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## Monitoring dairy protein aggregate structure allows to control the texture of emulsions

Catherine Garnier, T Loiseleux, P Gelebart, M Chevalier, Marie-Hélène Famelart, Thomas Croguennec, M Anton, A Riaublanc

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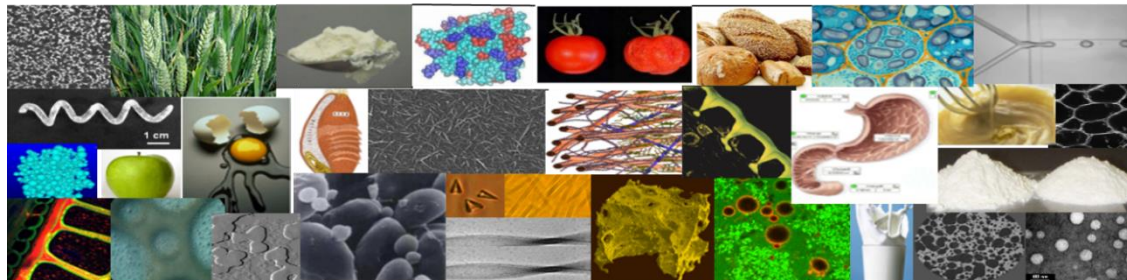
# Connectivité des gouttes de matière grasse par des agrégats protéiques et texturation des émulsions

**C. Garnier<sup>1</sup>, T. Loiseleux<sup>1</sup>, P. Gelebart<sup>1</sup>, M. Chevalier<sup>2</sup>, M.H. Famelart<sup>2</sup>, T. Croguennec<sup>2</sup>, M. Anton<sup>1</sup>, A. Riaublanc<sup>1</sup>**

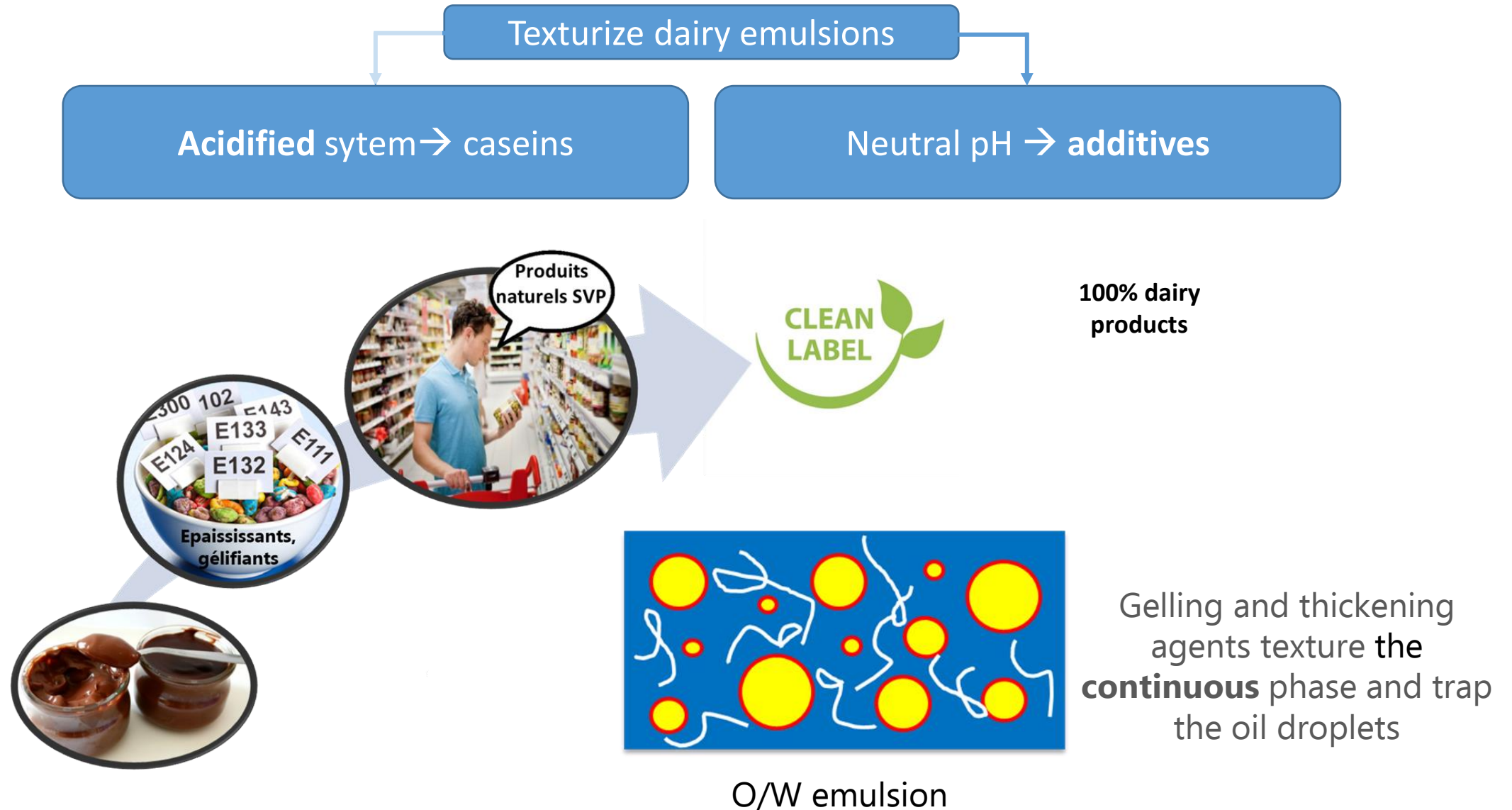
<sup>1</sup> UR1268 INRA, Biopolymères Interactions Assemblages, Nantes, France

<sup>2</sup> UMR1253 INRA, Science et Technologie du lait et de l'oeuf, Rennes, France

[catherine.garnier@inrae.fr](mailto:catherine.garnier@inrae.fr)



# Industrial context



# Scientific context

## Background

- ✓ Native whey proteins (NWP) have excellent emulsifying properties (Dickinson, 1999)
- ✓ NWP are sensitive to heat treatment and can form aggregates with different shapes and sizes after heating (Nicolai, 2011)
- ✓ Pure aggregates are not able to form small droplets and stable emulsions whereas by mixing with NWP, droplet size, stability and texture of emulsions can be controlled by modulating the **connection between droplets** (Surel, 2014).

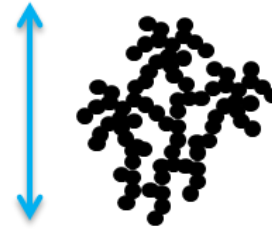


- ✓ To connect oil droplets, the **Ag size** and the **distance between droplets** are key parameters

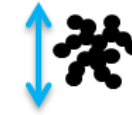
# Scientific context

✓ To connect oil droplets, the **Ag size** and the **distance between droplets** are very important.

## Ag size

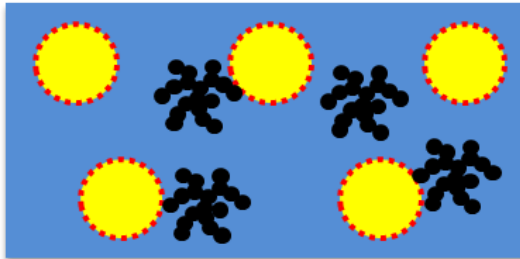


**Large aggregates:**  
connection on long  
distance



**Small aggregates:**  
connection on  
short distance

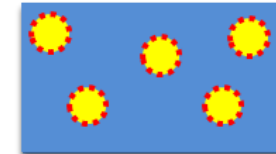
## Distance between droplets



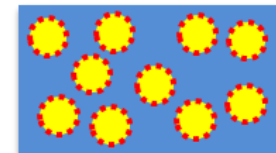
If the distance between droplets is larger than the aggregate size, connections are difficult

✓ Two ways to control the distance between droplets:

- ✓ **Dispersed phase:** droplets are closer with high concentration of anhydrous milk fat (AMF)
- ✓ **Droplet size:** modulated by the homogenisation pressure. At constant AMF volume fraction, the lower the homogenisation pressure, the larger the distance between droplets.



High pressure  
5% of AMF

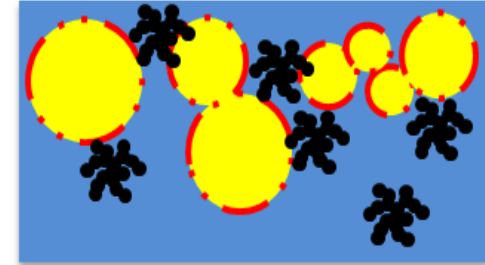


Low pressure  
10% of AMF

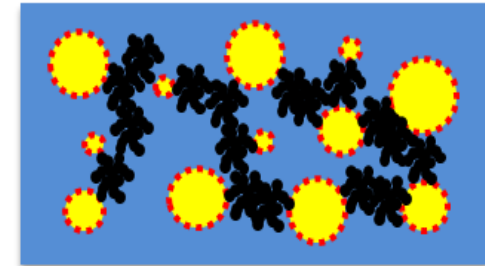
# Scientific context

To texture emulsions, a compromise has to be found between:

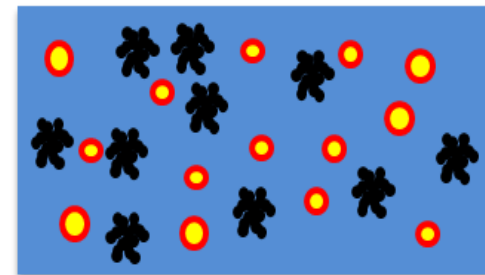
- ✓ The concentration of **NWP**
  - ✓ Enough NWP to stabilize emulsions and control droplet size
  - ✓ Not to much to allow aggregates to connect droplets (interface saturation)
- ✓ The concentration and the size of Ag to connect droplets
- ✓ The droplet size and the volume fraction of AMF to control the distance between them



Not enough NWP



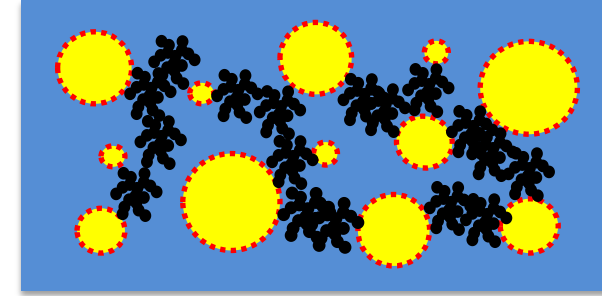
Appropriate amount of NWP



Too much NWP

# Objectives

- ✓ Use oil droplets to texture emulsion without hydrocolloids
- ✓ Connecting oil droplets with whey protein aggregates (Ag)



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## Aims of the study

Replace food additives like thickening or gelling agents in neutral dairy products or improve the texture of acid dairy products

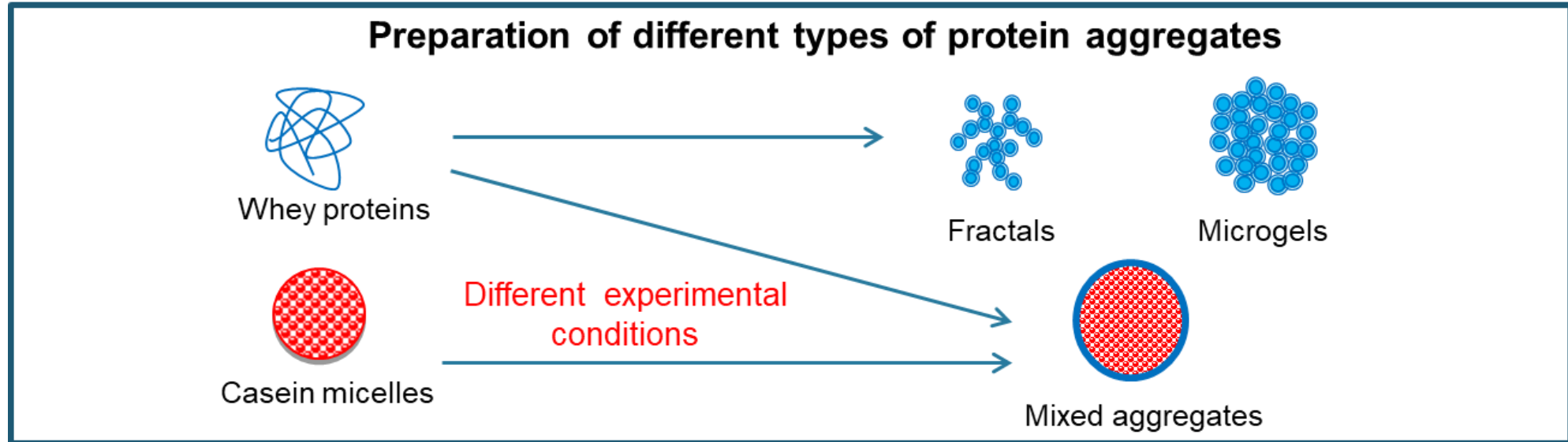
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Texturize even low fat content products

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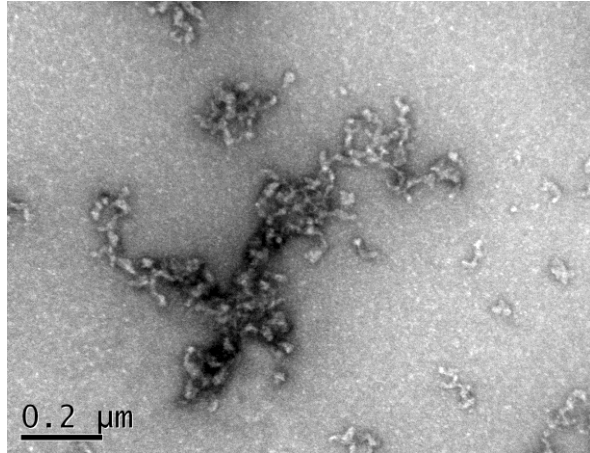
# What kind of aggregates ?





# What kind of aggregates ?

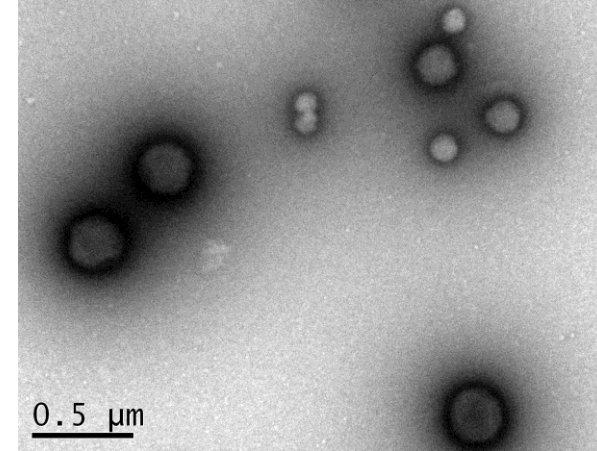
## Fractals



- Whey protein solution at 50 g/l
- **pH 7**
- **[NaCl] : 0 to 45 mM**
- 80°C - 2h

**Branched structures,**  
[NaCl]-dependent size dispersion  
**70 to 300 nm**

Heating  
conditions



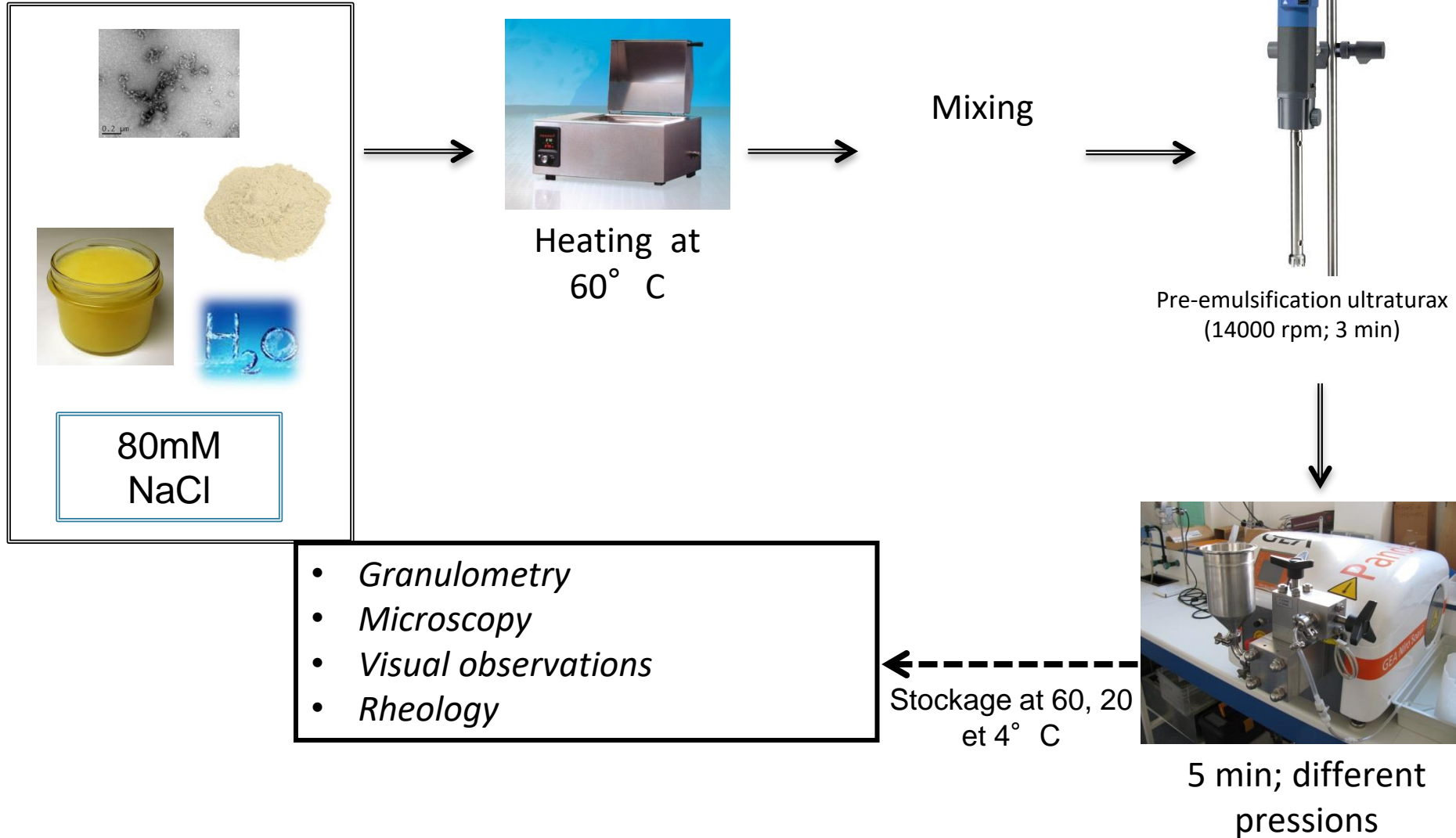
## Microgels



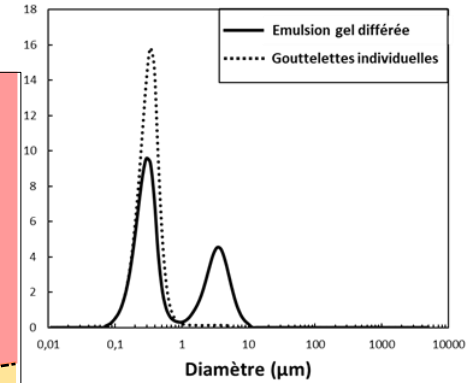
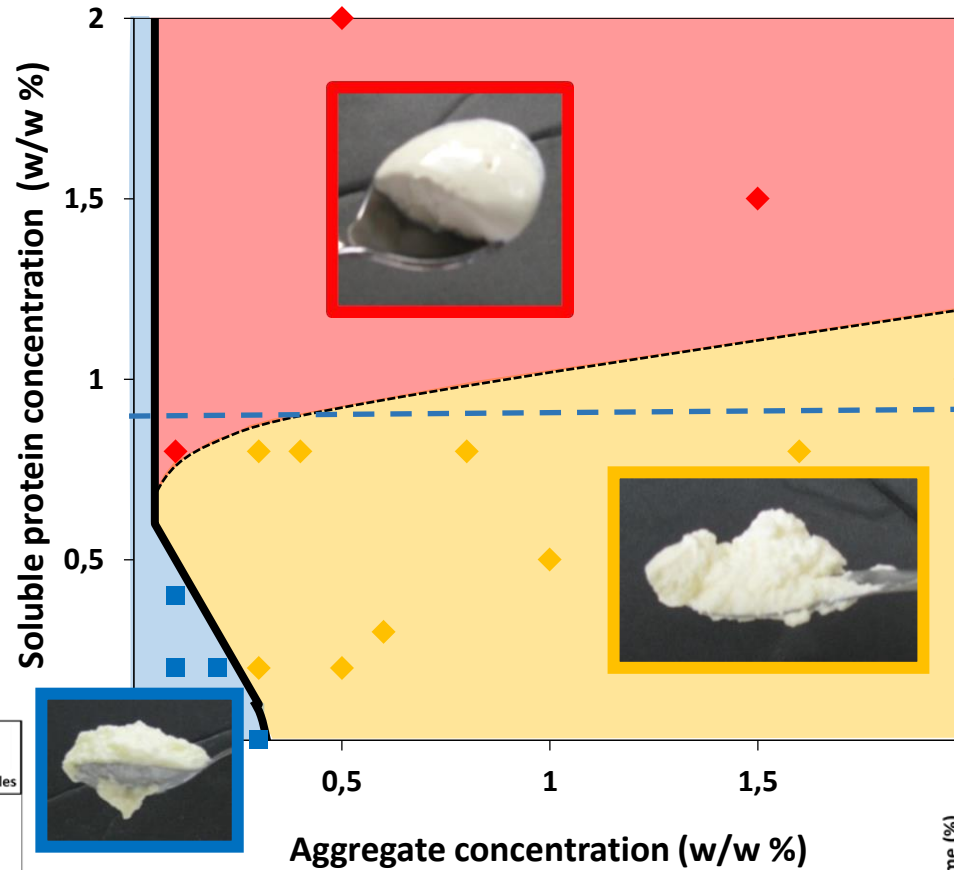
- Whey protein solution at 50 g/l
- **pH 5,8**
- 85°C - 1h

**Compact spherical structures,**  
monodisperse size  
**200 nm**

# Neutral emulsion fabrication



# State diagrams obtained with fractal aggregates (30 / 500)

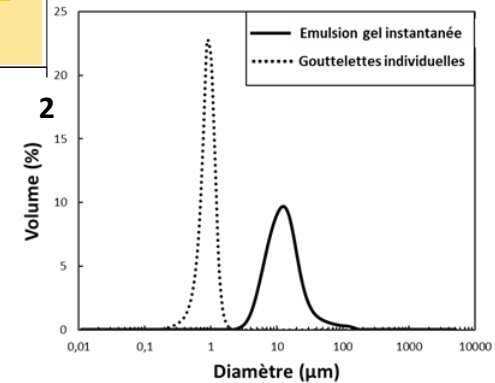
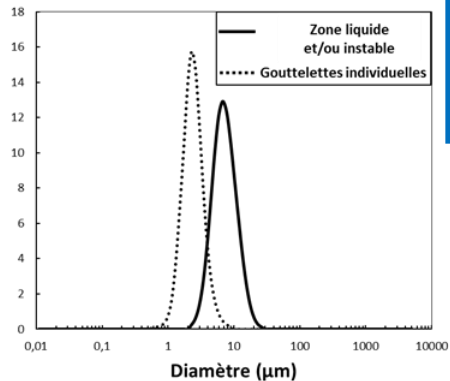


AMF(%)	Pression (bars)
5	100
<b>30</b>	<b>500</b>

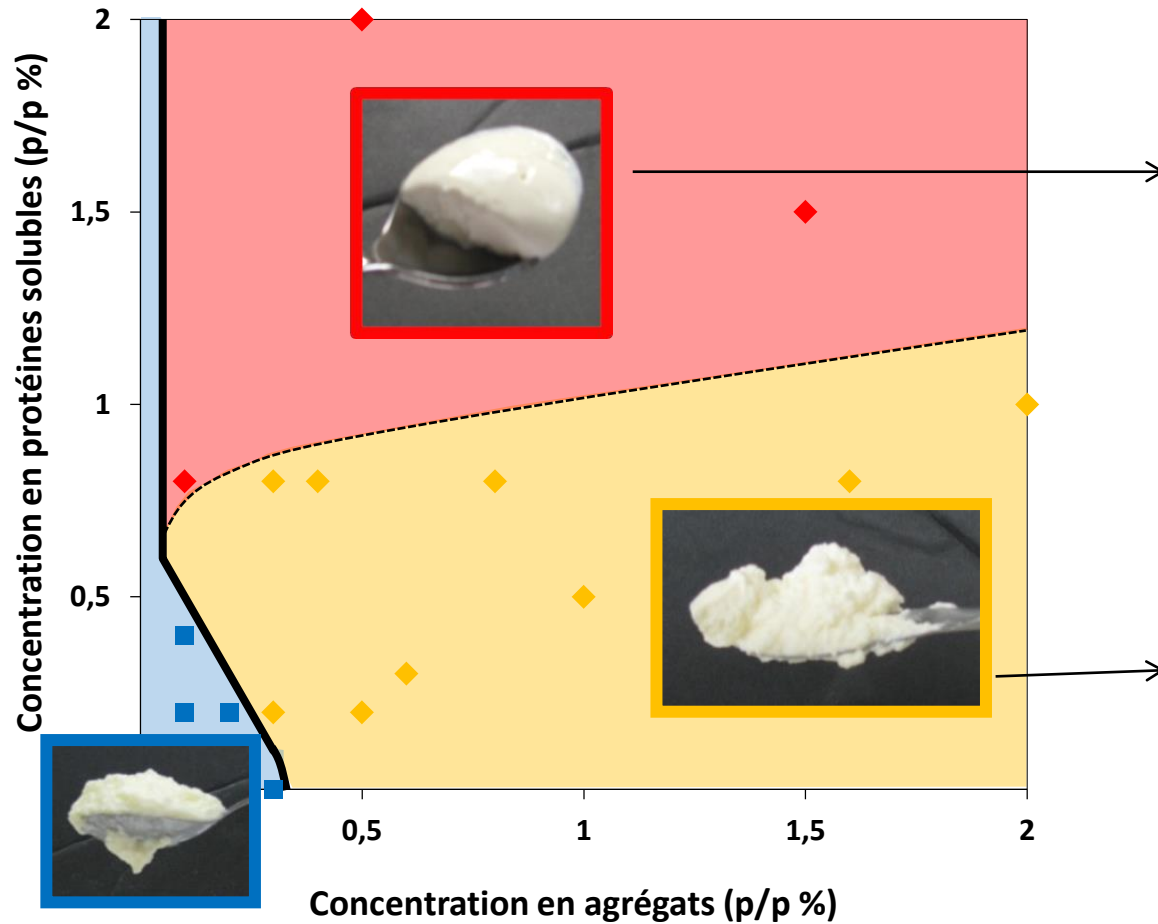
**Regions** Liquid or instable

Instant gel

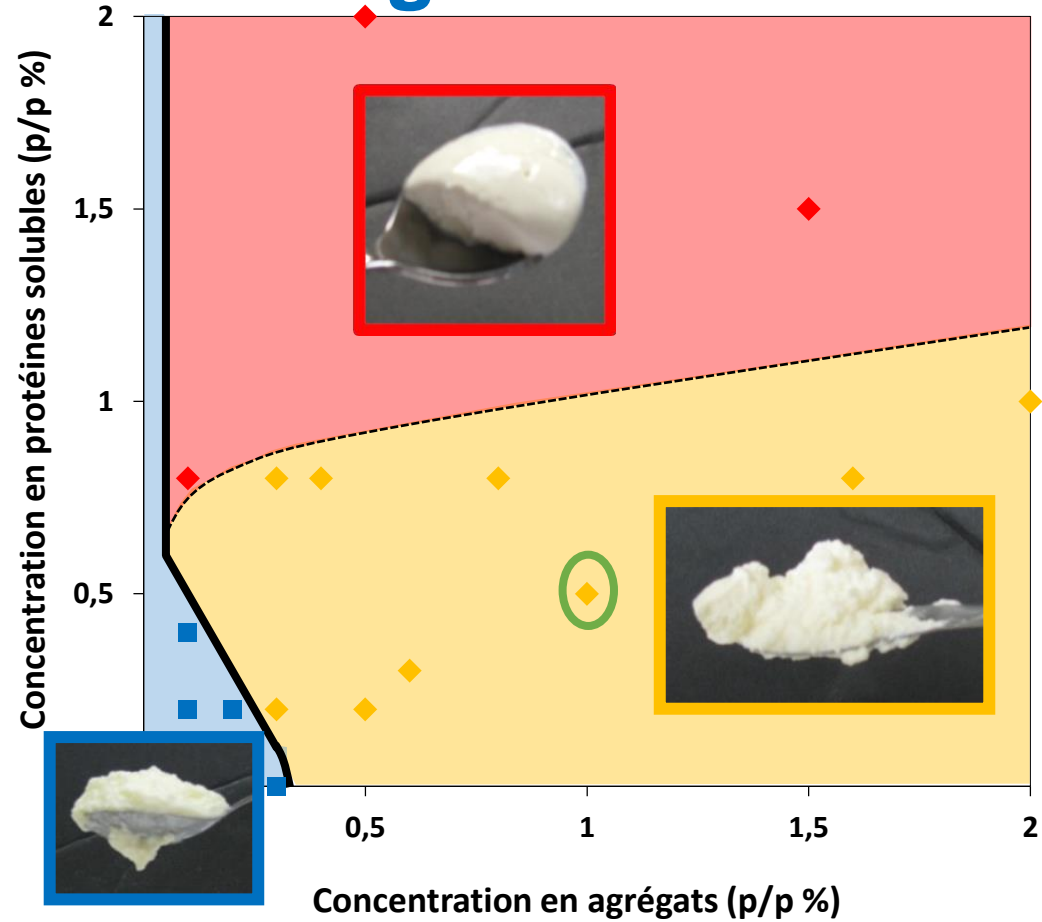
Delayed gel



# State diagrams obtained with fractal aggregates (30 / 500)

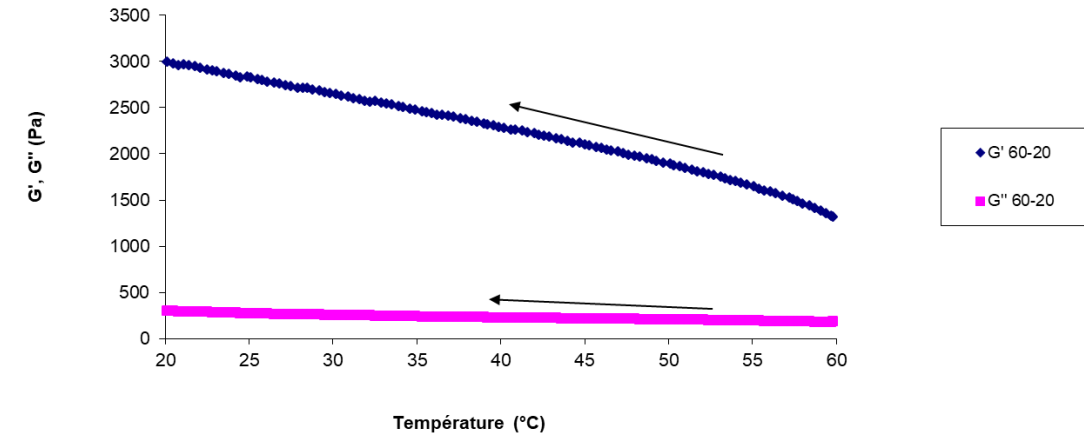


# Rheological behaviour

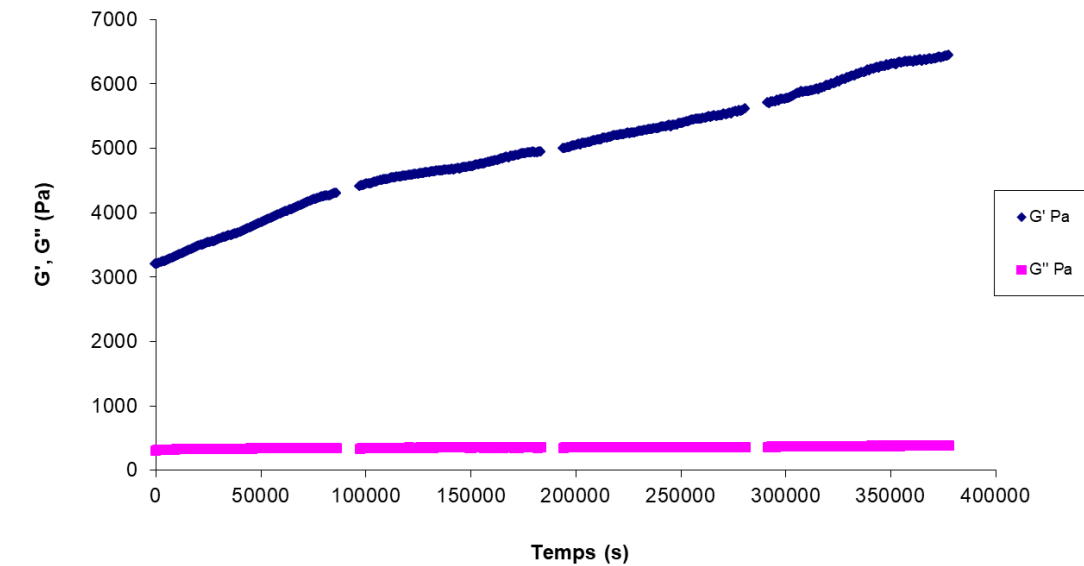


AR2000, TA Instruments  
 Plate-plate 40 mm  
 Gap 1 mm  
 $\gamma$  0,5%, 1 rad/s

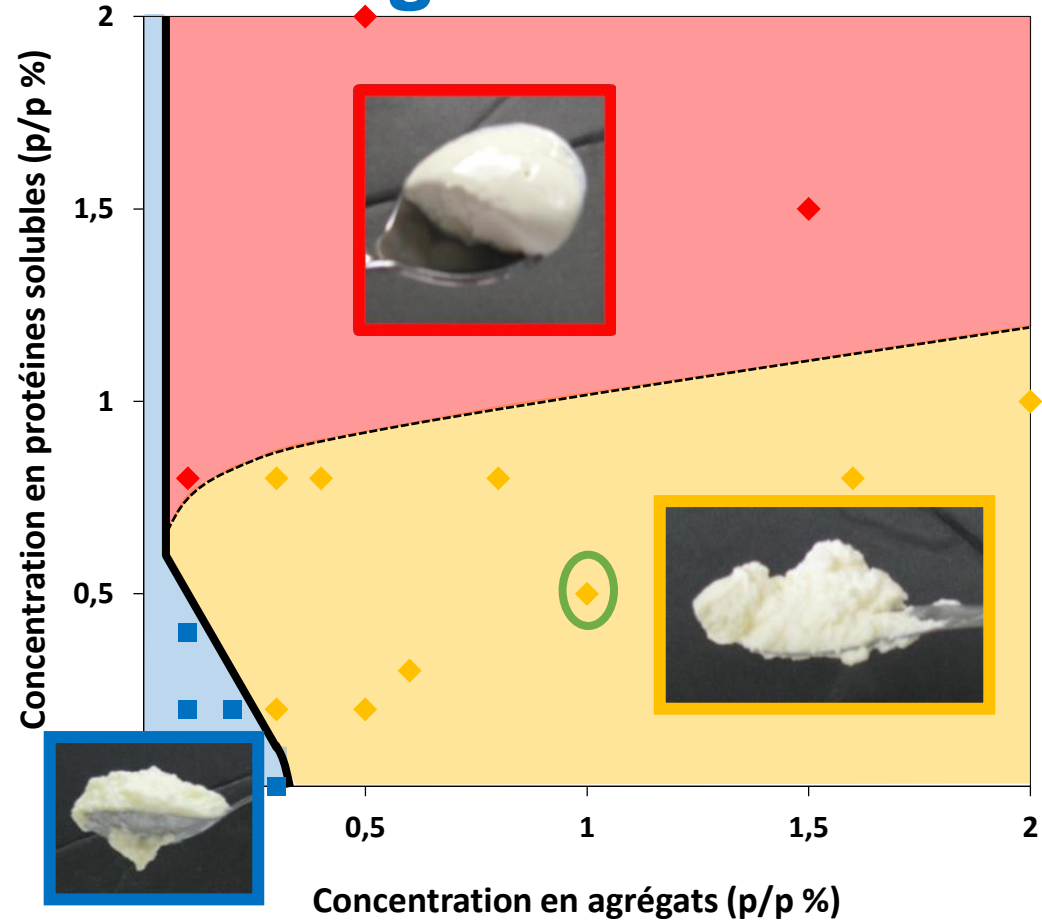
## Temperature sweep 60-20°C



## Time sweep 20°C 4 x 24 h

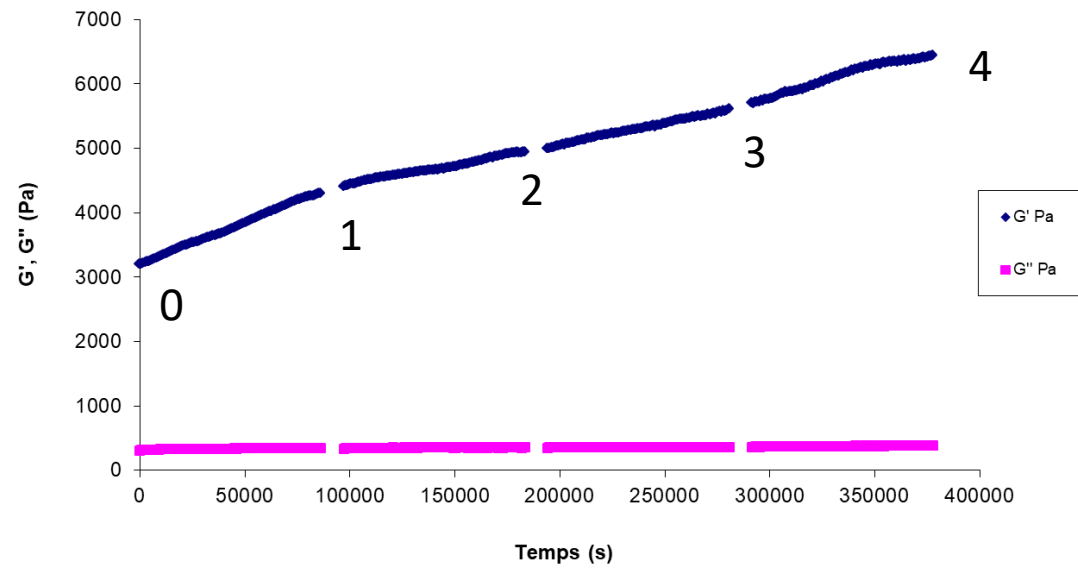


# Rheological behaviour

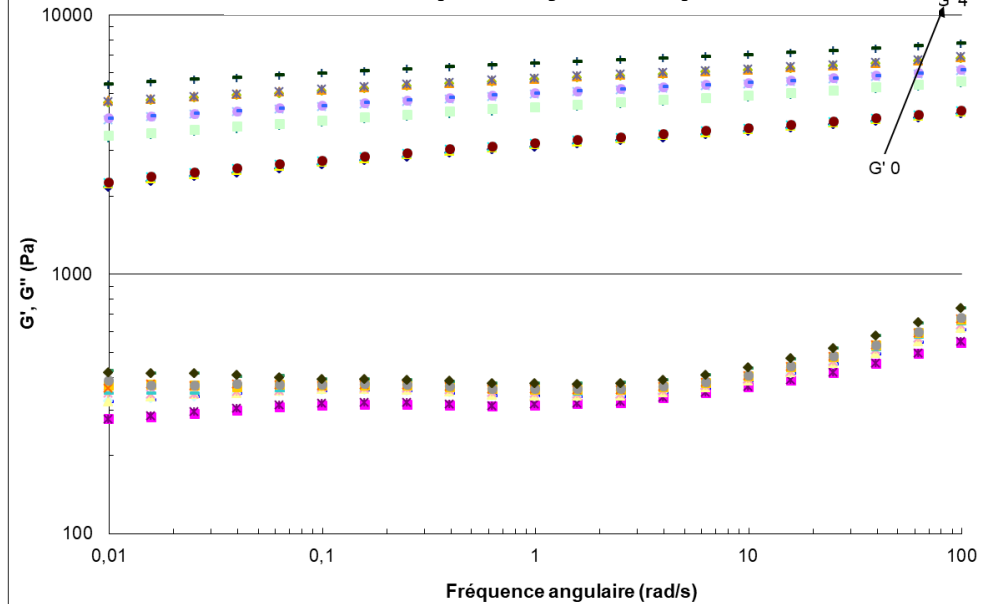


AR2000, TA Instruments  
 Plate-plate 40 mm  
 Gap 1 mm  
 $\gamma$  0,5%, 1 rad/s

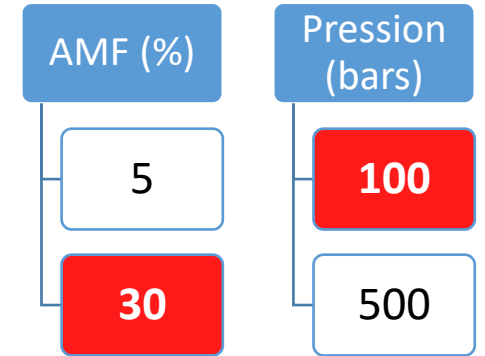
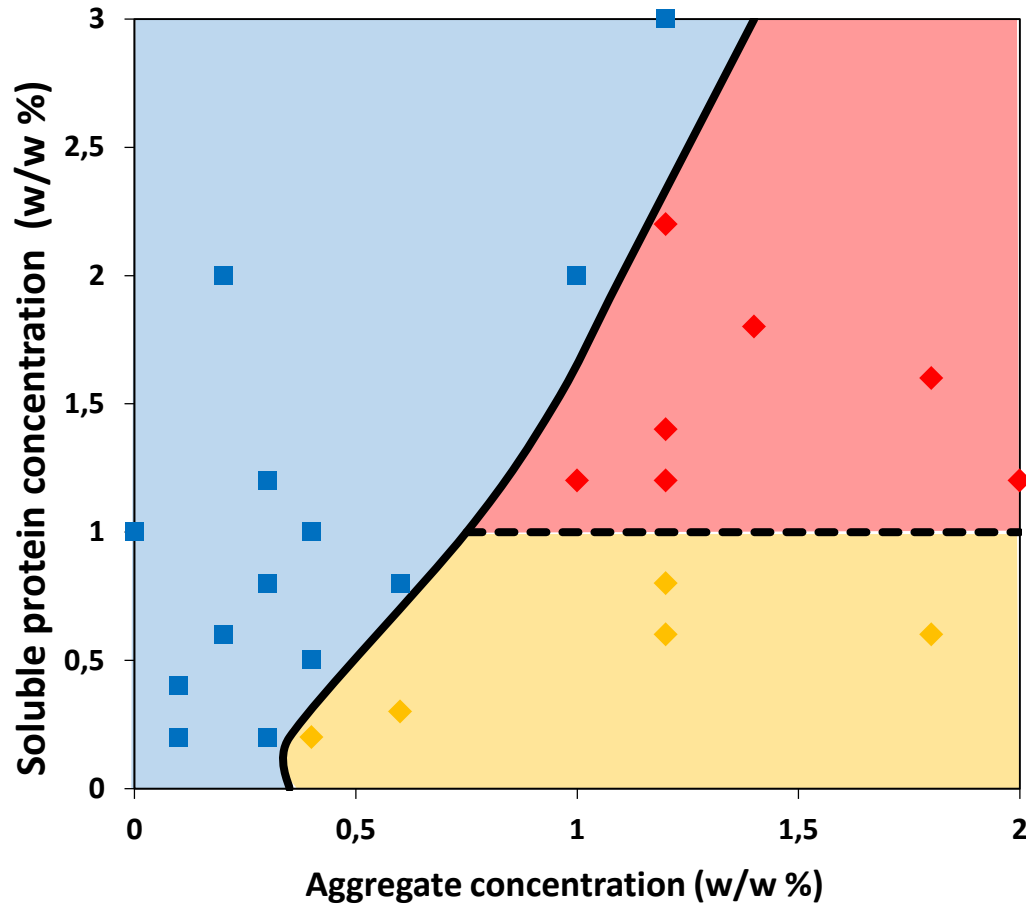
## Time sweep 20°C 4 x 24 h



## Frequency sweep 20°C



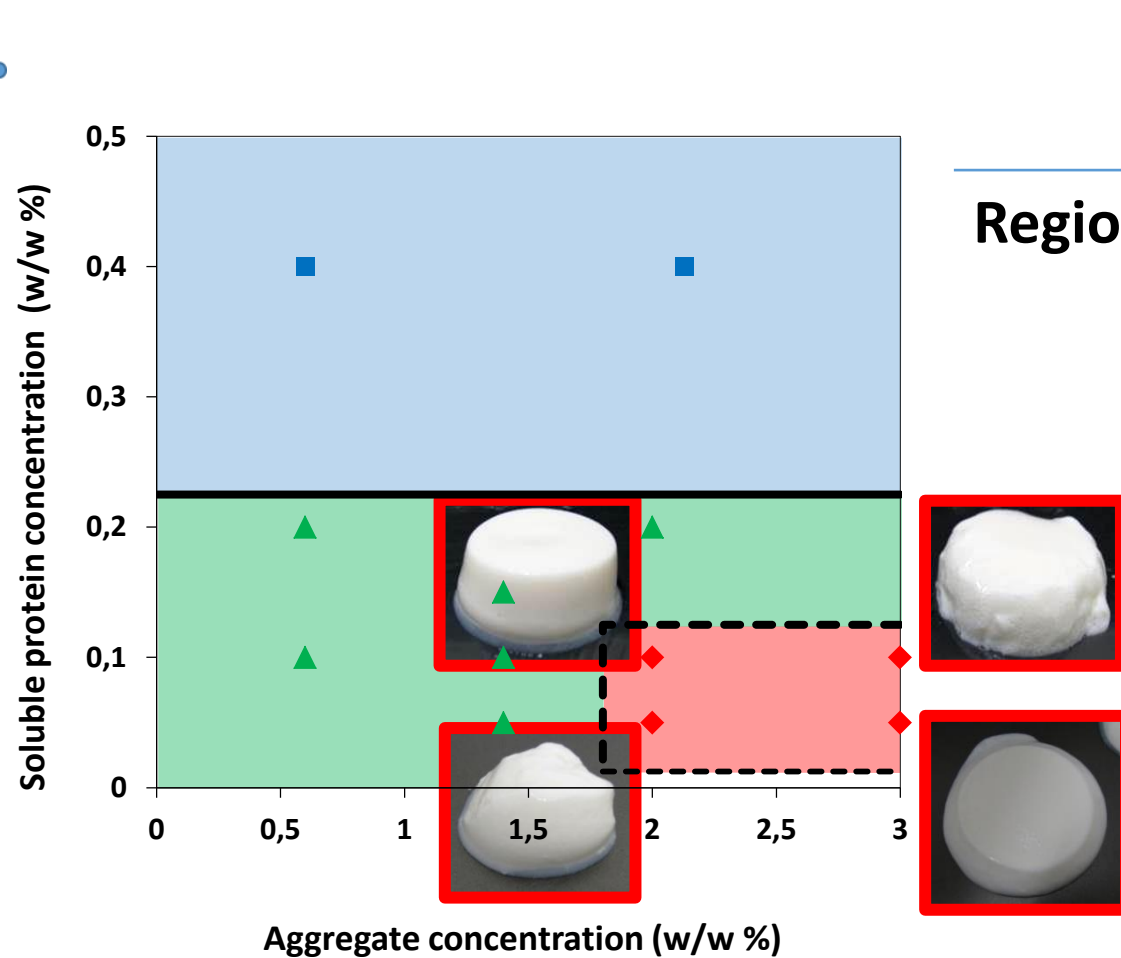
# State diagrams obtained with fractal aggregates (30 / 100)



**Regions**

- Liquid or instable
- Instant gel
- Delayed gel

# State diagrams obtained with fractal aggregates (5 / 500)



Regions

Liquid or instable

Heterogeneous

Delayed gel

~~Instant gel~~

MGLA (%)

5

30

Pression (bars)

~~100~~

500

Gels are able to reform after shearing



D7 (without breaking)

If [Ag] increases → liquid emulsion

Soluble proteins in aggregates



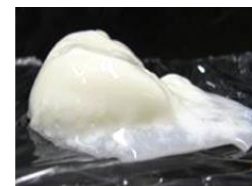
After breaking



D1



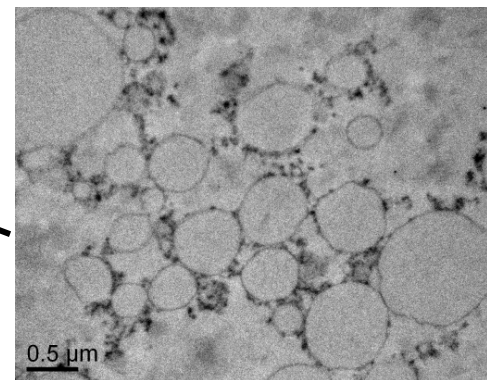
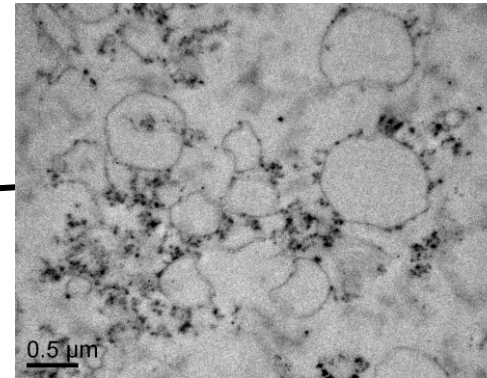
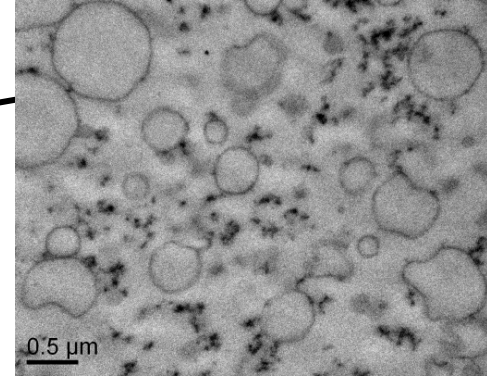
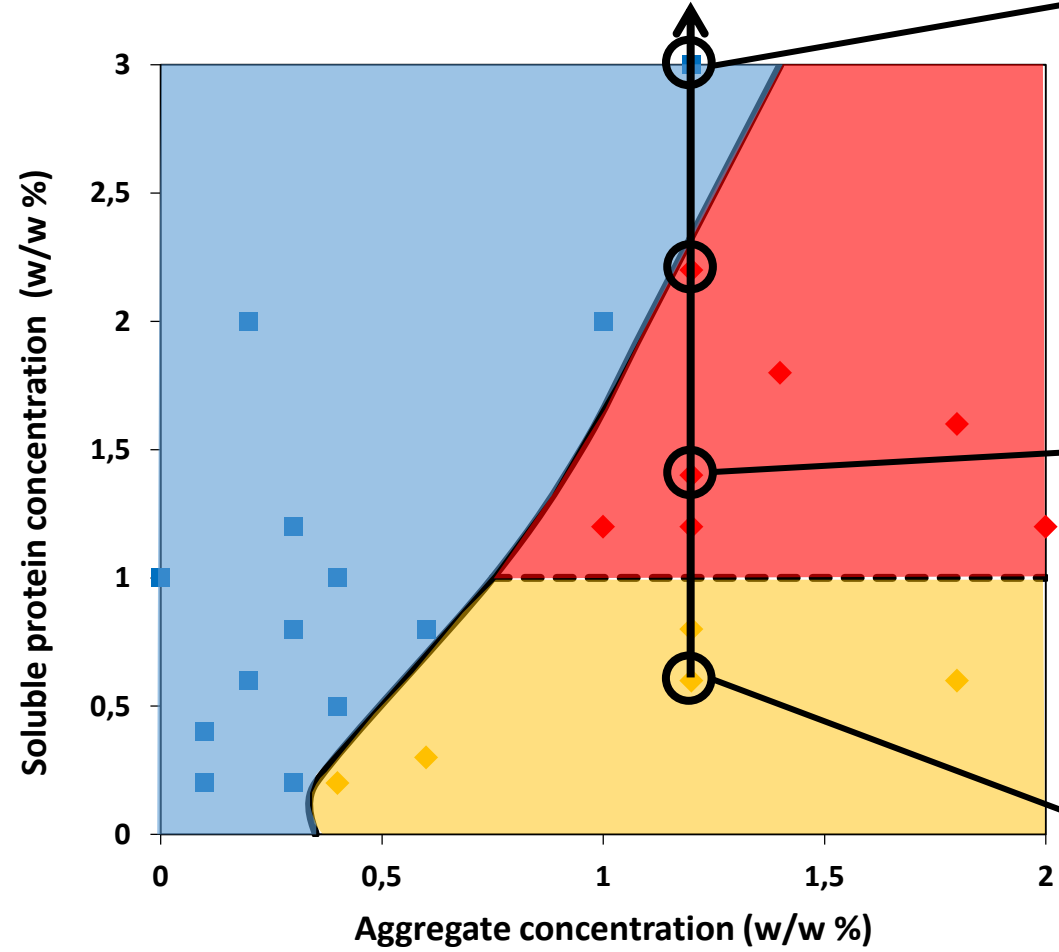
D3



D7



# Interface connectivity

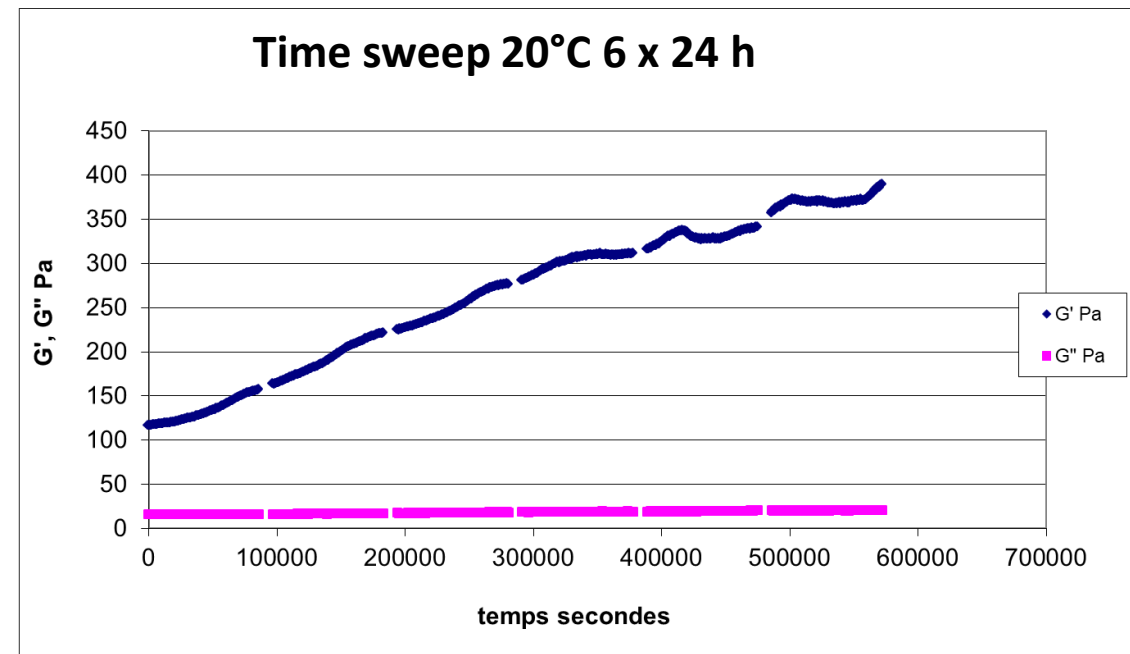
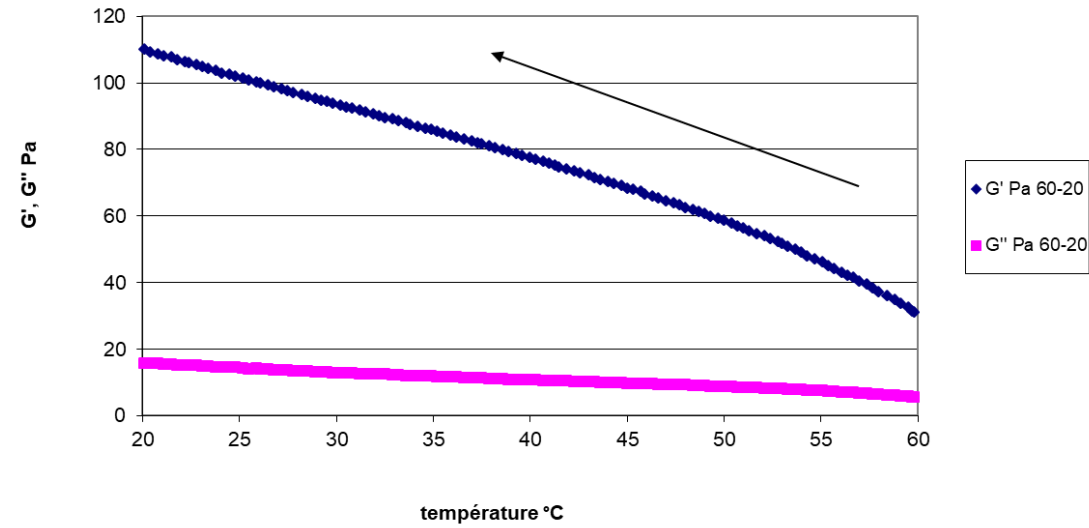
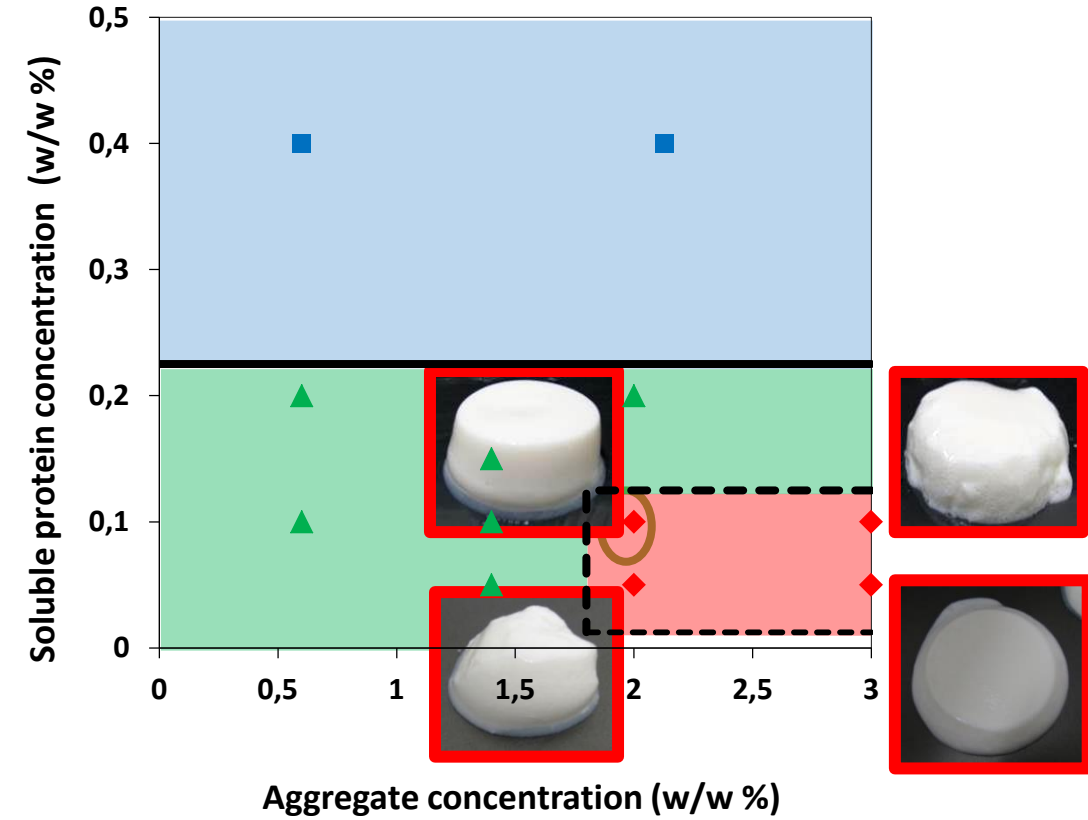


# Rheological behaviour



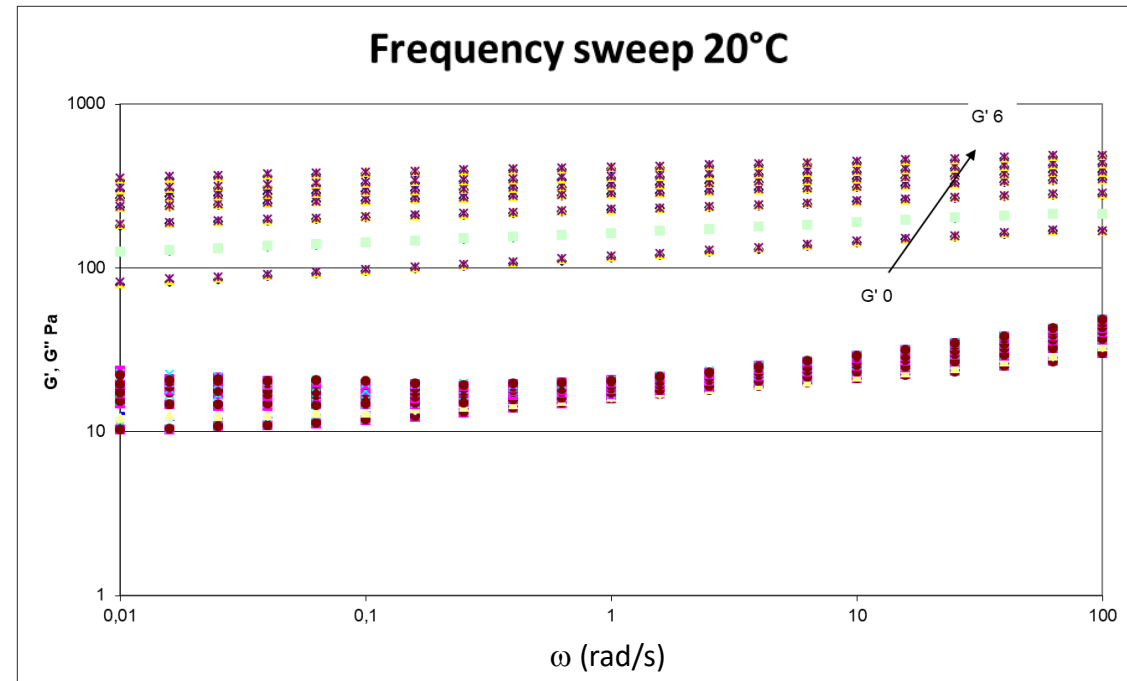
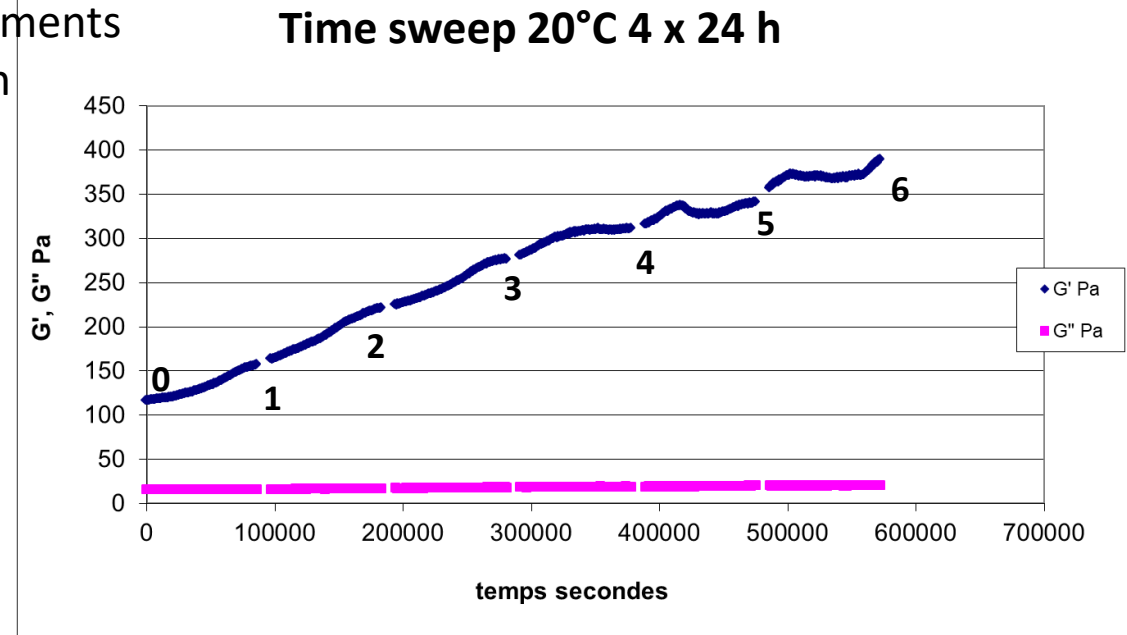
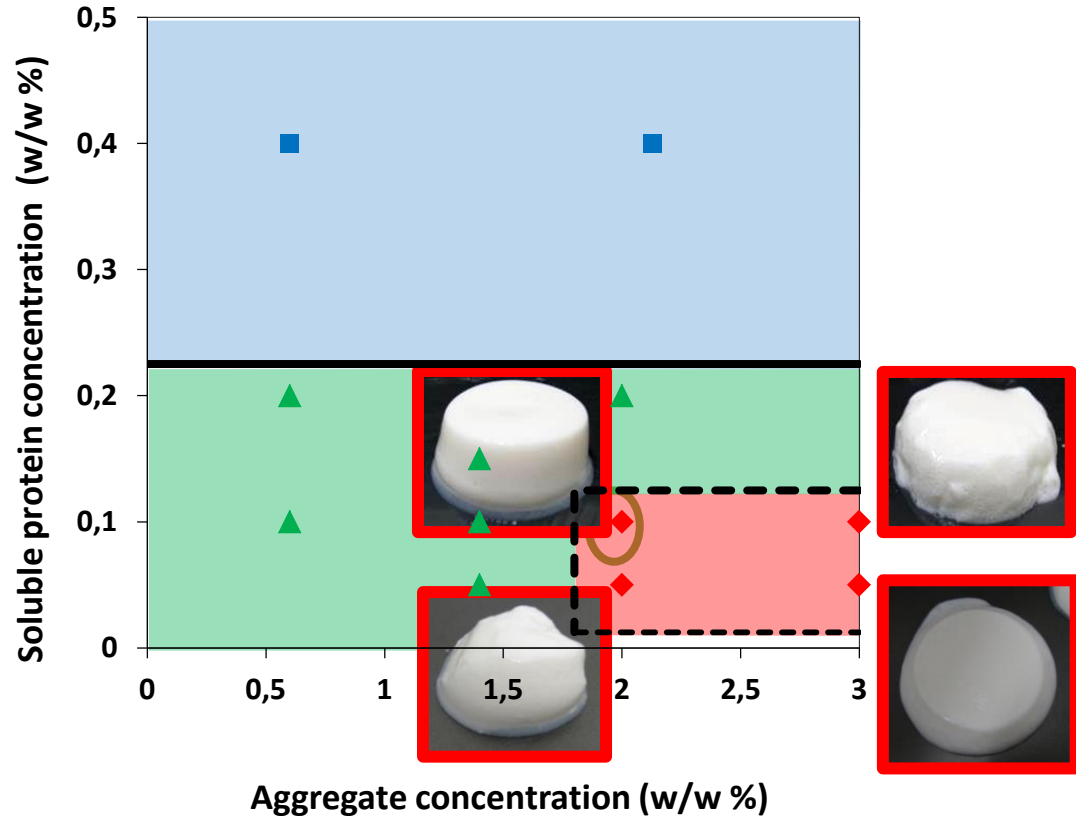
AR2000, TA Instruments  
 Plate-plate 40 mm  
 Gap 1 mm  
 $\gamma$  0,5%, 1 rad/s

Temperature sweep 60-20°C



# Rheological behaviour

AR2000, TA Instruments  
 Plate-plate 40 mm  
 Gap 1 mm  
 $\gamma$  0,5%, 1 rad/s



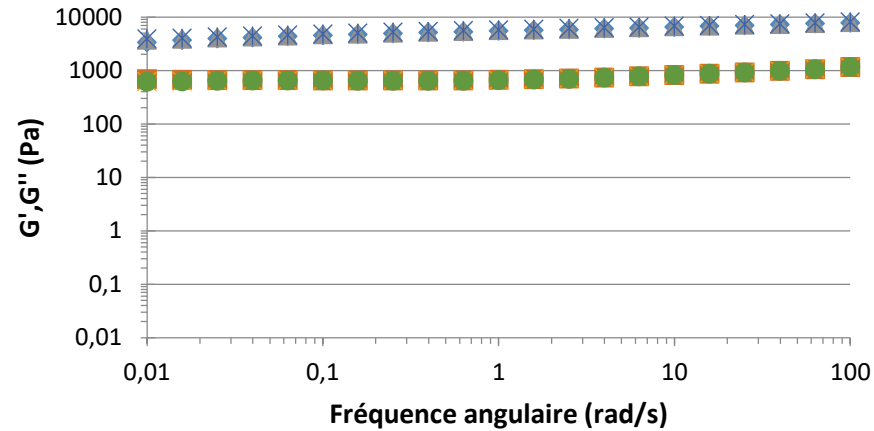
# Rheological behaviour



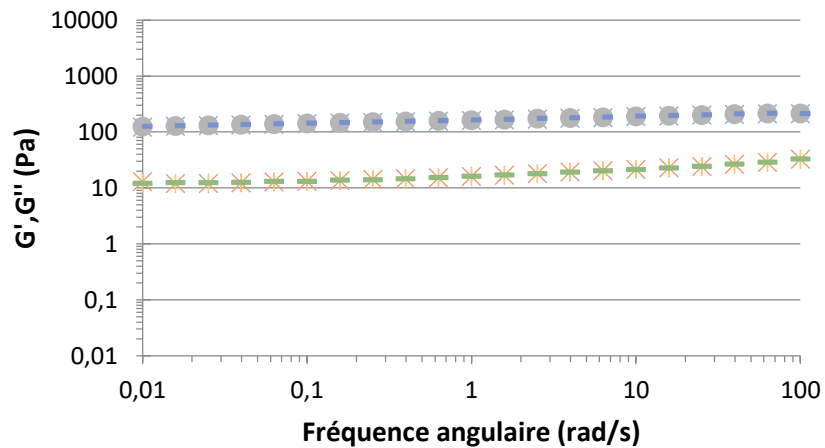
AR2000, TA Instruments  
Plate-plate 40 mm  
Gap 1 mm  
 $\gamma$  0,5%, 1 rad/s

6

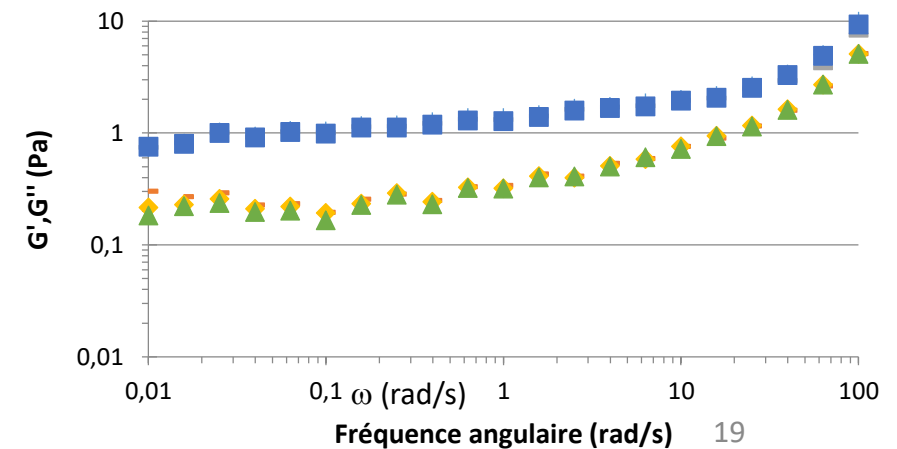
### AMF 30%; NP 0,5% ; Ag 1%



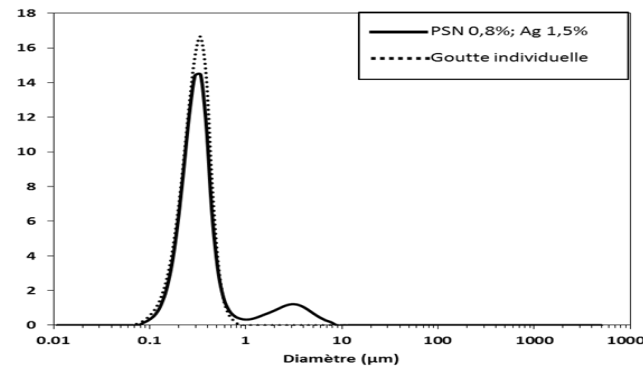
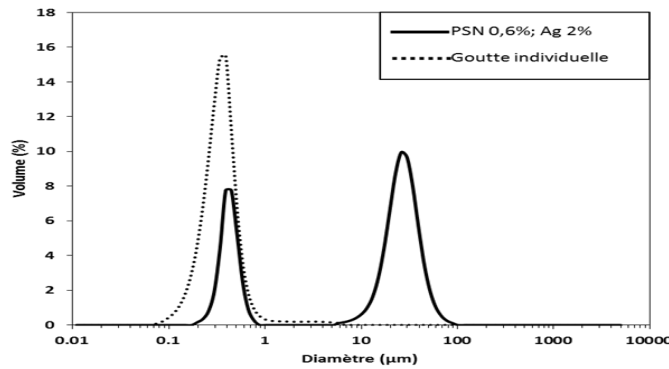
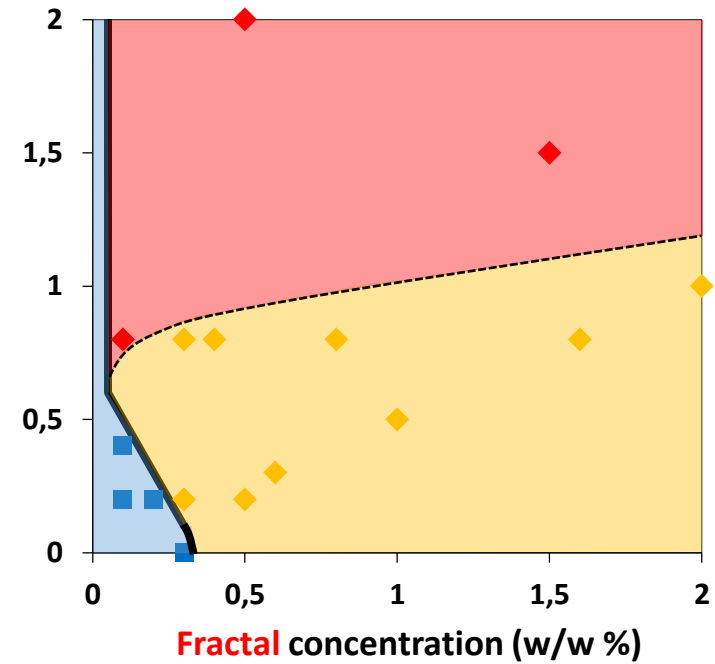
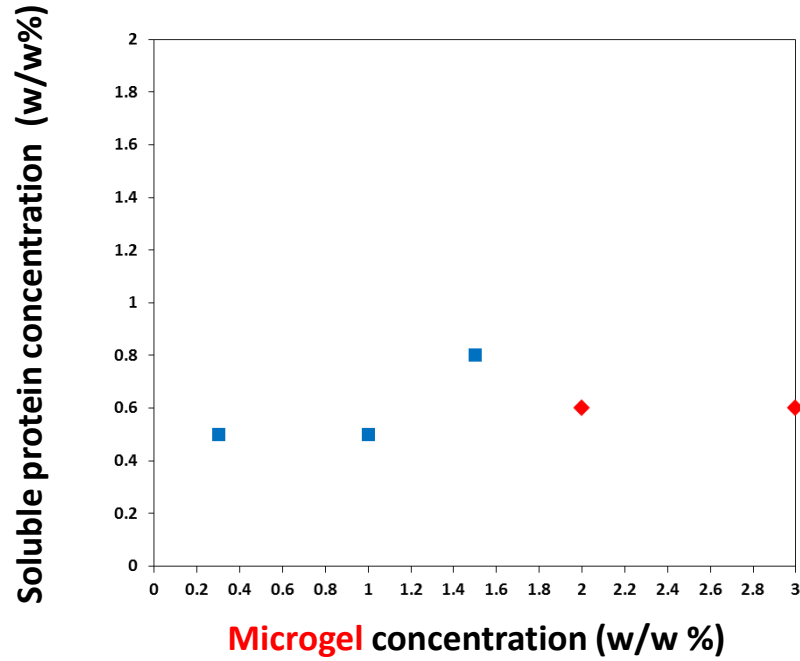
### AMF 5%; NP 0,1 %; Ag 2%



### AMF 5%; NP 0,1% ; Ag 3%



# State diagrams obtained with microgels (30 / 500)

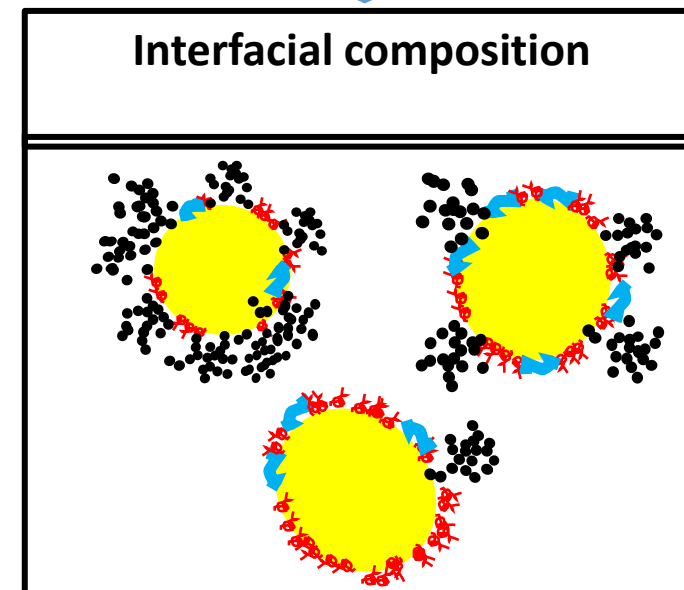
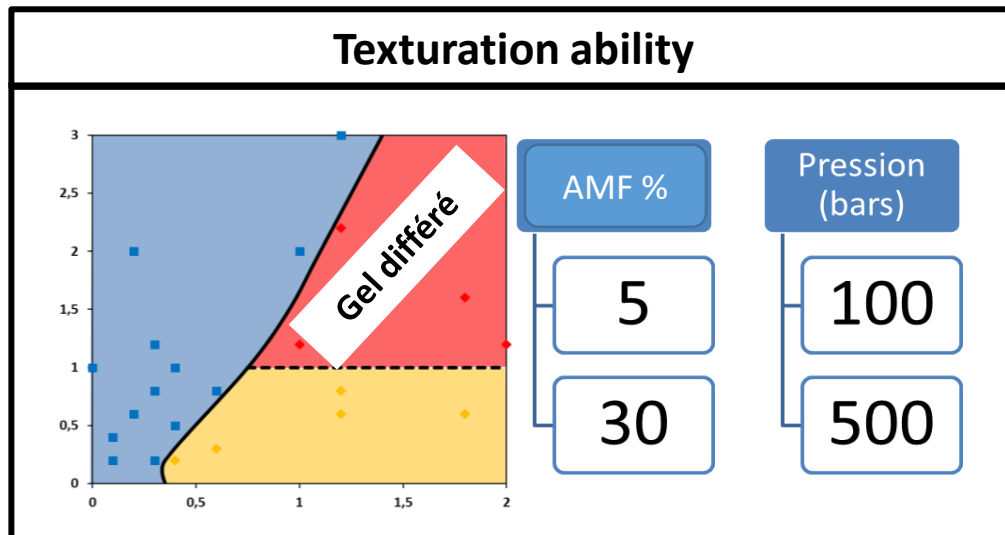
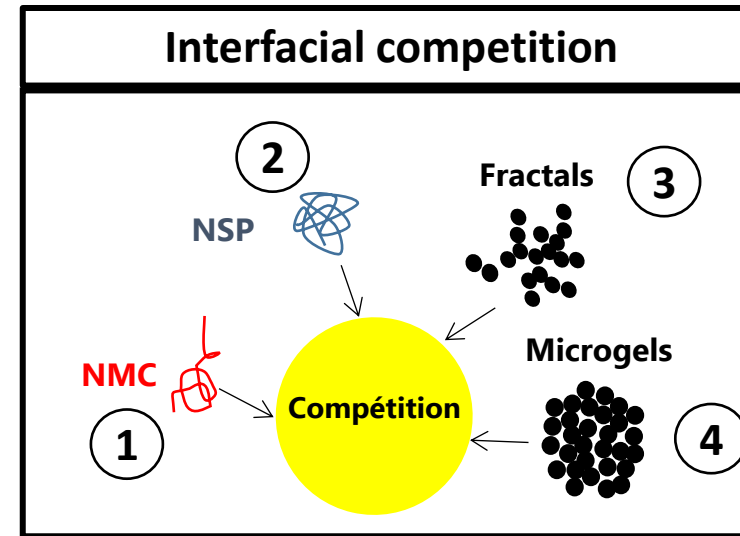
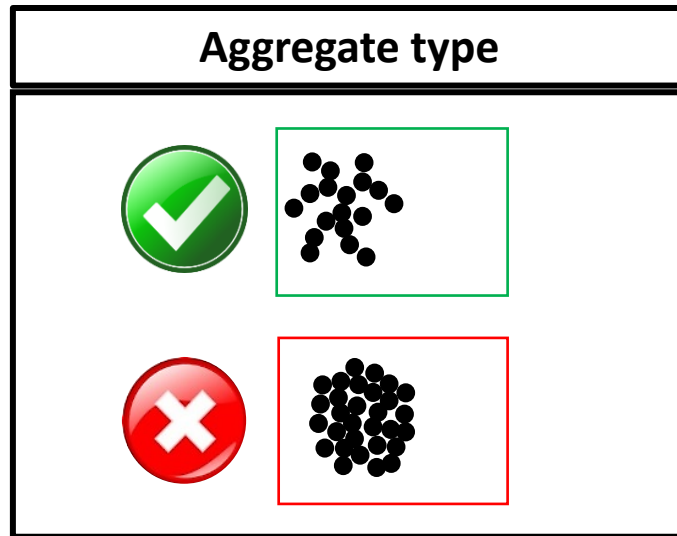


Few microgels

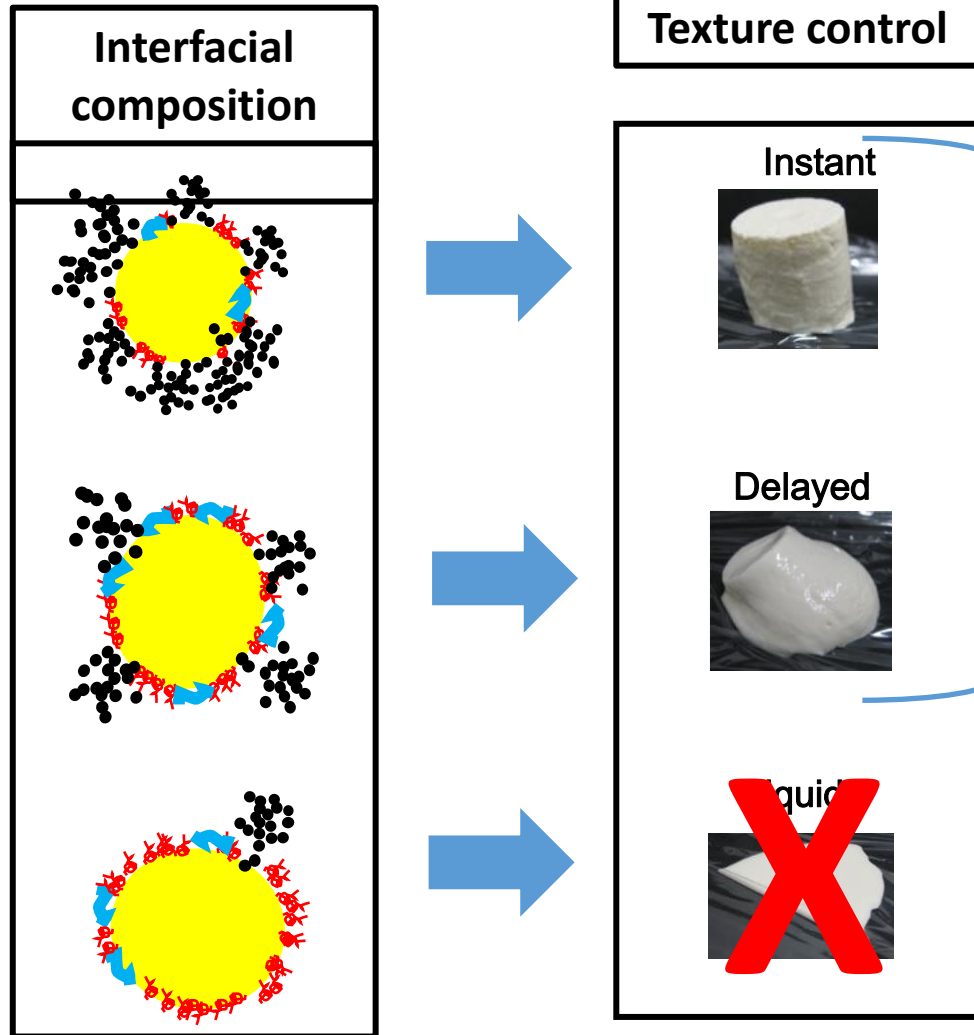
- ➔ Low affinity for the interface
- ➔ Less efficient to connect droplets



# For neutral emulsions



# For neutral emulsions



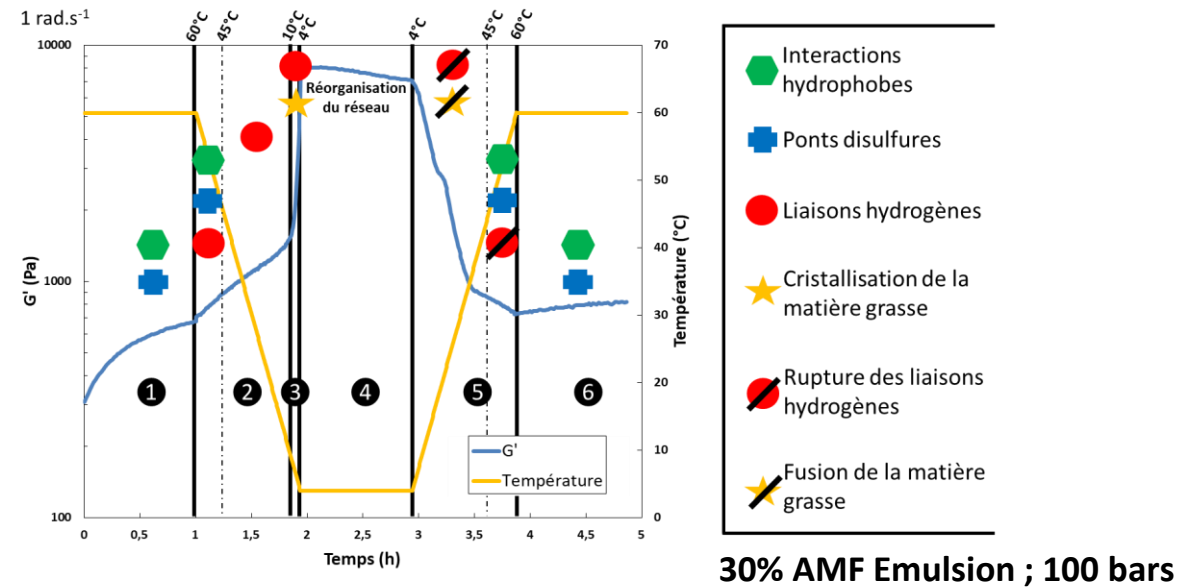
### Molecular interactions

**Pendant l'homogénéisation**

(Surel, 2014)

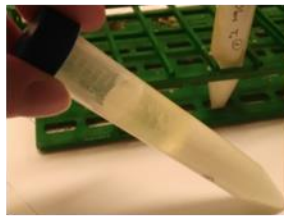
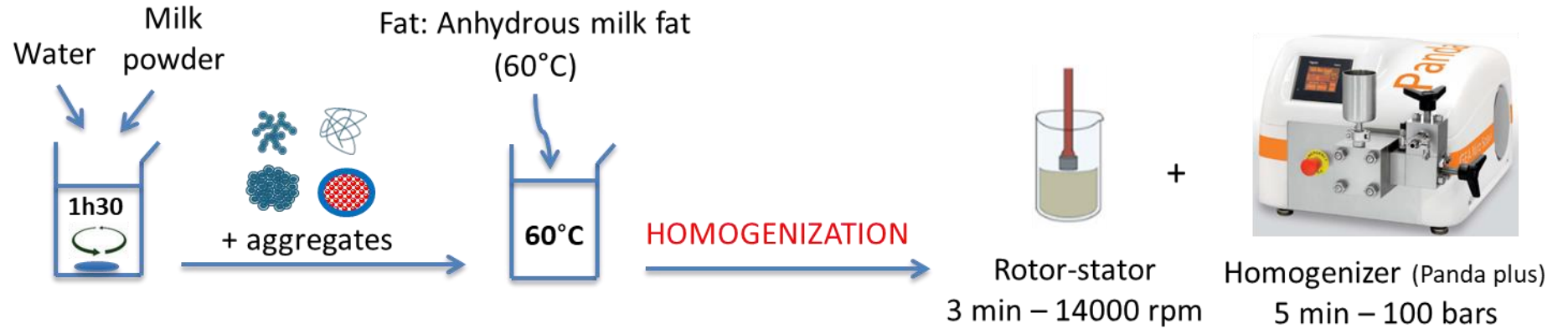
**Pendant le stockage**

- ✓ Disulfure bonds
- ✓ Hydrogen bonds
- ✓ Hydrophobic interactions
- ✓ Fat Crystallisation

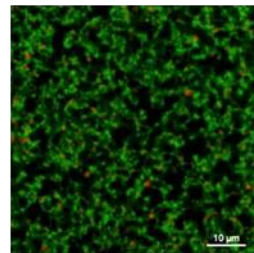


**Protein-protein interactions are predominant**

# Acidified dairy system



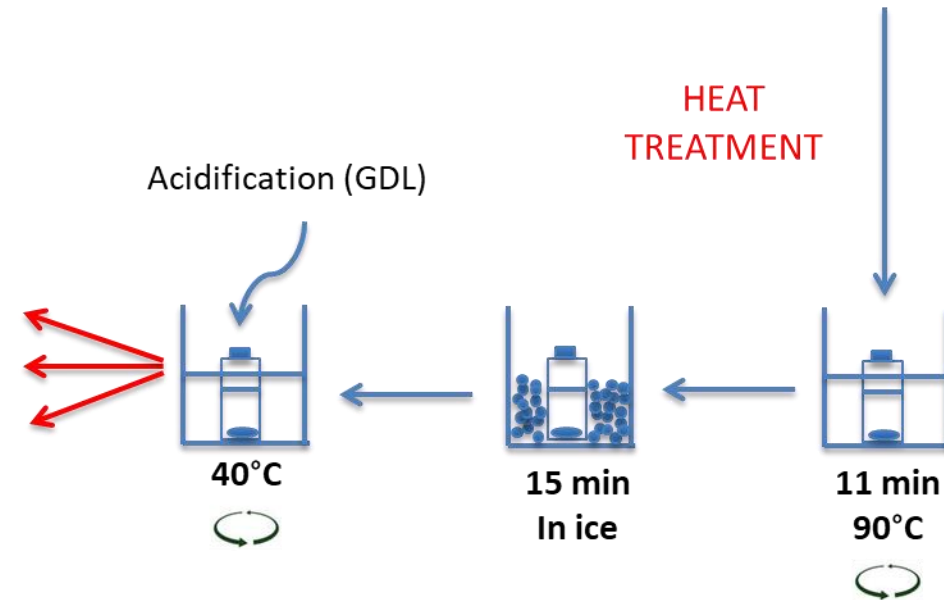
Analysis of syneresis



Microscopy

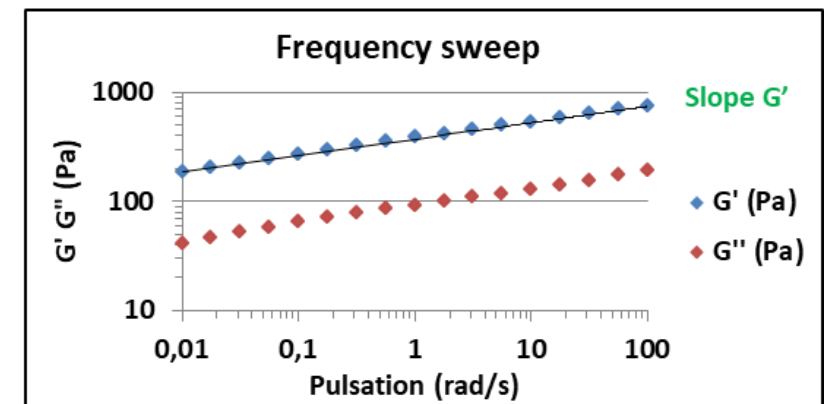
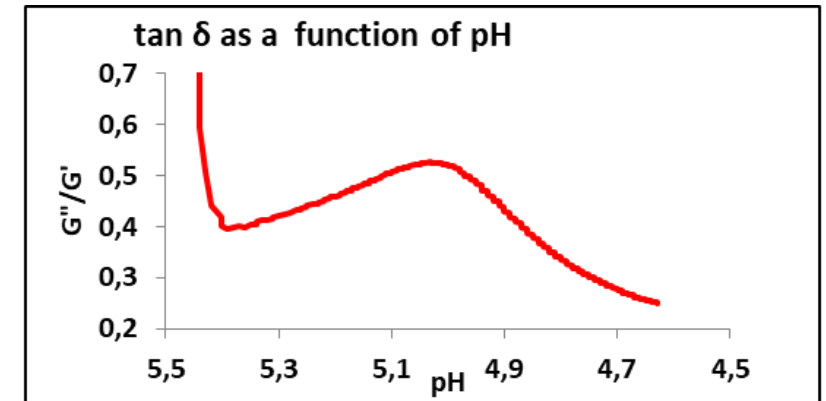
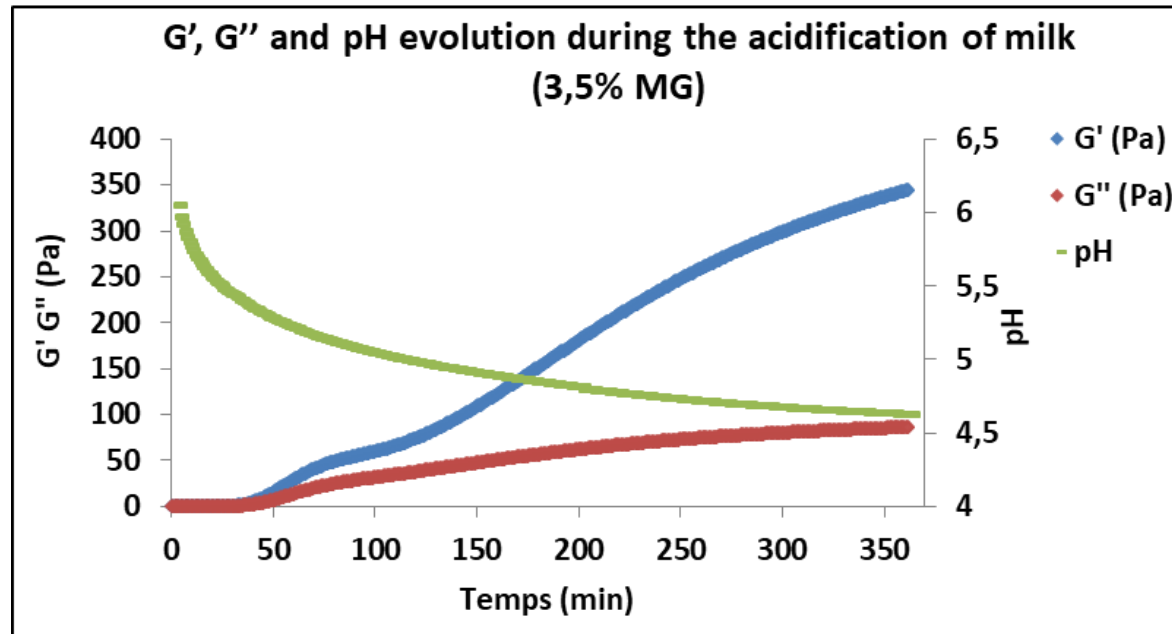


Rheological measurements

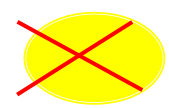




# Rheological behaviour of acidified dairy systems



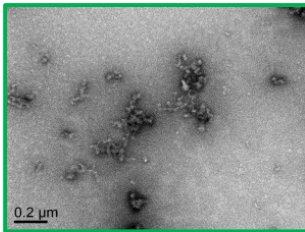
Sample	Gelation time (min)	Gelation pH	G' max (1 rad/s) (Pa)	Slope G' (FS)
No fat	29 min	5,44	234	0,164
3,5% AMF (100 bars)	29,4 min	5,45	340	0,150



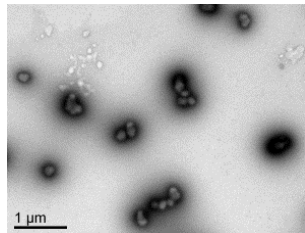
# Acid milk gel **without** fat



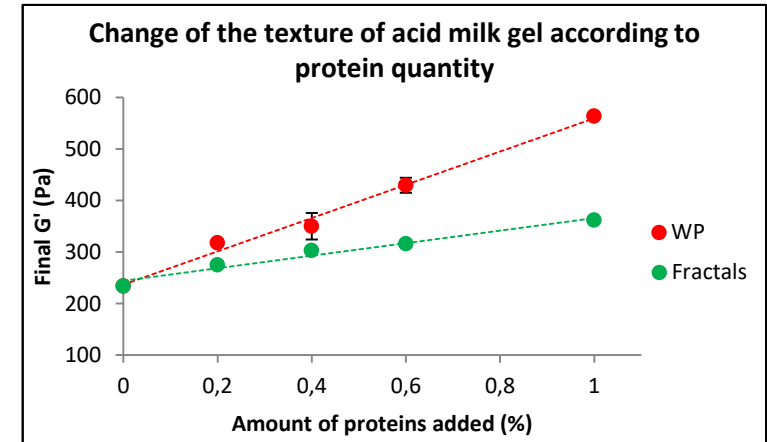
Better structuring and firmness with **increasing concentration**  
Decrease of syneresis



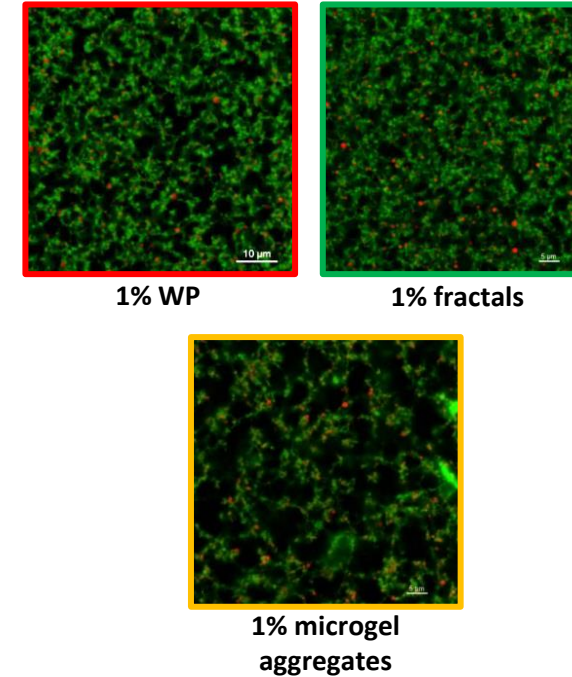
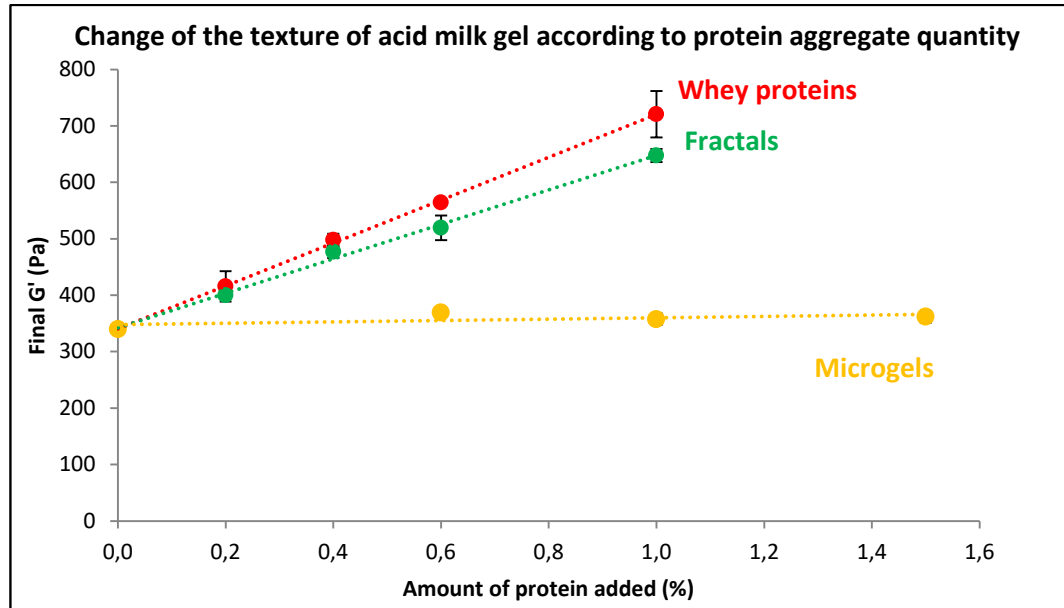
Good structuring and firmness  
Decrease of syneresis  
**Less efficient than WP**



No improvement of firmness and no decrease of syneresis  
**→ Protein enrichment of products**



# Acid milk gels with 3.5% fat and aggregates

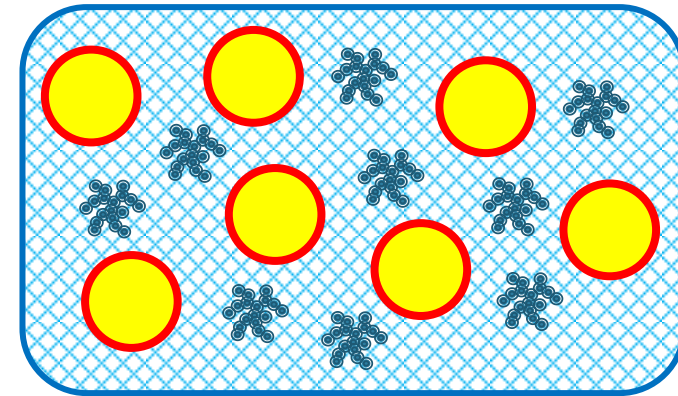
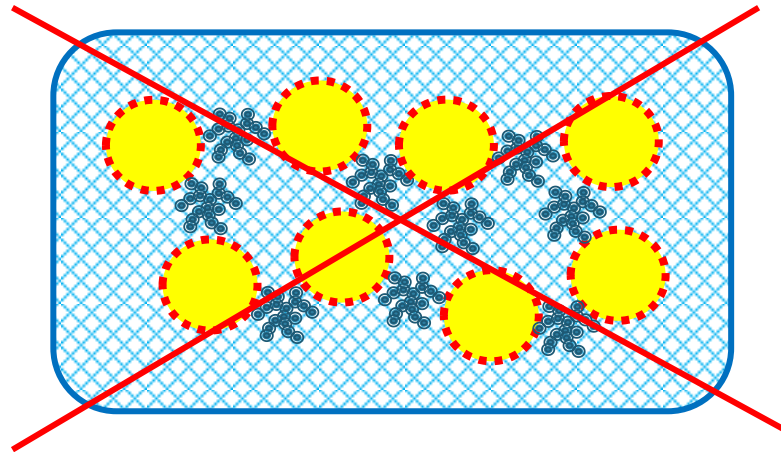


- WP and Fractals: **Increase of the gel strength** (slightly weaker with fractals)
  - **Similar aspect of protein network**
  - Same evolution with or without fat and WP/fractals → **impact on the interface?**
- Microgels: **constant** final  $G'$ , no modification with increasing concentration → **connection with the network?**

# Modulation of texture

At 3,5% fat :

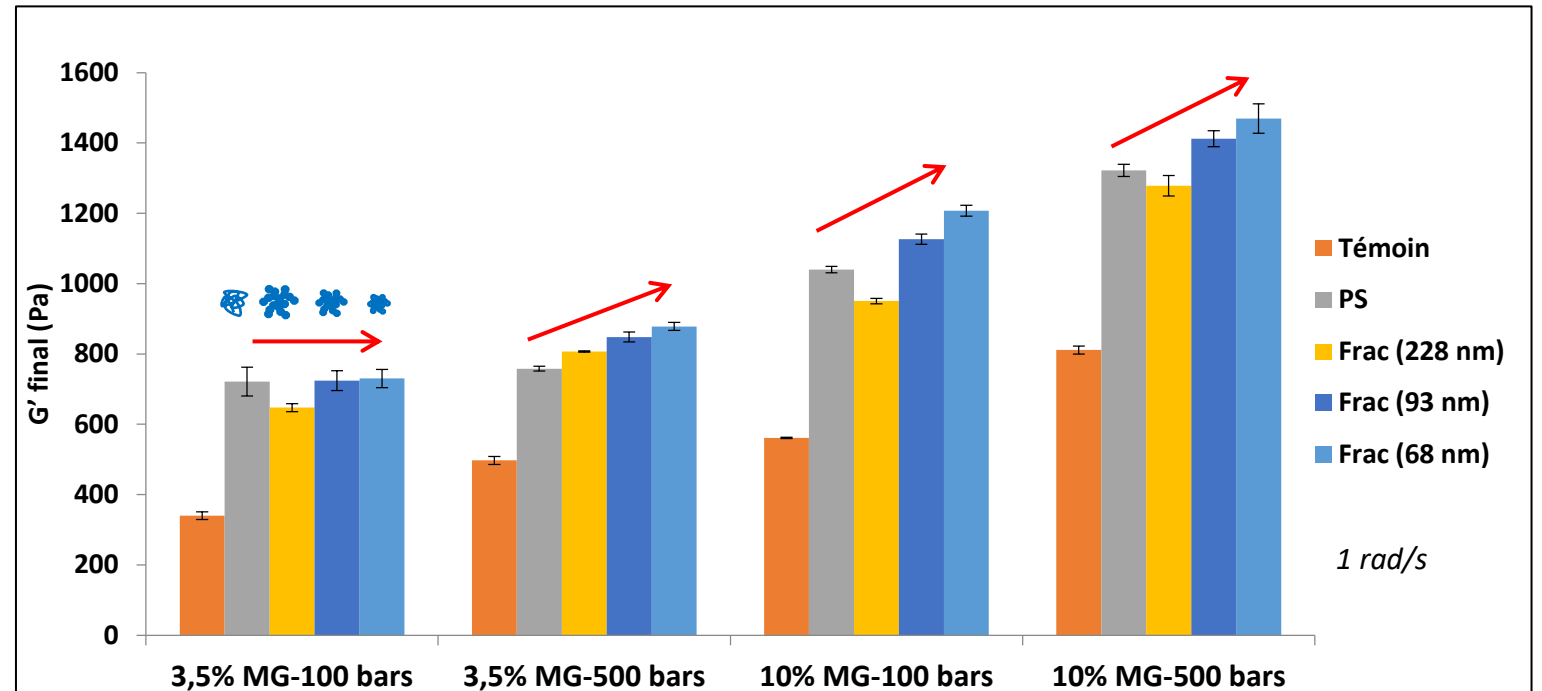
**interface totally occupied by caseins**  
aggregates play a rôle only in the continuous phase



# Effect of interfacial surface and of fractal aggregate size



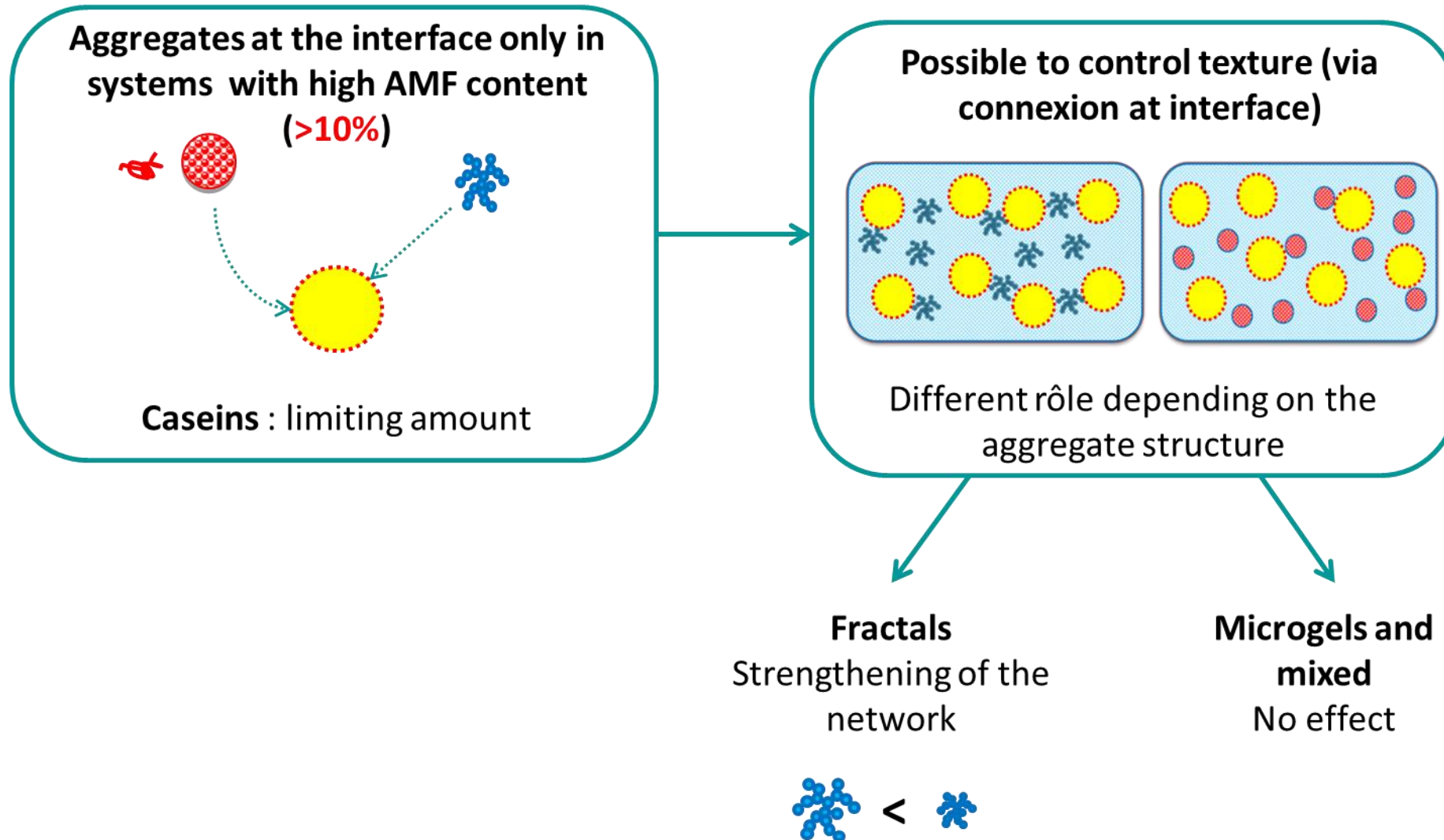
- Strong effect on interfacial surface increase on gel texture
- Weaker competition for interface when interfacial surface increases
- Stronger gels obtained when fractal aggregate size is lower



Final  $G'$  (pH 4.6) as a function of fractal aggregate size at a fixed concentration of 1% (w/w)



# For acidified systems



# Merci pour votre attention



## Projet PROFIL

**Joëlle Léonil**  
(Coordination scientifique)

**Morgane Raison**  
**Stéphan Rouverand**  
**Karine Le Roux**



Camille Jonchère, Valérie Beaumal,  
Bérénice Houinssou-Houssou,  
Véronique Solé, Geneviève Llamas,  
Bruno Novales...

