

# Structure of biological colloids revealed by drying cracks formation



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# LAB'S PRESENTATION



**A multidisciplinary and multiscale approach,  
reinforced by two high-calibre facilities:**

Dairy Platform



Biological Resource Centre



➤ **Structuration / destructuration mechanisms  
of food matrix:**

*from structural characterisation to digestion*

➤ **Dairy processing and cheese making:**

*toward sustainable dairy systems*

➤ **Microbial interaction:**

*food matrix and host cell*



# Controlling dairy powders properties

**Quite challenging**

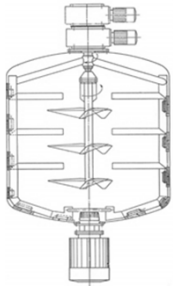

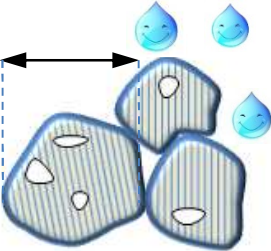
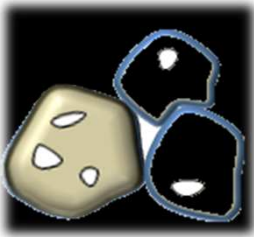
**Sticking & caking**  
*Glass transition, Hygroscopicity*




**SURFACE PROPERTIES**

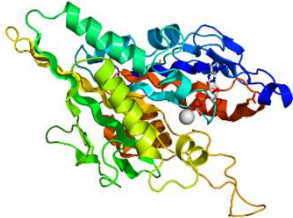
**Rehydration**  
*Surface composition & structure, Size, Porosity*

**Packing**  
*Density, occluded & interstitial air, size distribution*

**PARTICLE PHYSICAL PROPERTIES**

**Nutritional properties**  
*Denaturation / aggregation rate, etc.*



**MOLECULAR STRUCTURE**

Functional properties =  $f$  (particle intrinsic properties)  
**Insight on particle formation**

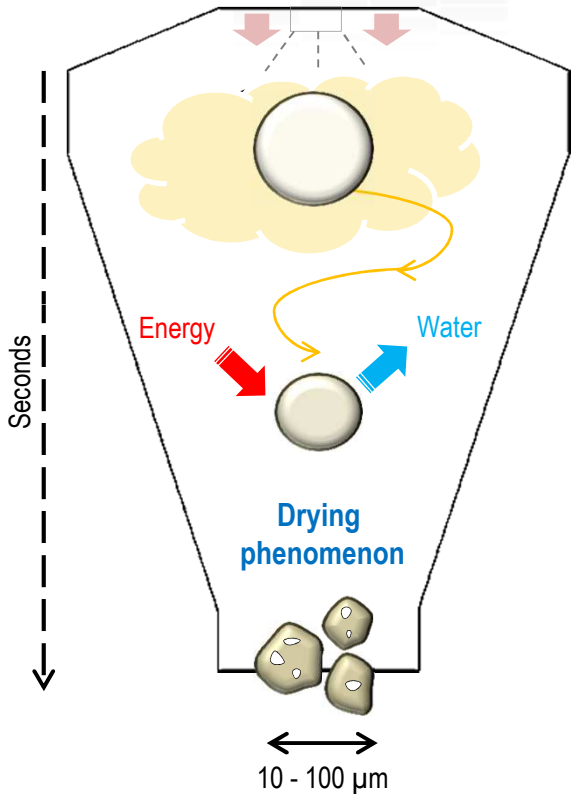
# A new strategy

From the industrial scale..



..to the droplet approach

Sadek et al., *Langmuir*, 2013, 29, 15606-15613.  
 Sadek et al., *Food Hydrocolloids*, 2015, 48, 8-16  
 Sadek et al., *Food Hydrocolloids*, 2016, 52:161-166.

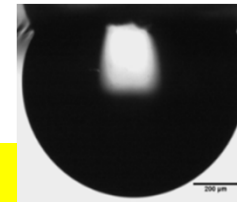


- Fast drying kinetics
- Complexity and costs



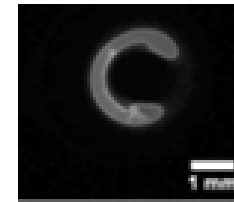
**SINGLE DROPLET**

Pendant



3D

Sandwiched



2D

- Kinetics of particle formation
- Material mechanical properties

**FLYING DROPLETS**

Mono disperse



Pressure nozzle



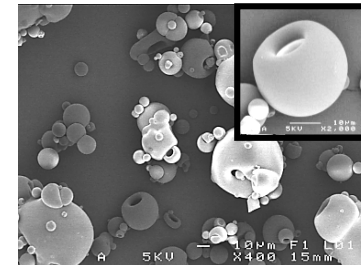
**Validation at Δ scale**  
 (size, temperature, time)

# Signature of milk proteins at multi-scale

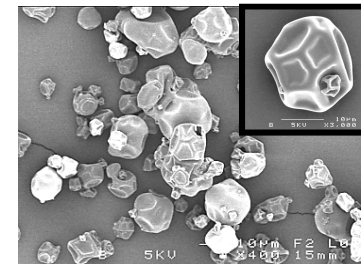


Spraying cone of droplets

Whey protein  
Isolates  
(WP)



Casein  
Micelles  
(NPC)



## Drying kinetics

Particle Size

500  $\mu\text{m}$

140  $\mu\text{m}$

42-56  $\mu\text{m}$

Drying temperature

20°C

190°C

210°C

→ ~1 s

Quantity

1 particle

~ g  
of particles

~ kg  
of particles

# Signature of milk proteins at multi-scale

Whatever the drying kinetics, same morphological behavior

- **Specific signatures** of WP and NPC proteins on the particle formation
- Different **kinds of drying behavior**
  - ✓ **Whey proteins = brittle material**
  - ✓ **Casein micelles = ductile material**



To what extent is the formation of particles affected by the protein material and its mechanical properties ?

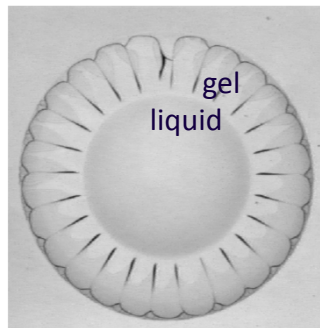
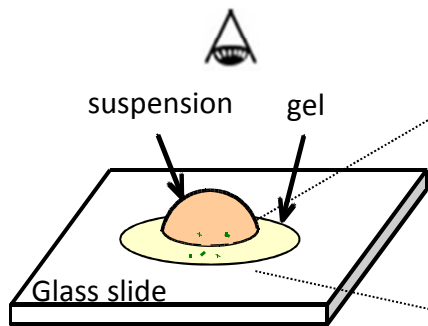


Studying model colloidal solutions for understanding more complicated biological systems

# Material & Method : investigation of mechanical behaviors

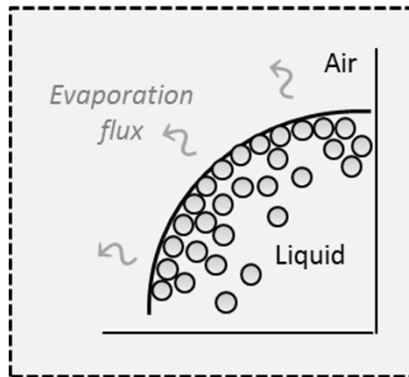
## Coupling cracks dynamics and micro-indentation

**Sessile droplet  
Cracks formation**



2cm top view

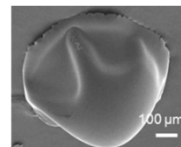
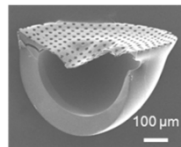
*Specific properties of  
concentrated phases*



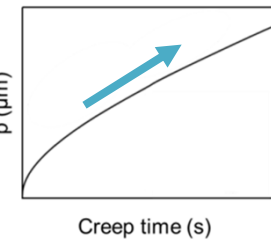
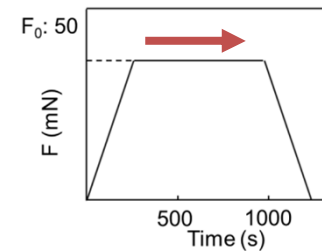
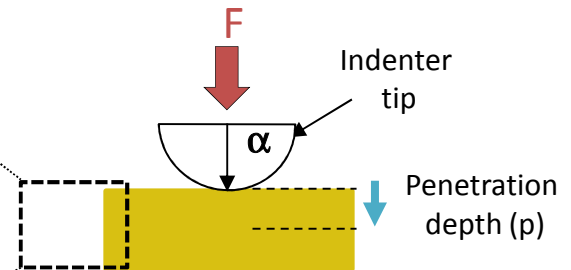
*Particle morphology*

Particle of whey proteins

Particle of casein micelles



**Micro-indentation  
Mechanical properties**



- Experimental conditions:**
- Temperature: 20°C
  - Relative humidity: 40%

# Material & Method : milk proteins and colloidal systems

- Study the drying behavior of **milk proteins**

## ☐ Whey proteins

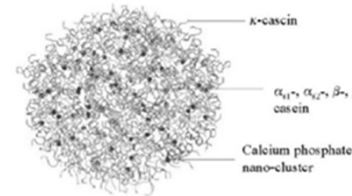
- Globular structure,  $D \approx 10\text{-}20\text{ nm}$
- Reconstituted from **WP powder (Whey Proteins)**



*Yohko, 2012*

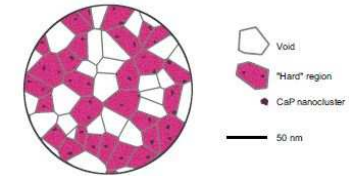
## ☐ Casein micelles

- Micellar, dynamic and hydrated structure,  $D \approx 10^2\text{ nm}$
- Reconstituted from **NPC powder (Native PhosphoCaseinates)**



*Holt & Horne, 1996*

Internal structure not known



*Bouchoux, 2010*

- Study the drying behavior of **colloidal systems**

## ☐ Dispersion of silica colloidal particles

Ludox TM50 :  $\varnothing = 22\text{ nm} \pm 2$

## ☐ Polymer chains on TM particles

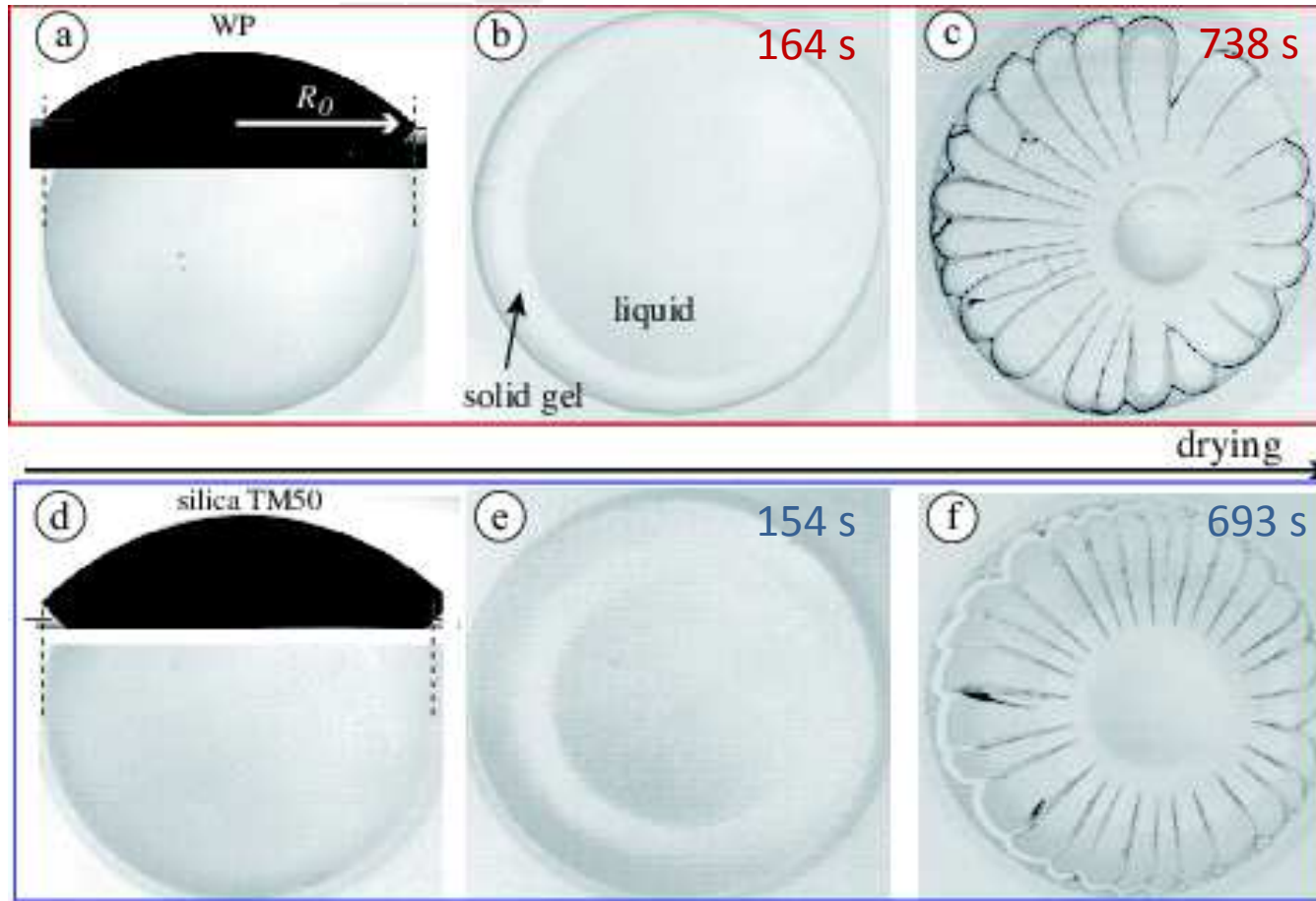
Ludox TM50 + PVP (40kDa)

[poly(vinylpyrrolidone)] < 0,01 mg.m<sup>-2</sup>

➡ PVP owns high affinity for silica surfaces



# Results – Drying process of sessile drops (WP / TM50)

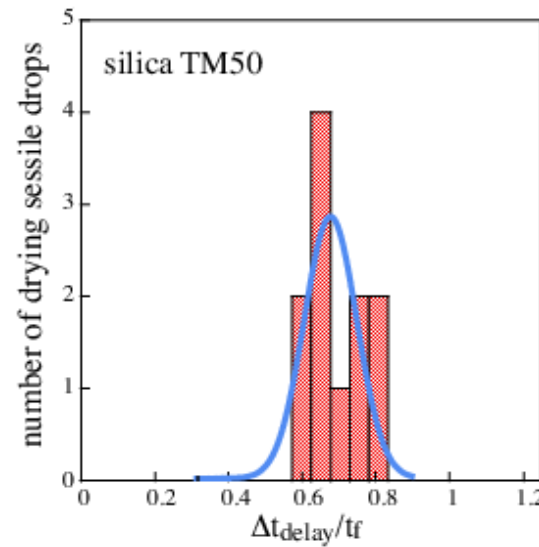
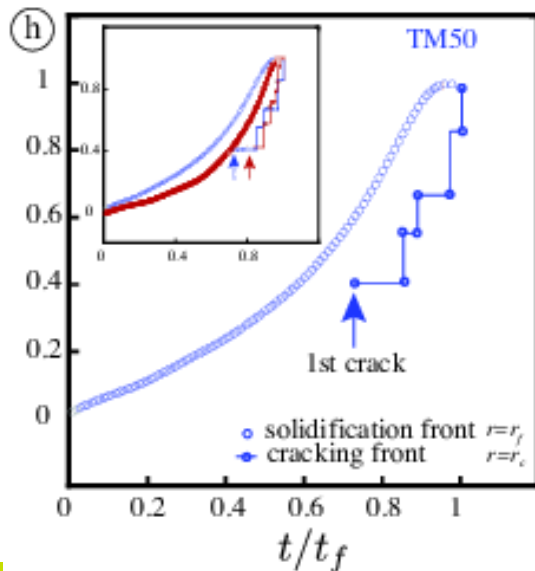
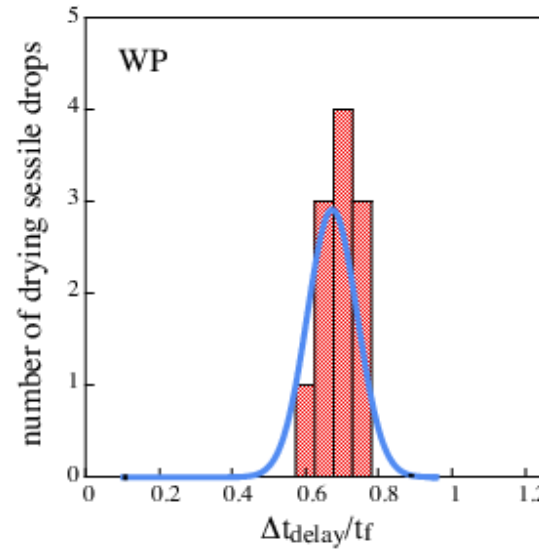
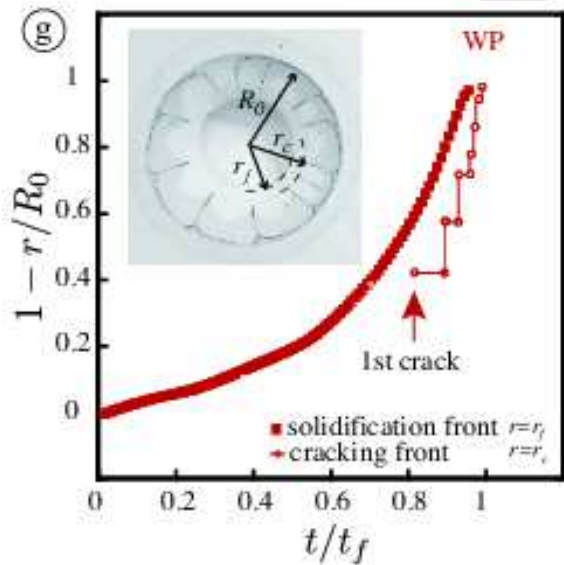


## Experimental conditions:

- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle :  $31 \pm 2^\circ$
- $2 R_0 = 8 \text{ mm}$
- Evaporation rate :  $8 \cdot 10^{-8} \text{ m} \cdot \text{s}^{-1}$

**Identical behavior**  
**Rapid nucleation of geometric, radial fractures**

# Results – Crack dynamics and delay time before cracking



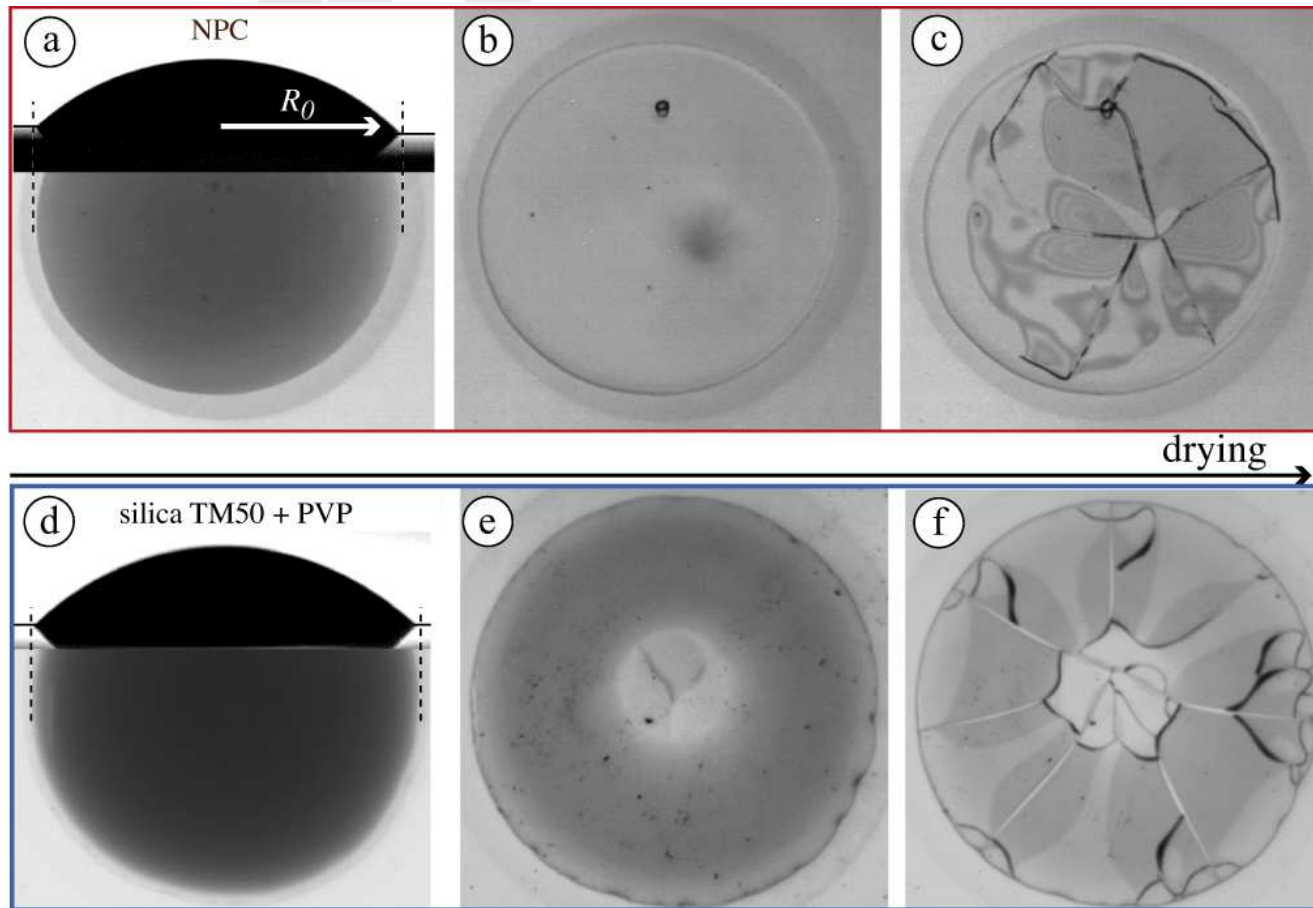
➤ Similar time evolution of the drying front location obtained for WP and TM50

➤ Similar statistics of duration elapsed before crack propagation :

✓  $334 \pm 41$  s for WP

✓  $311 \pm 61$  s for TM50

# Results – Drying process of sessile drops (NPC / TM50 + PVP)



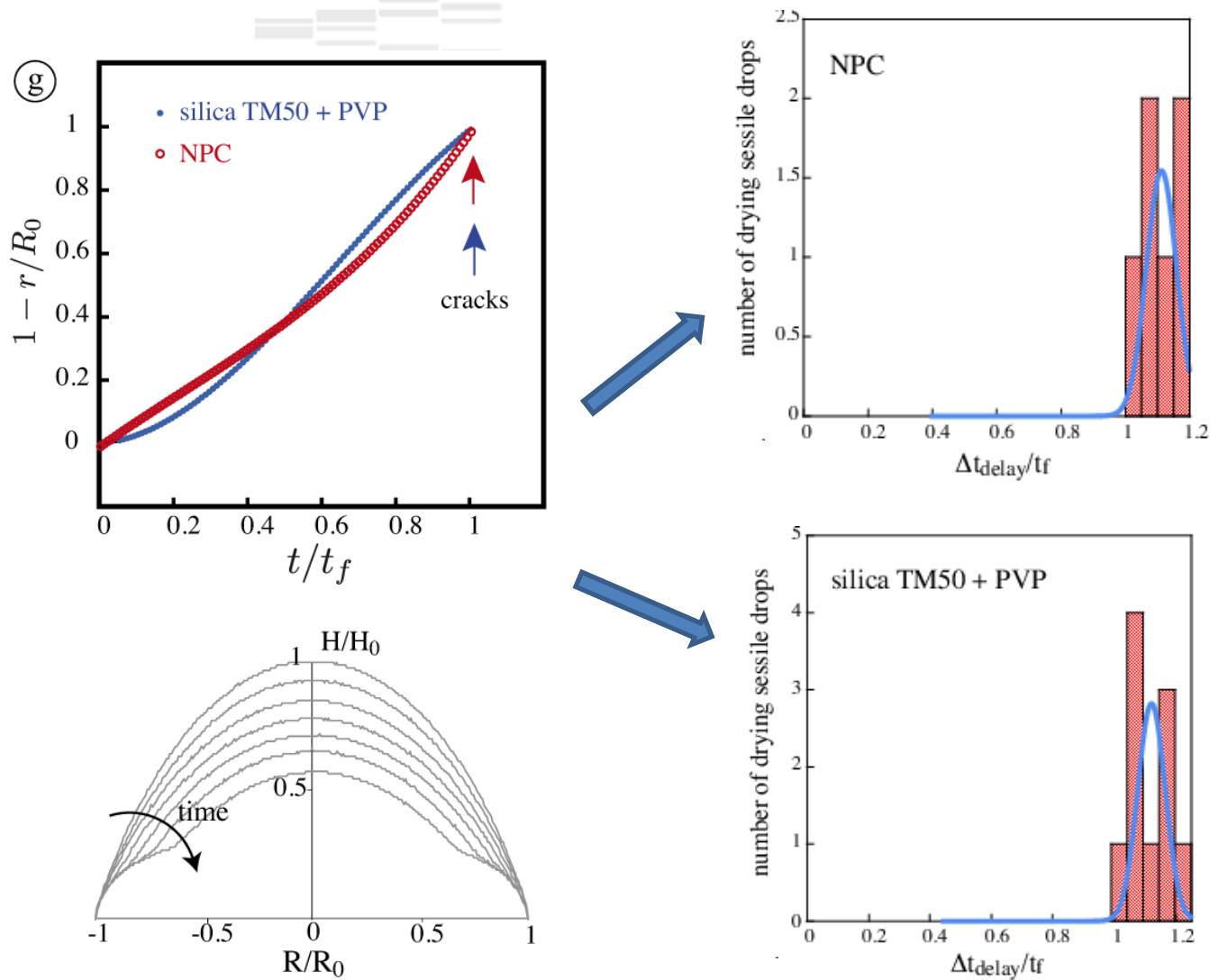
## Experimental conditions:

- Temperature: 20°C
- Relative humidity: 40%
- Initial contact angle :  $31 \pm 2^\circ$
- $2 R_0 = 8 \text{ mm}$
- Evaporation rate :  $8.10^{-8} \text{ m.s}^{-1}$

## Comparable behavior

Later nucleation of a few, random fractures

# Results – Crack dynamics and delay time before cracking

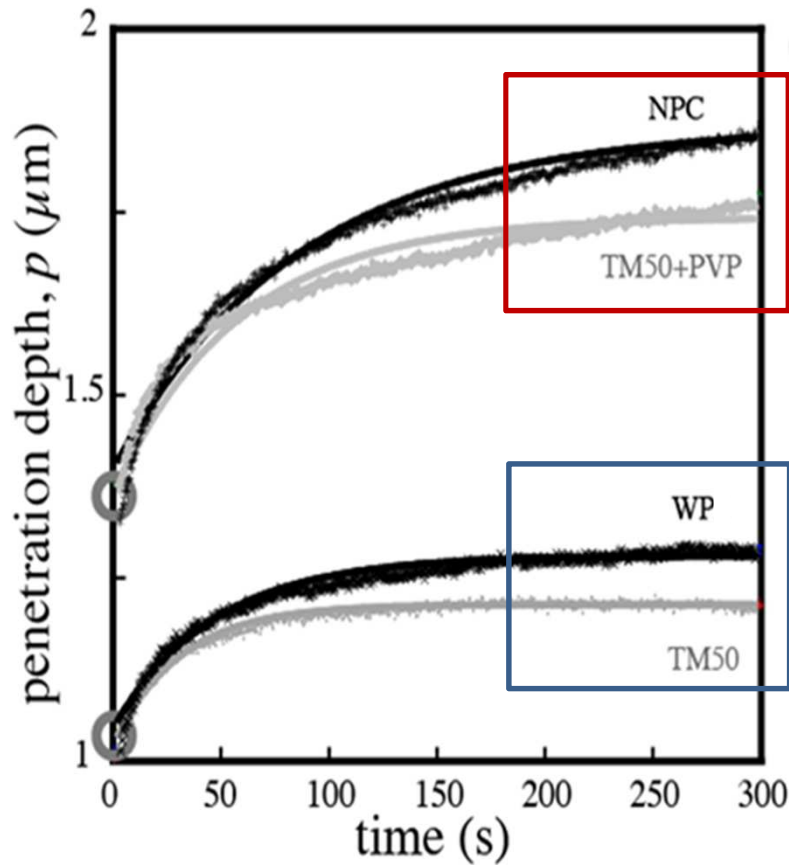
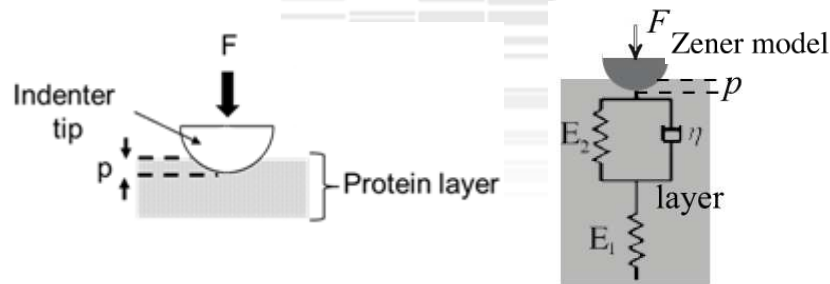


➤ Similar time evolution of the drying front location obtained for NPC and TM50 + PVP

➤ Similar statistics of duration elapsed before crack propagation:

- ✓  $834 \pm 50$  s for NPC
- ✓  $855 \pm 40$  s for TM50

# Results – Mechanical behavior & viscoelastic relaxation time



	Viscosity $\eta$ (GPa.s)	Elastic modulus $E_2$ (GPa)	Viscoelastic relaxation time, $t\eta$ (s)
WP	$99 \pm 5$	$3.50 \pm 1.10^{-3}$	$28 \pm 2$
TM50	$82 \pm 5$	$3.20 \pm 1.10^{-3}$	$26 \pm 2$
NPC	$119 \pm 5$	$0.96 \pm 1.10^{-3}$	$124 \pm 5$
TM50 + PVP	$115 \pm 5$	$0.98 \pm 1.10^{-3}$	$129 \pm 5$

- Penetration depth deeper for NPC and TM50 + PVP than for WP layer and TM50
- Values of viscoelastic relaxation time are similar between WP / TM50 and NPC / TM50 + PVP

# Conclusions

To what extent is the formation of particles affected by the protein material and its mechanical properties ?



Coupling cracking time (direct measurements) and micro-indentation (indirect measurements of mechanical properties)



**WP** : analogous mechanical behavior with TM50  
→ **Brittle plastic** characteristics of skin layer similar to non-interacting **hard sphere colloids**

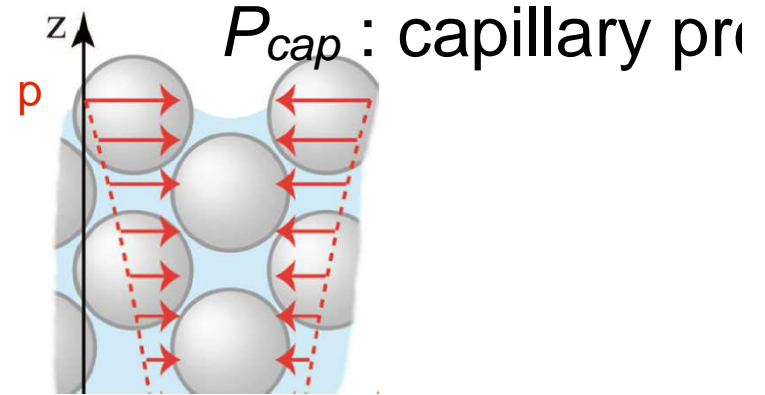
**NPC** : similar mechanical behavior with TM50 + PVP  
→ **Ductile plastic** property of skin layer similar to **soft colloids**

# Outlook – Relation between structure and drying stresses

Evaporation causes pressure gradient:  
Darcy law at the air/liquid interface

- Water pressure from Darcy flow:  $\frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial z^2}$
- $$D_p = \frac{E_p k}{\eta} : \text{diffusivity or "consolidation coefficient"}$$

$$V_E = -\frac{k}{\eta} \frac{\partial p}{\partial z} \Big|_{z=h}$$



- Mechanical stress  $\propto$  local pressure:

$$\sigma_y = -\alpha p \delta_y$$

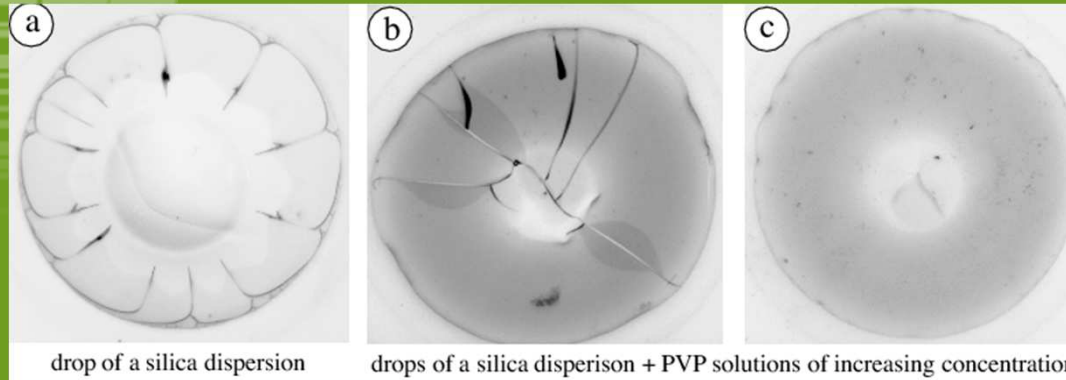
poroelasticity, Biot (1941)

Drying stress at the film/air interface:  $\sigma(z = h) \sim E \frac{t}{t_D}$  where  $t_D$  is the evaporation timescale ( $h/V_E$ )

max stress leading to crack when:  $\sigma(z = h) \sim -P_{cap} \sim 10 \frac{\gamma_{air/water}}{r_{pore}}$

Hypothesis: delay time before stress reaches max stress: viscoelastic timescale:  $t_\eta$

$$E \frac{t_\eta}{t_D} \sim 10 \frac{\gamma_{air/water}}{r_{pore}} \Rightarrow r_{pore}$$



*Merci*

*Thank you for your attention*



### More information

- Sadek et al., 2013, [Langmuir](#), **29**, 15606-15613
- Sadek et al., 2014. [Drying Technol](#), **32**, 1540-1551
- Sadek et al., 2014, [Dairy Sci Technol](#), **95**, 771-794
- Sadek et al., 2015, [Food Hydrocolloids](#), **48**, 8-16
- Sadek et al., 2016, [Food Hydrocolloids](#), **52**, 161-166
- Lanotte et al., 2018, [Col. Surf. A](#), **553**, 20-27



*Physics of drying Conference, 05-07 Nov. 2018*