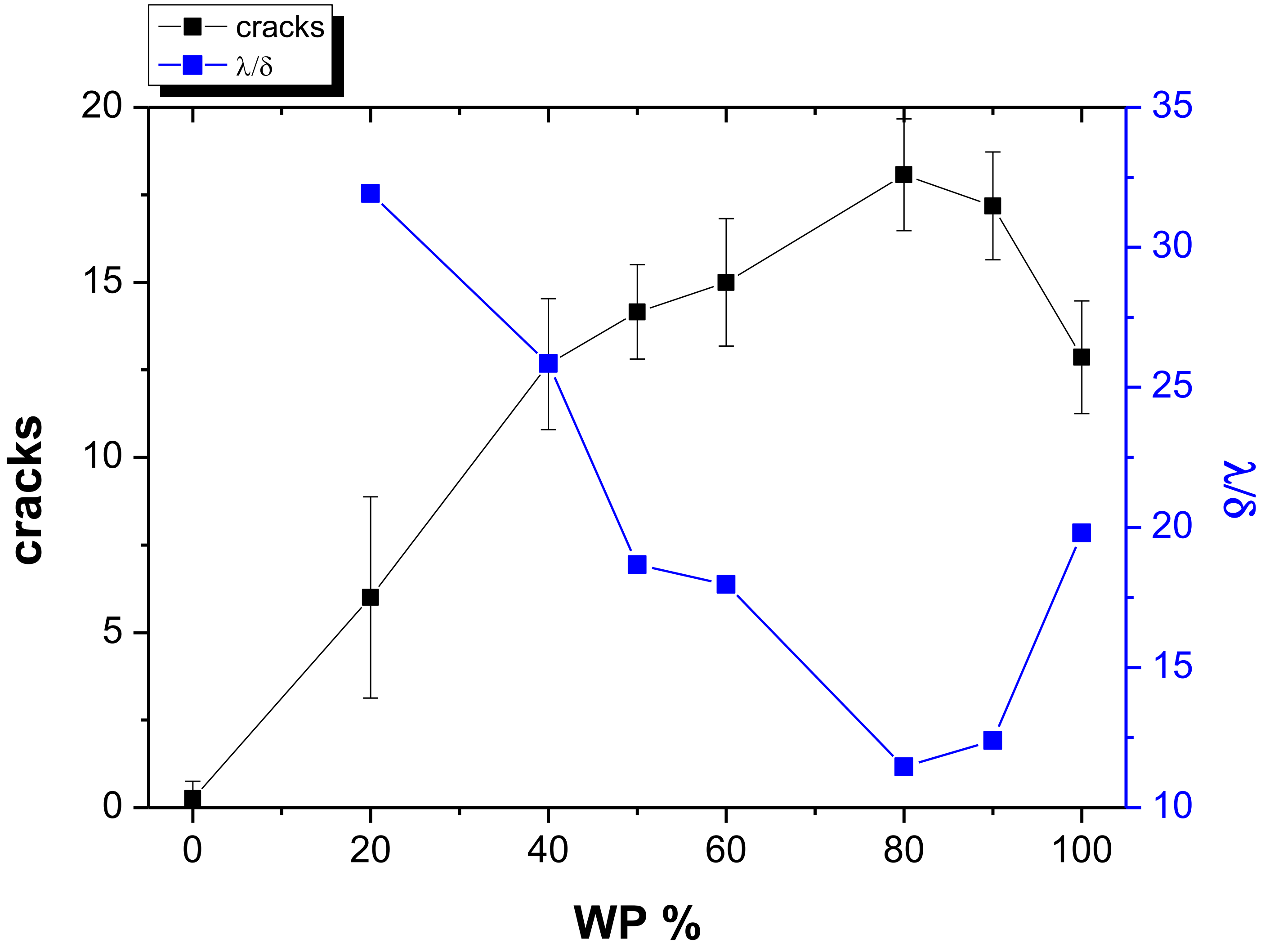


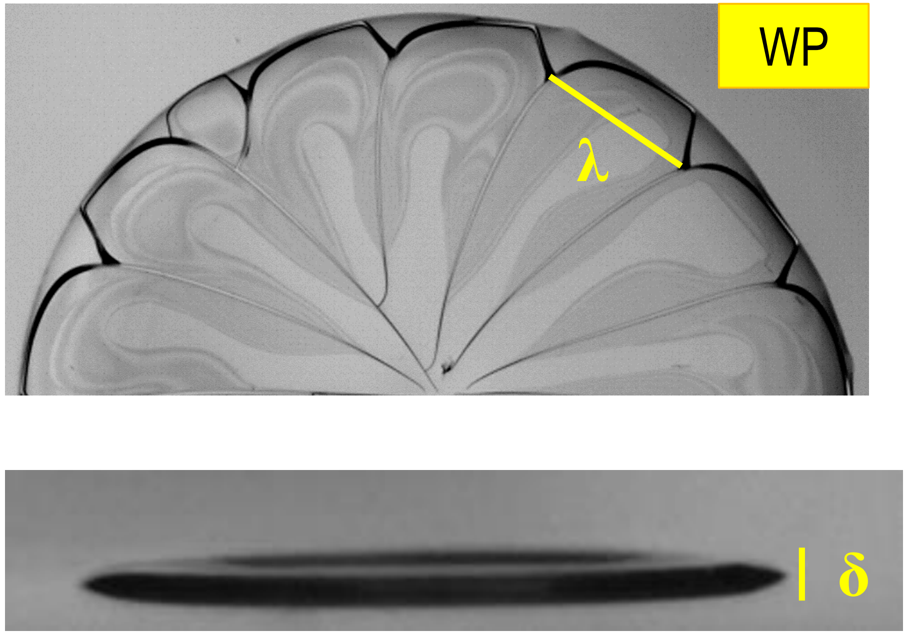
Increase of NPC% (2)

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

Impact of WPI percentage on radial crack formation

Colloidal mechanical properties

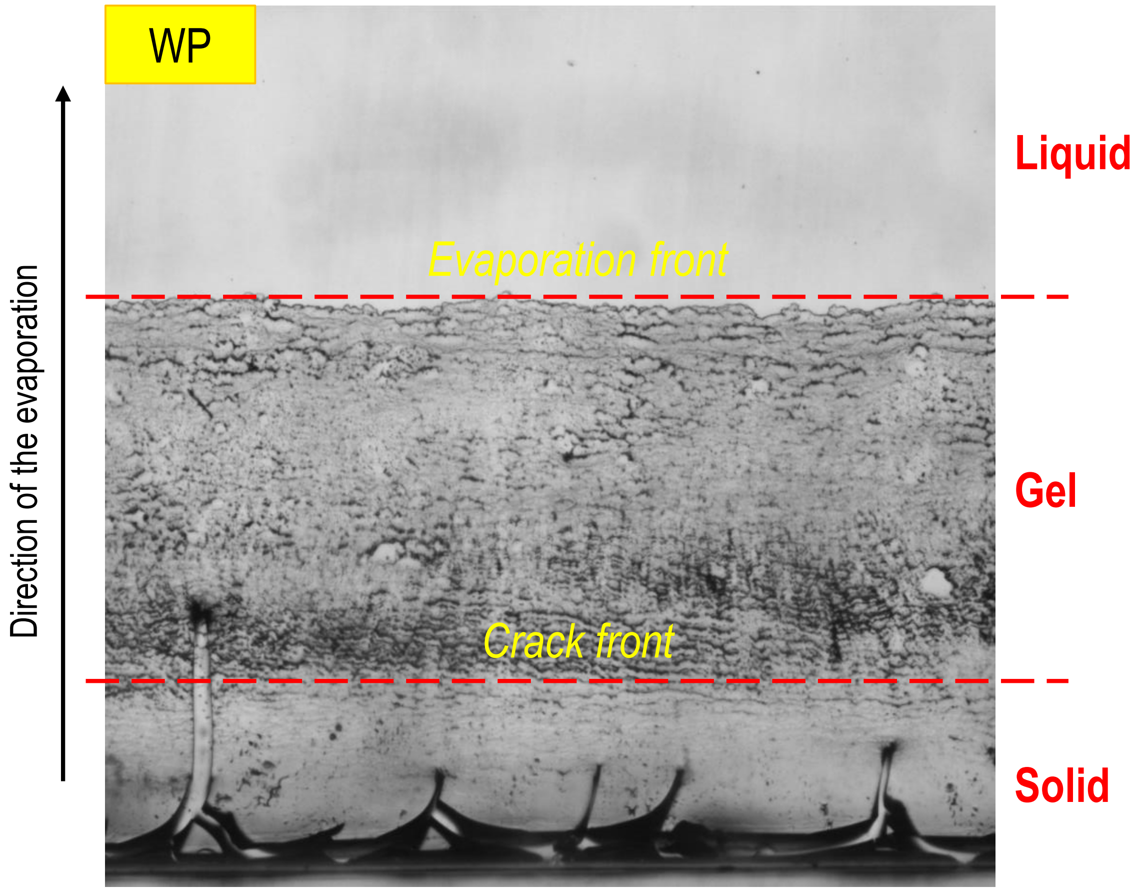




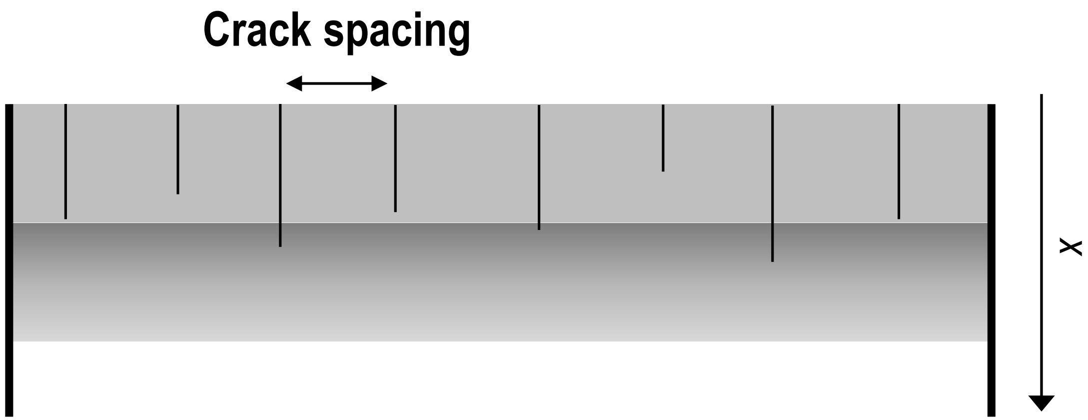
THE PRESENCE OF A LOW AMOUNT OF CASEIN MICELLES STRONGLY FOSTERS THE CRACK FORMATION

Evaporation in Hele-Shaw cells

Mono-directional drying process



Allain and Limat, PRL, 1995. Dufresne et al., PRL, 2003.



First crack

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

Particle size and
structure inhomogeneity (porosity)

Crack spacing

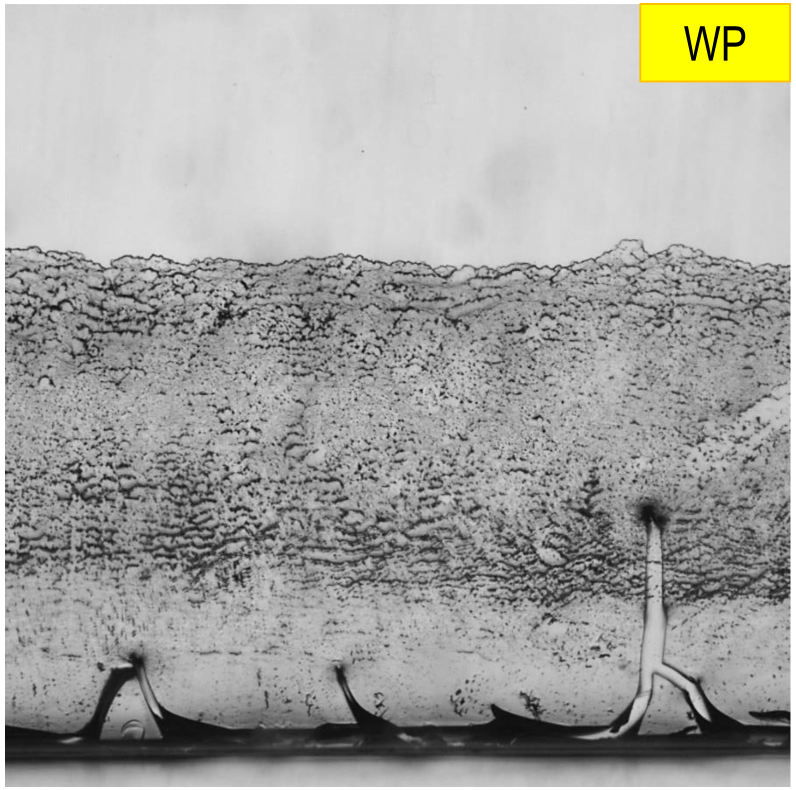
$$\sigma_{xx} = \tilde{E}\left[\left({}^{\partial u}/_{\partial x}\right) + C\right]$$

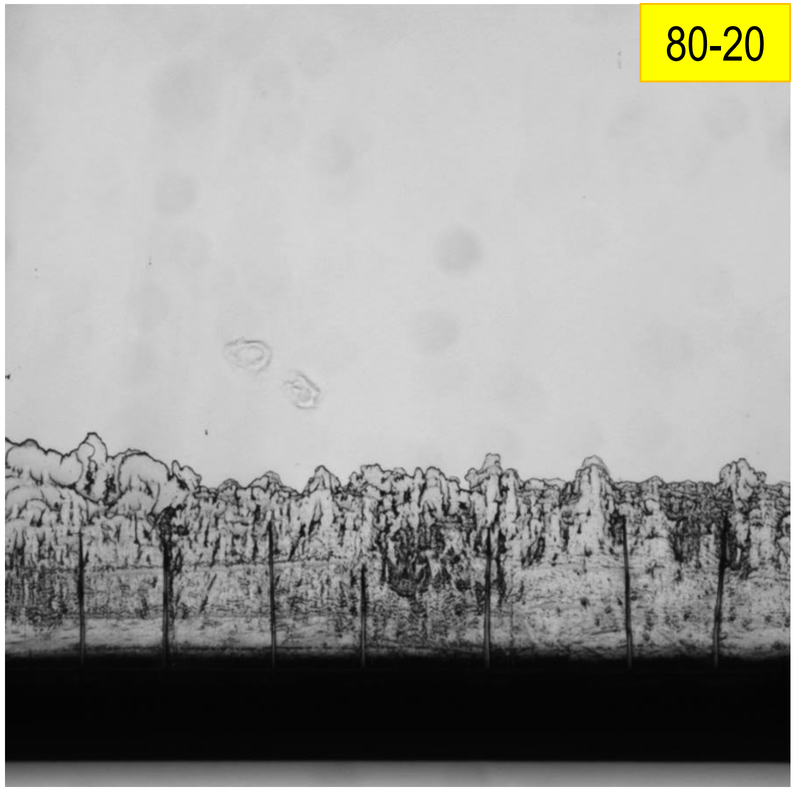
Stress balance
↓ crack relaxation ↑ water evaporation

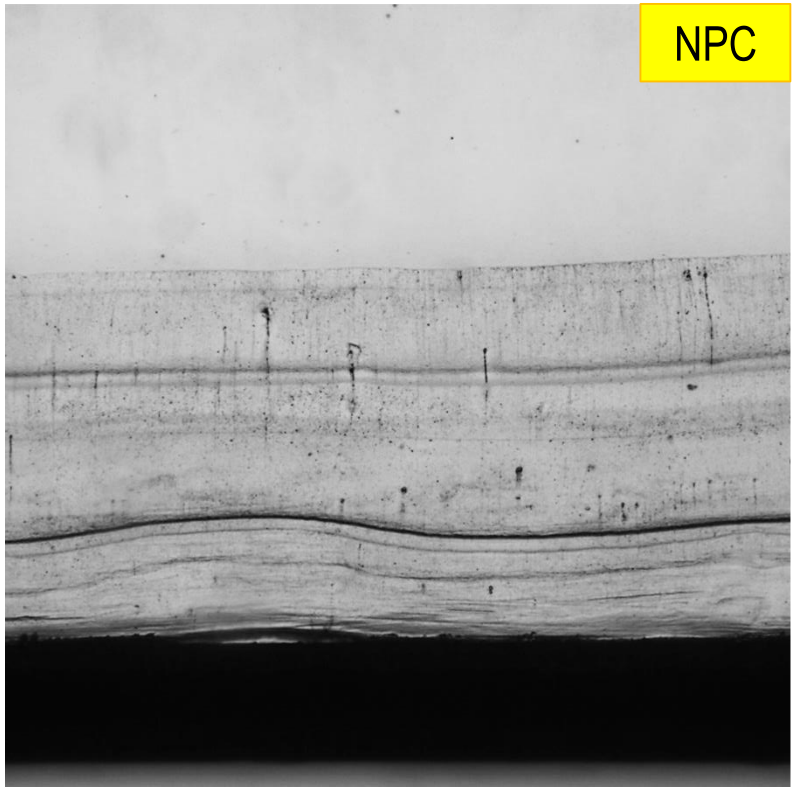
Mechanical properties and structure of the material

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

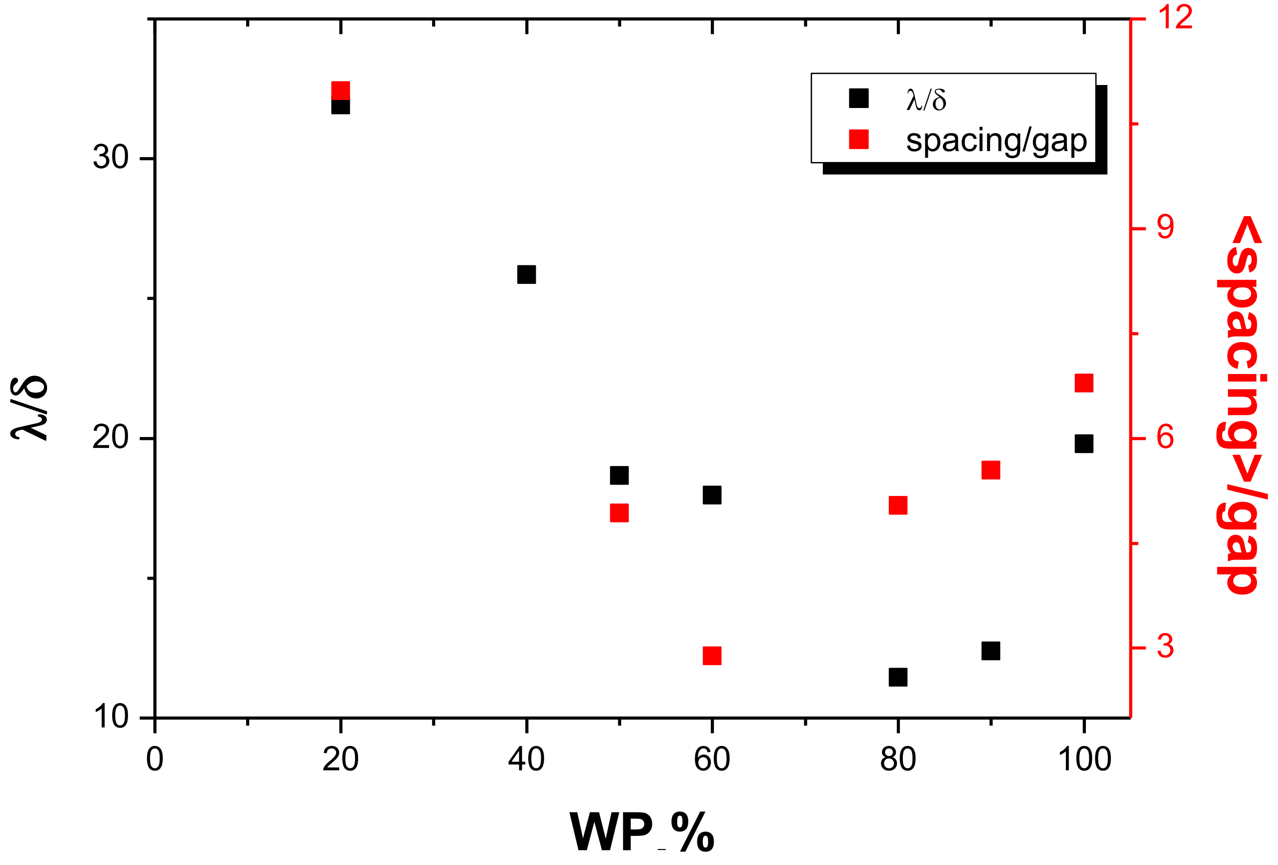
The number of cracks increases with the diminution of WP%

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

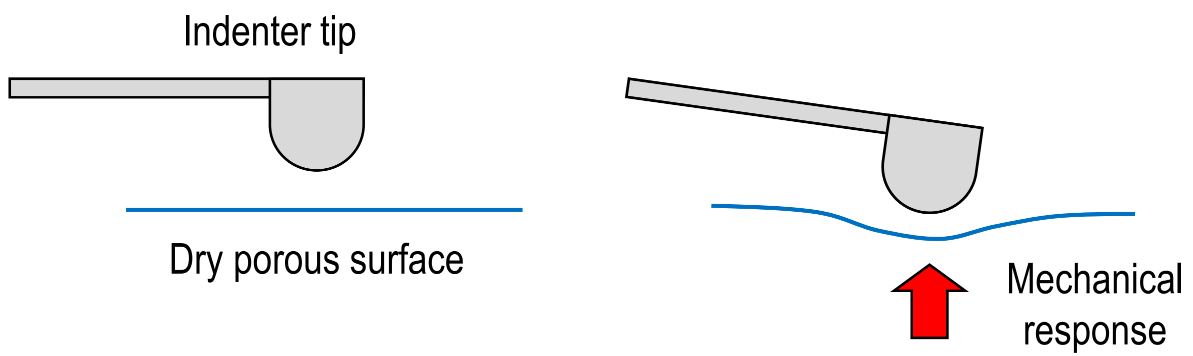
Slight shift of the minimum

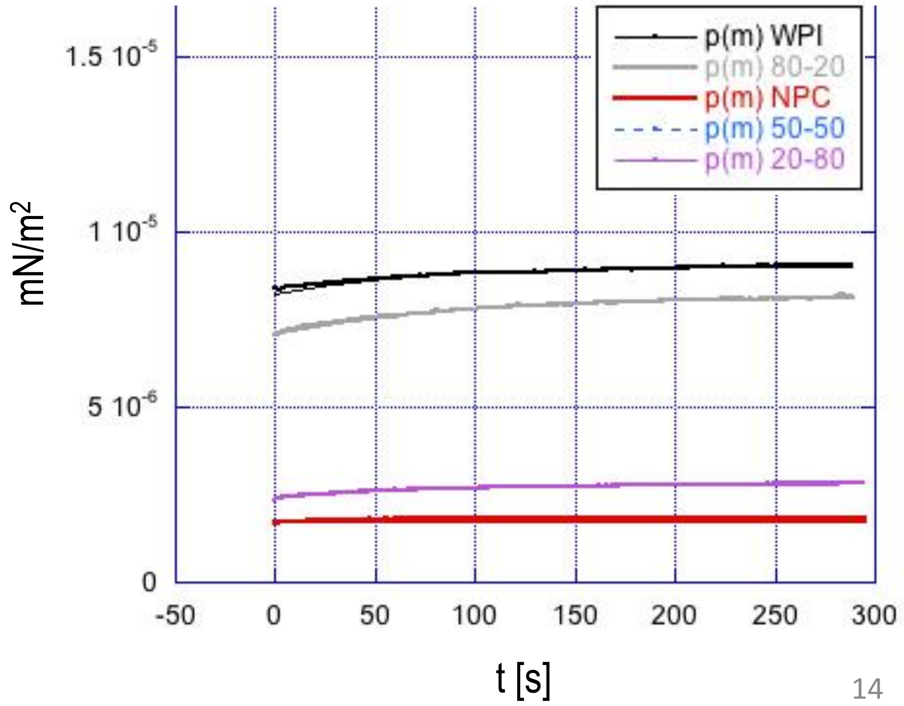
Need of more experimental tests
or geometry effect on crack occurrence?

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

Thank you for your attention