Heat treatment of concentrated milk protein system affect viscosity and enzymatic coagulation properties

François Martin, Luisa Azevedo-Scudeller, Arnaud Paul, Gaëlle Tanguy, Emeline Gousse, Florence Rousseau, Marie-Hélène Famelart, Romain Jeantet, Cécile Le Floch-Fouéré

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Context

- High added value products
- Expanding market

Dairy protein ingredients

- Many Properties
  - Coagulation
  - Setting agent
  - Emulsifier…
- Many outlets
  - Infant formulas
  - Cheese making
  - Bakery…

Highly concentrated protein product with increasingly complex physico-chemistry

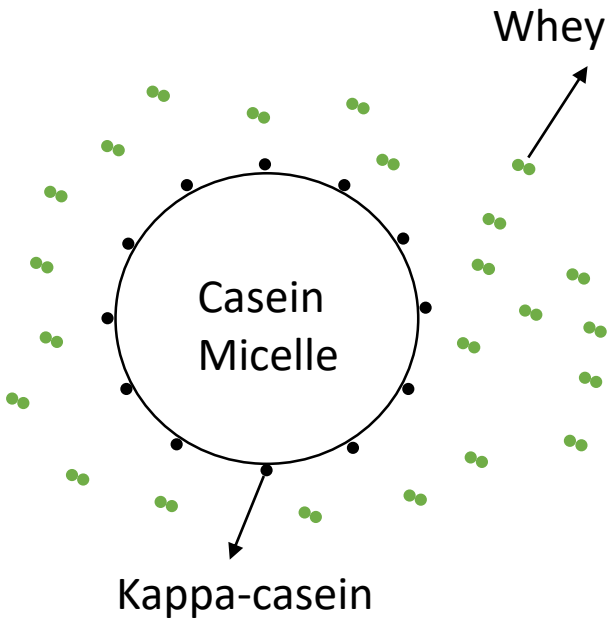
Process key stage : Heat treatment

More knowledge needed for controlling functionalities

Impact of heat treatments on highly concentrated dairy protein systems ?

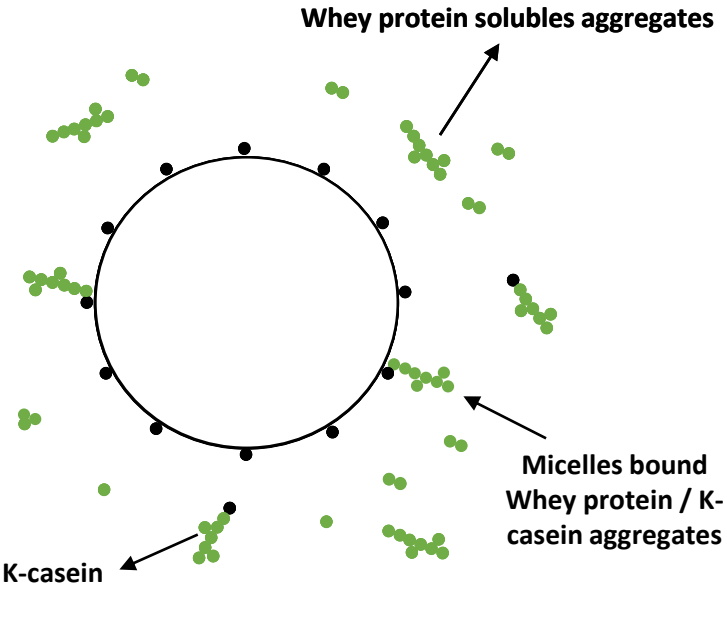
Scientific Background

Heat treatment of protein solution : what happens in the case of milk?



Process : Temperature / duration of heat treatment

Physicochemical conditions : pH, ionic strength, whey protein/Caseins ratio…

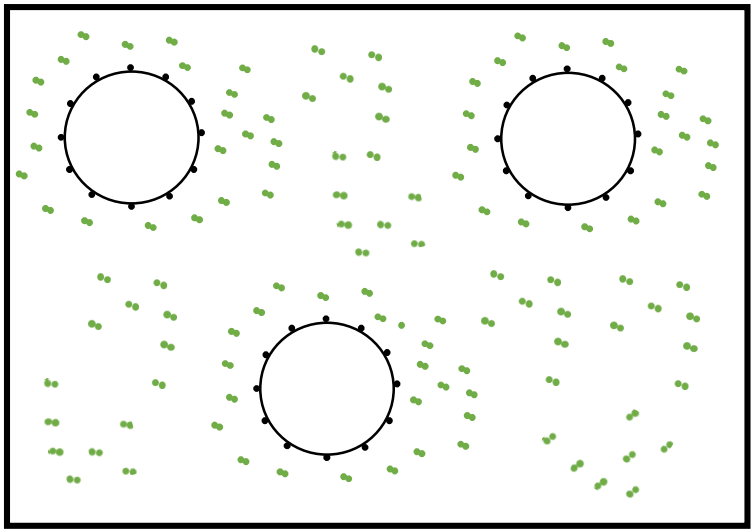


(Smits and Van Brouwershaven .1980 ; Singh and Fox, 1985,1987 ; Anema and Klostermeyer, 1997 ; Oldfield et al. 2000 ; Anema and Li. 2003, Anema, 2009 ; O'Connell and Fox. 2003 ; Singh 2004)

Scientific Background

Heat treatment of dairy solution with different protein concentration :

Heat treatment of milk

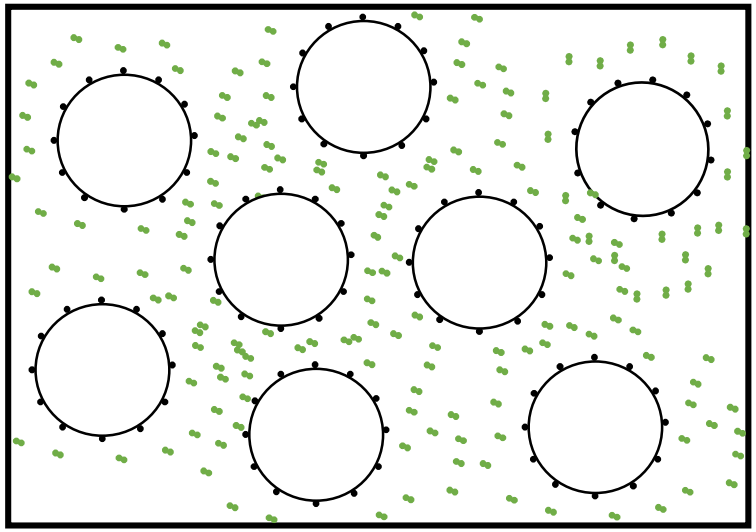


➢ [Protein] : 33 g/L

Many studies

(Smits and Van Brouwershaven .1980 ; Singh and Fox, 1985,1987 ; Anema and Klostermeyer, 1997 ; Oldfield et al. 2000 ; Anema and Li. 2003, Anema, 2009 ; O'Connell and Fox. 2003 ; Singh 2004)

Heat treatment of highly concentrated dairy protein systems

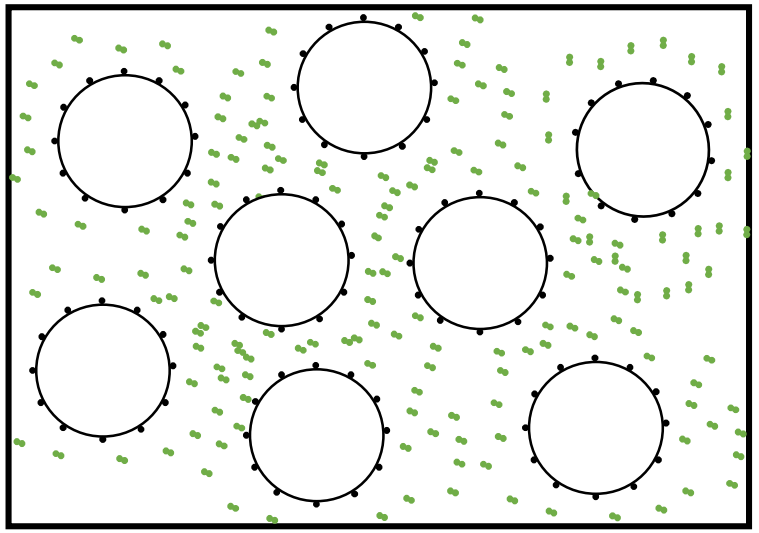


➢ [Protein] : 100-200 g/L

Only parcellar understanding

Research questions

Heat treatment of highly concentrated dairy protein systems



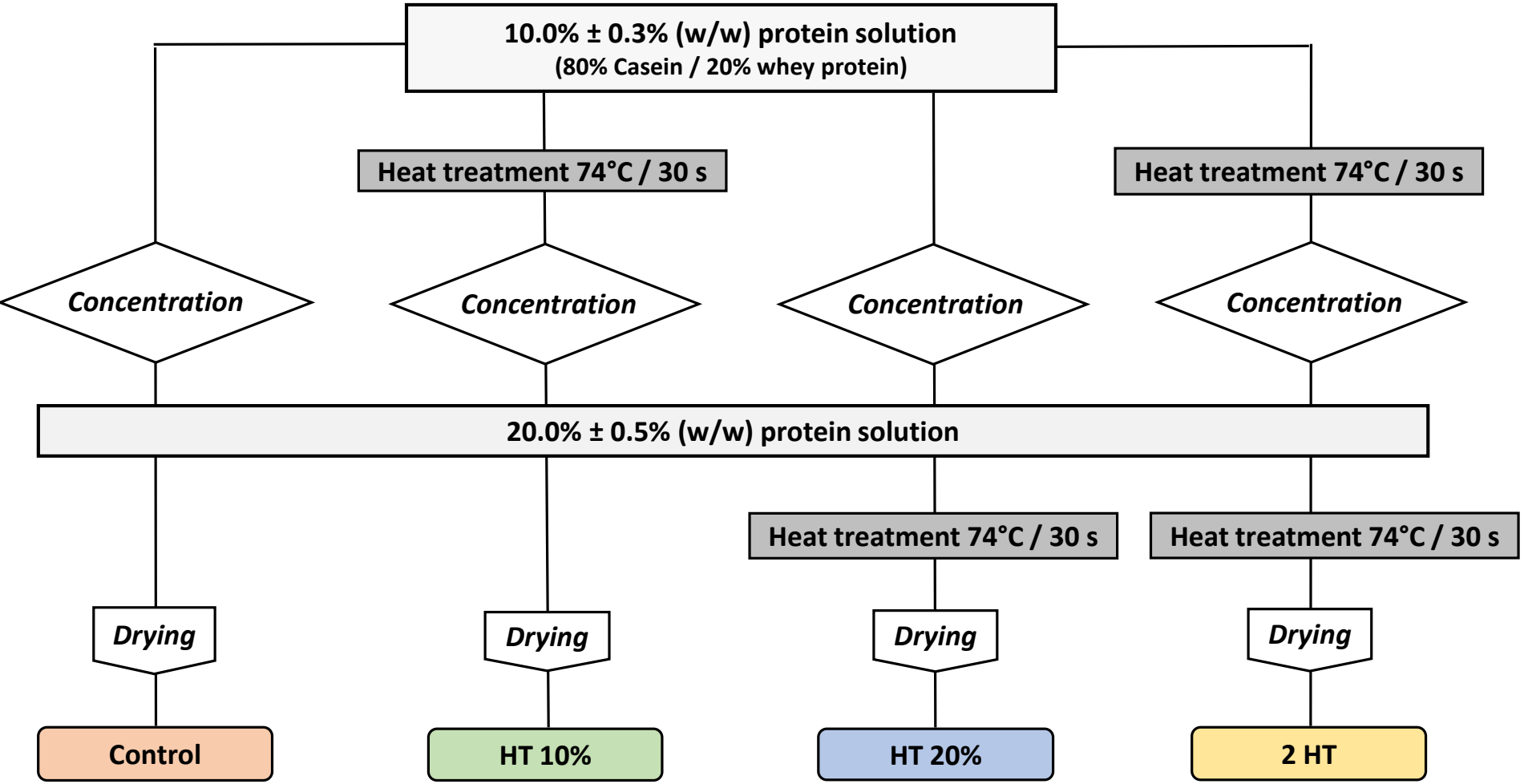
1/ Impact on heat-induced WP/Casein aggregation mechanisms ?

- Increase of collision probability
- Reaching of close packing of protein
  - Increasing formation of aggregates ?
  - Changes in whey protein/k-casein interaction ?
  - Changes in spatial location of protein complexes formed

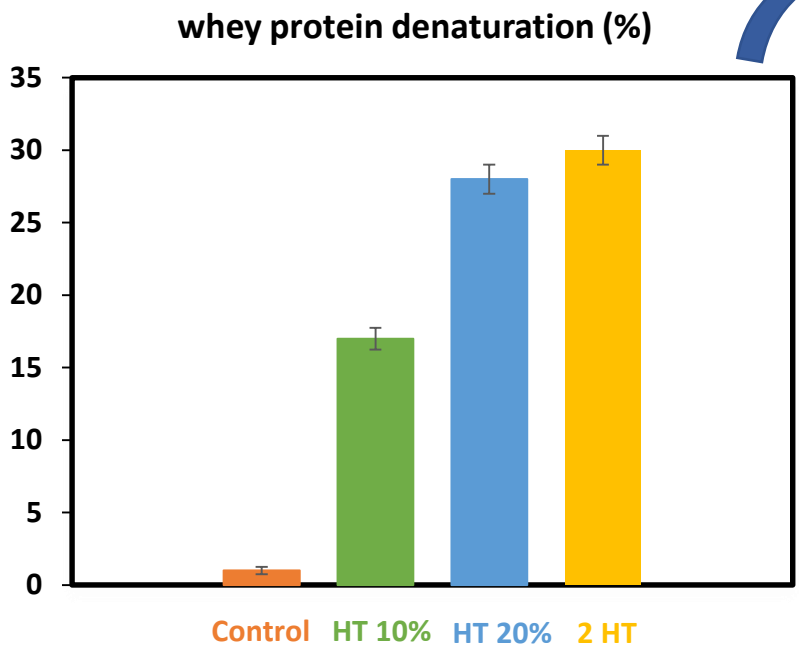
2/ What are the viscosity and coagulation properties of the resulting heat-treated solution ?

Experimental strategy

Experimental strategy



Results : Protein denaturation / aggregation



HT 20% / 2HT :

- Highest whey protein denaturation level
- 2 times more than **HT 10%** (17% -> 30 %)

Protein concentration -> parameter that influences whey protein denaturation / aggregation

Literature data

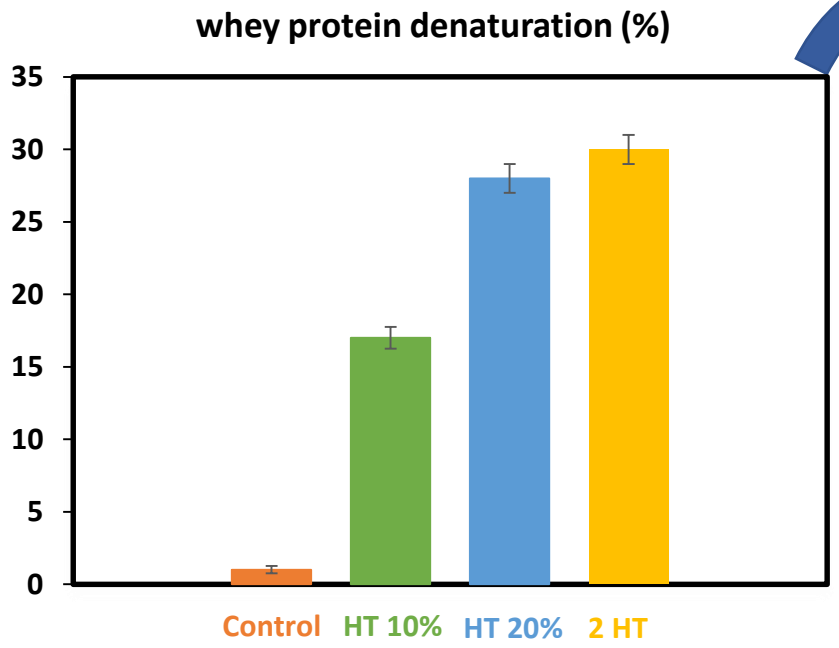
Denaturation level : 30/35 % ->
Heat treatment 80°C / 6 min

(Giroux et al. 2020) (Milk)

HT 20% / 2HT :
Very similar whey protein denaturation level (28 and 30 %)

No additive effect

Results : Protein denaturation / aggregation



Type of aggregates formed ?

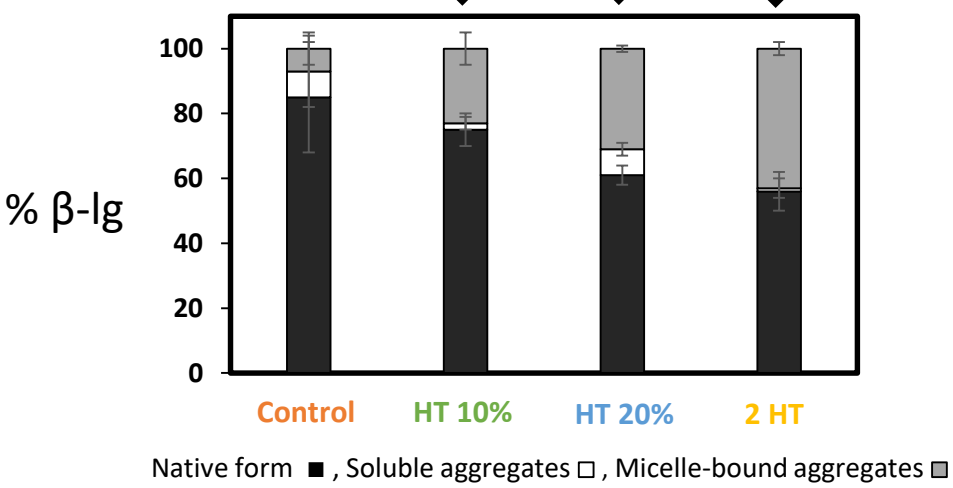
Whey proteins on the micelles or not ?

Coupled enzymatic and acid protein fractionation

(Noh et al.1989 ; Vasbinder et al. 2003)

Results : Protein denaturation / aggregation

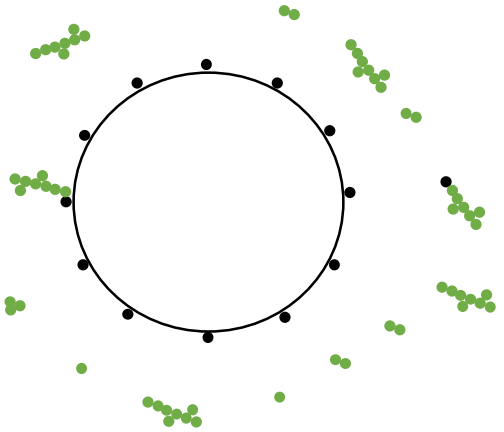
pH Heat treatment	10% protein	6.77	/	6.77
	20% protein	/	6.68	6.70

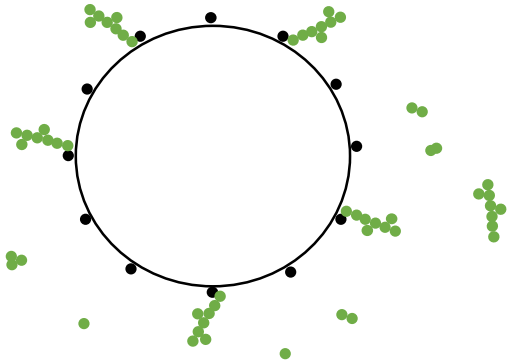


Literature data

~ 6.70/6.75 -> 80 % soluble aggregates

(Anema et al.2003)





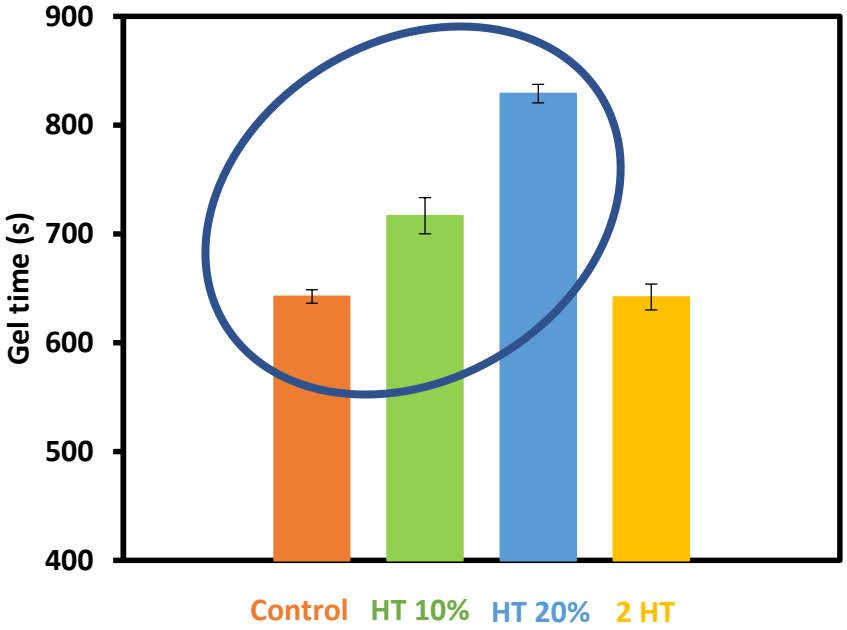
At least, 75 % micelle-bound aggregates

High protein concentration system

Different mechanism of k-casein / whey protein association

Result : Enzymatic coagulation properties

1/ Gel time



In agreement with milk based studies

↗ protein aggregates formation
↳ ↗ gel time

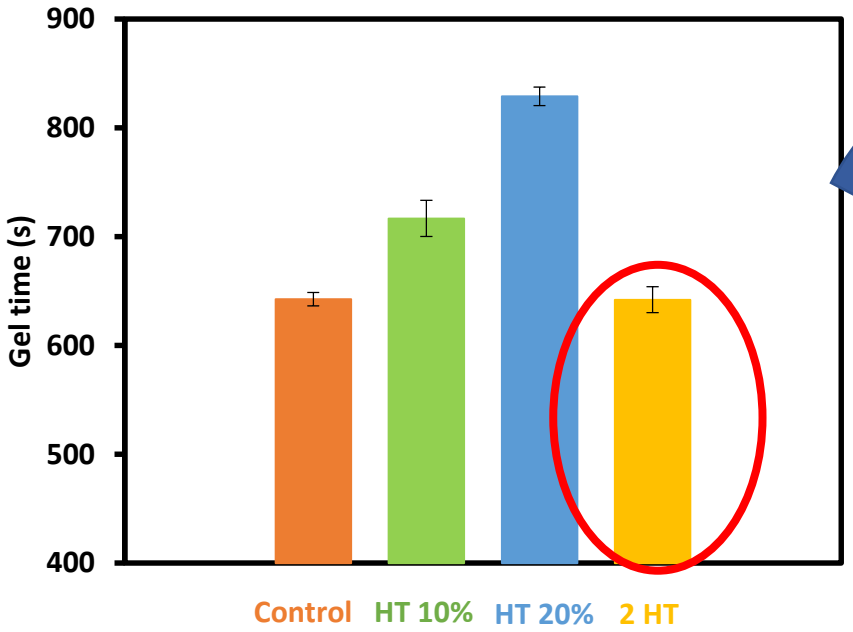
(Kethireddipalli et al. 2015; Vasbinder et al. 2003 ; Donato et Guyomarc'h. 2009)

K-casein/Whey protein complexes disrupt hydrolyzed casein micelle aggregation

- Steric hindrance
- Electrostatic repulsion

Result : Enzymatic coagulation properties

1/ Gel time



2HT singularity : More protein denaturation/aggregation than **HT 20%** but same gel time than **Control**

Mechanisms involved ?

Investigation of :

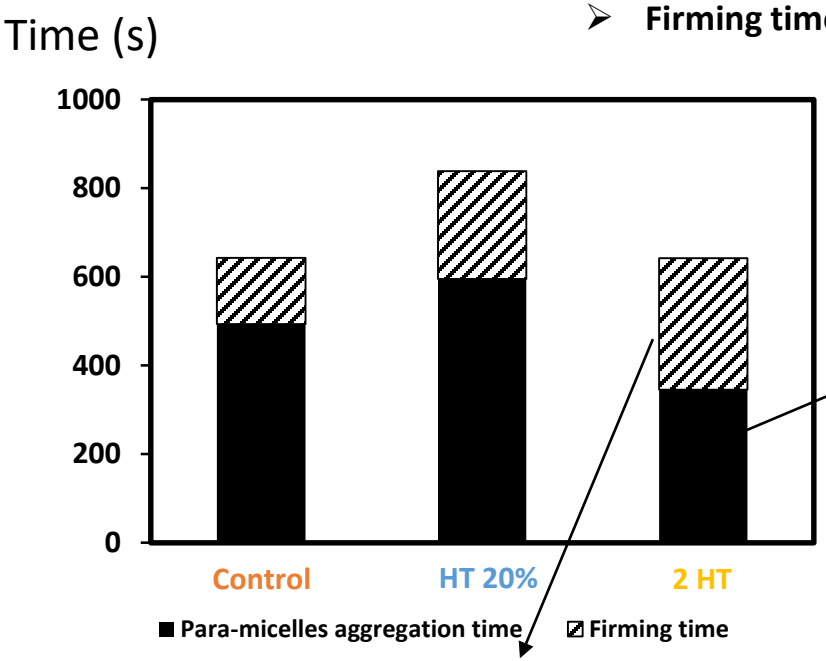
- Para casein micelles aggregation time
- Firming time

Result : Enzymatic coagulation properties

Investigation of :

- **Para casein micelles aggregation time**
- **Firming time**

Using a light backscattering technique (Payne and Castillo. 2007 ; Bauland and al. 2020)



Shortest para-micelles aggregation time

Longest firming time

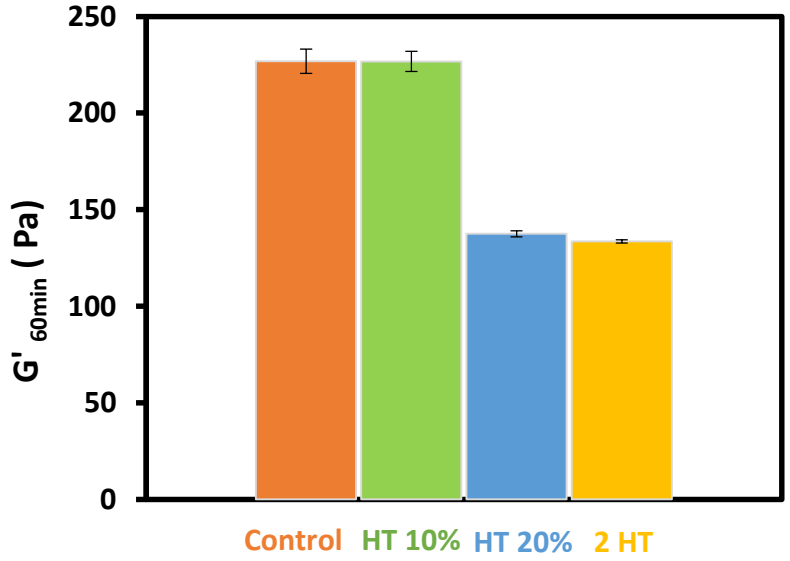
Impact of the 2 HT process scheme on :

- Casein micelles structure ?
  - *Futur outlook : SAXS study and K-casein hydrolysis*
- Physico-chemical environment ?

- Large number of K-casein/whey protein complexes on micelles
  - steric hindrance

Result : Enzymatic coagulation properties

2/ Storage Modulus 1h of coagulation



↗ **protein aggregates formation**

↘ **G'**

✓ ***HT 20% / 2 HT*** : Whey proteins aggregates and k-casein/WP complexes disrupt gel reorganisation and generate very weak gels

(Giroux et al. 2015 ; Perreault et al. 2017)

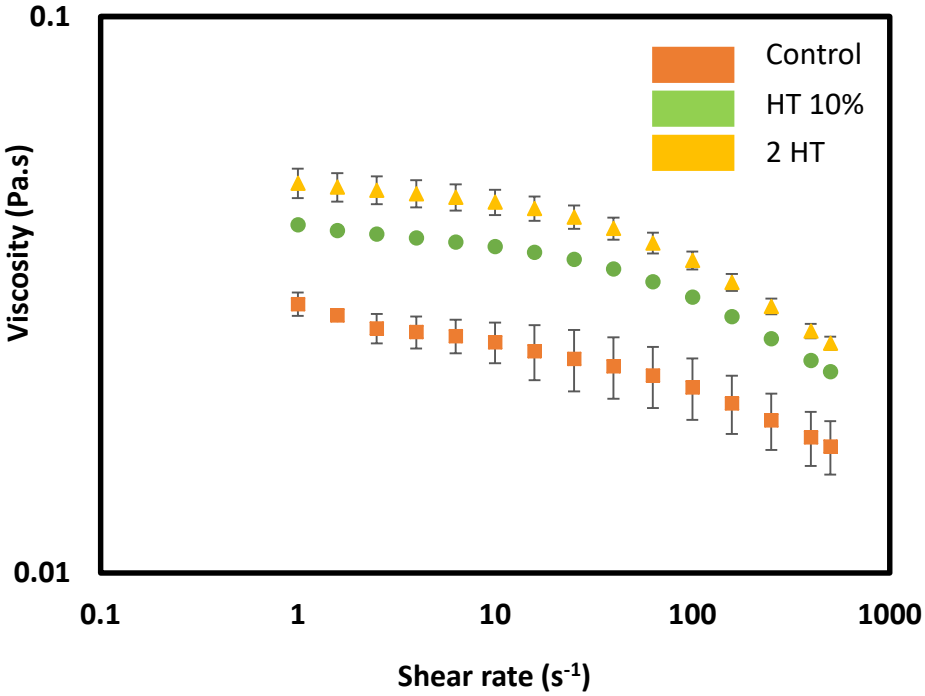
✓ **HT 10%** : Same gel strength as **Control** -> amount of whey proteins aggregates and k-casein/WP complexes seems to be insufficient to disrupt gel reorganisation

Aggregates quantity effect / threshold effect

Results : Viscosity changes

19,5 % protein

Control
HT 10%
2 HT



All samples -> **shear thinning behavior**

- The difference between the control and heat-treated products is greater than differences among heat-treated products

Higher protein denaturation level -> higher viscosity during shearing

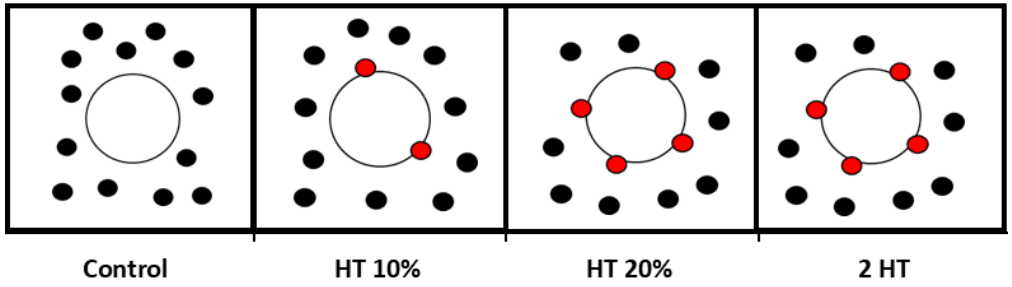
- Higher casein micelles voluminosity
- Higher water-binding capacity of whey protein aggregates >> native proteins

Anema et al, 2014

Take home message

Heat treatment of highly concentrated dairy protein systems :

1/ Impact on heat-induced WP/Casein aggregation mechanisms ?



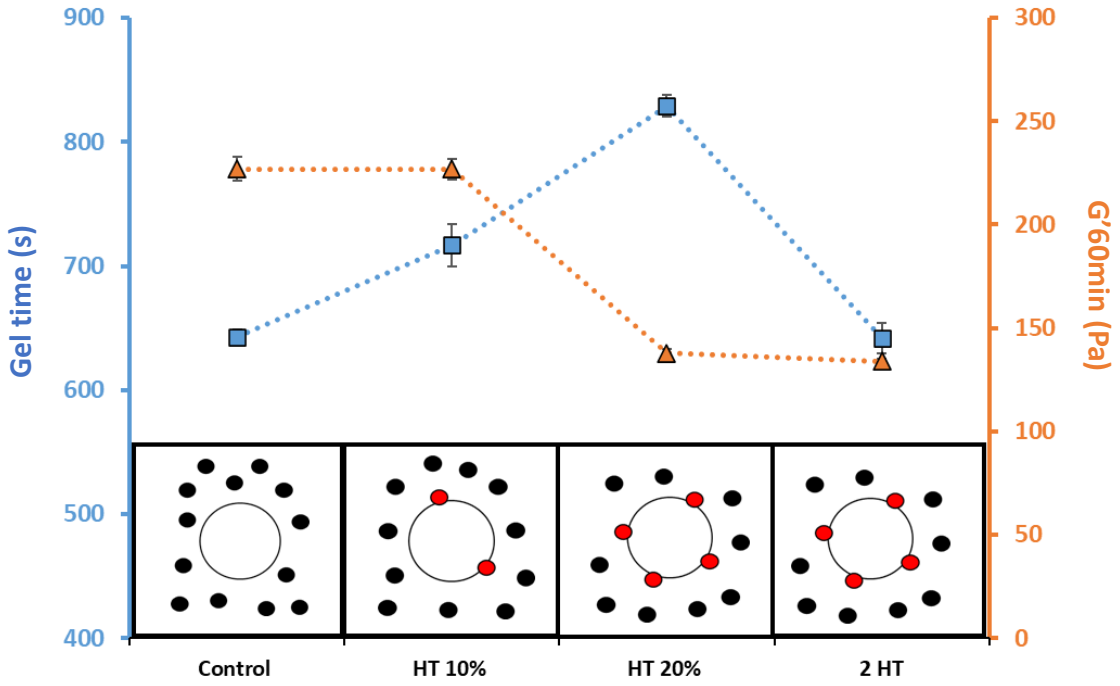
- Increase denaturation/aggregation of whey protein at 20 % (w/w) protein
- Protein denaturation -> no additive effect of heat treatment
- Drive K-casein/whey protein association toward major micellar aggregates

Take home message

Heat treatment of highly concentrated dairy protein systems :

2/ Impact on the coagulation properties of the resulting heat-treated solution ?

- K-casein/whey protein complexes -> increase gel time (especially by increasing the firming time), and lead to the formation of weak gels
- Few aggregates in the bulk -> gel produced have the same G' than control gel



Lines are guides for the eyes

Take home message

Heat treatment of highly concentrated dairy protein systems :

3/ Impact on viscosity of the resulting heat-treated solution ?

- Higher protein denaturation level -> higher viscosity during shearing
- The difference between the control and heat-treated products is greater than differences among heat-treated products

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Thanks