



MICRORHEOLOGY FOR SOFT MATERIALS

RHEOLASER

Rheolaser presentation – Secrets of Formulation III

Stability

Microrheology



MULTIPLE LIGHT SCATTERING



Backscattering intensity

STABILITY ANALYSIS

TURBISCAN RANGE





MS-DWS Interfering Backscattering waves

MICRORHEOLOGY

RHEOLASER & HORUS

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End use properties measurements



Shelf life, demulsification, flotation...



Drying, Open time, hardness, tablet swelling, crystalline state transition ...



Recovery, Gelation, Stiffness, Adhesion, Drug delivery....

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- 1. Soft materials
- 2. What is Microrheology?
- 3. Rheolaser: The instrument
- 4. Application examples



Why Rheology is important?

⇒ Because it allows to characterise end use properties like:



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Characteristics



□ Formulation in 1980's ⇒Surfactants

Goal: ⇒ Good dispersion



□ Formulation : Today ⇒ Surfactants + polymers

Gel like systems

Fluid like systems

Goal:

⇒ End use properties management / visco-elastic control

Decrease of the fat contents in food industry Improvement of spreadability of creams ... Environmental / health issues Better properties for drilling fluids



Properties

Most of the soft materials are visco-elastic (non newtonian)

→ Visco-elastic behavior depends on time scale observation





Properties

How to measure visco-elasticity?

⇒Oscillation analysis : Rheometer



Relation Stress / Strain depends on the visco-elastic properties





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Oscillation analysis

⇒Experiments are complex to perform:

- Find the right geometry
- Sampling is critical : volume, evaporation, drying...
- Risk of sample denaturation
- Intrusive measurement => no evolution (Rheolgy versus ageing time)



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⇒ Thanks to Brownian motion the particle feels the viscoelastic structure:



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Experimental set up



⇒MS-DWS principle of measurement

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MS-DWS

⇒Measurement of particles mobility in opaque media





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MS-DWS

⇒Particle Mean Square Displacement (MSD)



Particle Mean Square Displacement

Mean Square Displacement





Particle Mean Square Displacement

Soft material properties affect the MSD of the particles Purely Viscous Particle is free to move



DWS measures displacement of many particle

Stability



DATA ACQUISITION :

Particle Mean Square Displacement (MSD) Case 3 : Visco-elastic product



C Formulaction 2009

DWS measures displacement of many particle



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MEAN SQUARE DISPLACEMENT

⇒ MSD is the viscoelastic signature



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⇒3 parameters to monitor end use properties

- Solid/Liquid balance SLB : firmness, texture, shape stability, etc...
- Elasticity Index EI : gelation, mesh size, cross-linking, etc...
- Macroscopic Viscosity Index MVI : flowability, stability, thickening power, etc...



⇒ FOR EASY SAMPLES COMPARISON

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DATA TREATMENT

⇒ Kinetic analysis









SPECIFICATIONS

A unique tool to measure viscoelastic properties

- Easily : 1 tube (4-20 ml) / 1 click
- 6 measuring positions
- Viscoelastic analysis
 - ⇒ Non contact
 - ⇒ No denaturation
 - ⇒ No stress
- Simple parameters vs aging time
 - ⇒ Elasticity Index
 - ⇒Solid-Liquid balance
 - ⇒ Macroscopic Viscosity Index





time



- 1. Soft materials
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R6+

⇒2 gelatins were prepared, using 2 grades of gelatin
 ✓Gelatin A (LOW level of gel)
 ✓Gelatin B (HIGH level of gel)

⇒Gelation process:

✓ Products are first heated \rightarrow homogenous liquid

(gelatin and water + introduction of TiO_2 in order to have scatterers)

 \checkmark Sample is then cooled down \rightarrow solidification

(liquid warm sample is introduced in RheoLaser, following the gelation process)



1) GELATION PROCESS Study of 2 gelatins





- At short time : liquid behavior
- At longer time: Solid behavior => Gel



Polymer network

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1) GELATION PROCESS Study of 2 gelatins





 \Rightarrow Gelatin B forms faster than A (at SLB = 0,5)

- Gel time B = 13 min
- Gel time A = 33 min







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Computation of Network Size



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2) DRUG DELIVERY SYSTEMS Silica gel versus pH



R6+

No particles added

Experiment: Silica gel rheological behavior versus pH

- Gel at acid pH (Stomach pH = 2 3.5)
- Degradation at basic pH (Duodenum pH > 7)



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Formulaction Smart scientific analusis



No particles added

⇒ Elasticity index monitors gelation and gel destruction versus aging time









I work on emulsions, I want to produce low fat emulsions, which **kind of** polymer and which concentration can I choose to keep similar end-use properties?





3) EMULSION AND POLYMER Polymer effect



I work on emulsions, I want to produce low fat emulsions, which **kind of** polymer and which concentration can I choose to keep similar end-use properties?



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3) EMULSION AND POLYMER Polymer effect





Adding polymer – particularly xanthan and guar gums - to replace oil in emulsions enables to save money in the components cost

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4) STABILITY Study of delayed creaming : sample description



Applications:

⇒ Analyse the stability properties of emulsions stabilized with a polymer
 ⇒ Analyse the microstructure evolution

⇒ Application field : cosmetic emulsions, flavoured emulsions, food...

Experiment:

⇒ analysis of emulsions : stabilised with xanthan at different concentrations



Oil in water emulsion : 20% vegetable oil, 2% tween 20, 1% NaCl + xanthan (0.12%; 0.15%; 0.25%; 0.40%)

Data:

⇒ Monitoring of the Macroscopic Viscosity Index versus ageing time







 \Rightarrow MSD curves evolve versus time \rightarrow return to the left = signature of destabilisation



Polymer concentration	0.12%	0.15%	0.25%	0.40%
Breaking time (MVI drop)	4 hours ¼	11 hours	5 days ½	42 days
Stability (macroscopic)	65 hours	168 hours	>> 40 days	>> 100 days

⇒ The more thickener is added to the sample, the longer is the stability time (time before the MVI drops)
⇒ The Rheolaser observation is faster than eye observation !

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Rheolaser compares end use properties related to visco-elasticity

- Easily : no parameters needed, no configuration of the instrument
- Results do not depend on the operator
 - ⇒ sampling in glass cell
- At rest thanks to a non contact optical measurement
- Versus aging time on the very same sample
- By monitoring the evolution of simple parameters like:
 - Elasticity Index
 - Macroscopic Viscosity Index
 - Solid-Liquid balance



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