Chocolate Flow

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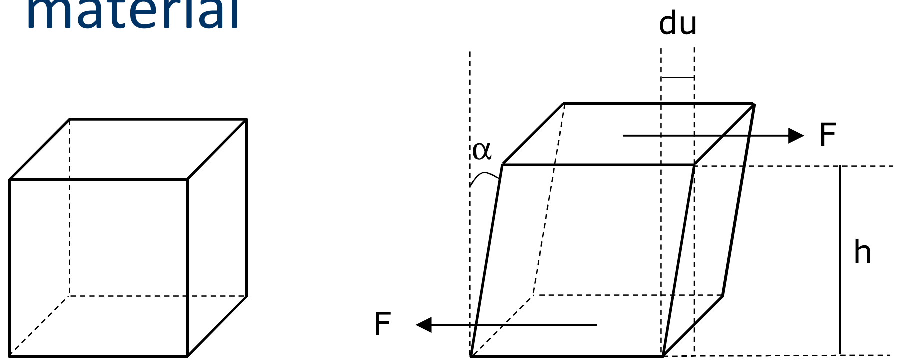
Outline

- Food rheology
- Suspension rheology
- Emulsifiers
- Practical excercise

Food rheology

- **Rheology attemps to define a relationship between the stress acting on a given material and the resulting deformation and/or flow that takes place**

- Stress (σ_s): force per unit of surface area, expressed in Pascal (Pa = N/m^2)
- Normal stress: perpendicular to the surface
- Shear stress: parallel to the surface
- Strain: dimensionless quantity of relative deformation of a material



$$\sigma_S = \frac{F}{A}$$

$$\gamma = \frac{du}{h} = tg\alpha$$

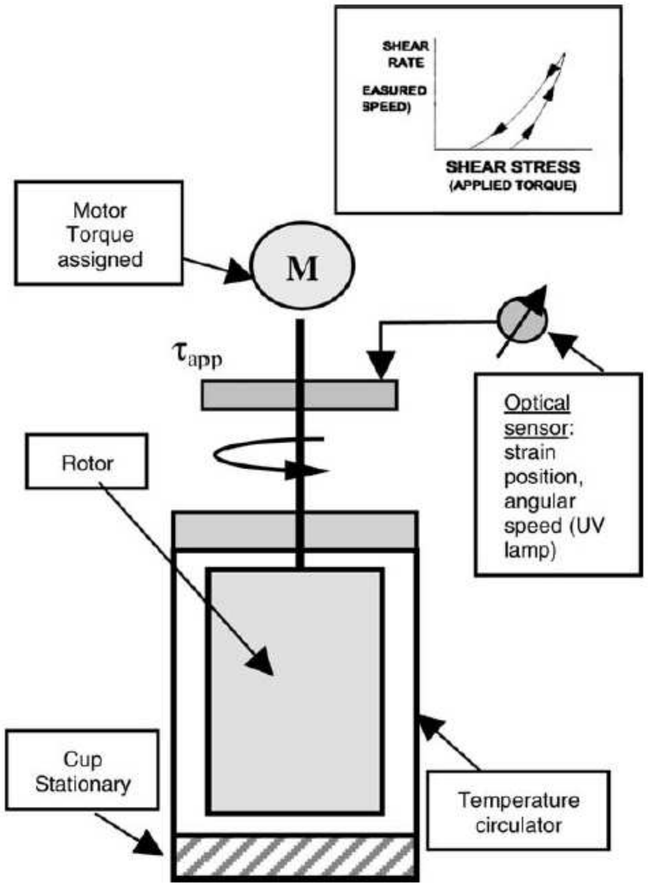


Fig. 10. Controlled stress rheometer with Searle operation mode.

Rheological test selection

- Different groups of testing methods:
  - Flow (laminar!!)
  - Static
  - Dynamic
- Depend on:
  - Aim of the research
  - Type of product
- Limitations:
  - Rheometer sensitivity
  - *E.g.*: gels and solid materials do not flow
  - *E.g.*: low viscosity solutions: static and dynamic measurements difficult to perform

Rheological test selection

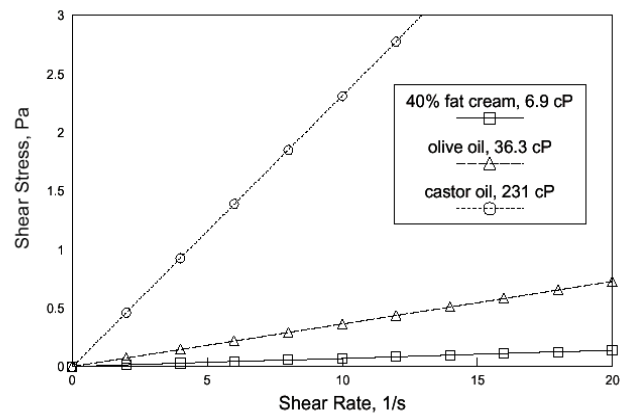
- Flow curves: shear stress as function of shear rate
- **Choose temperature!!**
- In case of fluids the deformation will keep changing as a function of time and as such a shear or strain rate (s^{-1}) is given by:

$$\dot{\gamma} = \frac{d\gamma}{dt}$$

- In case of an ideal viscous liquid:

$$\sigma_S = \eta \dot{\gamma}$$

  – with η (Pa.s) being the dynamic viscosity



Rheological test selection

- In case of linear viscous behavior (Newtonian), η is a material constant which is temperature dependent but does not depend on the shear rate is (1cP = 1 mPa.s)

Fluid	η, 0°C (mPa.s)	η, 20°C (mPa.s)	η, 30°C (mPa.s)
Water	1,79	1,00	
Milk	4,28	2,12	
Melasse		6600	
Olive oil			84,0

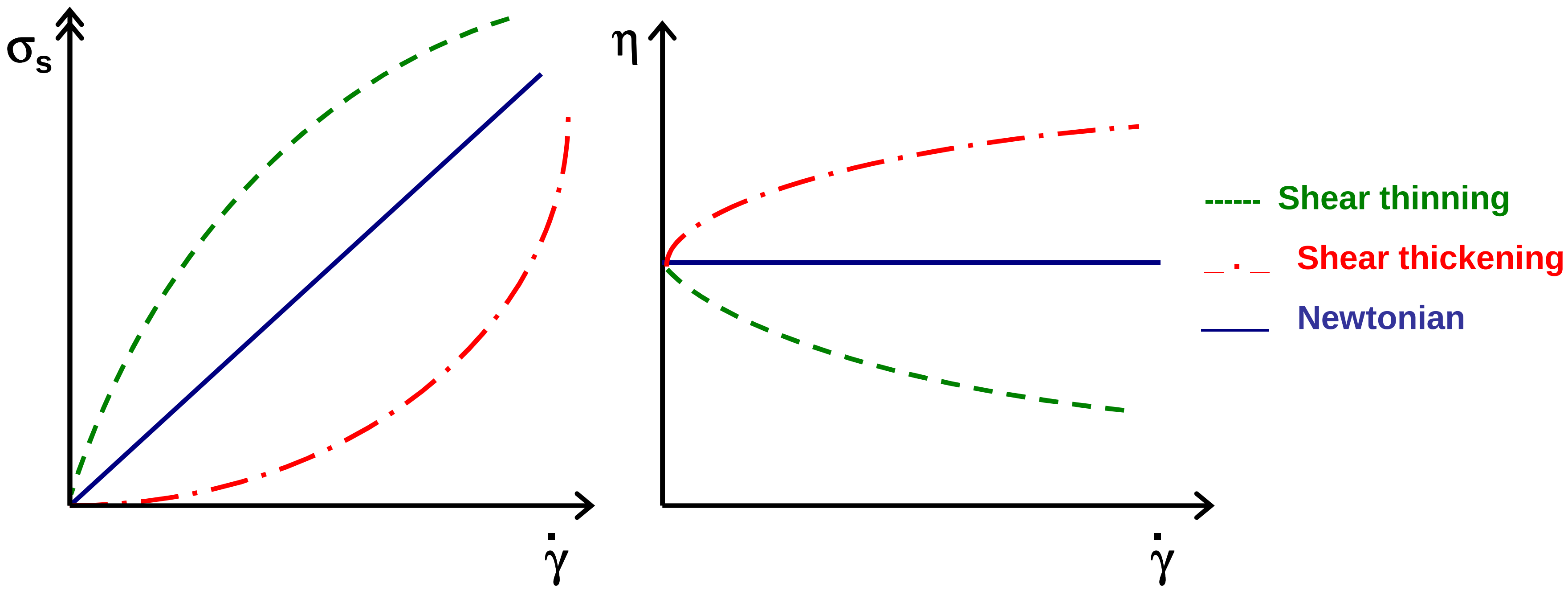
Rheological test selection

- Non-Newtonian fluids: viscosity depends on shear rate
- An apparent viscosity can be defined:

$$\eta^* = \frac{\sigma_S}{\dot{\gamma}} \qquad \eta^* = f\left(\dot{\gamma}\right)$$

  - Pseudo-plastic behavior (*shear-thinning*): η* decreases with increasing shear rate
  - Dilatant behavior (*shear-thickening*): η* increases with increasing shear rate
- Variation of shear rate or shear stress
- Define useful regions

$$\sigma_s = f(\gamma)$$



Food rheology

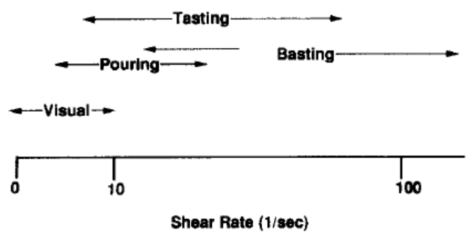
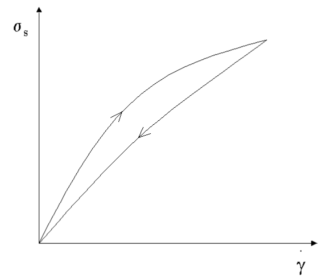


Fig. 5. Shear rates operating under different methods employed in thickness perception for barbecue sauce.

Situation	Shear Rate Range / s^{-1}	Examples
Sedimentation of fine powders in liquids	10^{-6} - 10^{-3}	Medicines, paints, salad dressing
Levelling due to surface tension	10^{-2} - 10^{-1}	Paints, printing inks
Draining off surfaces under gravity	10^{-1} - 10^{1}	Toilet bleaches, paints, coatings
Extruders	10^{0} - 10^{2}	Polymers, foods soft solids
Chewing and swallowing	10^{1} - 10^{2}	Foods
Dip coating	10^{1} - 10^{2}	Paints, confectionery
Mixing and stirring	10^{1} - 10^{3}	Liquids manufacturing
Pipe flow	10^{0} - 10^{3}	Pumping liquids, blood flow
Brushing	10^{3} - 10^{4}	Painting
Rubbing	10^{4} - 10^{5}	Skin creams, lotions
High-speed coating	10^{4} - 10^{6}	Paper manufacture
Spraying	10^{5} - 10^{6}	Atomisation, spray drying
Lubrication	10^{3} - 10^{7}	Bearings, engines

Rheological test selection

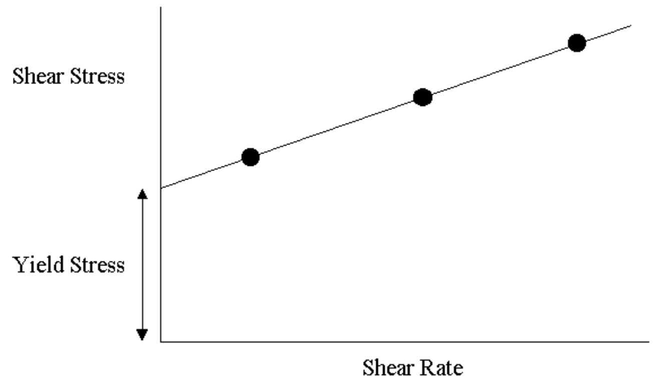
- For certain fluids the relationship between σ_s and the shear rate depends on time and thus on the history
- Time dependent behaviour often points at structural changes (Thixotropy , Rheopexy)
- Necessary to apply pre-shear?
- Hysteresis recording: increasing shear rates followed by decreasing shear rates

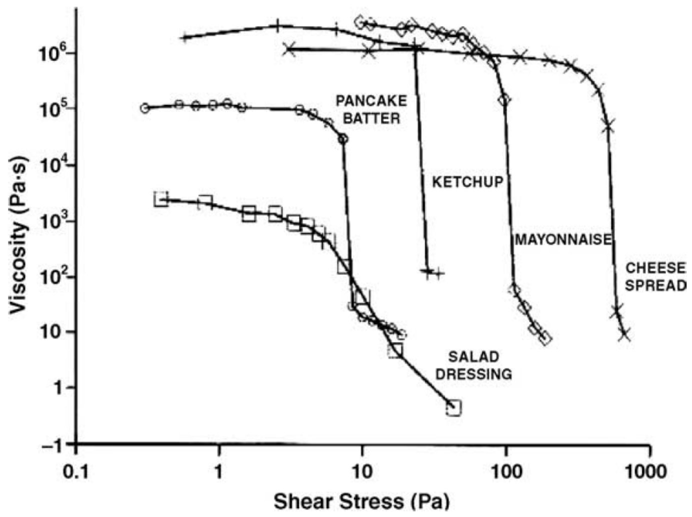


- Flow curve test procedure:
  - Steady state flow step: waiting for equilibrium at each point
  - Stepped flow step: maintain each shear rate certain time, then average
  - Continuous ramp: continuously increase shear rate (or stress)

Flow measurements

- **Yield stress**: minimal shear stress required to initiate flow
- Concept subject for debate
- Dependent on analytical procedure:
  - Extrapolation of flow data to zero shear rate
  - Gradual increase shear stress
- Technological importance:
  - Suspension and emulsion stability
  - Chocolate: air release during vibrations, enrobing, shell making, moulding





Food rheology

- *Power law model:*

$$\sigma_s = k\dot{\gamma}^n$$

  - No yield stress σ_0

- *Herschel-bulkley:*

$$\sigma_s = \sigma_0 + k\dot{\gamma}^n$$

  - k = consistency coefficient
  - n = flow behavior index

- *Bingham Model*:

$$\sigma_s = \sigma_0 + \eta_B\dot{\gamma}$$

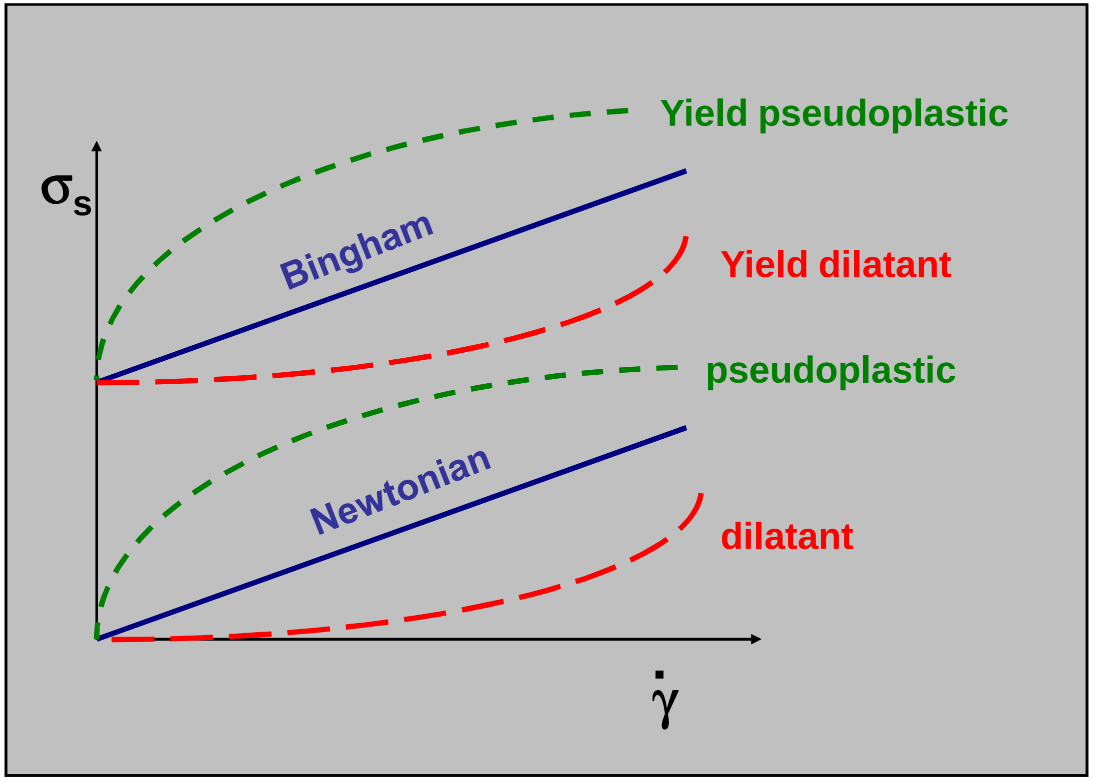
  - η_B = Bingham viscosity
  - Often to simple

- *Casson-model:*

$$\sigma_S^{1/2} = \sigma_{CA}^{1/2} + \eta_{CA}^{1/2} \cdot \dot{\gamma}^{1/2}$$

  - σ_{CA} = Casson yield stress
  - η_{CA} = Casson viscosity

Herschel-Bulkley	n	σ_0
Newtonian	1	0
Shear-thickening	1<n<∞	0
Yield shear thickening	1<n<∞	>0
Shear-thinning	0<n<1	0
Yield Shear-thinning	0<n<1	>0
Bingham plastic	1	>0



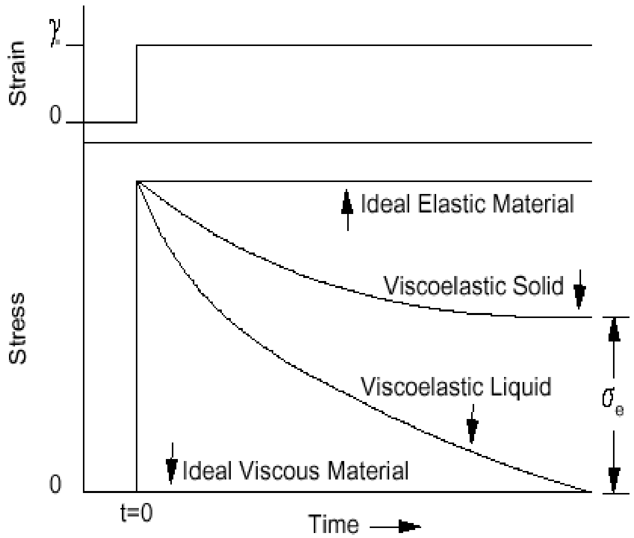
Food rheology

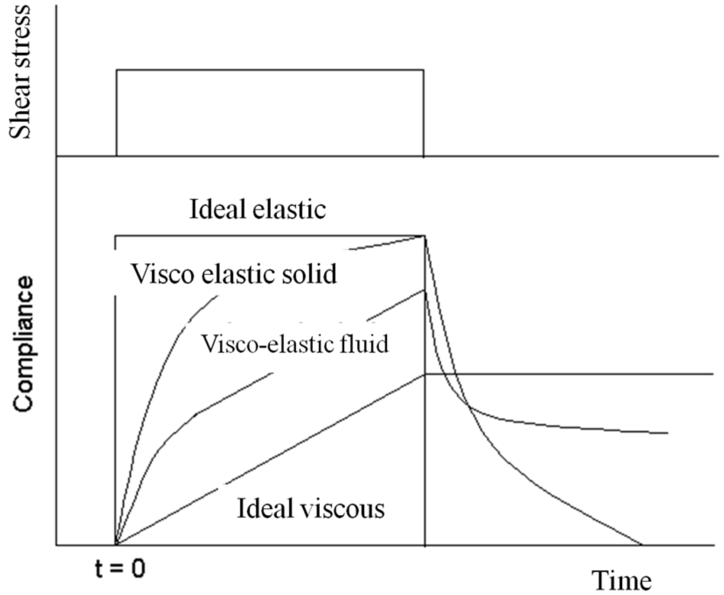
- A visco-elastic material behaves non-linear elastic when stress is applied, but on removal of the stress it does not return completely to its original state.

- This indicates that a permanent deformation has taken place: the material acts partially viscous.

Static measurements: viscoelastic behaviour

- **Stress relaxation:** the sample is subjected to an instantaneous constant deformation and the decrease in stress, necessary to maintain the deformation, is monitored as a function of time
- **Creep test:** the sample is subjected to an instantaneous stress and the strain (creep) is monitored as a function of time





Dynamic or oscillatory measurements

- Allow studying the rheological behavior of viscoelastic materials in a relatively short time frame
- The sample is subjected to a sinusoidal varying stress or strain
- The variation of the strain γ as a function of time *t* can be written as:

$$\gamma = \gamma_0 \sin(\omega t)$$

with γ_0 : the maximum strain or strain amplitude

ω : angular speed (rad.s^{-1}) of the oscillatory motion

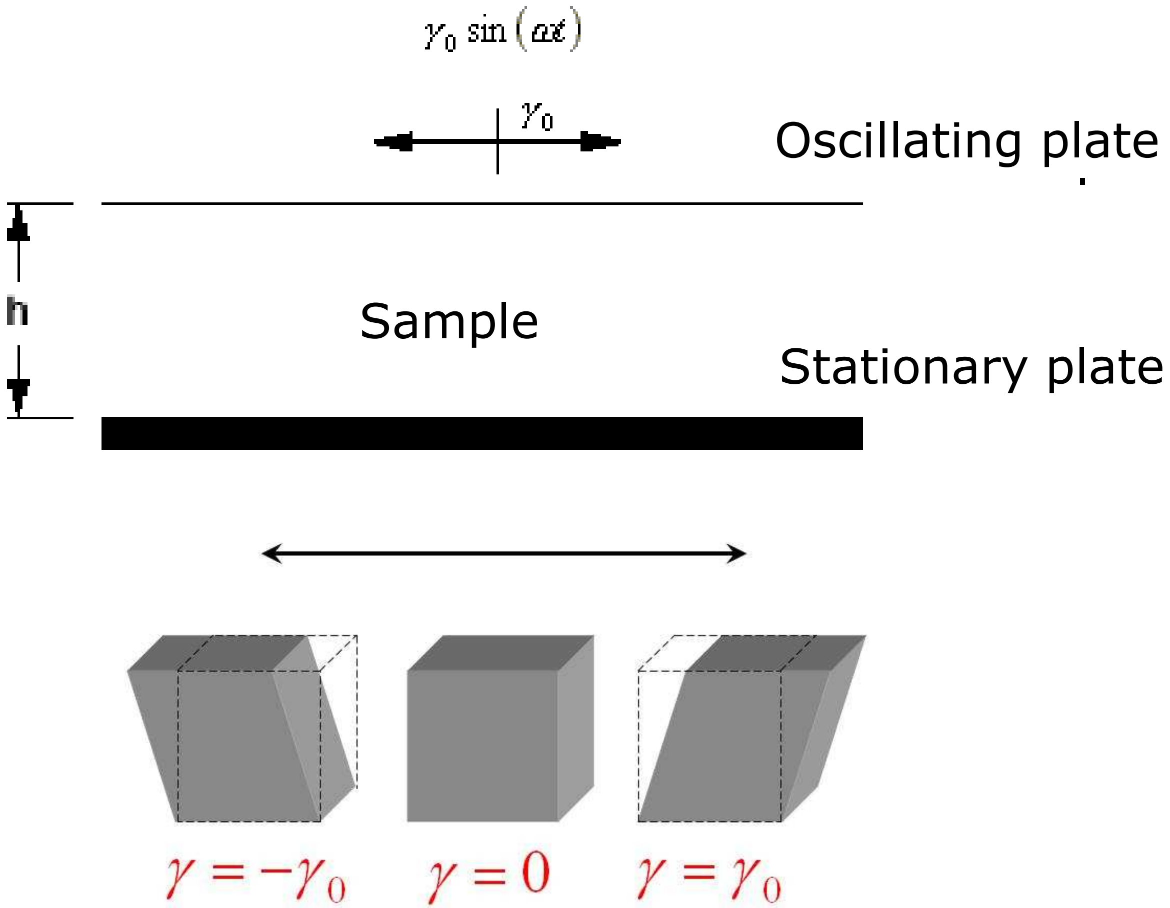
- The resulting stress σ_S is given by:

$$\sigma_S = \sigma_{S,0} \sin(\omega t + \delta)$$

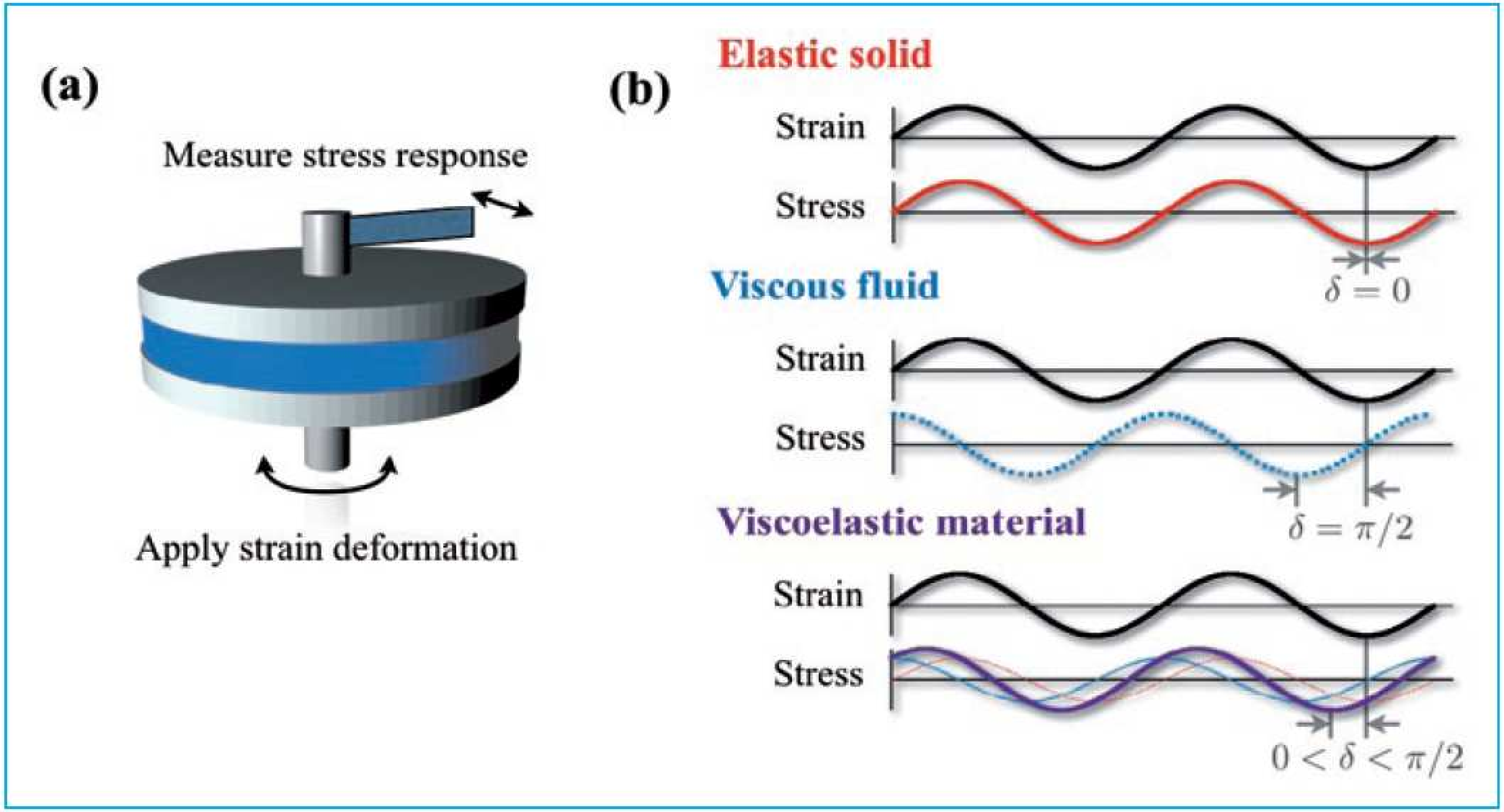
with $\sigma_{S,0}$: the maximum stress (stress amplitude)

δ (°) : the phase shift between stress and strain

Dynamic or oscillatory measurements



Dynamic or oscillatory measurements



G.I.T. Laboratory Journal 3-4/2007, pp 68-70, GIT VERLAG GmbH & Co. KG, Darmstadt

Dynamic or oscillatory measurements

- One amplitude and one frequency is imposed
- Other amplitude and phase angle are measured
- Moduli are calculated:

$$G' = \left(\sigma_{S,0}/\gamma_0\right)\cos\delta$$

$$G'' = \left(\sigma_{S,0}/\gamma_0\right)\sin\delta$$

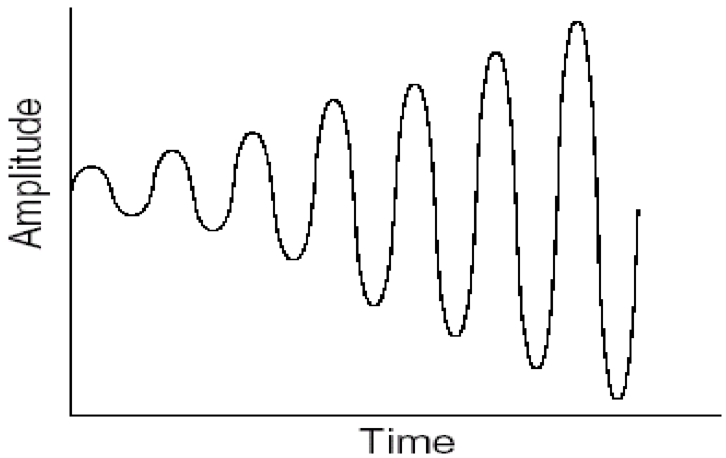
$$G^* = \frac{\sigma_0}{\gamma_0} = \sqrt{(G')^2 + (G'')^2}$$

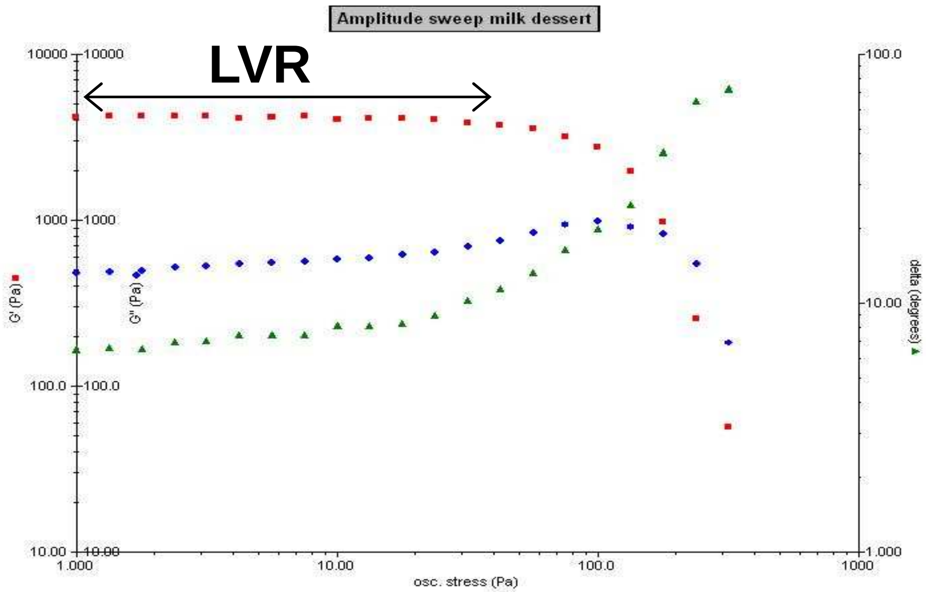
- G’ (Pa): storage or elastic modulus (represents solid behavior)
- G” (Pa): loss modulus (represents fluid behavior)
- G* (Pa): ratio between stress and strain amplitude

Dynamic or oscillatory measurements

- **Non-destructive tests**: microstructure is maintained when performed within linear viscoelastic region (LVR)
- Stress or strain is gradually increased and stress to strain ratio should be constant (at strain > LVR: G* starts to decrease)
- Amplitude should be fixed below this critical value
- **Types of tests**
  - Stress or strain ramp (LVR, structure rigidity) at fixed frequency
  - Frequency sweep at fixed amplitude
  - Time sweep: temperature, frequency and amplitude fixed
  - Temperature ramp: fixed frequency and amplitude
  - Combinations of different tests

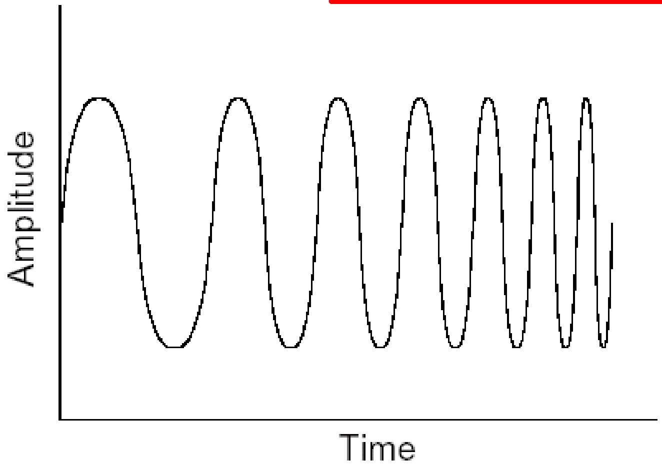
Food rheology





Food rheology

Weak gel: moduli dependent on deformation rate



Strong gel: moduli independent on deformation rate

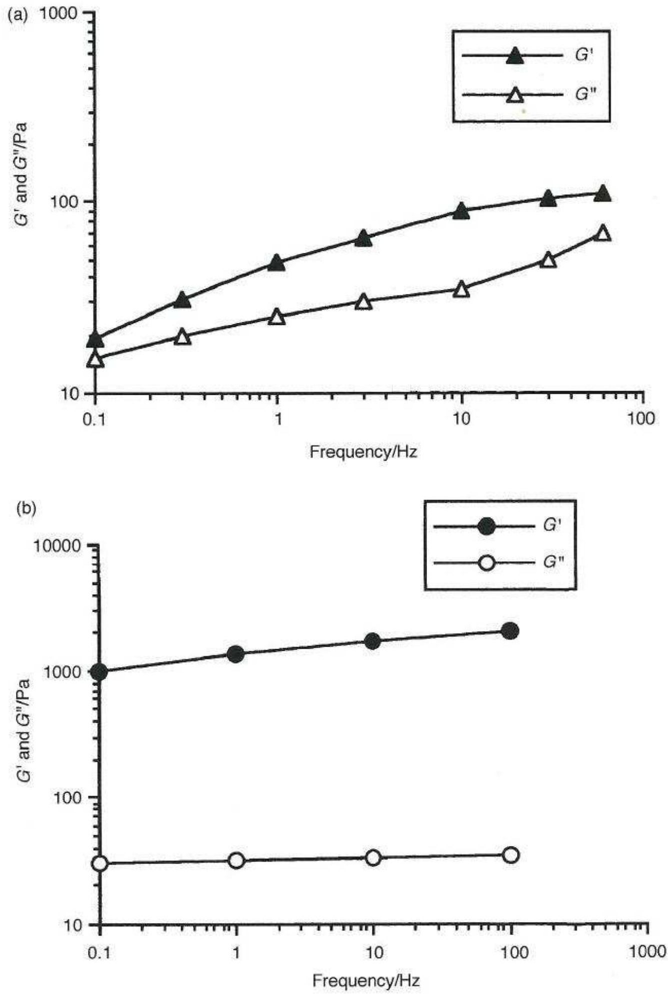


Fig. 1.8 (a) G' and G'' of 1% xanthan gum solution as a function of frequency. (b) G' and G'' of 1.5% amylose gels as a function of frequency.

Food rheology

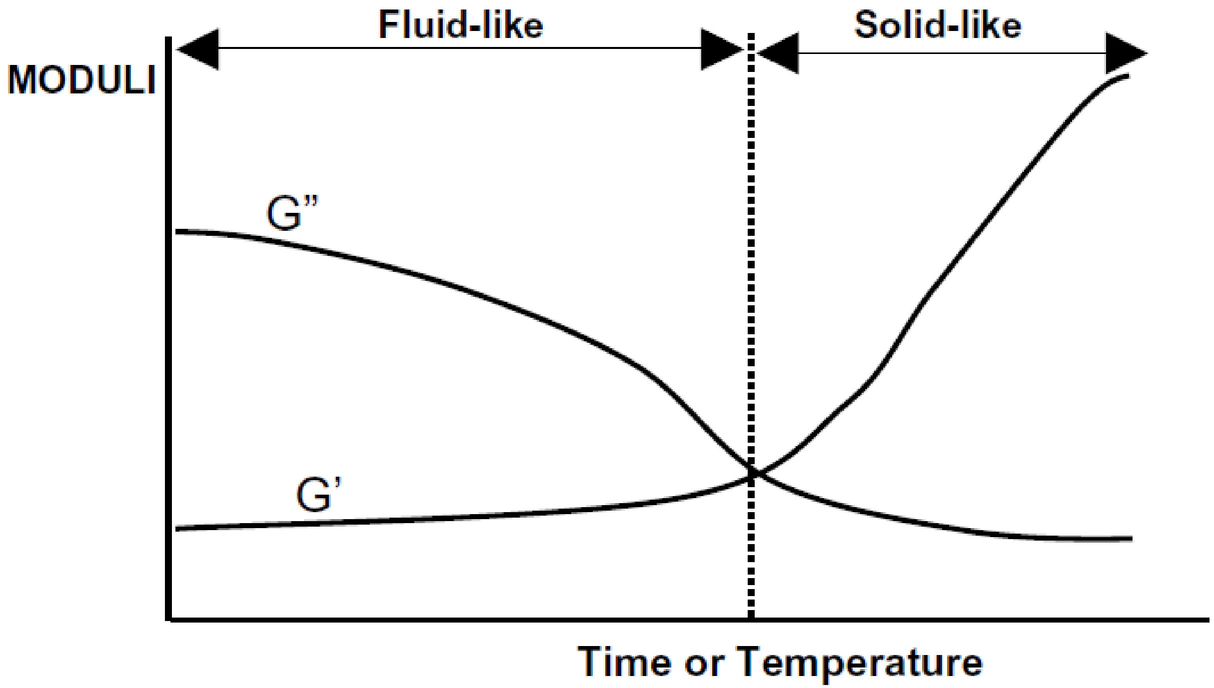
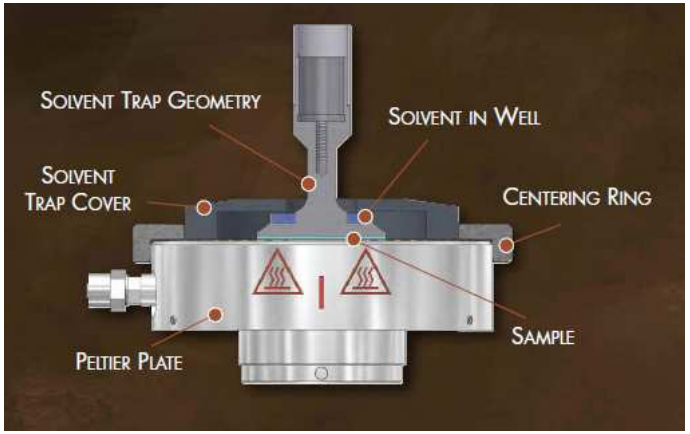
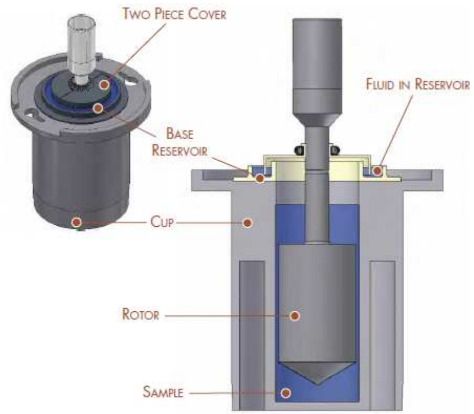


Fig. 2. Viscoelastic response of a material undergoing gelation.

Geometry selection

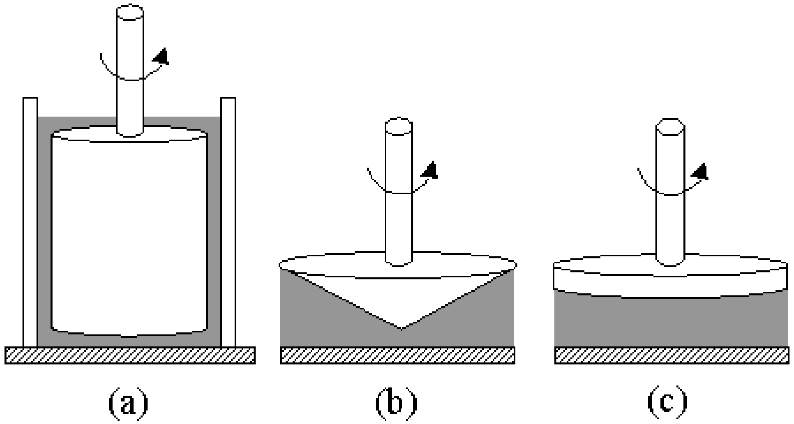
- Choice is very important and depends on type of product and type of test
- Product parameters:
  - Highly viscous or highly elastic
  - Size particles
  - Sedimentation?
  - Syneresis/slip
  - Destruction followed by restructuring after loading
- Test parameters:
  - Required heating/cooling rate
  - High or low shear rates
  - Evaporation

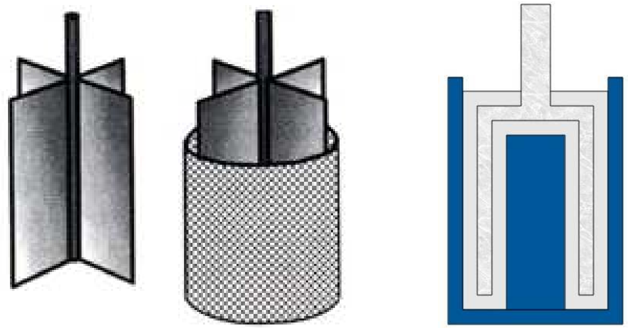


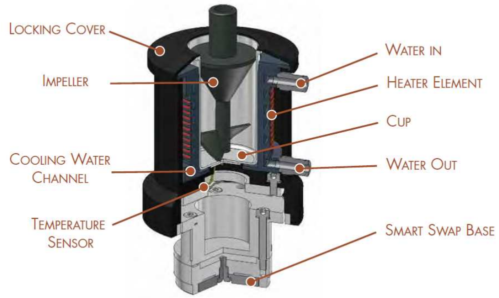


Geometry selection

- Concentric cylinders
  - Higher sensitivity for low viscosity fluids
  - Less evaporation
  - Limited heating and cooling rates
- Plate-plate
  - Shear rate gradient (not constant)
  - Suitable for samples containing particles
- Cone-plate
  - Uniform shear rate
  - Not suitable for particles
- Others: double gap (high sensitivity), vane (less sample destruction), starch pasting cell (limits sedimentation

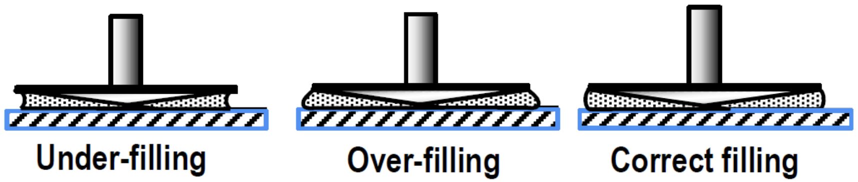






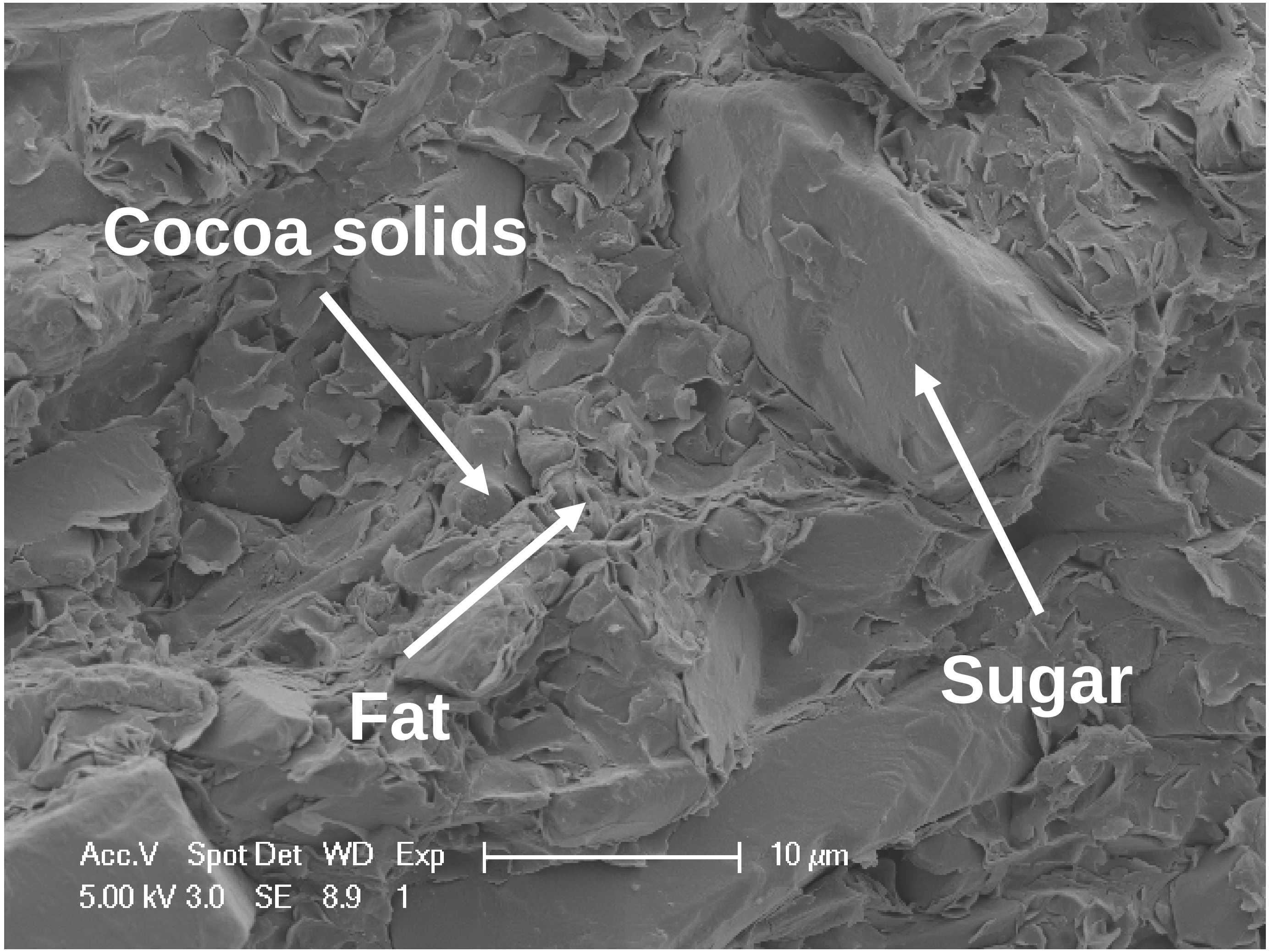
Geometry selection

- Pay extra attention to:
  - Sample loading
  - Homogeneous sampling (uniform batch)
  - Pre-treatment of sample (may influence results)
  - Temperature equilibration



Proper loading of sample after closing the gap for cone and parallel plate geometry systems

Suspension rheology



Suspension rheology

- Molten chocolate is a suspension of solid particles (sugar, cocoa solids and/or milk solids) in a continuous fat phase (cocoa butter and milk fat)
- Flow behaviour of molten chocolate is described by:
  - Yield stress (Pa): minimum stress acquired to initiate flow

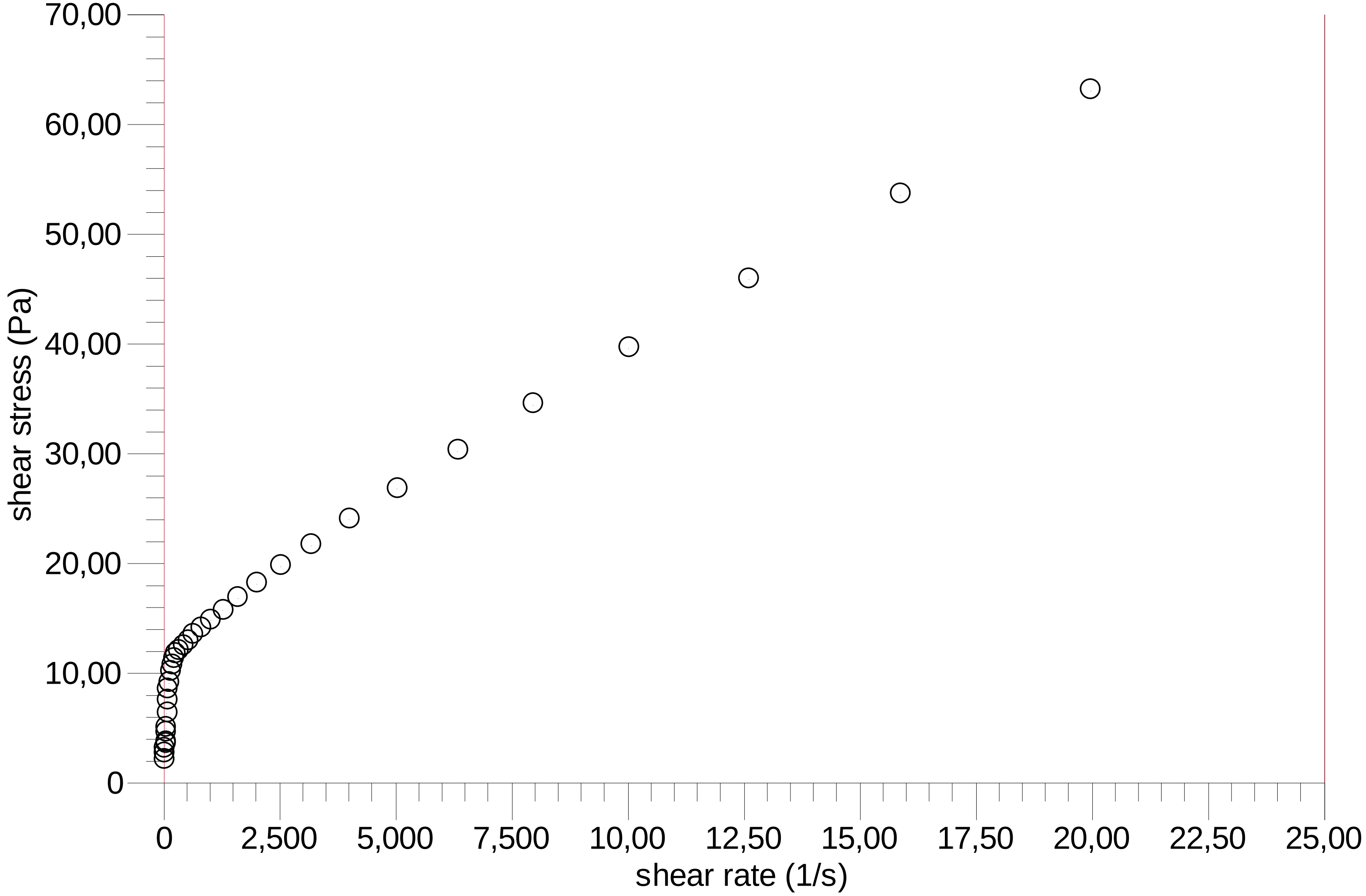
    → low shear rate part of flow curve

    ~ fat content, particle interactions, specific surface area, mean particle size
  - Plastic viscosity (Pa.s): resistance against flow once it's moving

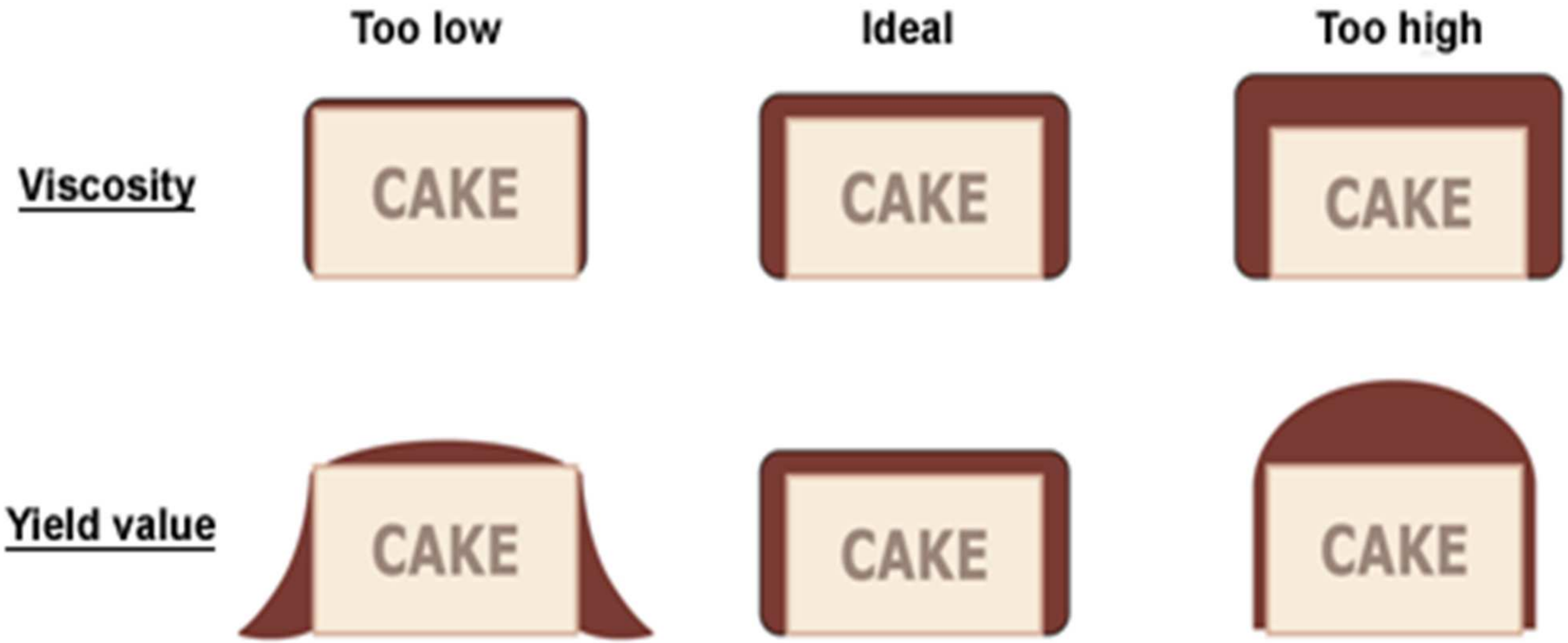
    → high shear rate part of flow curve

    ~ fat content, packing efficiency

Suspension rheology



Suspension rheology



Suspension rheology

Main factors influencing suspension rheology:

- Particle volume fraction ϕ
- Particle size distribution PSD
- Maximum packing volume fraction ϕ_m
- Particle shape
- Particle density
- Surface roughness
- Wetting properties of suspended particles in continuous phase
- Adsorbed agents on the particle surface
- Aggregation
- Continuous phase viscosity

Suspension rheology

- Maximum particle volume fraction ϕ_m:
  - Maximum amount of particles which can be packed in a given volume
  - Depends on PSD

- Viscosity control is realized by optimizing ϕ_m, although limited by the sensitivity of the palate

- For non-interacting multimodal spherical particles, the lowest viscosity for any ϕ corresponds to the maximum value of ϕ_m

Particle volume fraction ϕ and maximum packing volume fraction ϕ_m

Bimodal distribution – ϕ = 0,64

Viscosity decrease

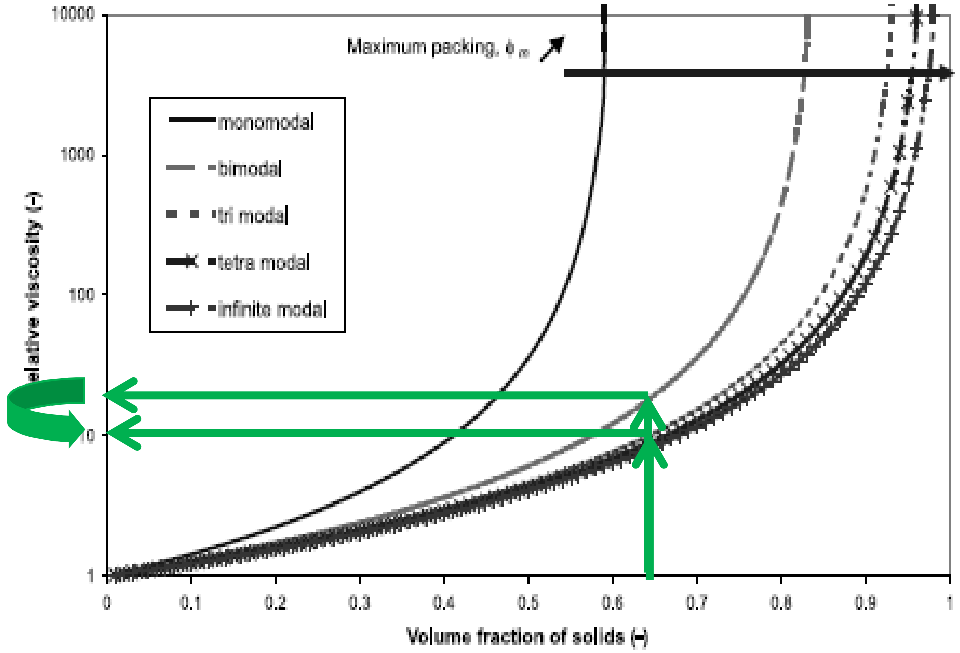
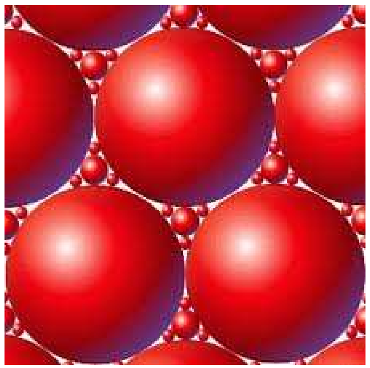


Fig. 1. Relative viscosity vs. solid volume fraction for best multimodal systems (Farris, 1968).

Trimodal distribution – ϕ = 0,64



Particle volume fraction ϕ and maximum packing volume fraction ϕ_m

Bimodal distribution – $\phi = 0,64$

Trimodal distribution – same η_r

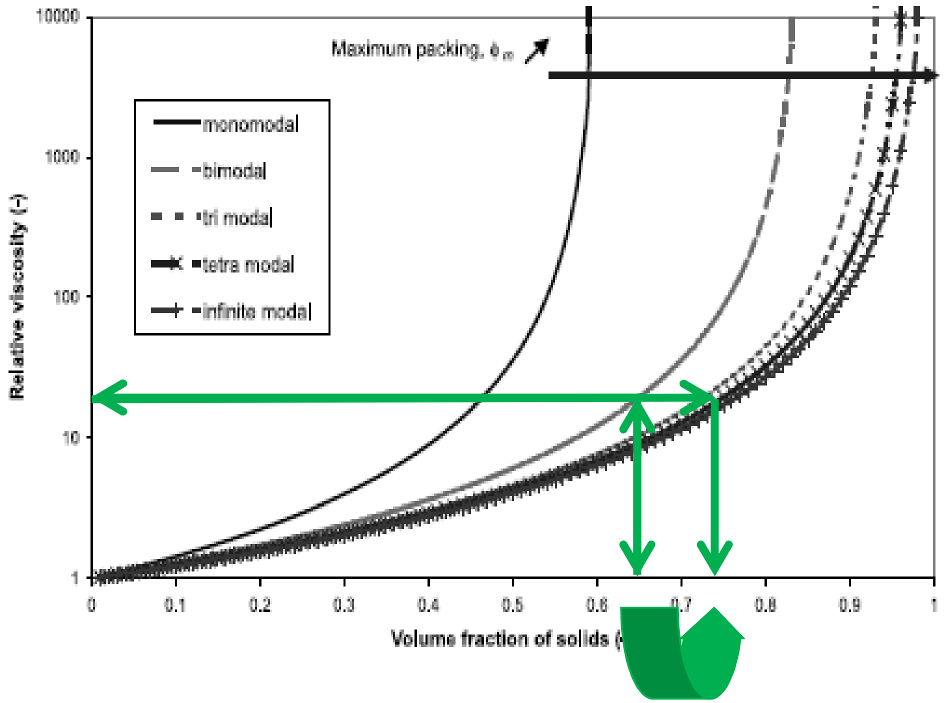


Fig. 1. Relative viscosity vs. soli systems (Farris, 1968).

Particle volume fraction increase

Particle size distribution

- Diameter ratio $\lambda = D_{large}/D_{small}$

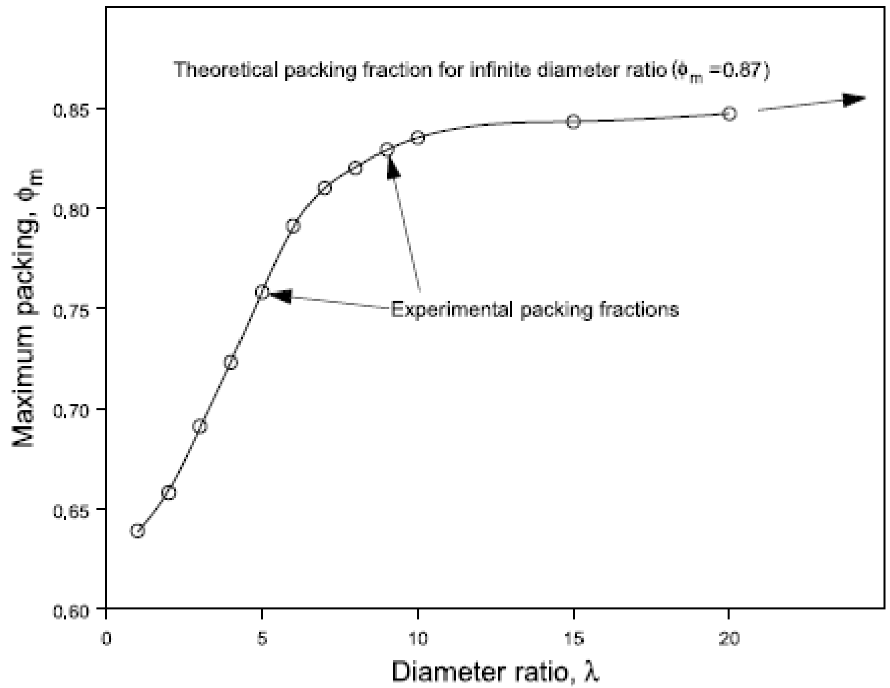


Fig. 5. Graph of maximum packing fraction for different diameter ratios (McGeary, 1961; Lee, 1970).

Particle size distribution

- Blend ratio ξ: fraction of a particle class in relation to the other classes

Optimum blend ratio of monospheres at a concentrations of 64% (Farris, 1968)

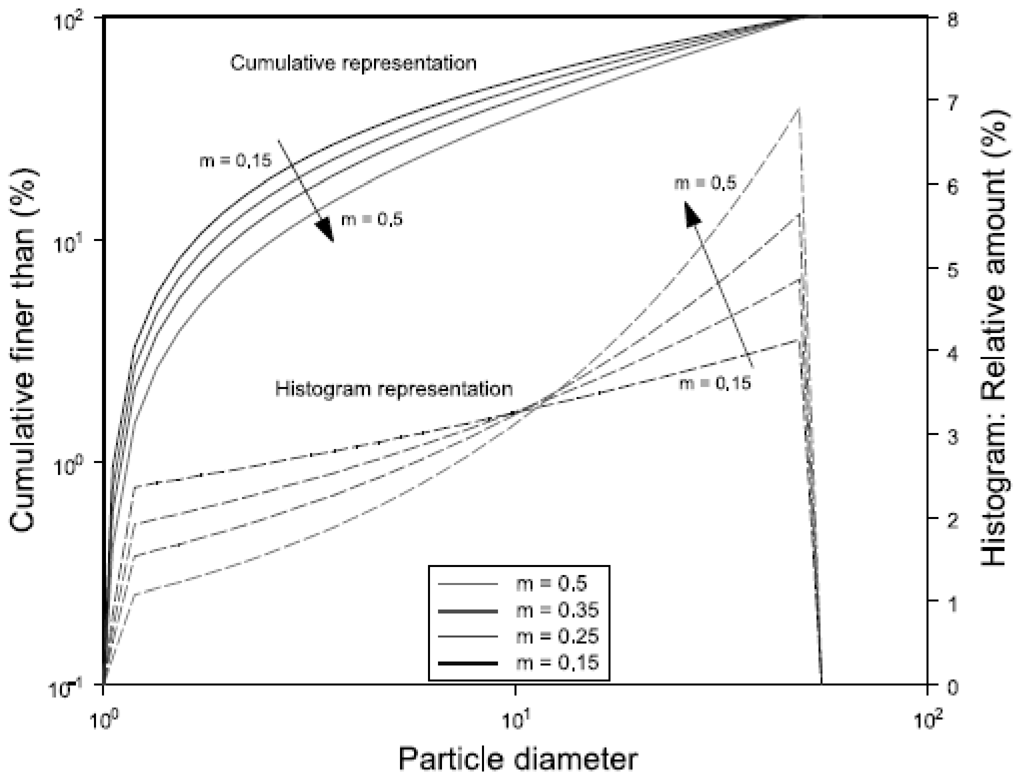
Mode	Very fine	Fine	Medium	Coarse
Bimodal	–	37%	–	63%
Trimodal		22.5%	32%	45.5%
Tetramodal	16.5%	21.5%	27%	35%

Particle size distribution

$$\frac{\text{CPFT}}{100\%} = \frac{D^m - D_S^m}{D_L^m - D_S^m}$$

ϕ_m is maximized for m ≈ 0,37

Viscosity optimisation leads to increase in yield stress!



Servais *et al.* (2002)

Particle shape

Maximum packing volume fractions of blends of monodispersed particles (Funk & Dinger, 1993)

Packing efficiency (%)		Mode
Spheres	Cubes	
100[0.60] = 60	44	Unimodal
100[0.60 + 0.40 × 0.60] = 84	69	Bimodal
100[0.84 + 0.16 × 0.60] = 94	82	Trimodal
100[0.94 + 0.064 × 0.60] = 97	90	Tetramodal

Food suspensions tend to display a packing efficiency ϕ_m in between these extremes

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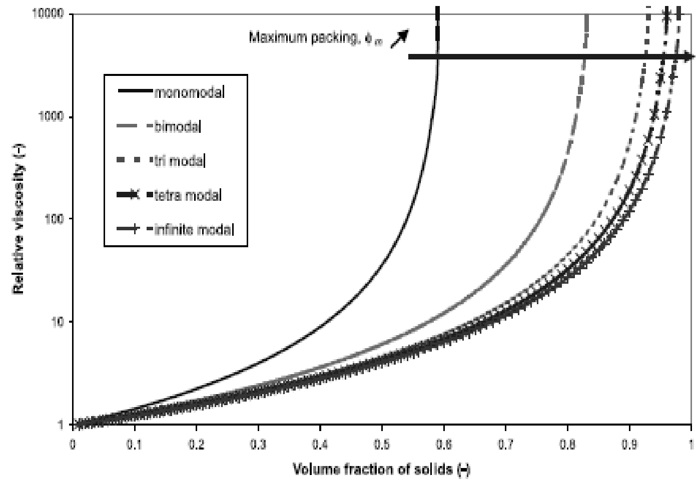
Food suspensions tend to display a packing efficiency ϕ_m in between these extremes

Particle density

- Different ingredients have a different density (g/cm^3)
- Keep in mind: replacement on weight basis of solid ingredients

$\Rightarrow$ Different ϕ!

$\Rightarrow$ Different flow behaviour!



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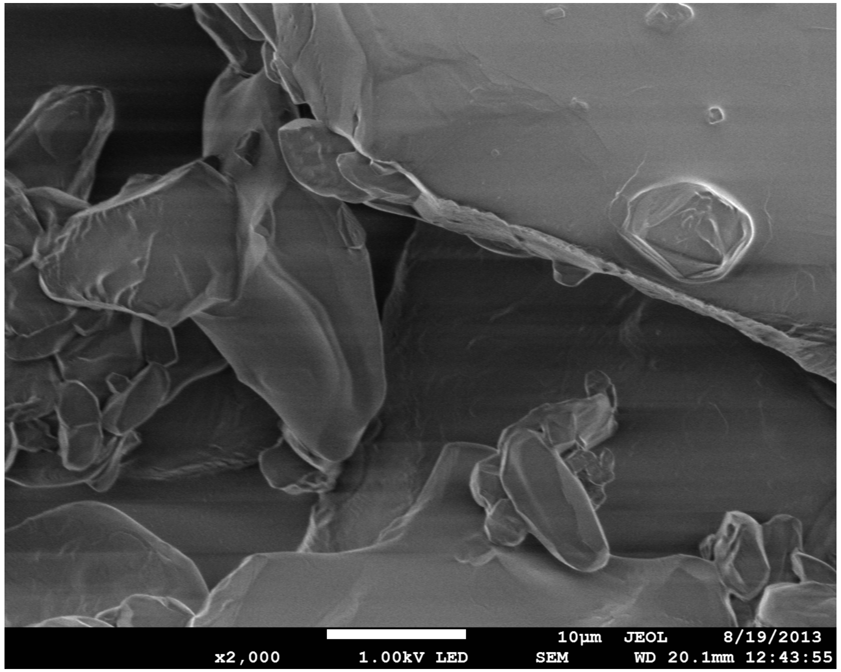
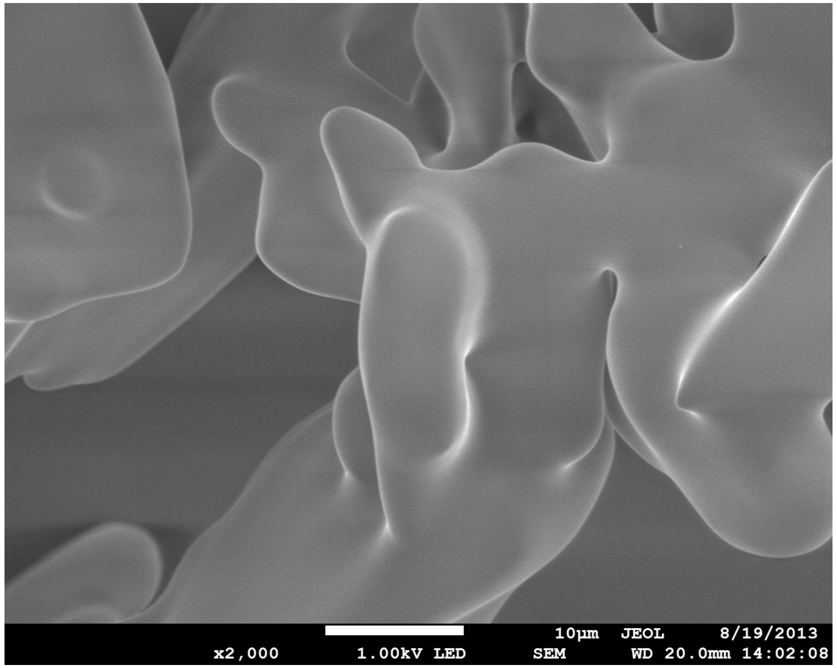
Surface roughness



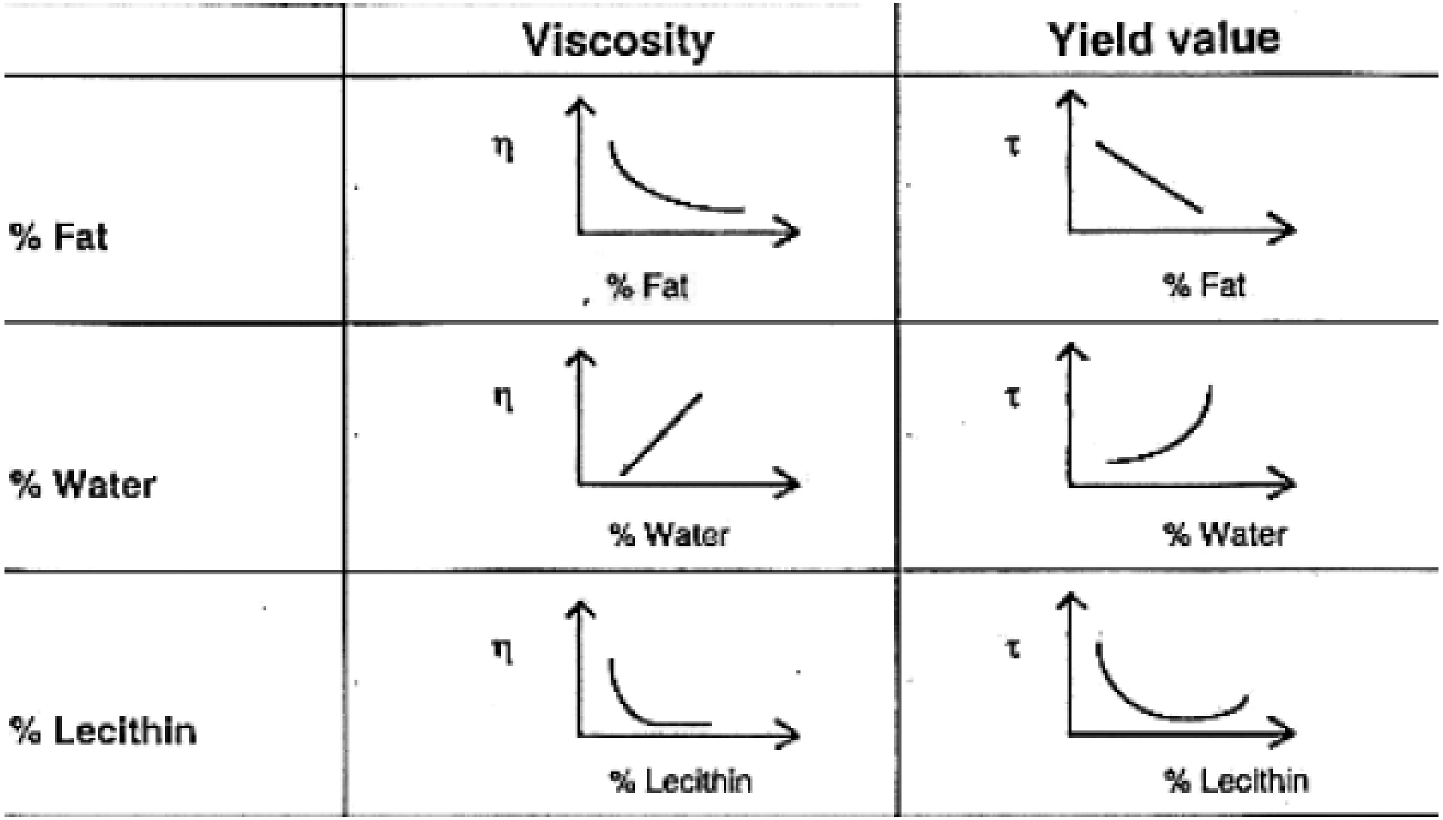
Sucrose



Polydextrose

Suspension rheology

Aggregation – interparticle forces



Continuous phase viscosity

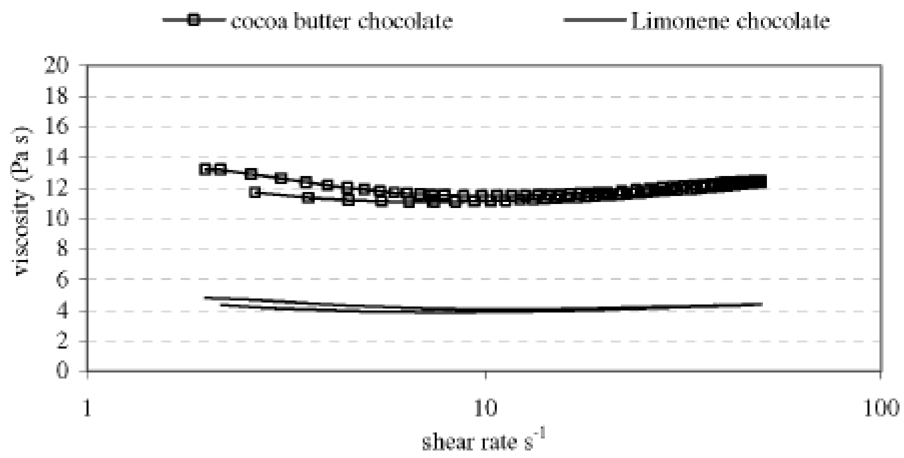
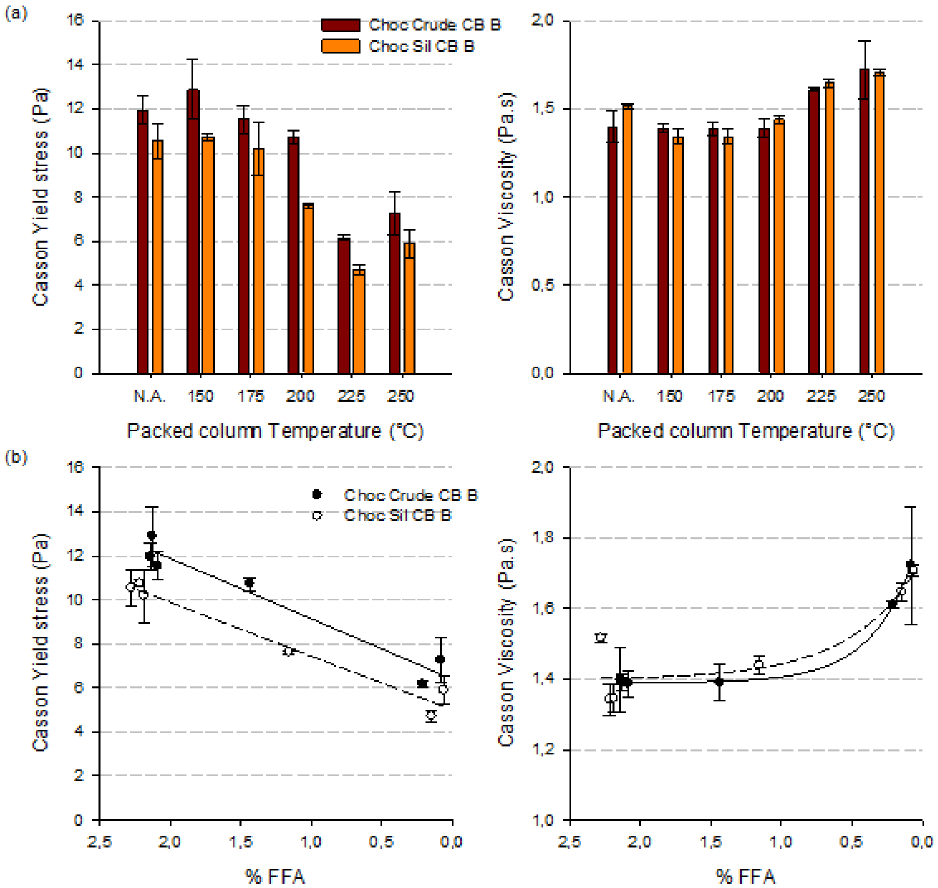


FIGURE 1. Viscosity of 2 reduced-fat chocolates (25%wt fat) at 40°C - After a 15 minute pre-shear at 50 s^{-1}, the shear rate was increased from 2 to 50 s^{-1} in 3 minutes, held at 50s^{-1} for 1 minute and then decreased from 50 to 2 s^{-1} in 3 minutes using concentric cylinders.

Do *et al.* (2008)

Continuous phase viscosity



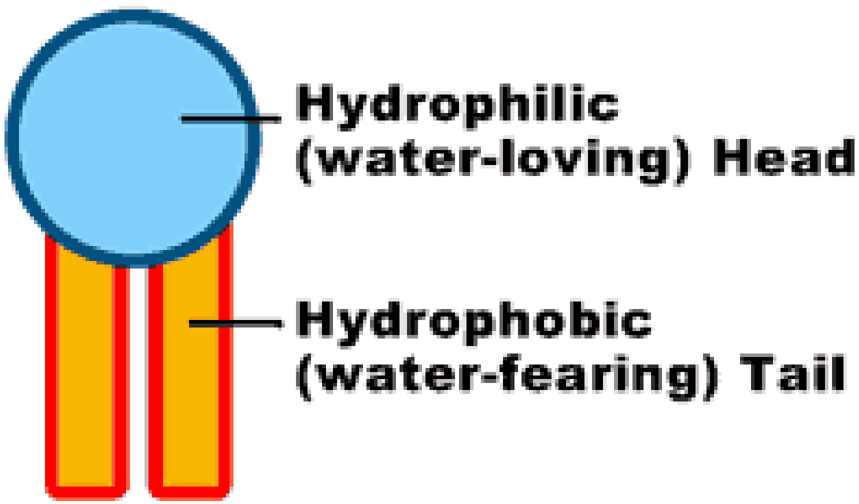
Reference: De Clercq, N. (1994). Changing the cocoa butter functionality. PhD thesis, Ghent University

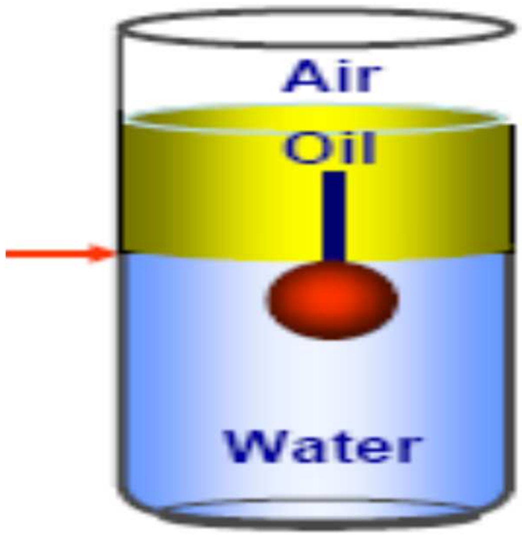
Emulsifier functionality

What is an emulsifier?

= amphiphilic molecule:

- Hydrophilic part preferring to be in an aqueous (polar) environment
- Lipophilic part preferring to be in a lipid (nonpolar) environment

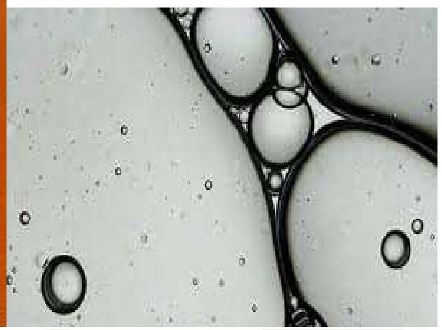




Emulsifier functionality

Functions

- Emulsion
  - Stabilisation
  - Destabilisation
- Starch interaction
- Protein interaction
- Crystal modifiers
- Wetting Agents
- **Viscosity reducing**
- ...



Emulsifier functionality

Product

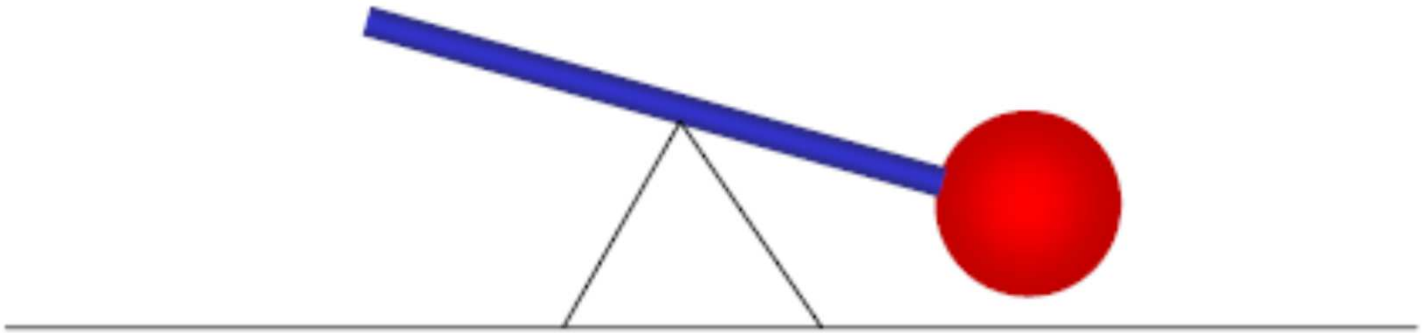
- Bread and Rolls
- Cake Mixes
- Cookies and crackers
- Dressings
- Margarine and shortenings
- Confectionaries, **chocolate**
- Desserts and toppings
- Dairy products
- …

Emulsifier functionality

HLB

= Hydrophilic-lipophilic balance

- A low HLB number: lipophilic in character (w/o)
- A high HLB number: hydrophilic in character (o/w)



Low HLB values

The lipophilic (hydrophobic) part is dominating

High HLB values

The hydrophilic part is dominating

Emulsifier functionality

HLB *versus* application

Field of application	HLB
Anti-foaming agent	1–3
Water-in-oil emulsifier	3–6
Wetting agent	7–9
Oil-in-water emulsifier	8–18
Detergent	13–15
Solubiliser	15–18

Emulsifier functionality

EMULSIFIER	HLB
Oleic acid	1.0
Acetylated monoglycerides	1.5
Sorbitan trioleate	1.8
Glycerol dioleate	1.8
Sorbitan tristearate	2.1
Propyleneglycol monostearate	3.4
Glycerol Monoleate	3.4
Glycerol monostearate	3.8
Acetylated monoglycerides (stearate)	3.8
Sorbitan monooleate	4.3
Propylene glycol monolaurate	4.5
Sorbitan monostearate	4.7
Calcium stearoxyl-2-lactylate	5.1

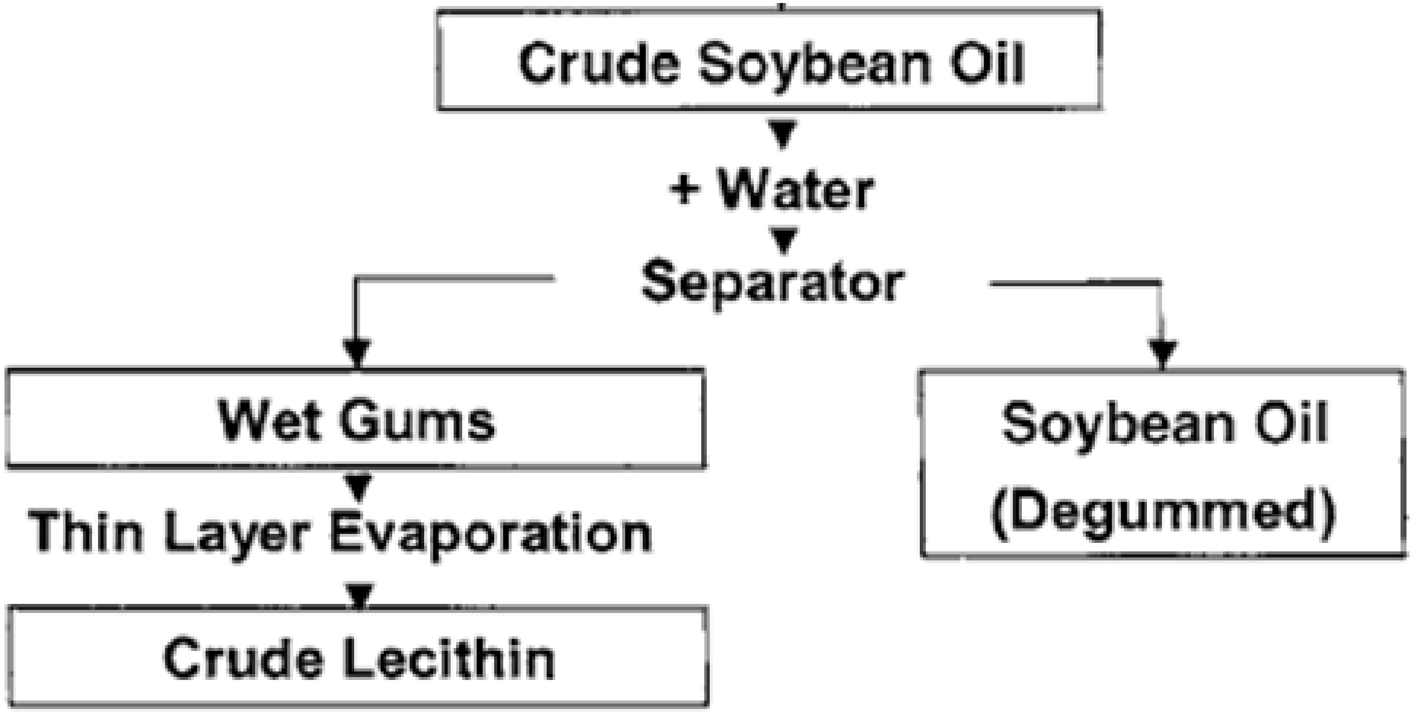
Emulsifier functionality

EMULSIFIER	HLB
Glycerol monolaurate	5.2
Sorbitan monopalmitate	6.7
Soy lecithin	8.0
Diacetylated tartaric acid esters of monoglycerides	8.0
Sodium Stearoyl lactylate	8.3
Sorbitan monolaurate	8.6
Polyoxyethylene (20) sorbitan tristearate	10.5
Polyoxyethylene (20) sorbitan trioleate	11.0
Polyoxyethylene (20) sorbitan monostearate	14.9
Sucrose monolaurate	15.0
Polyoxyethylene (20) sorbitan monooleate	15.0
Polyoxyethylene (20) sorbitan monopalmitate	15.6

Emulsifier functionality

- Lecithin and fractions (quantum satis)
- Polyglycerol polyricinoleate PGPR (max. 0.5%)
- Synthetic lecithin YN ~ lecithin

Production of lecithin



Emulsifier functionality

Lecithin is defined as a mixture of polar and neutral lipids with a polar lipid content (insoluble in acetone) of at least 60%:

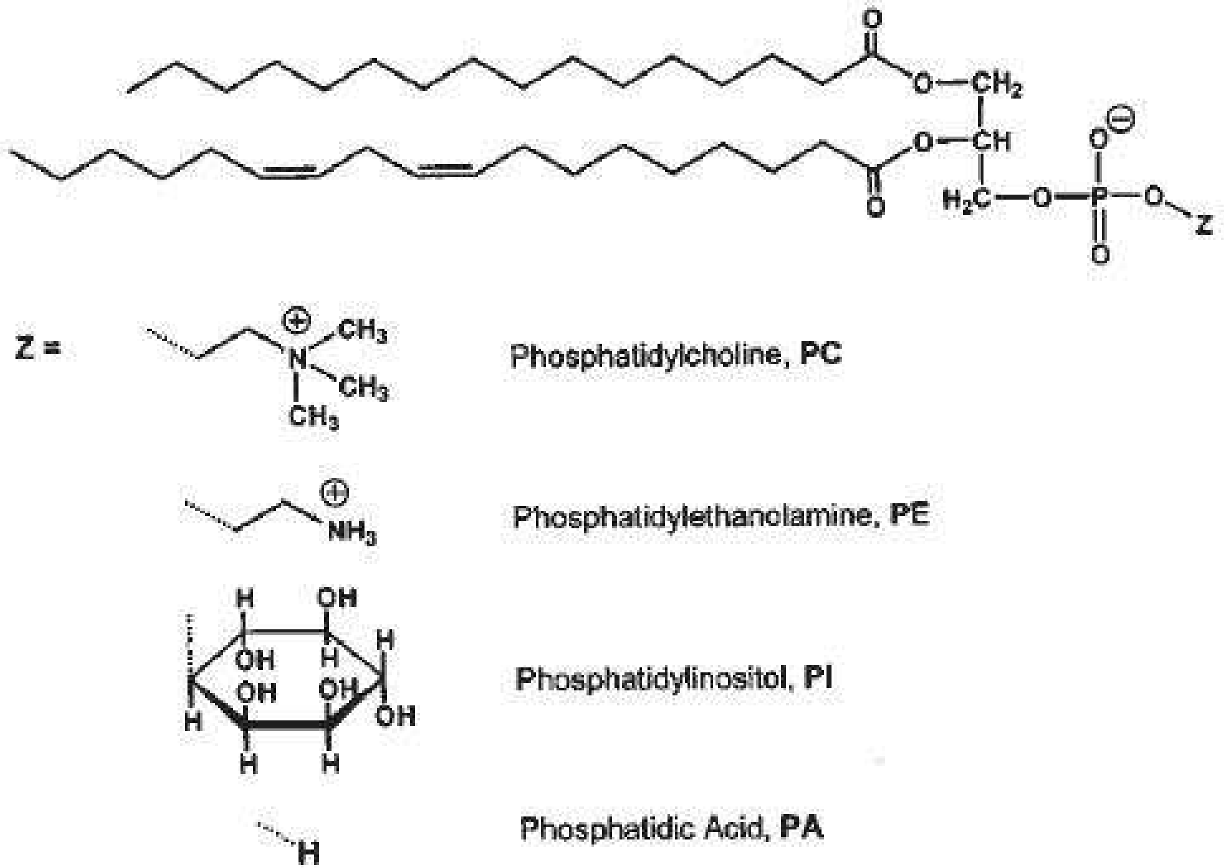
- Polar lipids: phospholipids and glycolipids → active components
- Neutral lipids: triglycerides and free fatty acids
- Minor components: carbohydrates, proteins, (glyco)sterols, fibre, minerals, ...

Emulsifier functionality

Phospholipids:

- 1,2-diacyl-sn-glycerol-3-phosphate (PA)
- 1,2-diacyl-sn-glycerol-3-phosphate linked to an alcohol
  - Aminoalcohol: choline (PC) and ethanolamine (PE)
  - Polyvalent alcohol: inositol (PI) and glycerol (PG)
  - Hydroxyamino acid: serine (PS)
- 1-monoacyl-sn-glycerol-3-phosphate (linked to an alcohol) or 2-monoacyl-sn-glycerol-3-phosphate (linked to an alcohol) = lysophospholipids

Phospholipids



Emulsifier functionality

Phospholipids:

- Two fatty acids are rarely of the same chemical nature; fatty acid attached to second carbon atom of glycerol is more unsaturated than the one attached to the first carbon atom
- Phospholipids are more unsaturated than the oils they are obtained from
- Dry bean storage and efficient front-end dehulling of beans prior to grinding keep the phospholipase D enzyme activity low, which prevents the undesired hydrolysis of PC into PA
  - Smooth degumming of the oil
  - PC, PI and LPC: easily hydratable phospholipids
  - PE and PA: low hydrating properties (can be increased applying acid-degumming)

Phospholipids

Table Phospholipid composition of liquid vegetable lecithins by ^{31}P-NMR

Phospholipid	**Soy**	**Sunflower**	**Rapeseed**
PC	15	16	17
PE	11	8	9
PI	10	14	10
PA	4	3	4
Other phospholipids	7	6	6
All phospholipids	47	47	46

Differences within one variety can be even larger, due to variation in crop conditions, storage, seed treatment and extraction conditions.

Reference: van Nieuwenhuyzen, W. & Tomas, M.C. (2008). Update on vegetable lecithin and phospholipid technologies. European Journal of Lipid Science and Technology, 110, 472-486.

Phospholipids

Table Fatty acid composition of vegetable lecithins

Fatty acid	Soy	Sunflower	Rapeseed
C16:0	16	11	7
C18:0	4	4	1
C18:1	17	18	56
C18:2	55	63	25
C18:3	7	0	6
Others	1	4	5

Reference: van Nieuwenhuyzen, W. & Tomas, M.C. (2008). Update on vegetable lecithin and phospholipid technologies. European Journal of Lipid Science and Technology, 110, 472-486.

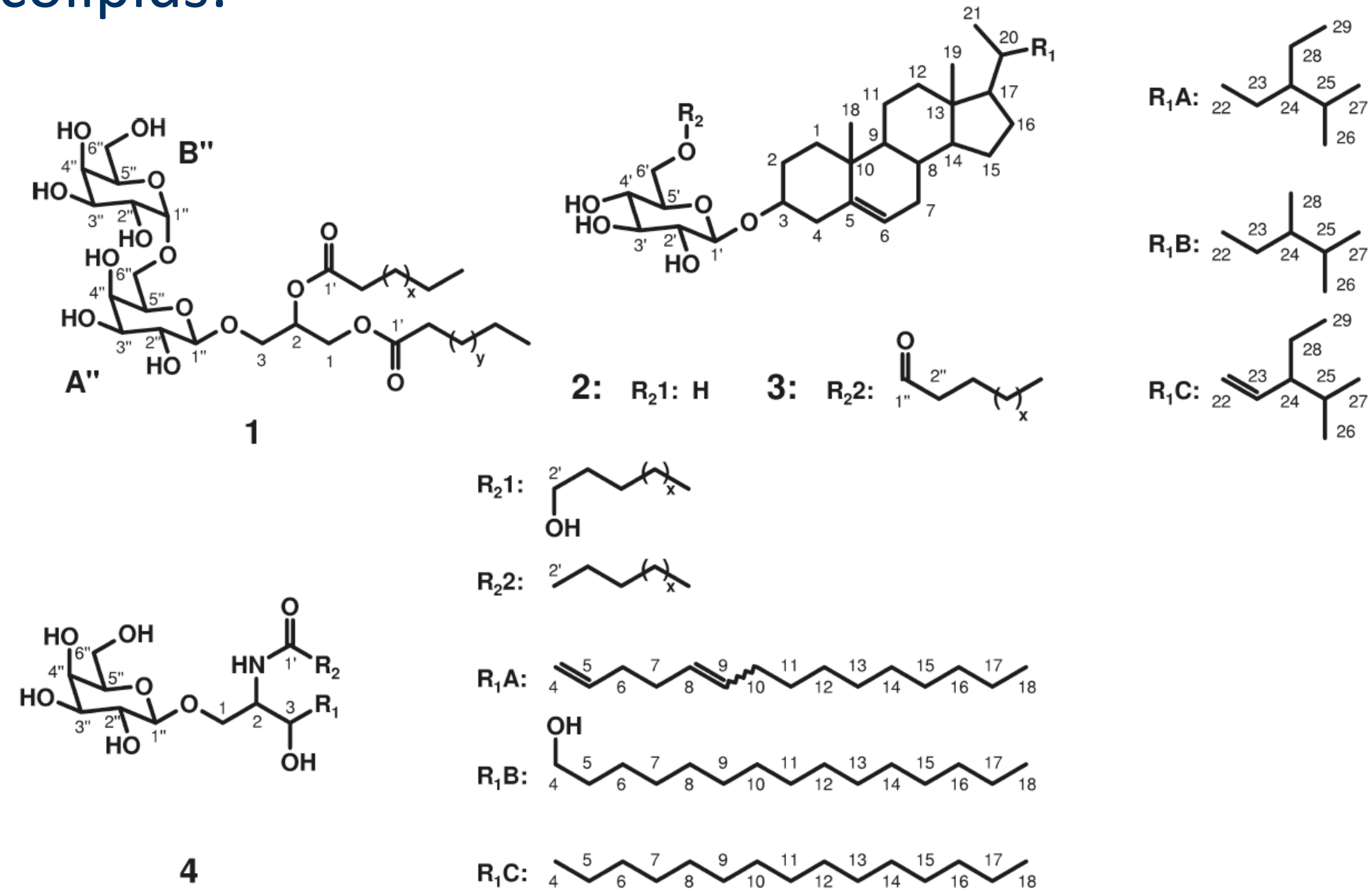
Emulsifier functionality

Glycolipids:

- Selmair & Koehler (2009) observed that soy bean, sunflower and rapeseed lecithin all contained the same major glycolipid classes, namely (1) digalactosyl diacylglycerides, (2) sterol glucosides, (3) acylated sterol glucosides and (4) cerebrosides, but in different quantities
- Soy lecithin: 13% glycolipids (AI basis) (source: Lucas Meyer brochure)
- Rapeseed lecithin: 20% glycolipid (AI basis) (source: Lucas Meyer brochure)

Emulsifier functionality

Glycolipids:



Selmair & Koehler (2009)

Polar lipids – solvent fractionation

Table Solubility of various components of lecithins in water and in organic solvents

Polar lipid	**Water**	**Acetone**	**Hexane**	**Ethanol**
PC	Dispersible	-	+	+
PE	Dispersible	-	+	±
PI	Dispersible	-	+	-
Glycolipid	Dispersible	-	±	+
Lysophospholipid	+	-	±	+

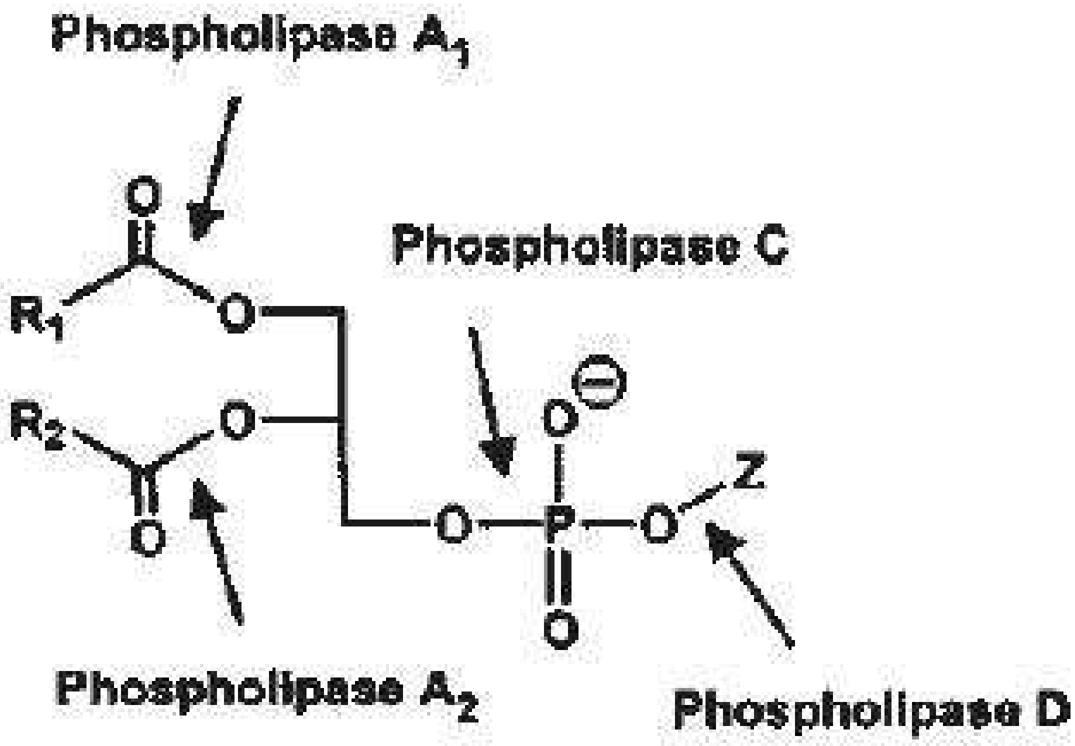
+: highly soluble; −: practically insoluble; ±: partially soluble

Emulsifier functionality

Polar lipids – solvent fractionation

	Crude lecithin	De-oiled lecithin
Phospholipids		
Phosphatidylcholine	9-17	20-23
Phosphatidylethanolamine	8-15	16-21
Phosphatidylinositol	8-11	12-18
Phosphatidic acid	3-10	7-11
Other phospholipids	5-10	8-13
Total phospholipids	**~56**	**~86**
Glycolipids	**~6**	**~10**
Neutral lipids		
Triglycerides	35-40	2
Free fatty acids	2	0.25
Sterols	1-2	0.25
Total neutral lipids	**38-44**	**2.5**

Phospholipids – enzymatic modification



Quality aspects of lecithin:

- Acetone insoluble matter (AI): approximate indication for the amount of phospholipids, glycolipids and carbohydrates

- Toluene insoluble (TI): consists of residual fibre, but sometimes particulate contaminants may be introduced during processing (*e.g.* filter aids)

- Hexane insoluble (HI): used in North and South America as an alternative for TI

Emulsifier functionality

Quality aspects of lecithin:

- Acid value (AV): represents the acidity contributed by phospholipids and free fatty acids (sometimes deliberately for viscosity reasons)

- Peroxide value (PV): measure of degree of oxidation

  ~ PV in lecithin is mostly the result of residual hydrogen peroxide used for bleaching

- Moisture: higher moisture levels than 1% usually indicate a greater potential for spoilage or chemical degradation

Quality aspects of lecithin

Table Legal purity specifications of food-grade lecithin

Parameter	FAO/WHO Codex Alimentarius	European Union E322	Food Chemical Codex
AI (%)	> 60	> 60 Hydrolyzed > 56	> 50
HI (%)			< 0,3
TI (%)	< 0,3	< 0,3	
Moisture (%)			< 1,5
Drying loss (%)	< 2,0	< 2,0	
AV (mg KOH/g)	< 36	< 35 Hydrolyzed < 45	< 36
PV (meq O_2/kg)	< 10	< 10	< 10

Reference: van Nieuwenhuyzen, W. & Tomas, M.C. (2008). Update on vegetable lecithin and phospholipid technologies. European Journal of Lipid Science and Technology, 110, 472-486.

Lecithin

- For bulk storage, a temperature of around 40°C under dry conditions is recommended. It is advised to use adequate tanks with stirring facilities for keeping the stored lecithin homogeneous
- At 20-30°C, lecithin can easily be stored for over a year without significant changes in product quality and functional properties
- For smooth chocolate production, a good standard lecithin with constant phospholipid composition is desired
- Sourcing of identity-preserved (IP) non-GMO soy lecithin for the European market will become limited, which presents a market opportunity for high-quality IP sunflower and rapeseed lecithins

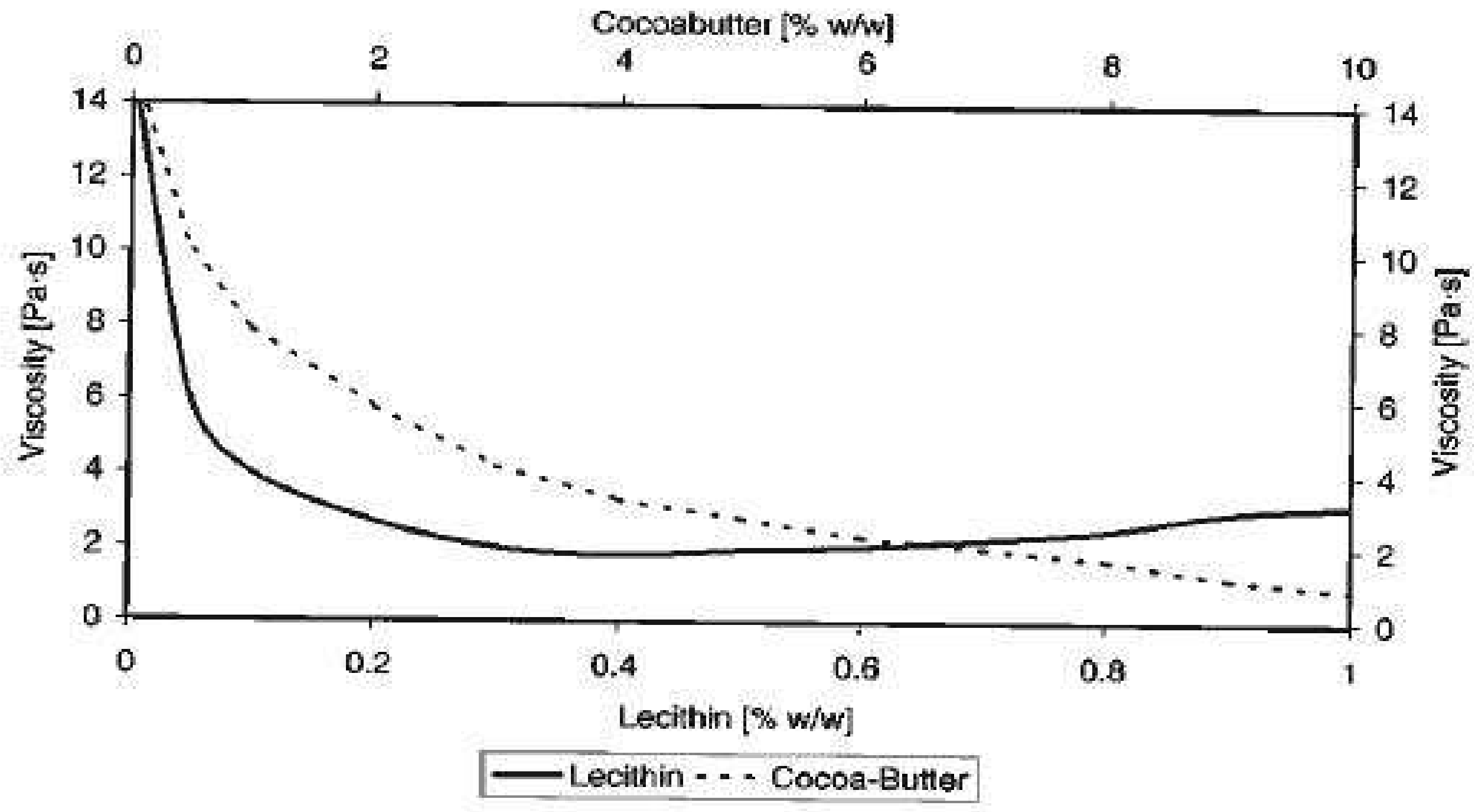
Emulsifier functionality

Lecithin

- Benefits of using lecithin in chocolate production:
  - Reduction of yield stress and viscosity
  - Excellent flow properties during tempering, moulding or enrobing
  - Cost savings on cocoa butter
  - Reduction of the total processing time
  - Tolerates water absorption

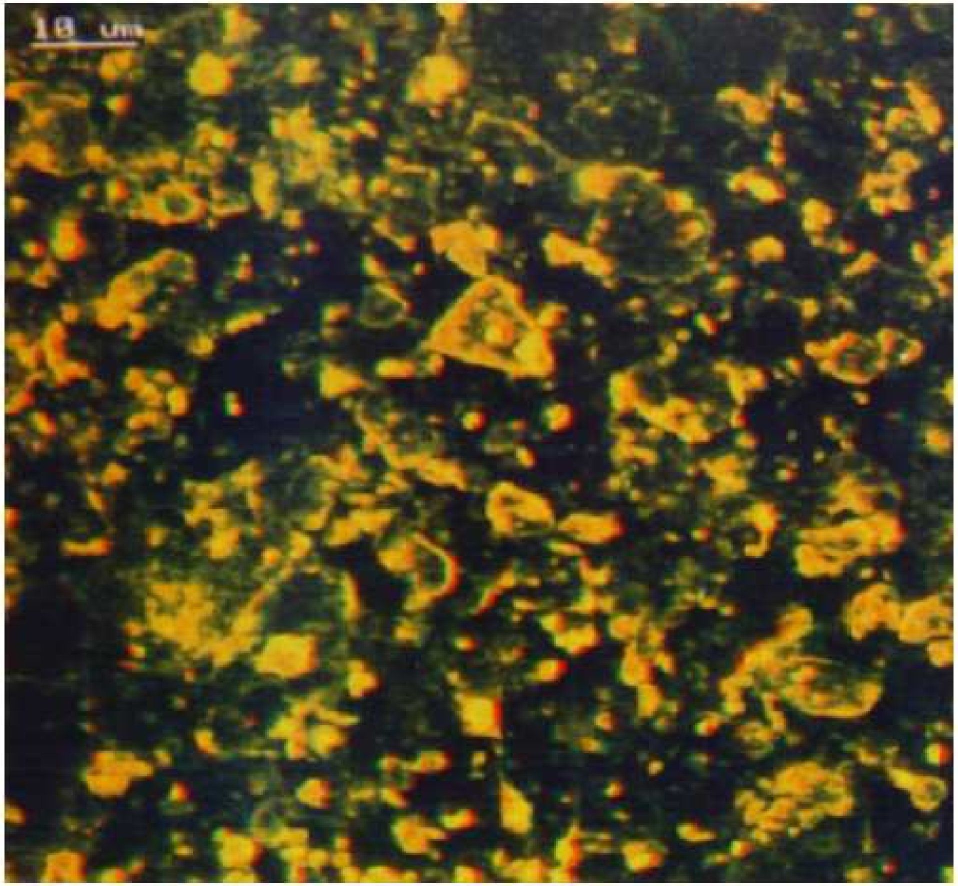
- The EU approved food additive E322 covers all standard, physically fractionated and enzymatically hydrolysed lecithins

Emulsifier functionality



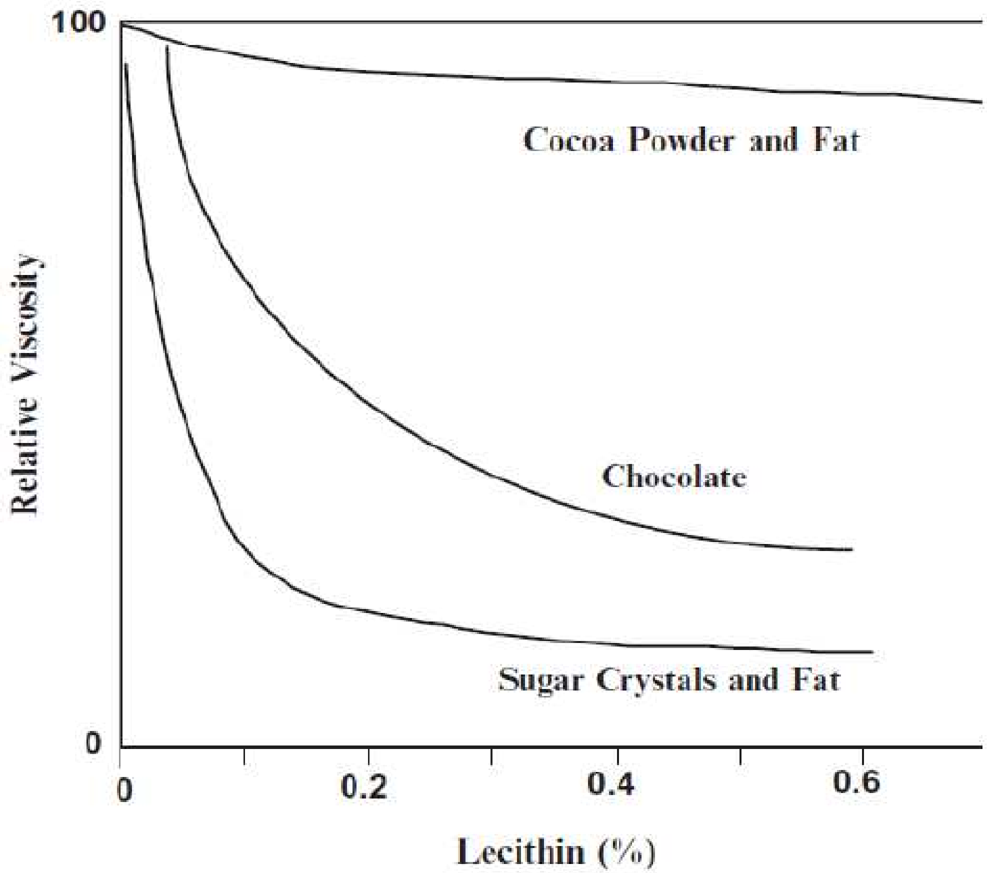
Reference: Bueschelberger, H.-G. (2004). Lecithins. In: Emulsifiers in Food Technology, R.J. Whitehurst (Ed.), Blackwell Publishing, 1-39.

Emulsifier functionality



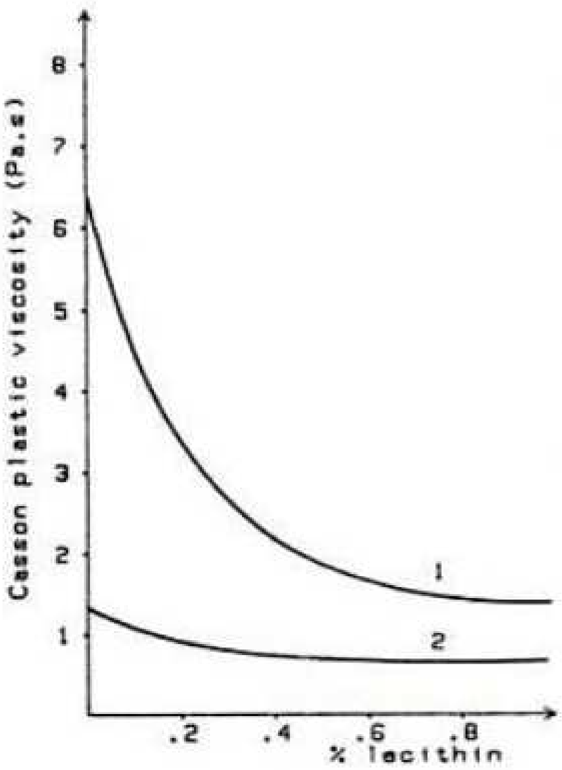
Reference: Vernier, F.C. (1997). Influence of emulsifiers on the rheology of chocolate and suspensions of cocoa or sugar particles in oil. PhD thesis, University of Reading, UK.

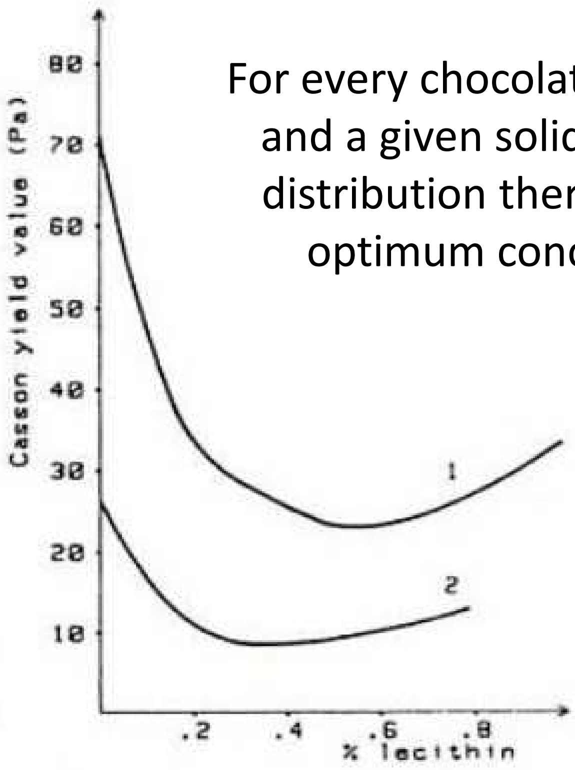
Emulsifier functionality



Reference: Minifie, B.W. (1980). Chocolate, Cocoa and Confectionery, 2nd Edition, Avi Publishing Co. Inc., Westport, Connecticut.

Emulsifier functionality

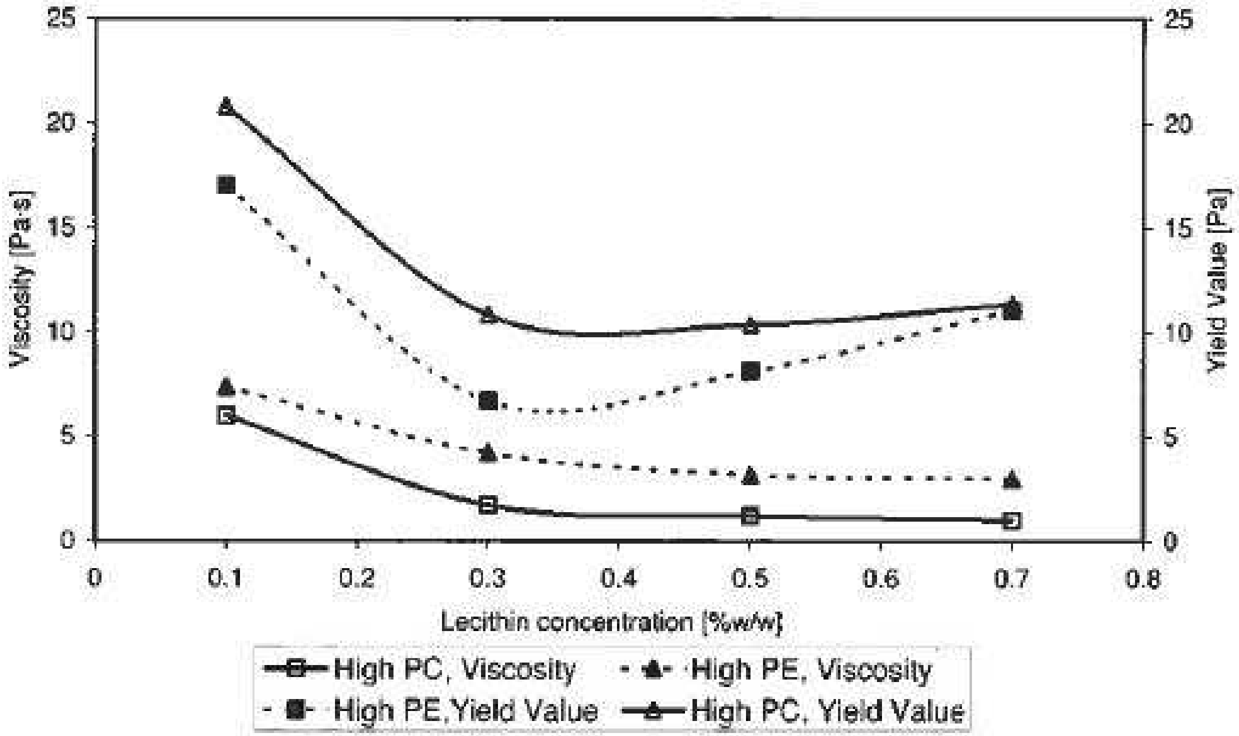




For every chocolate composition and a given solid particle size distribution there is a certain optimum concentration.

Reference: Chevalley, J. (1994). Chocolate Flow Properties. In: Industrial Chocolate Manufacture and Use, 2nd Edition, Blackie A&P.

Emulsifier functionality



Reference: Bueschelberger, H.-G. (2004). Lecithins. In: Emulsifiers in Food Technology, R.J. Whitehurst (Ed.), Blackwell Publishing, 1-39.

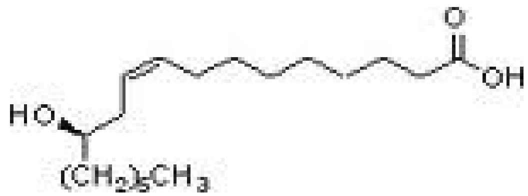
Emulsifier functionality

PGPR (E476)

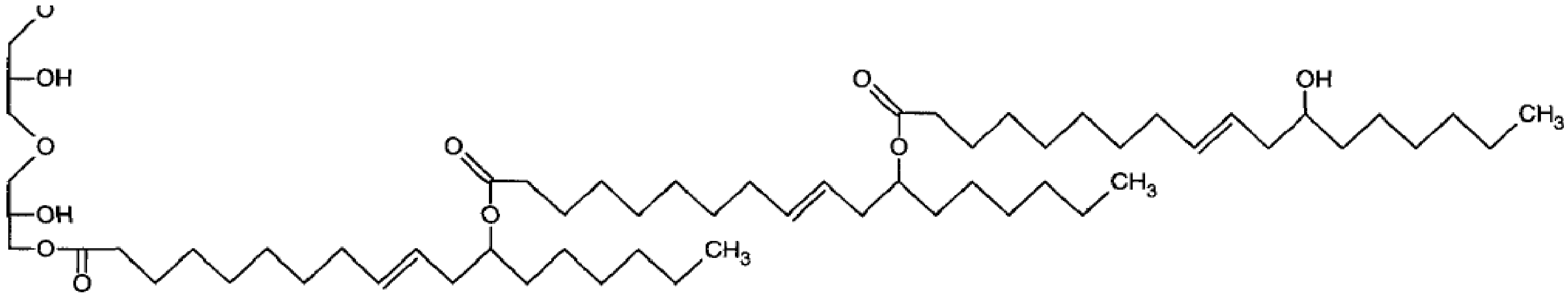
= complex mixture of partial esters and esters of polyglycerol condensed with linearly interesterified castor oil fatty acids

- Polyglycerol moiety
    - Predominantly di-, tri- and tetraglycerols (min. 75%)
    - Limited amount of polyglycerols equal to or higher than heptaglycerols (max. 10%)

- Fatty acid moiety
    - Condensed ricinoleic acid (80-90%)
    - Average of five residues per molecule of the condensed product



PGPR



Chemical structure of PGPR, here triglycerol triricinoleate (Wikman, 2008)

Emulsifier functionality

PGPR

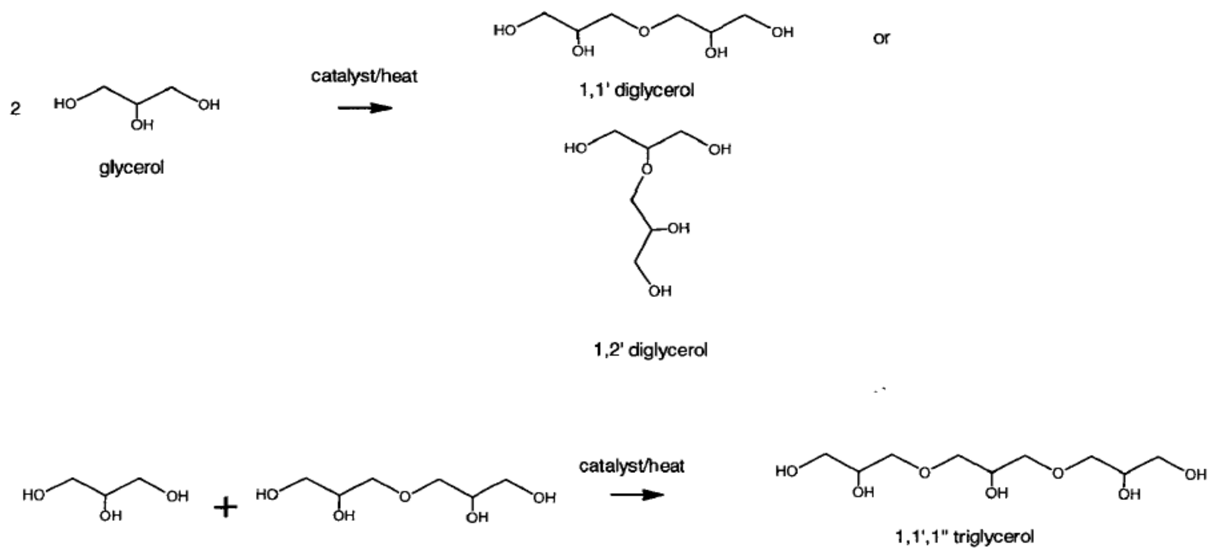
- Surface-active properties:
  - Powerful water-in-oil emulsifier, stable w/o-emulsion at high water contents (80%)
  - Improver of flow properties in chocolate and vegetable fat coatings, esp. the yield stress

- HLB ≈ 1.5 (Rector, 2000)

Manufacturing process of PGPR:

1) Preparation of polyglycerol

- Heating glycerol to T above 200°C in the presence of a small amount of alkali
- Predominantly straight-chain: 1- and 3-hydroxy groups are more active than 2-hydroxy group



Wikman, 2008

Emulsifier functionality

Manufacturing process of PGPR:

2) Preparation of castor oil fatty acids

- Hydrolysis of castor oil with water and steam at 400 psi pressure
- Washing step
- Castor oil: 80-90% ricinoleic acid, 3-8% oleic acid, 3-7% linoleic acid and 0-2% stearic acid

3) Fatty acid condensation

- Heating castor oil fatty acids at elevated temperatures under vacuum
- Acid value of 35 mg KOH/g ~ average of five fatty acid residues per molecule
- Simple linear esterification = desired reaction
- Cyclic esterification = undesired reaction → no evidence for the presence of this type of cyclic material

Manufacturing process of PGPR:

4) Partial esterification of the condensed castor oil fatty acids with polyglycerol

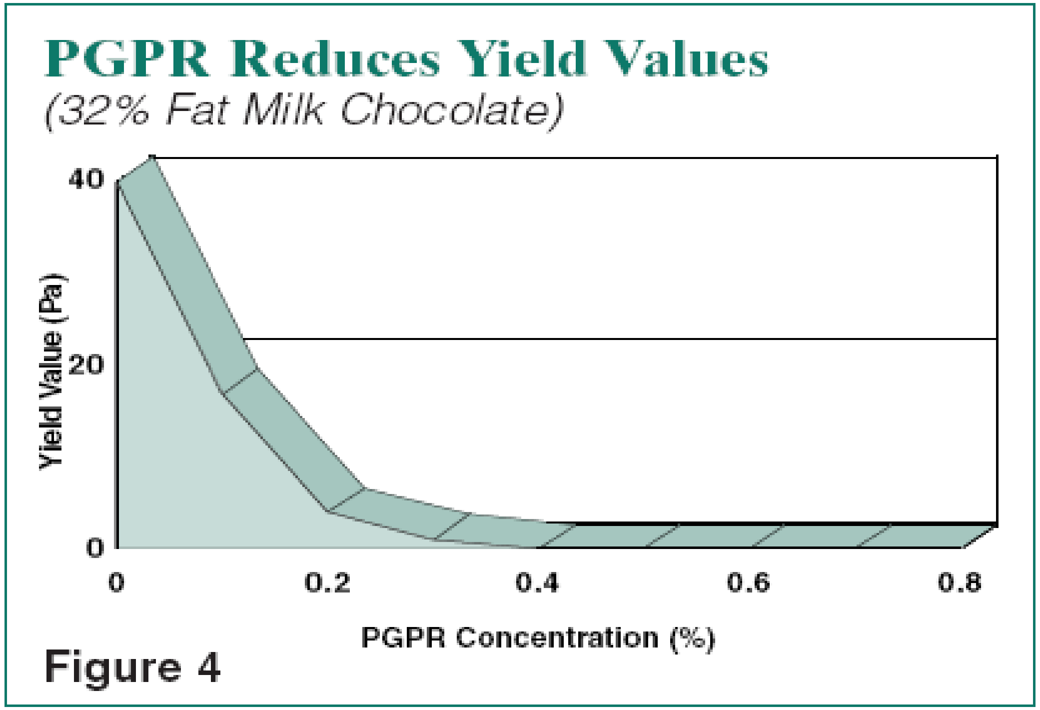
- Similar conditions as those for fatty acid condensation
- Reaction continues until suitable acid value

Emulsifier functionality

Chemical specifications of PGPR

- Acid value: max. 2 mg KOH/g
- Hydroxylvalue: 85-100 mg/g
- Iodine value: 80-90 g I_2/100 g
- Refractive value at 65°C: 1.4635-1.4665

Emulsifier functionality



Rector (2000)

Emulsifier functionality

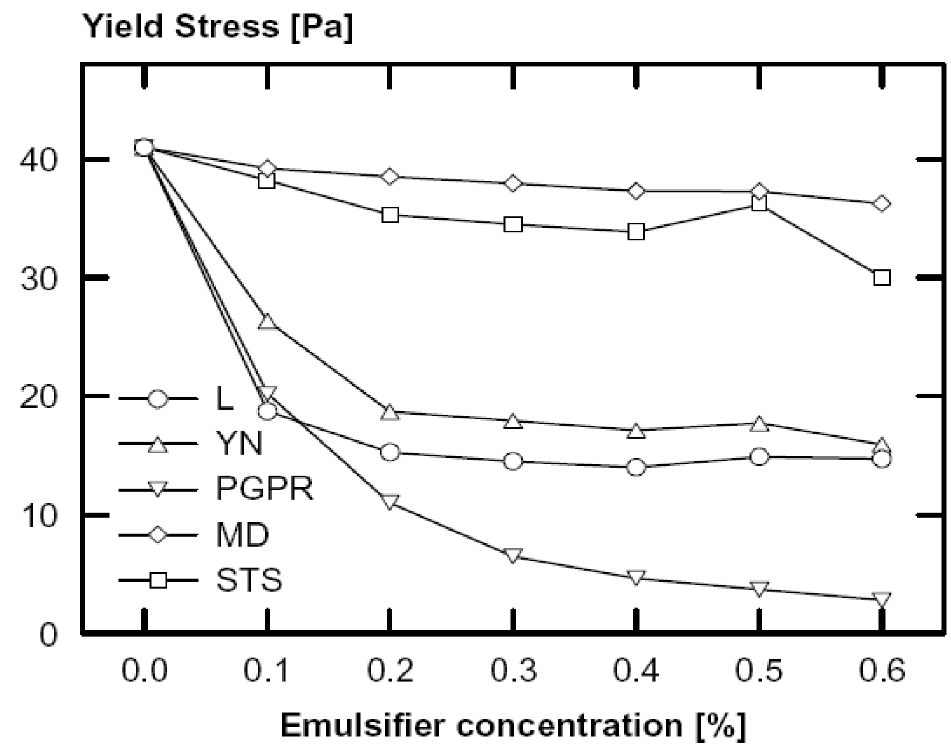


Fig. Effects of selected emulsifiers on the yield stress of dark chocolate. L: lecithin; YN: ammoniumphosphatide; PGPR; MD: mono- and diglycerides; STS: sorbitan tristearate (Schantz *et* al., 2003)

Emulsifier functionality

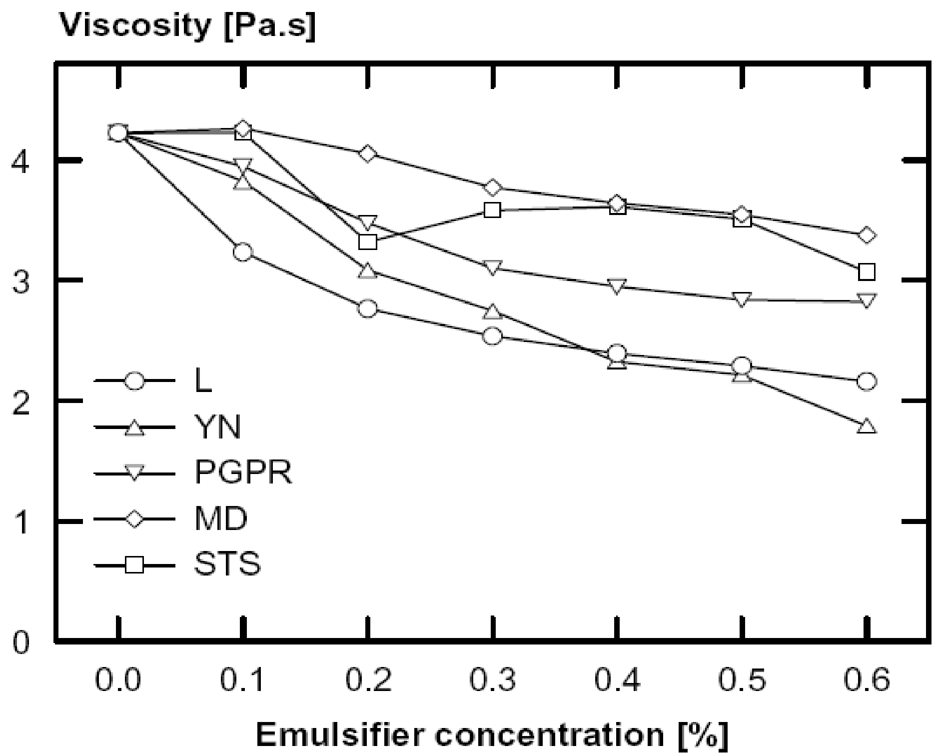


Fig. Effects of selected emulsifiers on the viscosity of dark chocolate. L: lecithin; YN: ammonniumphosphatide; PGPR; MD: mono- and diglycerides; STS: sorbitan tristearate (Schantz *et* al., 2003)

Emulsifier functionality

Lecithin-PGPR blends (Schantz & Rohm, 2005)

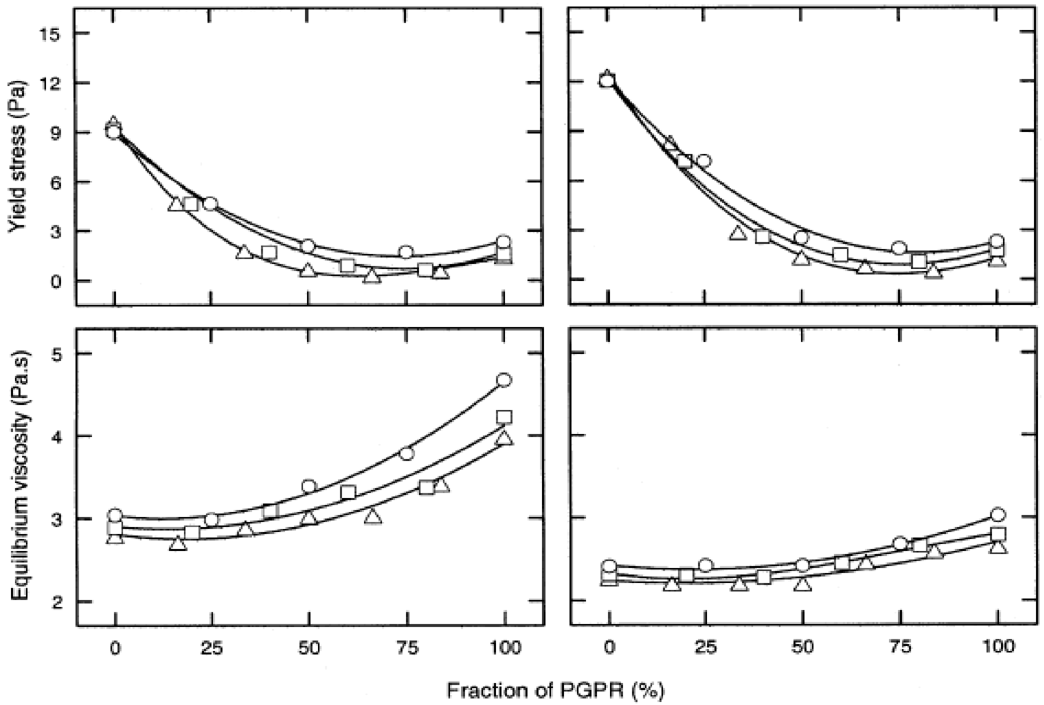
Milk chocolate

• Yield stress minima:

Lecithin/PGPR 30/70

• Equilibrium viscosity minima:

Lecithin/PGPR 75/25



Dark chocolate

• Yield stress minima:

Lecithin/PGPR 30/70

• Equilibrium viscosity minima:

Lecithin/PGPR 50/50

Fig. Yield stress and equilibrium viscosity of milk chocolate (left) and dark chocolate with varying emulsifier content (circles: 4 g/kg; squares: 5 g/kg; triangles: 6 g/kg) as a function of emulsifier blending. Experimental data were fitted by a second-order polynomial (4 g/kg) and by third-order polynomials (5 and 6 g/kg)

Practical excercise

- Base dark chocolate: 32.4% fat, including 0.4% soy lecithin

- Flow behaviour using ICA46 method:
  - Melting in oven at 52°C for 1h
  - Concentric cylinders at 40°C
  - Pre-shear at 5 s^{-1} for 15 min
  - Stepped shear at 2, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 s^{-1} for 16 s (upward flow curve)
  - σ_{CA} = 11.7 Pa
  - η_{CA} = 2.08 Pa.s

Practical excercise

- Task:
  - Mixing fat + emulsifiers until a final fat content of 34% (emulsifiers included) using Stephan mixer
  - Ingredients:
    - Cocoa butter
    - Emulsifiers: Standard lecithin, PC-enriched lecithin and PGPR

  - Group 1: σ_{CA} = rank 3 (lowest value); η_{CA} = rank 1 (highest value)
  - Group 2: η_{CA} = rank 3
  - Group 3: σ_{CA} = rank 1


KEEP
CALM
AND
GO WITH
THE FLOW