Passive microrheology as a useful tool for milk gel analyses

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Passive microrheology as a useful tool for milk gel analyses

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Colloidal, Macromolecular & Biological Gels: Formulation, Properties & Applications
July 10-14 2016
Hernstein, Austria
A full range to characterize dispersions:

- Without denaturation
- With easy operation
- From Formulation to Application

**TURBISCAN**

STABILITY & SIZE

Dispersion stability & size by multiple light scattering

**FLUIDICAM**

RHEOLOGY ON CHIP

Flow rheology by microfluidics

**RHEOLASER**

MICORORHEOLOGY

Zero shear microrheology

THERMAL ANALYSIS

Thermal analysis by microrheology

**DISPERSSION STATE**

SIZE
Dispersibility, aggregation...

STABILITY
Size variation, migration...

**RHEOLOGY**

FLOW BEHAVIOR
Injectability, sprayability...

STRUCTURE AT REST
Gelling, stability...

**THERMAL ANALYSIS**

PHASE TRANSITION
Crystallization, melting...

FROM FORMULATION TO APPLICATION

www.formulaction.com
Coherent light source

$L^*$ (penetration depth)

sample

Backscattering (BS) sensor 135°
Core technologie
Multiple light scattering

- Coherent light source
- Backscattering (BS) sensor 135°
- Sample

Turbiscan
Static Multiple Light Scattering

- Stability analysis
- Size determination

Rheolaser range
Diffusing Wave Spectroscopy
- passive microrheology

- Bulk rheological properties
- Gel time
Diffusing Wave Spectroscopy

Principle

LIGHT SOURCE

SPECKLE IMAGE

INTERFERING WAVES
Analysis of backscatterd light in dynamic mode

= Mean Square Displacement curves give information about bulk rheology
Gel point determination is quite complicated.

Usually people do it the easy way:

\[ \text{gel point is } G' = G'' \text{ (at one frequency)} \]

Actually:

\[ G' \sim G'' \sim \omega^n \]

Definition according to Winter and Chambon
Rheolaser Master
Gel point determination

Control parameter CP (t, T, conc., etc.)

Factor «a»
Factor «b»

Liquid
Gel

MSD (nm²)

Decorrelation time (s)

MSD 0. CP₀
MSD 1. CP₁
MSD 2. CP₂
MSD 3. CP₃
MSD 4. CP₄
MSD N. CPₕ

\[ \text{Liquid} \]
\[ \text{Gel} \]

\[ a^* \]
\[ b^* \]

\[ \text{b}^* \text{ MSD (nm}^2\text{)} \]

\[ \text{a}^* \text{ Decorrelation time (s)} \]

\[ \text{CP₀ - a₀. b₀} \]
\[ \text{CP₁ - a₁. b₁} \]
\[ \text{CP₂ - a₂. b₂} \]
\[ \text{CP₃ - a₃. b₃} \]
\[ \text{CP₄ - a₄. b₄} \]
\[ \text{CPₕ - aₕ. bₕ} \]

Furst et al., PRL 100, 146001 (2008)
Objective:
Studying milk gels (cheese and yogurt) with Rheolaser (DWS)
Milk
An introduction

Complex System

3% Proteins
80% caseins
Hydrophilic casein
Hydrophobic casein
20%
Whey proteins

Fat globules
Minerals
Composition of cow milk

- Water (87.5 %)
- Fat (3.7 %)
- Proteins (3.3 %)
- Glucides (4.7 %)
- Minerals (0.7 %)
- Others: enzymes, vitamins, pigments (0.1 %)

Changes during lactation!
Introduction

Cheese
### Cheese making

#### Introduction

<table>
<thead>
<tr>
<th>MILK PREPARATION</th>
<th>CURDLING</th>
<th>CURD PROCESSING</th>
<th>RIPING</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical, thermal processing. Milk adjustment</td>
<td>Rennet (ferment) addition</td>
<td>Cutting, salting, washing, etc.</td>
<td>Several days to several months</td>
</tr>
</tbody>
</table>

**Influence of milk preparation and study of the curdling step with diffusive wave spectroscopy**
1. Milk preparation

- Homogenization of fat droplet size
- Pasteurization of milk
- Adjusting milk properties by adding cream, proteins, pH
2. Curdling

Hydrophilic casein

Cut off of hydrophilic part – loss of steric and electrostatic repulsion

Flocculation: gel point (percolation point)

Coagulation: somewhere during gel curing

Hydrophobic casein
Results

in collaboration with
Cheese making
General results

Typical evolution of MSD curves

- Liquid milk
- Milk gel
- Plateau height

33°C, no CaCl₂, rennet

Elasticity Index (nm²)

1. Enzymatic reaction
2. Flocculation
3. Formation of coagulation
4. Maximum elasticity of coagulum
5. Syneresis

 MSD (nm²)

Decorrelation time (s)
The pasteurized milk forms a stronger milk gel

Cheese making
Influence of pasteurization

Whole milk pasteurized at 70°C
Unpasteurized whole milk
33°C. no CaCl2. rennet

The pasteurized milk forms a stronger milk gel
Cheese making
Observation of syneresis

Whole milk pasteurized at 70°C
Unpasteurized milk
33°C C. pas de CaCl2. rennet

Decrease of EI = Restructuration (syneresis ?)
Rheolaser allows the observation of syneresis
1. Milk with CaCl$_2$ addition forms gel earlier and with a higher gel strength
2. Milk with CaCl$_2$ undergoes syneresis earlier and more strongly → curd cutting has to be done earlier
Cheese making

Influence of pH

pH adjusted with GDL (glucono-δ-lactone)

1. The lower the pH, the better works the enzyme, the faster is gel formation
At 70°C → milk gel formation
At 85°C → only slight flocculation observed
Cheese making
Flocculation time – Rheolaser vs. Optigraph

**Optigraph**

Laser → Sample → Detector

Measures the increase of laser power to maintain 4 mV at the detector

Purely optical method, No correlation with rheological properties

Formagraph – not anymore produced
At 70°C → milk gel formation
At 85°C → only slight flocculation observed

Whole milk pasteurized at 70°C
Whole milk pasteurized at 85°C

Optigraph indicates « gel formation »

Elasticity Index (nm²)

Time (min)

33°C, no CaCl₂, rennet
Cheese making
Influence of high temperature
Cheese making

General results

Typical evolution of MSD curves

- Liquid milk
- Milk gel
- Plateau height
- 33°C, no CaCl₂, rennet

![Graph showing MSD curves with annotations](image_url)

- Enzymatic reaction
- Flocculation
- Formation of coagulation
- Maximum elasticity of coagulum
- Syneresis

www.formulaction.com
Cheese making
Time cure superposition

Liquid

Gel

MSD 0. CP

MSD 1. CP

MSD 2. CP

MSD 3. CP

MSD 4. CP

MSD N. CP

Control parameter CP (t, T, conc., etc.)

Factor «a»

Factor «b»

b* MSD (nm²)

a* Decorrelation time (s)

Gel Point

CP₀ CP₁ CP₂ CP₃ CP₄ CP₅
<table>
<thead>
<tr>
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<th>Rheolaser (min)</th>
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<tr>
<td>w/o CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>24.2 ± 0.2</td>
</tr>
<tr>
<td>with CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12.9 ± 0.4</td>
</tr>
<tr>
<td>Milk. 3.3% proteins</td>
<td>9.2 ± 0.4</td>
</tr>
<tr>
<td>Milk. 4% proteins</td>
<td>11.6 ± 0.1</td>
</tr>
<tr>
<td>Milk. 5% proteins</td>
<td>14.2 ± 0.1</td>
</tr>
<tr>
<td>Unpasteurized Milk. 5%</td>
<td>16.3 ± 0.4</td>
</tr>
<tr>
<td>proteins</td>
<td></td>
</tr>
<tr>
<td>Pasteurized Milk. 5%</td>
<td>14.5 ± 0.6</td>
</tr>
<tr>
<td>proteins</td>
<td></td>
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</table>
## Cheese making

**Flocculation time – Rheolaser vs. Optigraph**

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<th>Rheolaser (min)</th>
<th>Optigraph (min)</th>
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<tr>
<td>w/o CaCl₂</td>
<td>24.2 ± 0.2</td>
<td>23.8 ± 0.1</td>
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<tr>
<td>with CaCl₂</td>
<td>12.9 ± 0.4</td>
<td>15.7 ± 0.3</td>
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<td>Milk. 3.3% proteins</td>
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<td>10.6 ± 0.1</td>
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<td>Milk. 5% proteins</td>
<td>14.2 ± 0.1</td>
<td>17.6 ± 1.9</td>
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Rheolaser and Optigraph have similar results. In all cases, visual observation with spoon test are closer to Rheolaser.
Milk gels for cheese preparations were studied

- Rheolaser determines similar values for flocculation time in comparison to Optigraph

- Rheolaser detects also « gel strength » and gel formation

- Rheolaser observes syneresis

- Rheolaser can use 6 independent positions

- What else?
3. Curd cutting

Cutting is a very important step:

- Is it done too early – network is too loose and whey protein is loss

- Is it done too late – network is too strong and humidity is enclosed

Quality problems (taste, shape, etc) and yield loss!
Cheese making
Where is the ideal curd cutting time

Typical evolution of MSD curves

- Liquid milk
- Milk gel
- Plateau height

33°C, no CaCl₂, rennet

- Enzymatic reaction
- Flocculation
- Formation of coagulation
- Maximum elasticity of coagulum
- Syneresis
New project on curd cutting time determination in collaboration with the Agriculture Engineering School Toulouse (INPT) and several companies in France.
Thank you for your attention!

INP Purapn:
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