Formulation Engineering of "Pickering Emulsions" novel functionalities and potential applications

Tom Mills, Fotis Spyropoulos

Overview

- Emulsions - Pickering
- Pickering particles
- Mixed systems
- Applications in foods

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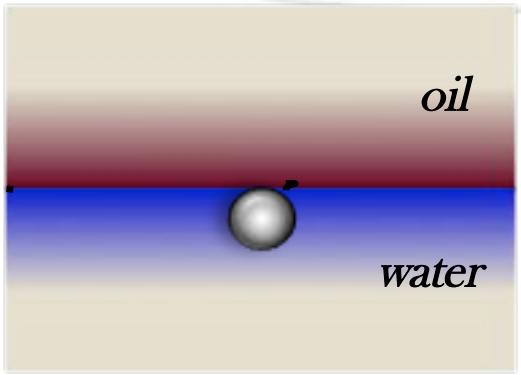
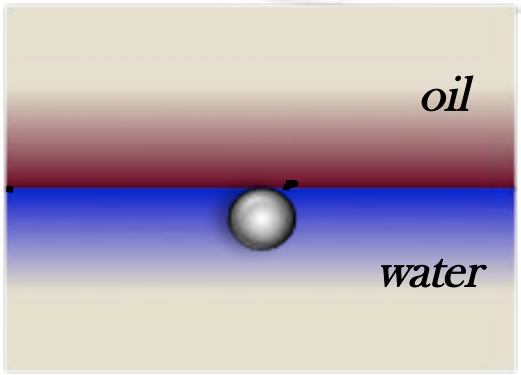
- Applications in foods

Emulsifier or Particle Stabilised Emulsions



Emulsifiers:

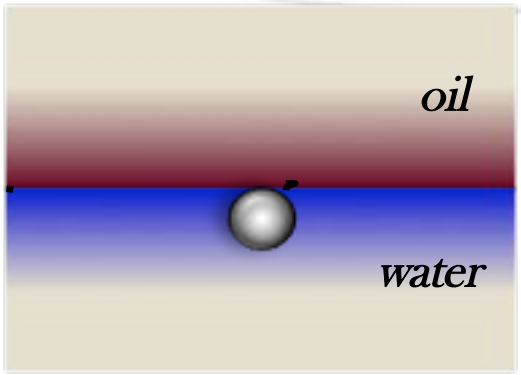
Emulsifier or Particle Stabilised Emulsions



Emulsifiers:

- Small size (<1nm)
  - more mobile and thus adsorb at the interface faster

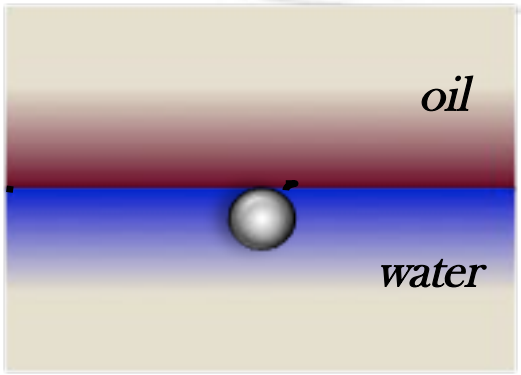
Emulsifier or Particle Stabilised Emulsions



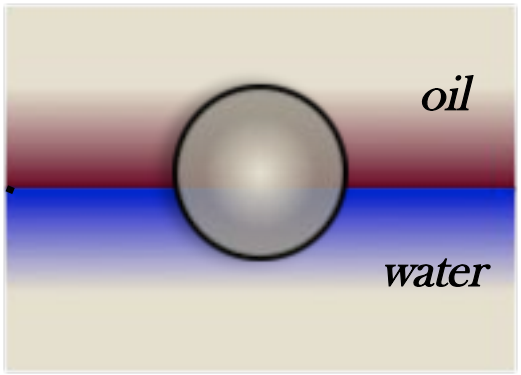
Emulsifiers:

- Small size (<1nm)
  - easily adsorb and desorb from the interface thus more susceptible to coalescence
  - (detachment energy<10kT)

Emulsifier or Particle Stabilised Emulsions

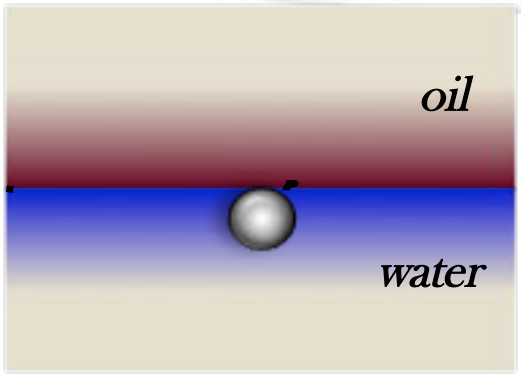


Emulsifiers:



Particles:

Emulsifier or Particle Stabilised Emulsions



Emulsifiers:

- Small size (<1nm)
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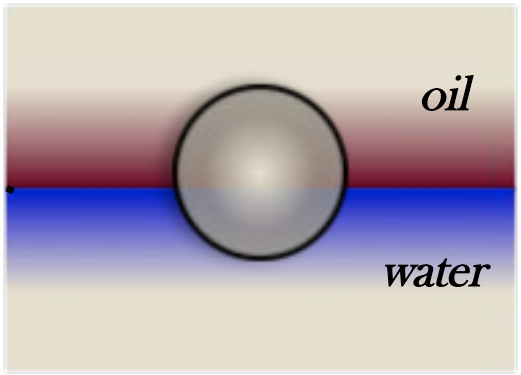
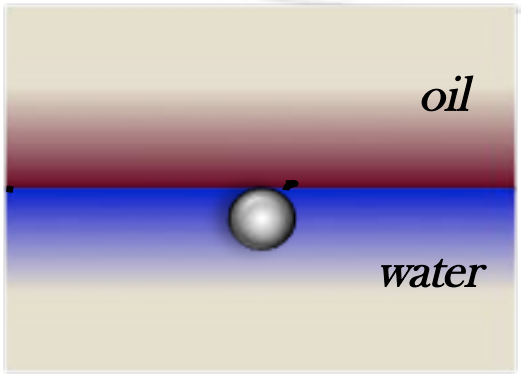


Particles:

- Bigger in size (>100nm)
  - less mobile and thus adsorb at the interface slower

Emulsifier or Particle Stabilised Emulsions



Emulsifiers:

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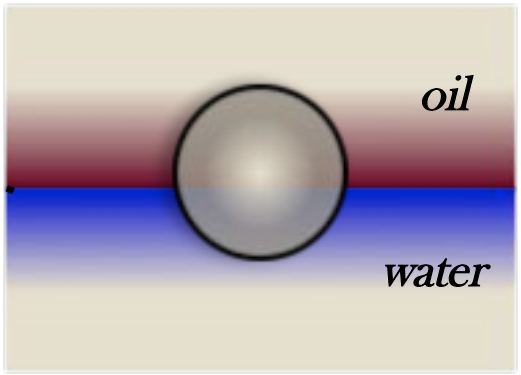
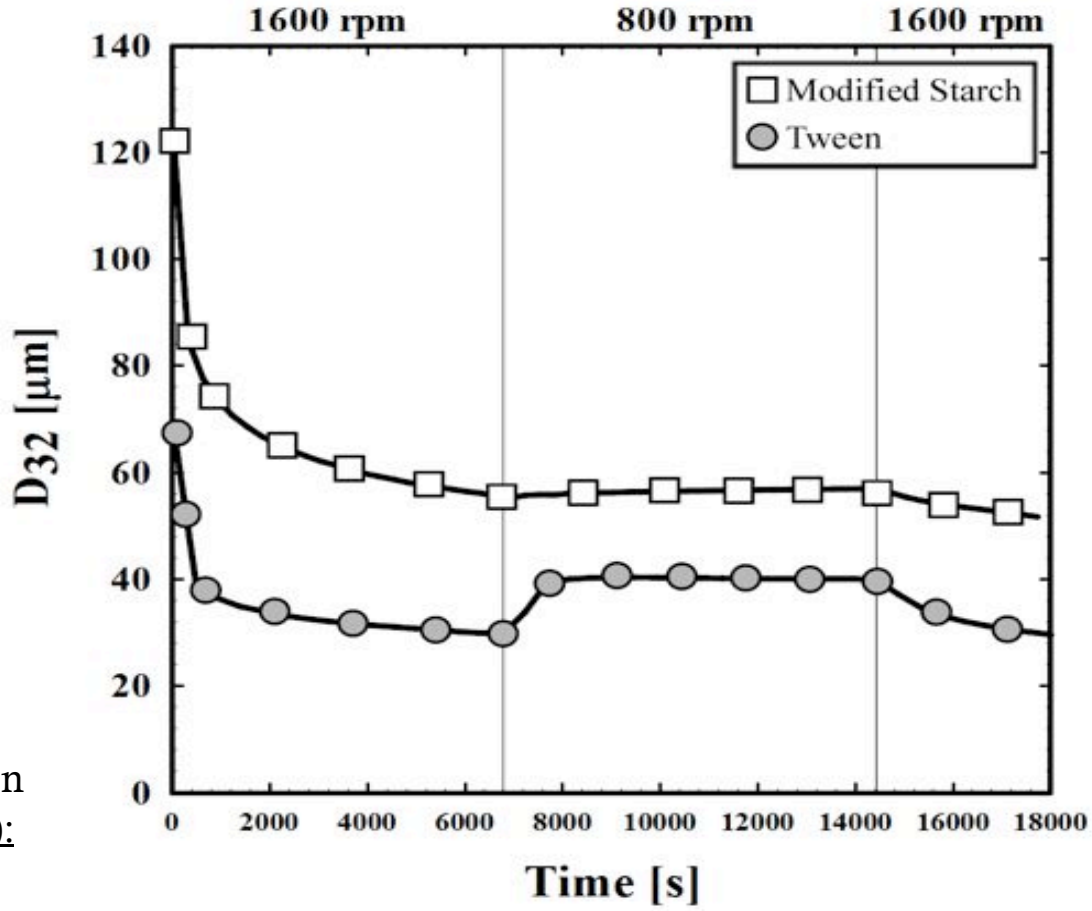


Particles:

- Bigger in size (>100nm)
  - irreversibly adsorbed at the interface excellent long-term stability against coalescence
  - Detachment energy >3000kT

Pickering Emulsions

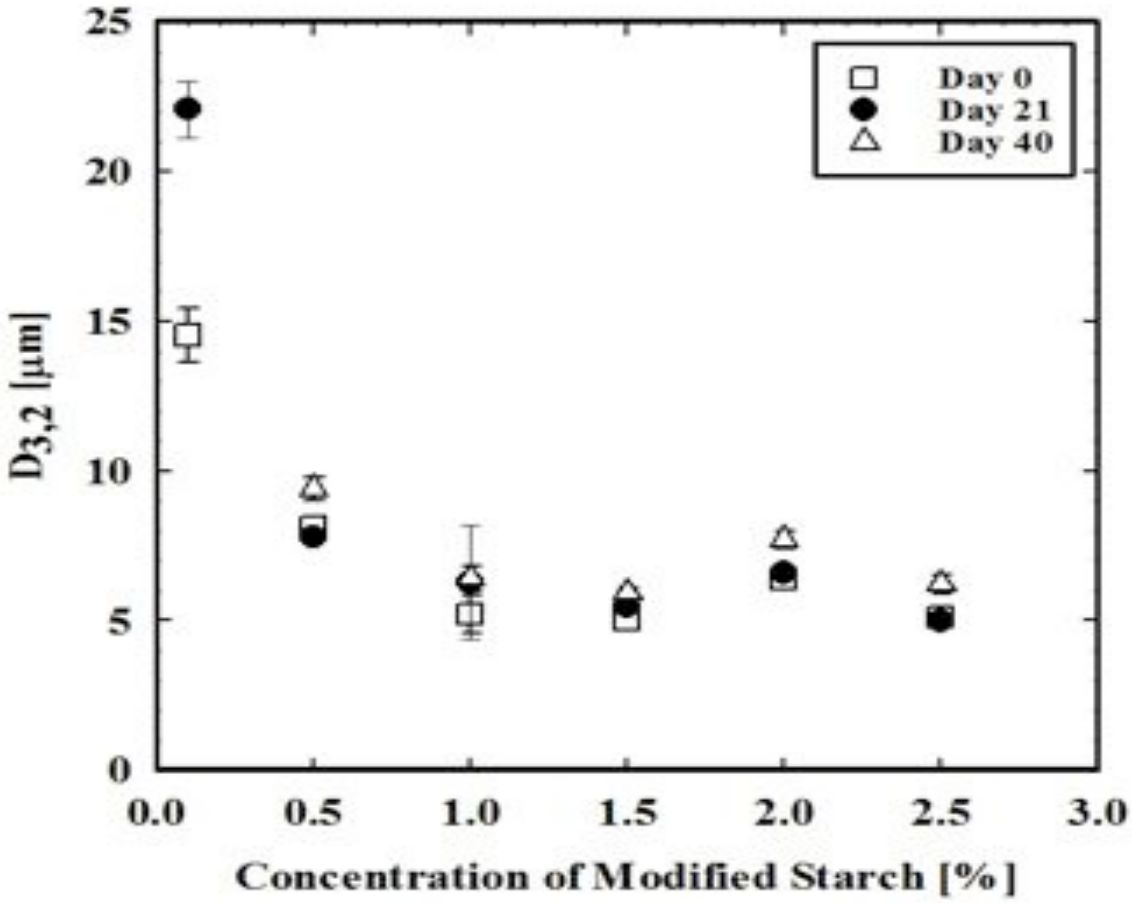
- Stability during processing



Niknafs, N., F. Spyropoulos and I. T. Norton (2011). Journal of Food Engineering **104**(4): 603-611.

Pickering Emulsions

- MS emulsions have good storage stability



Overview

- Emulsions - Pickering
- Pickering particles
- Mixed systems
- Applications in foods

Pickering Emulsions

- Pickering particles
  - Silica
  - Alumina
  - Titanium dioxide
  - Clay particles

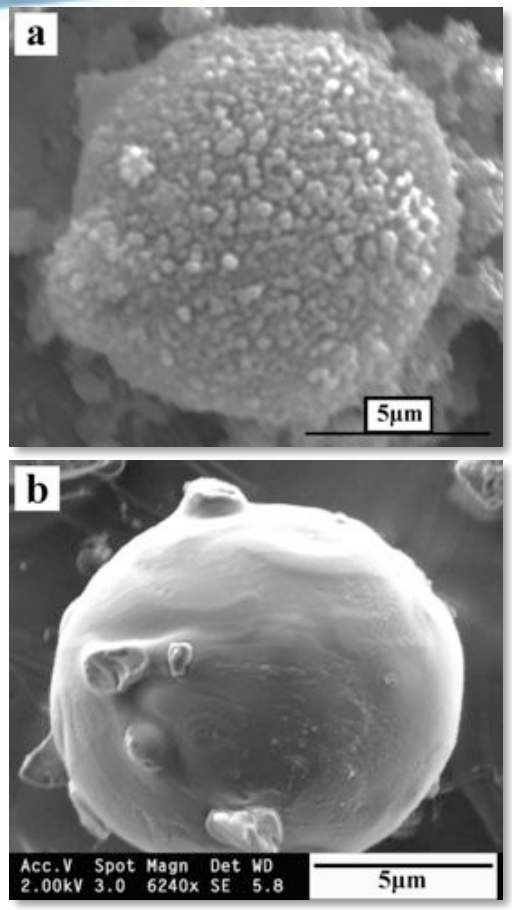


Figure 1. Micrographs of a particle-stabilised **(a)** and an emulsifier-stabilised **(b)** emulsion droplet.

Pickering Emulsions

- Pickering particles
  - Silica
  - Alumina
  - Titanium dioxide
  - Clay Particles

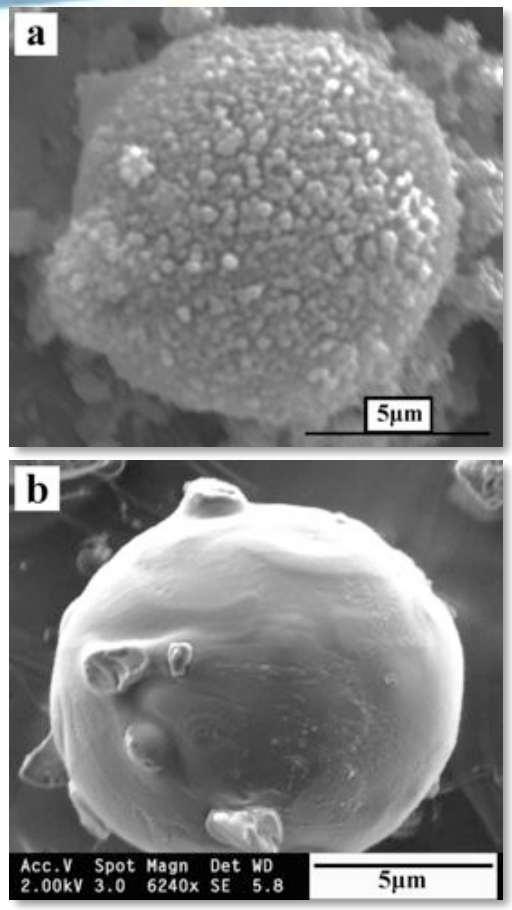


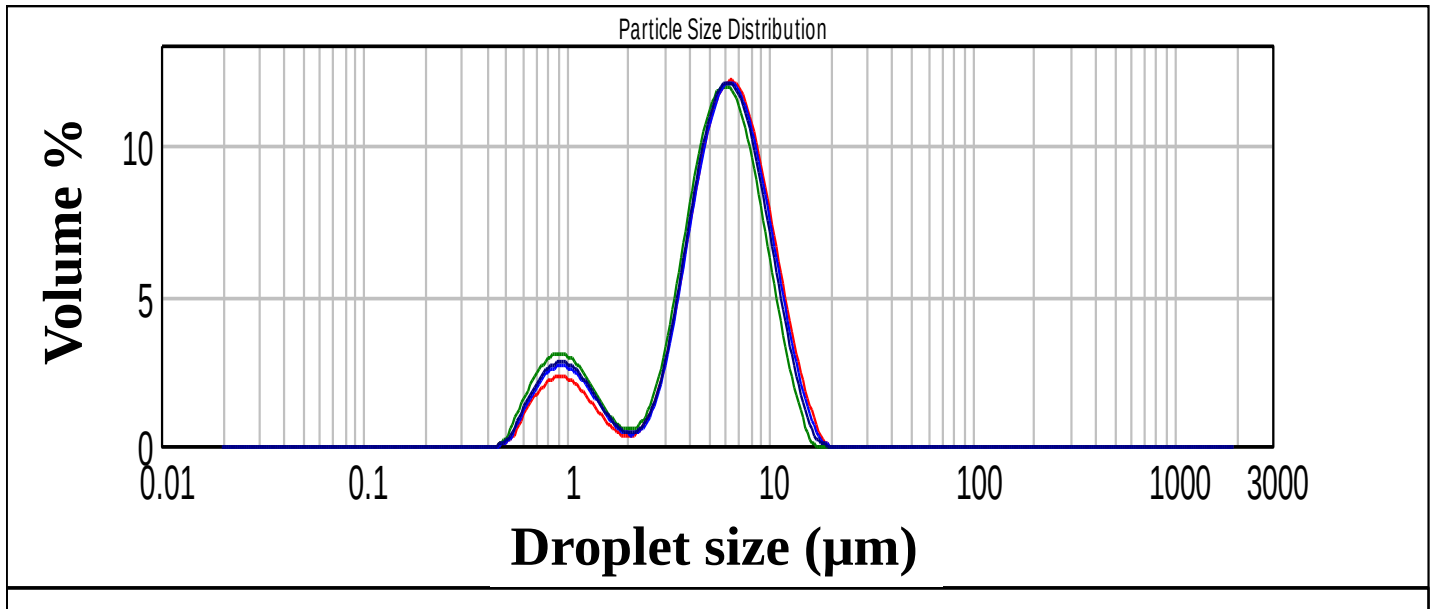
Figure 1. Micrographs of a particle-stabilised **(a)** and an emulsifier-stabilised **(b)** emulsion droplet.

Pickering Emulsions

- Silica
- High pressure homogeniser - 500 bar
- 1% silica, 20% oil

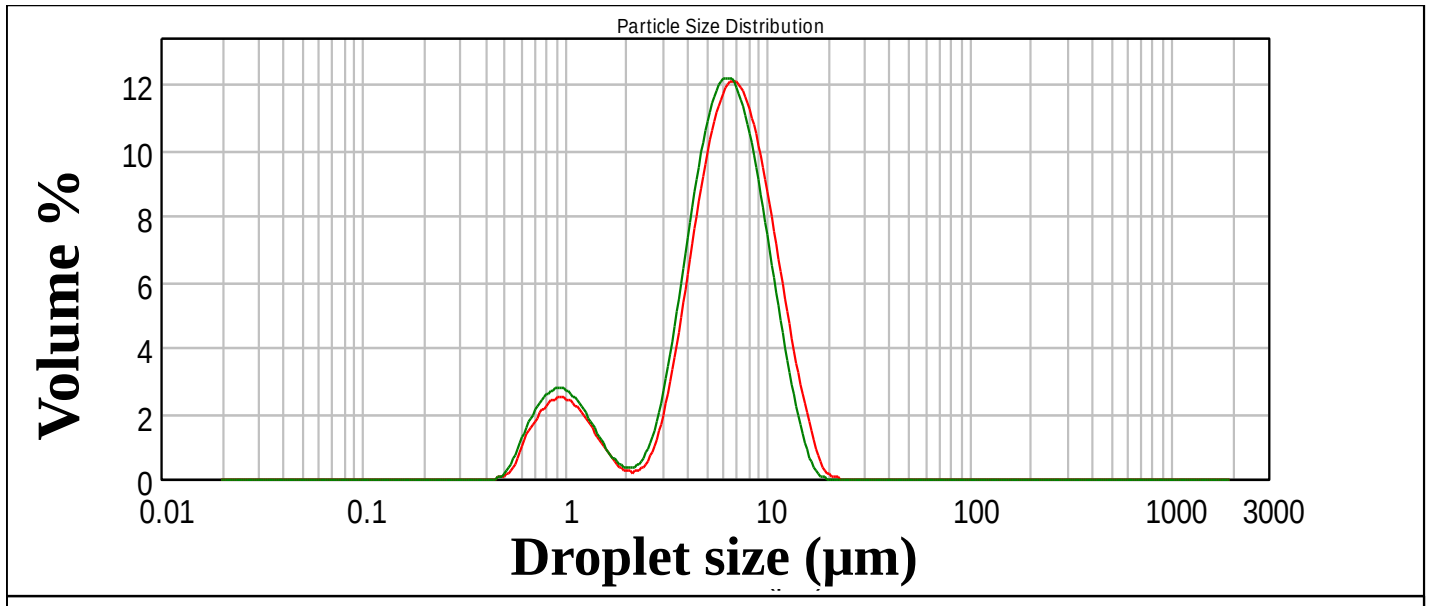
Pickering Emulsions Silica

- Distribution with passes



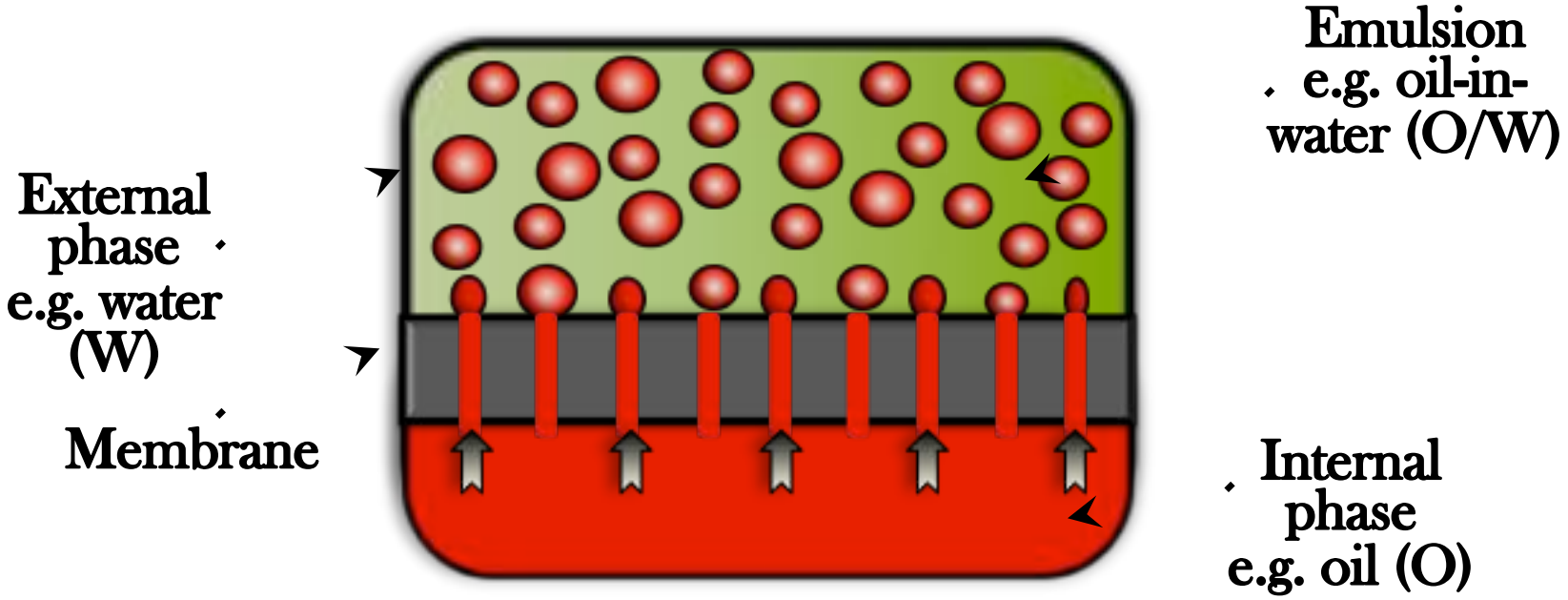
Pickering Emulsions Silica

- Stability over 7 days



Membrane Emulsification

- The method involves using pressure to force the to-be-internal/ dispersed phase to permeate through a membrane into the external/continuous phase.

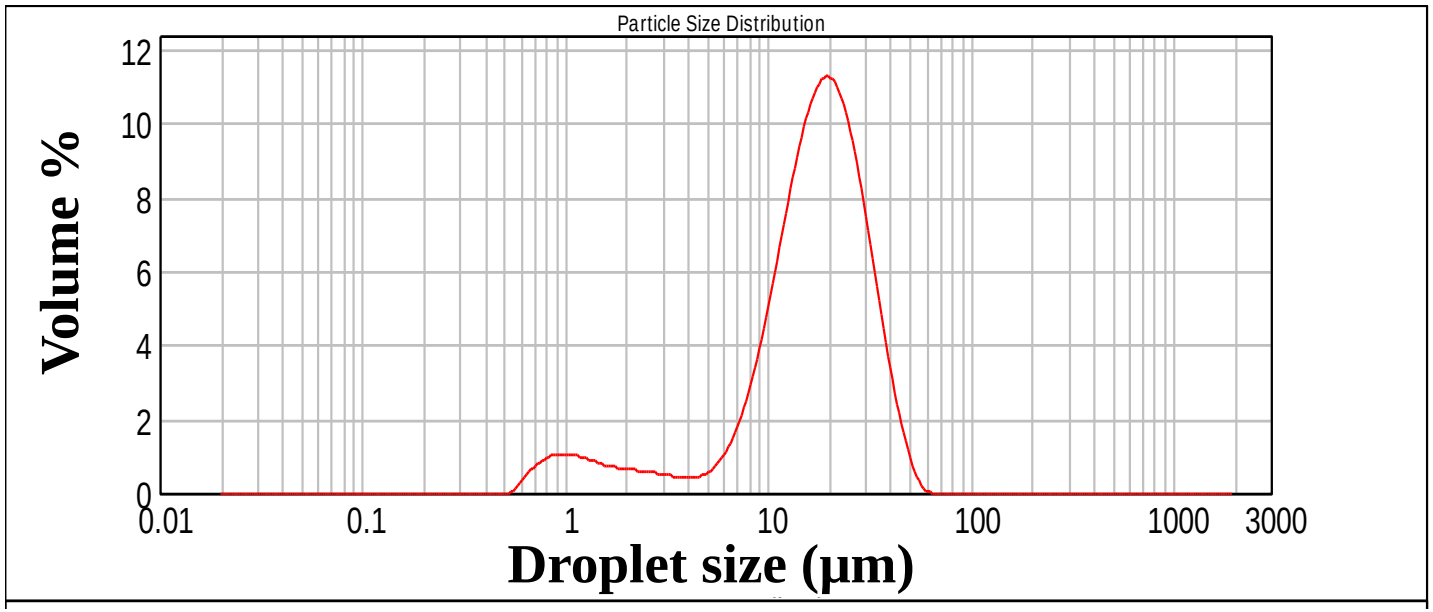


Pickering Emulsions

- Silica (aggregates)
- Membrane emulsification
- 1% silica, 20% oil

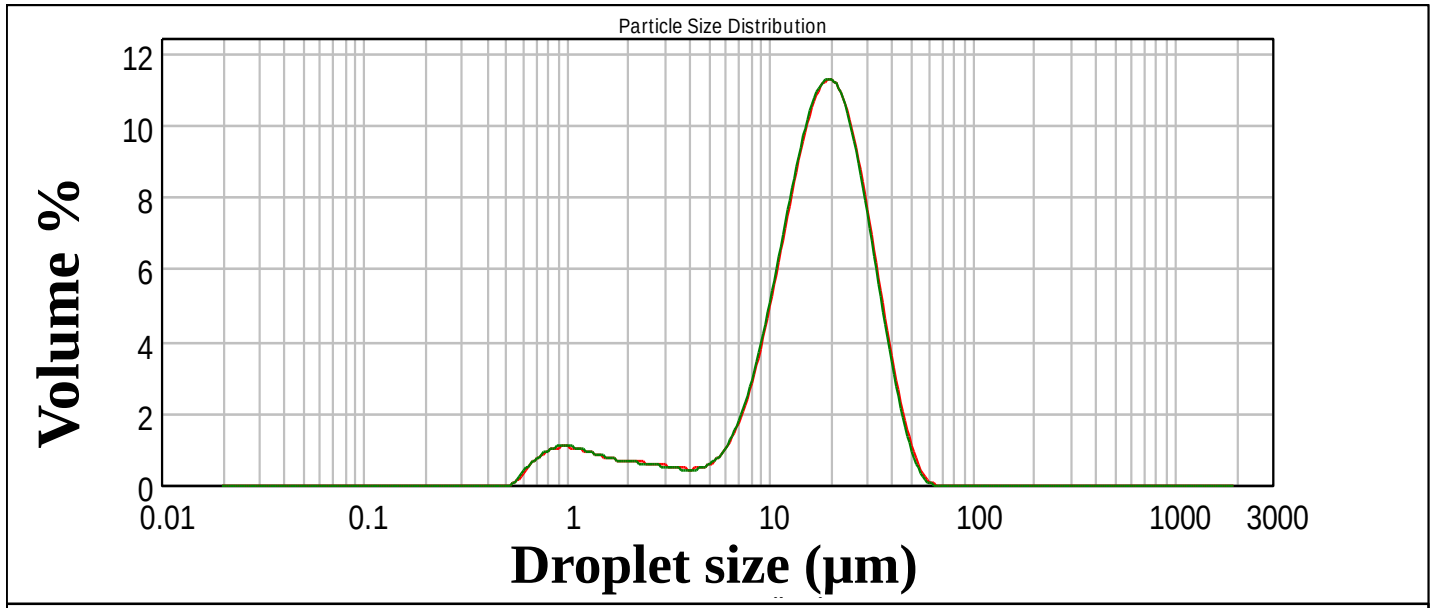
Pickering Emulsions Silica

- Droplet size distribution created



Pickering Emulsions Silica

- Stability over 7 days

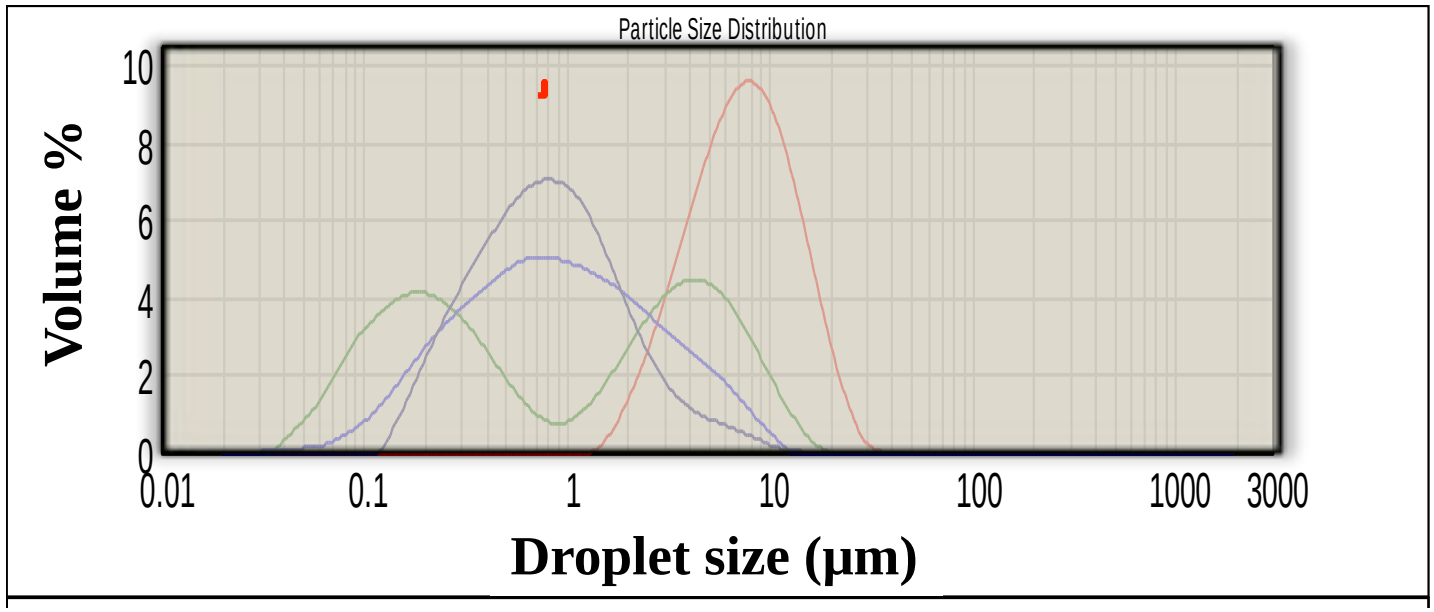


Pickering Emulsions

- Modified starch (MS) (aggregates)
- High pressure homogeniser 200 bar
- 1% starch, 20% oil

Pickering Emulsions Modified Starch

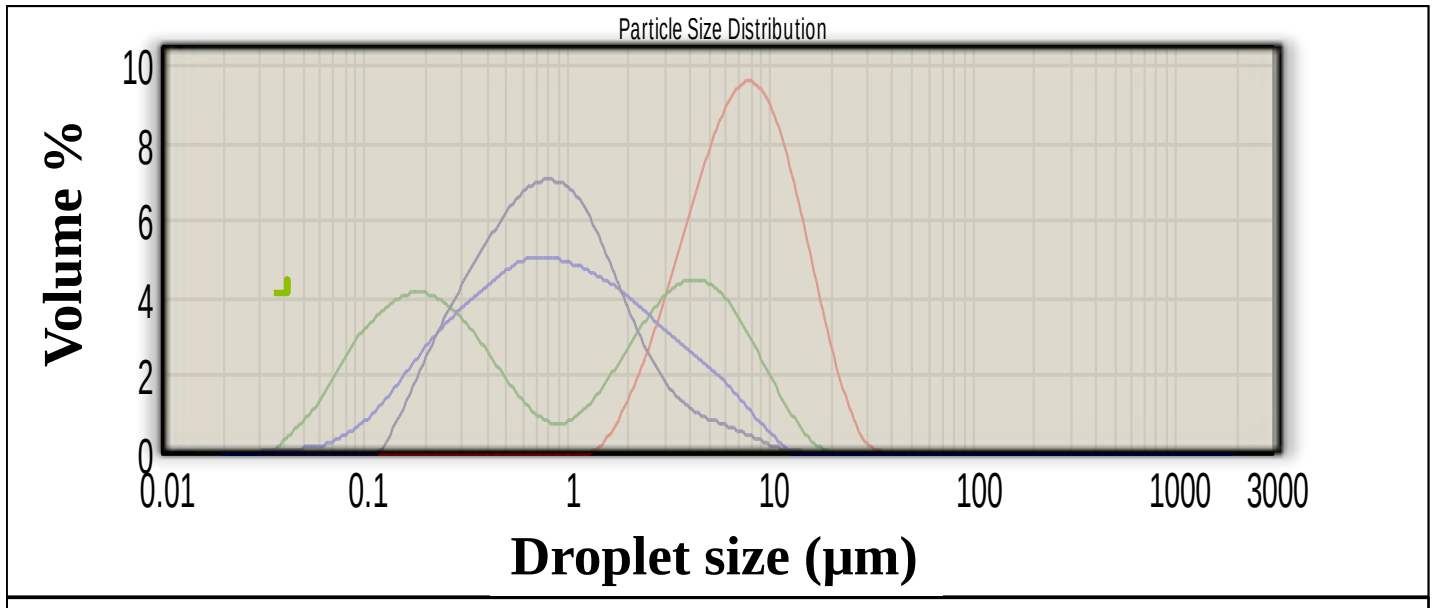
- 1% Modified starch, 20% oil – 200 bar



-- **Pass 1**

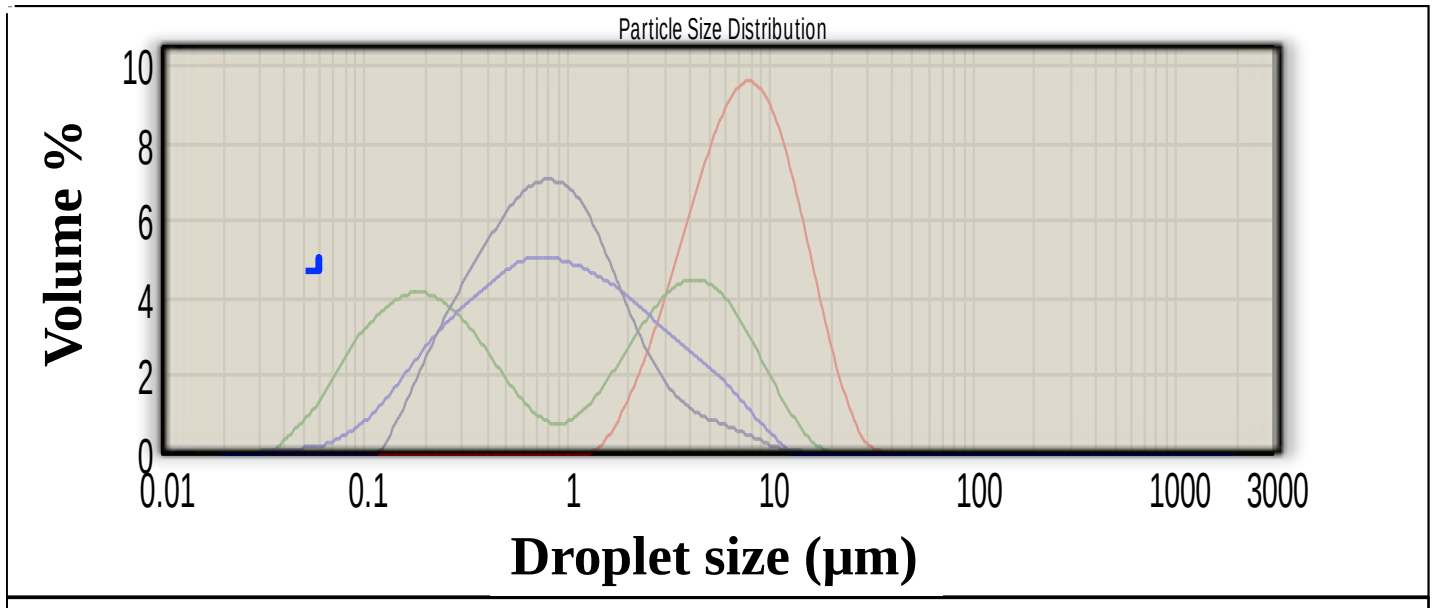
Pickering Emulsions Modified Starch

- 1% Modified starch, 20% oil – 200 bar



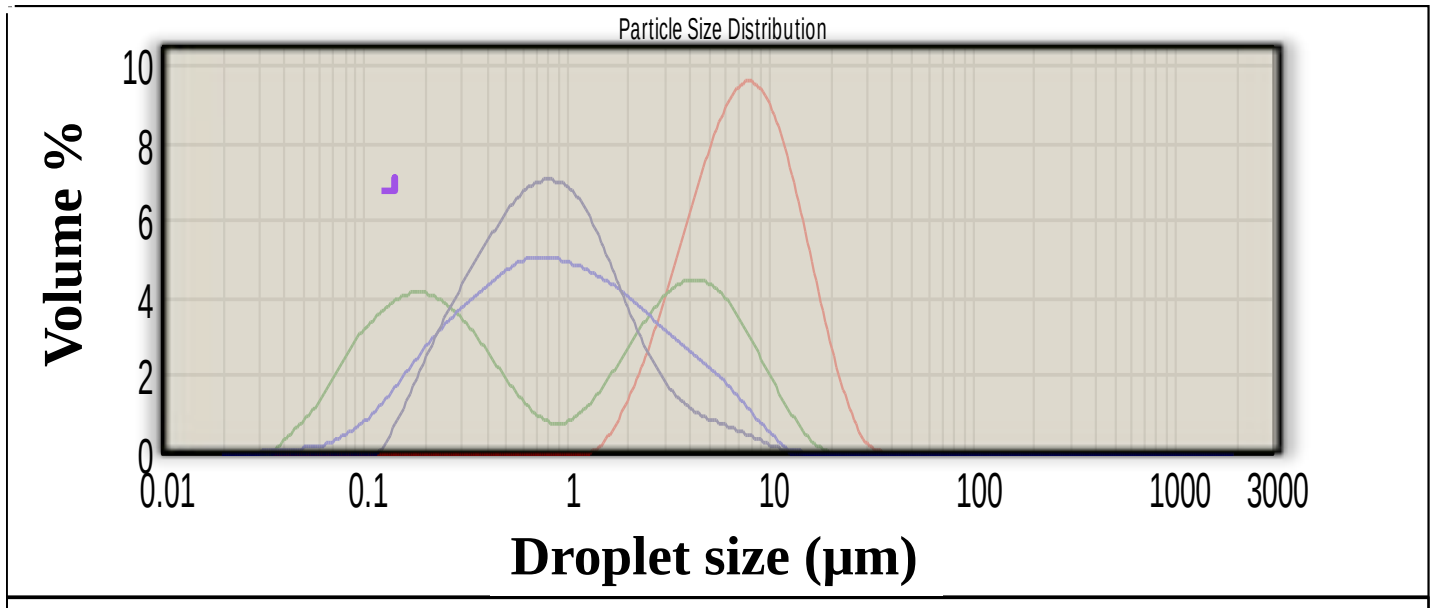
Pickering Emulsions Modified Starch

- 1% Modified starch, 20% oil – 200 bar



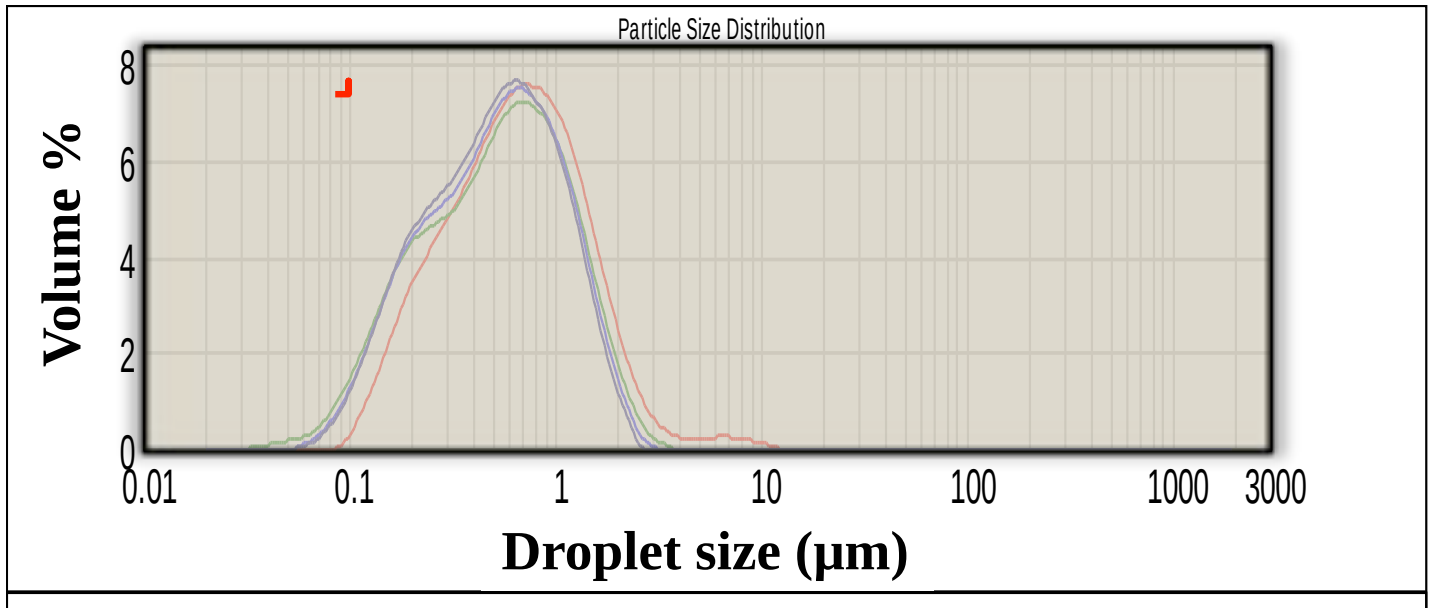
Pickering Emulsions Modified Starch

- 1% Modified starch, 20% oil – 200 bar



Pickering Emulsions Modified Starch

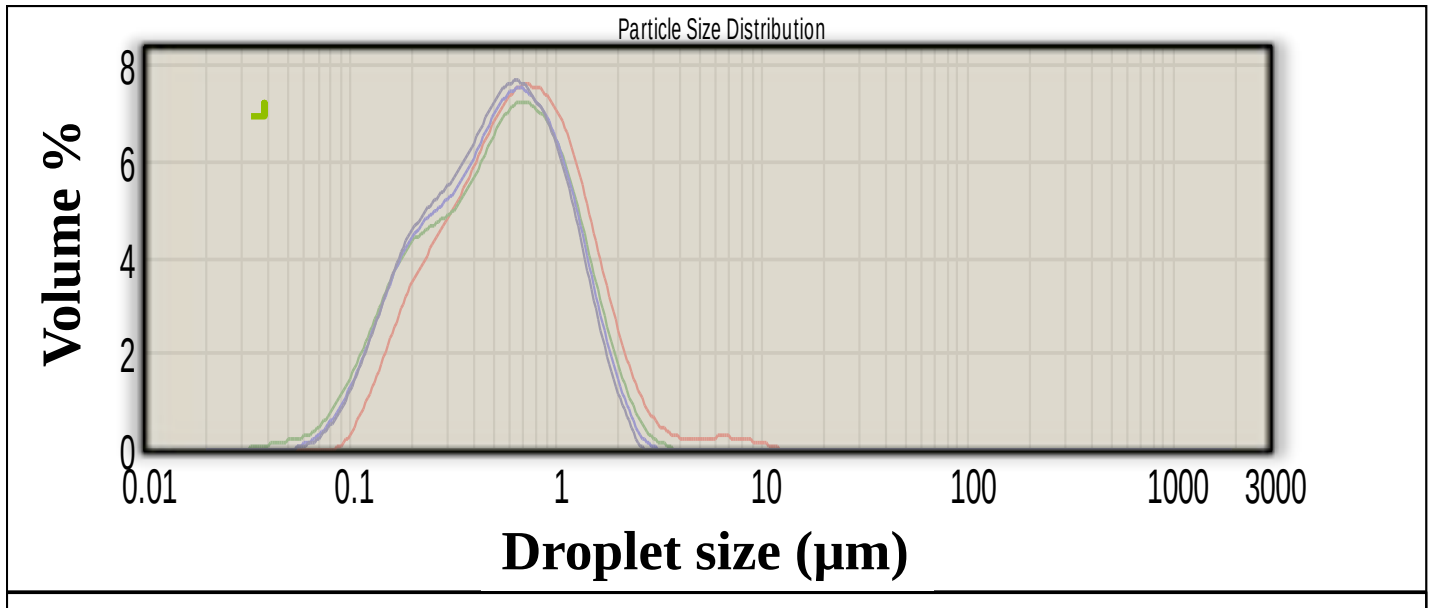
- 1% Modified starch, 20% oil – 200 bar



-- **Pass 5**

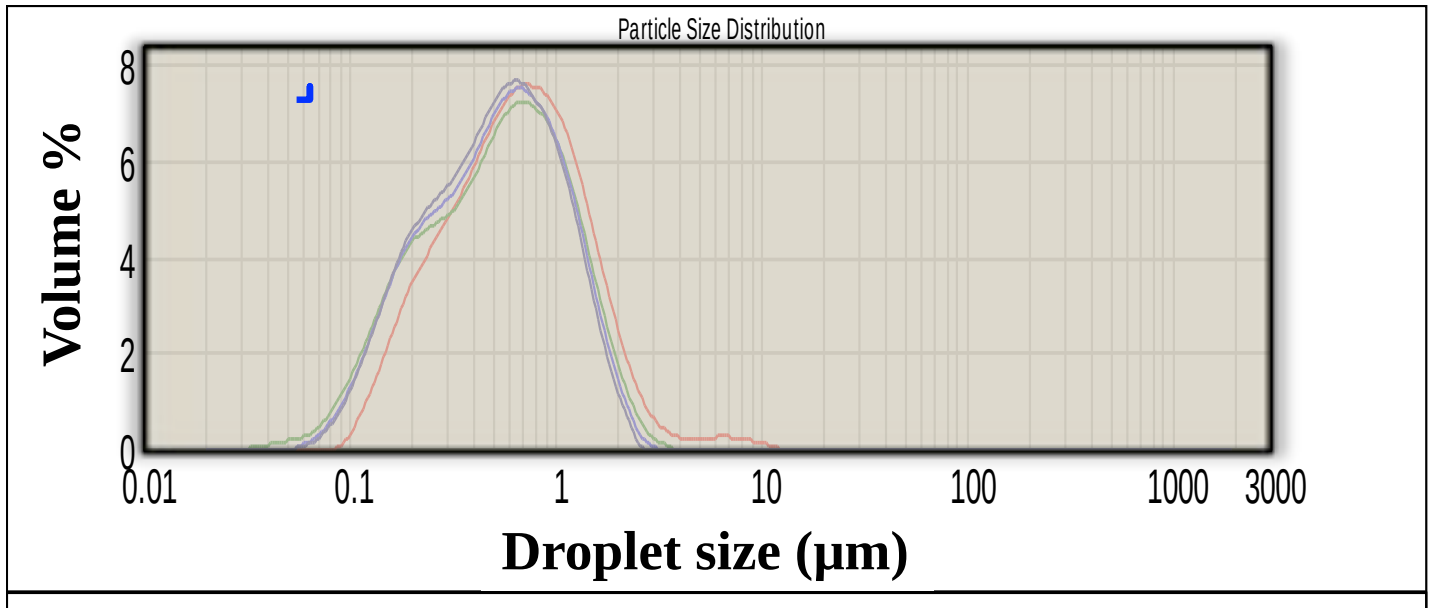
Pickering Emulsions Modified Starch

- 1% Modified starch, 20% oil – 200 bar



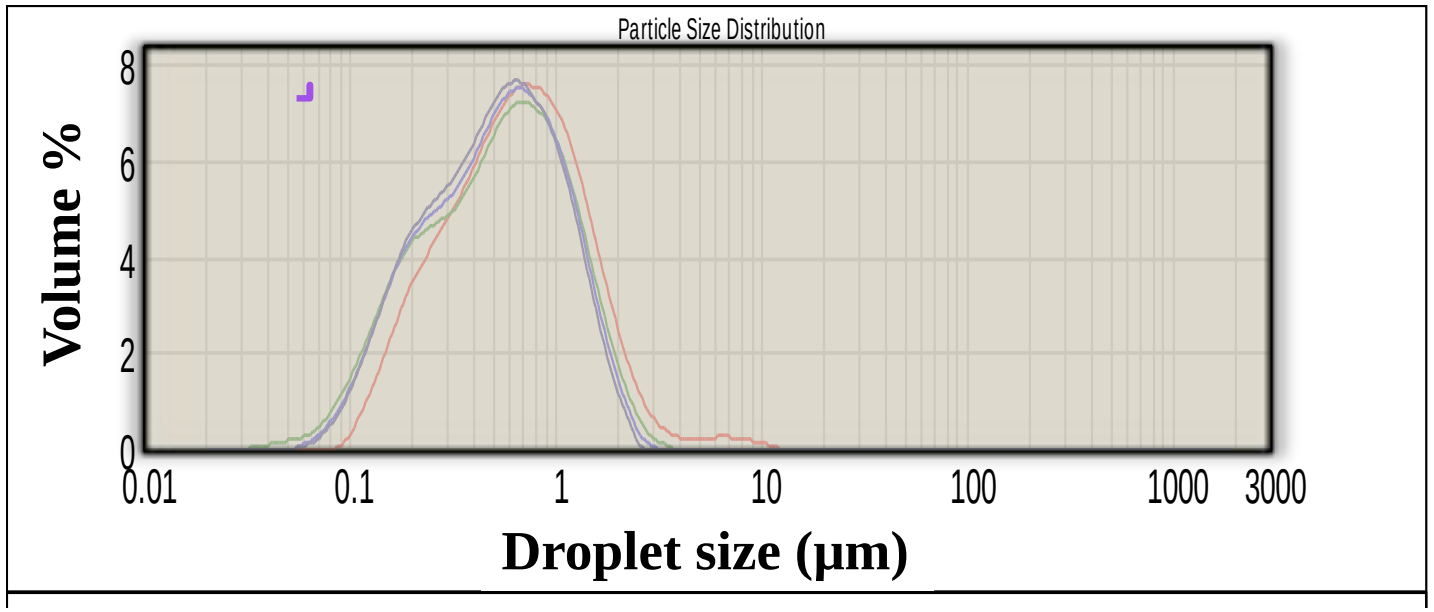
Pickering Emulsions Modified Starch

- 1% Modified starch, 20% oil – 200 bar



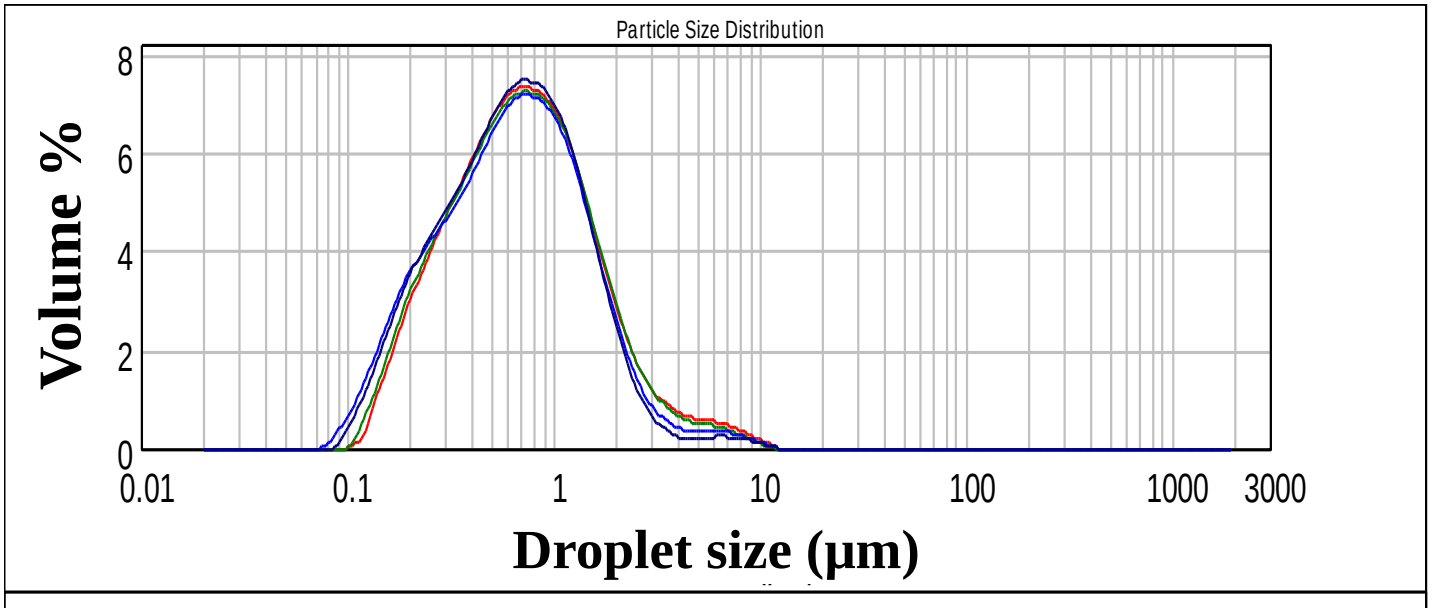
Pickering Emulsions Modified Starch

- 1% Modified starch, 20% oil – 200 bar



Pickering Emulsions Modified Starch

- Stability over 21 days

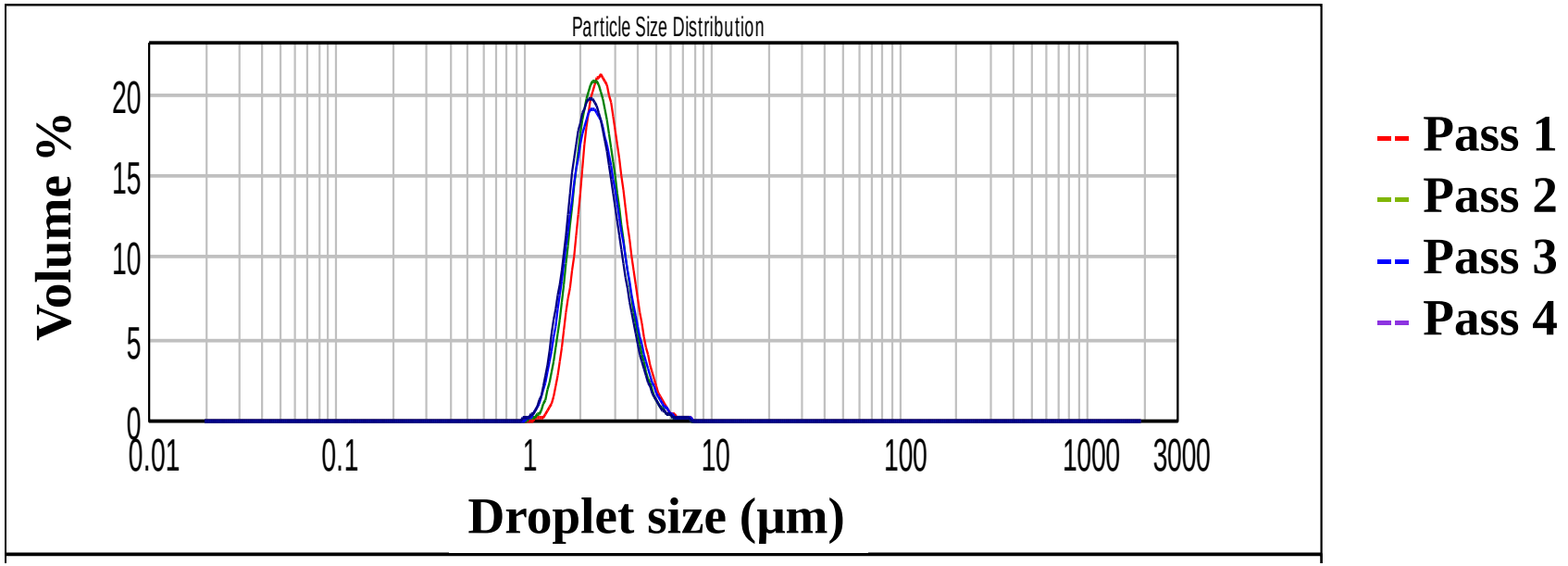


Pickering Emulsions

- Microcrystalline cellulose (MCC) (aggregates)
- High pressure homogeniser 200 bar
- 1% MCC, 20% oil

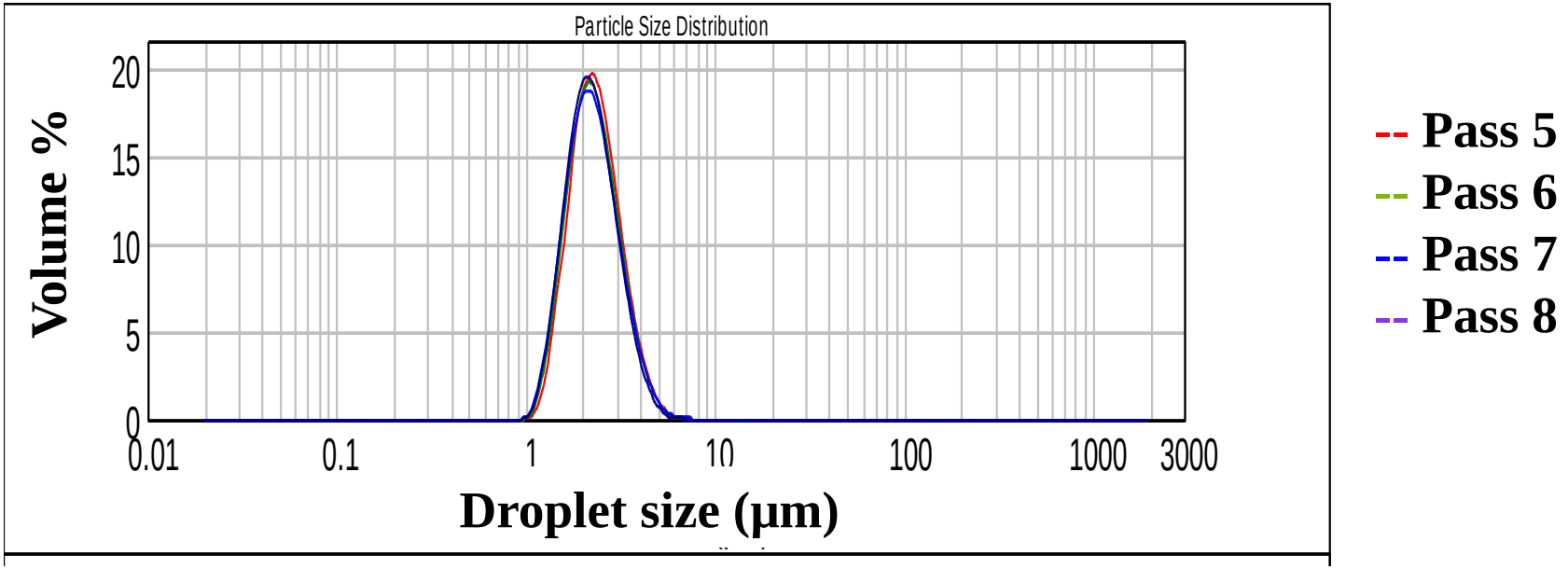
Pickering Emulsions Microcrystalline Cellulose

- 1% Microcrystalline cellulose, 20% oil



Pickering Emulsions Microcrystalline Cellulose

- 1% Microcrystalline cellulose, 20% oil



Pickering Emulsions Microcrystalline Cellulose

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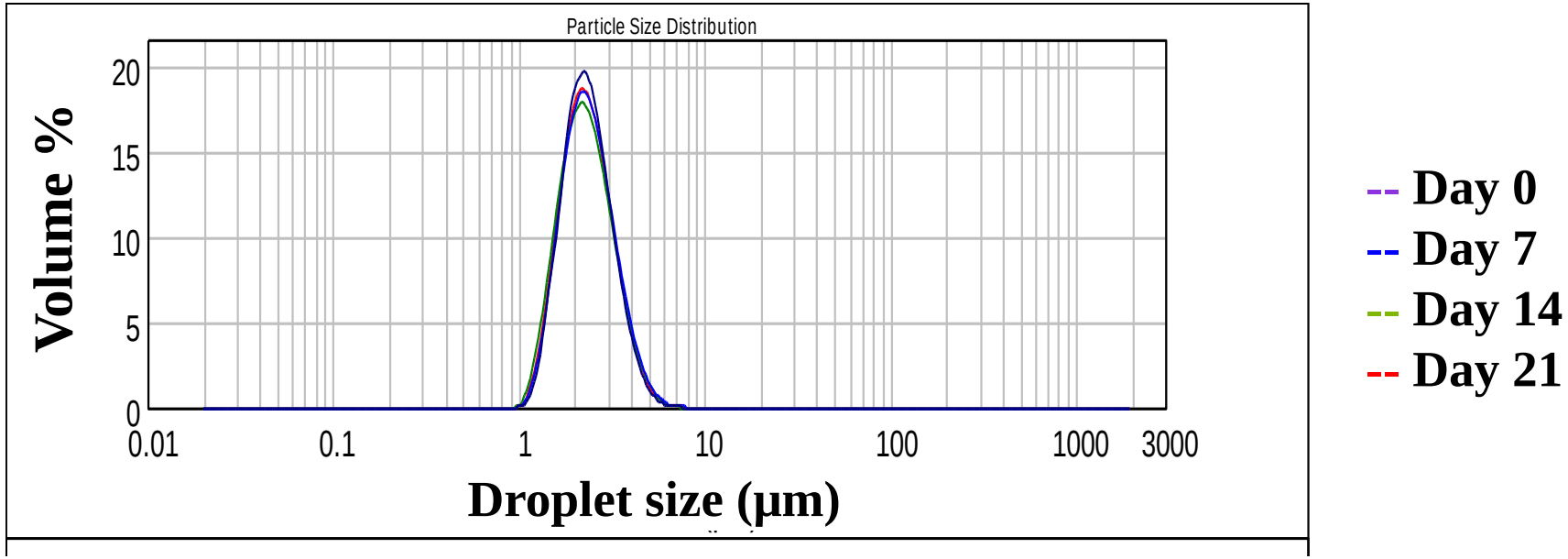


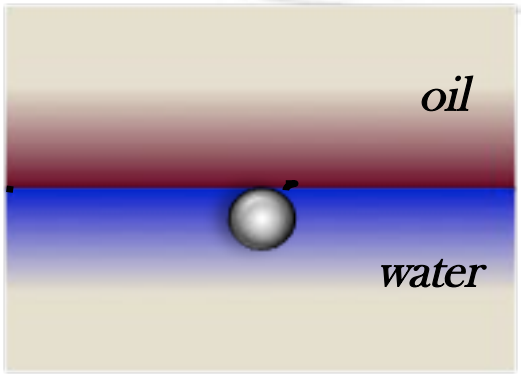
Summary

- Emulsions can be created using Pickering particles
- Particle size and properties control emulsion function
- Different processing techniques can be used
- Wettability of the particles control how they function

Overview

- Emulsions - Pickering
- Potential particles
- Mixed systems
- Applications in foods

Emulsifier or Particle Stabilised Emulsions



Emulsifiers:

- Small size (<1nm)
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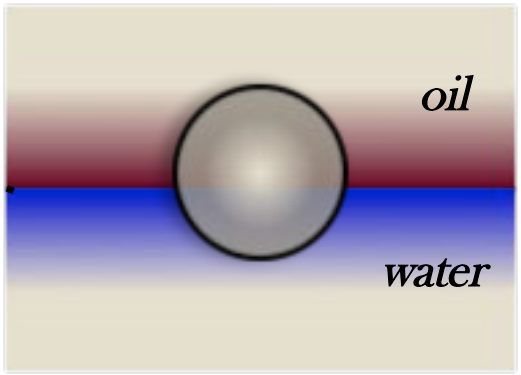


Particles:

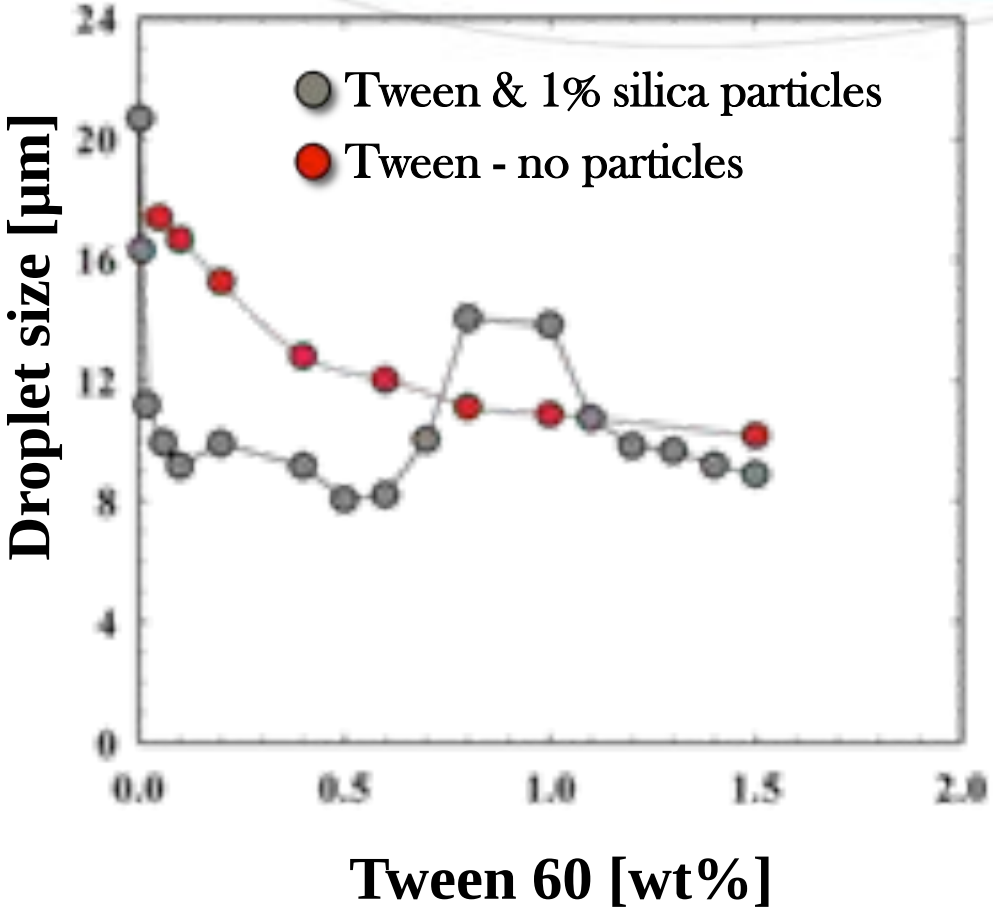
- Bigger in size (>100nm)
  - irreversibly adsorbed at the interface excellent long-term stability against coalescence
  - Detachment energy >3000kT

Emulsifier & Particle Stabilised Emulsions

- Fast adsorption at the interface (emulsifiers) but also excellent long-term stability (particles) to minimise coalescence and reduce droplet size
- Control the positioning of the particles at the interface via material functionality

Pichot R., Spyropoulos F., Norton I.T., 2009. *J. Colloid Interface Sci.*, 329, 284-291.

Emulsifier & Particle Stabilised Emulsions



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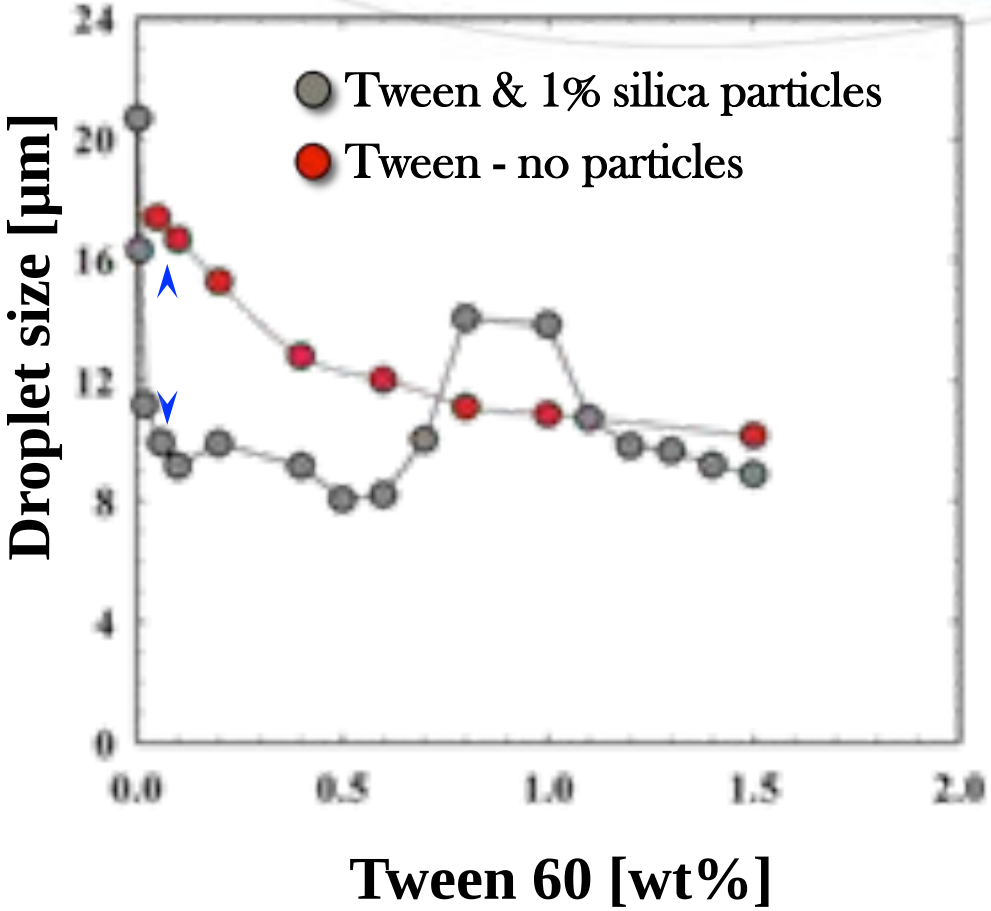
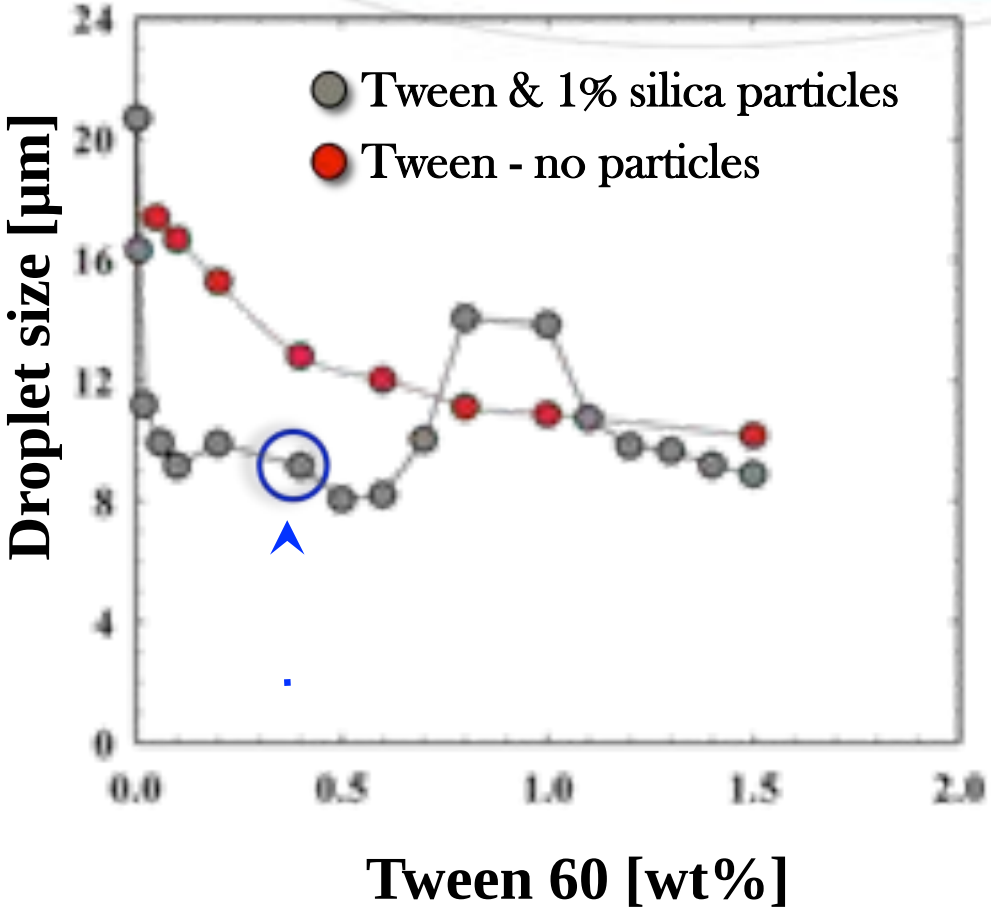


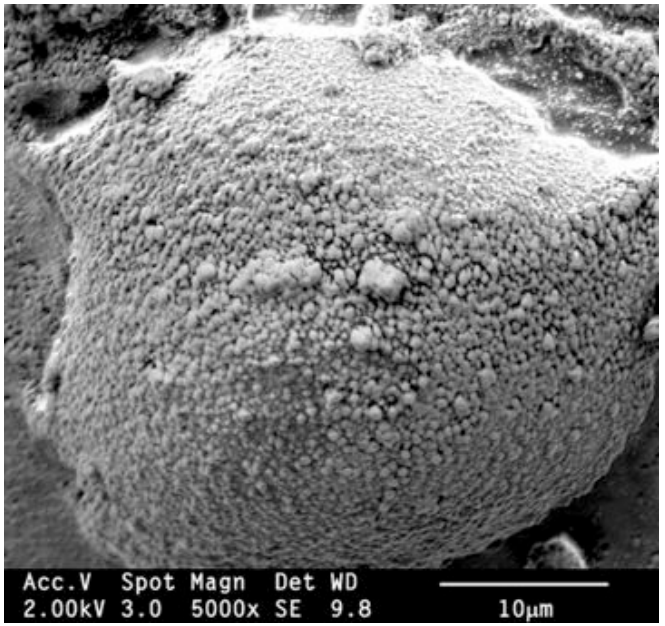
Droplet size is reduced

Pichot R., Spyropoulos F., Norton I.T., 2009. *J. Colloid Interface Sci.*, 329, 284-291.

Emulsifier & Particle Stabilised Emulsions



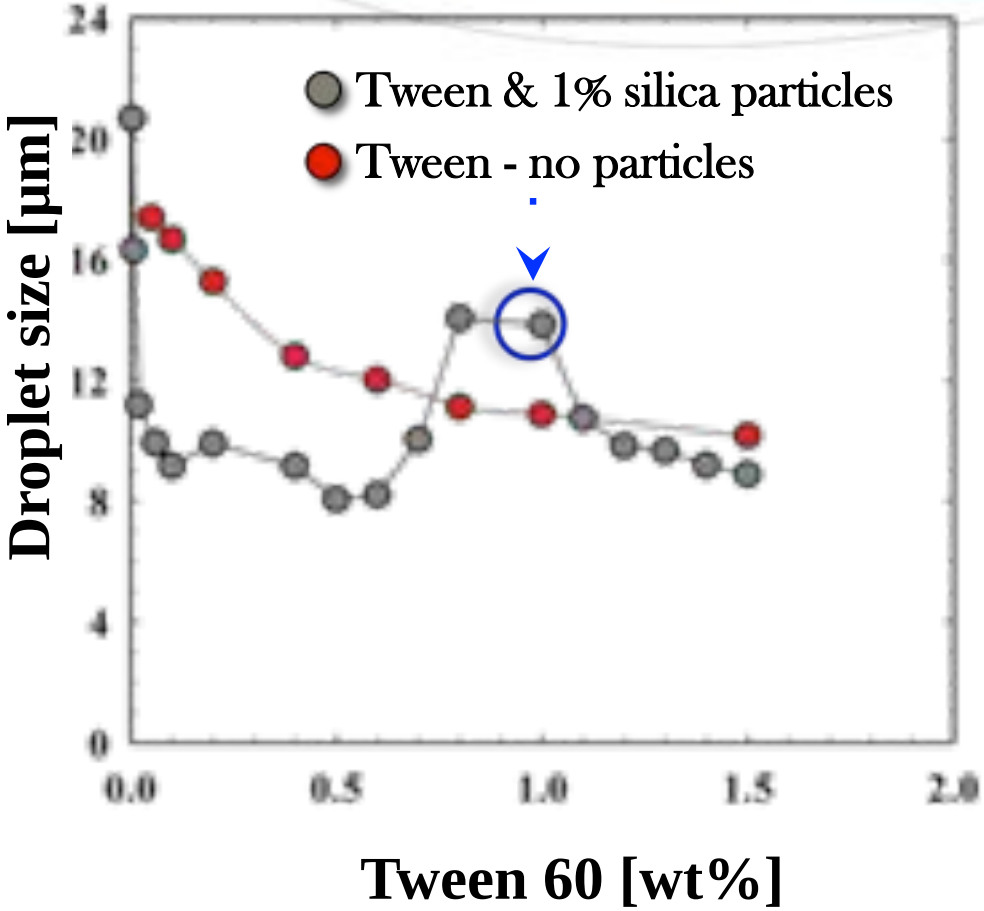
0.4wt% Tween & 1wt% particles



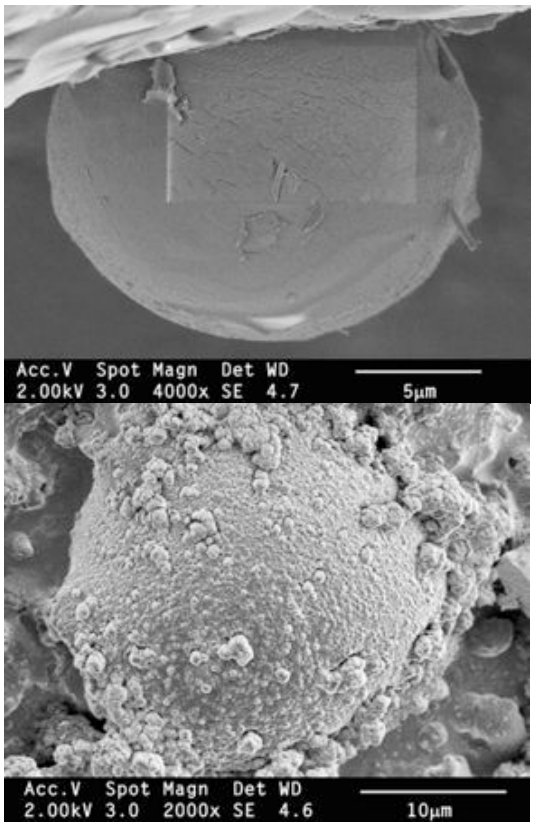
Particle positioning is controlled

Pichot R., Spyropoulos F., Norton I.T., 2009. *J. Colloid Interface Sci.*, 329, 284-291.

Emulsifier & Particle Stabilised Emulsions



1wt% Tween & 1wt% particles



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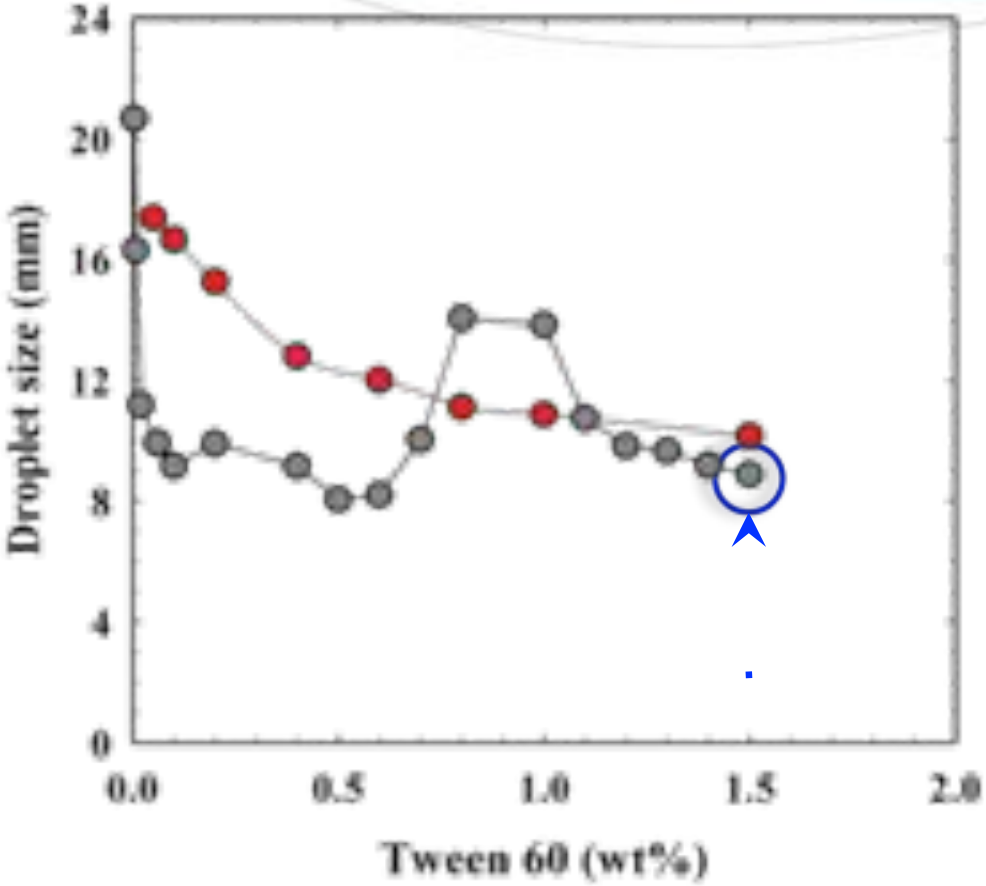
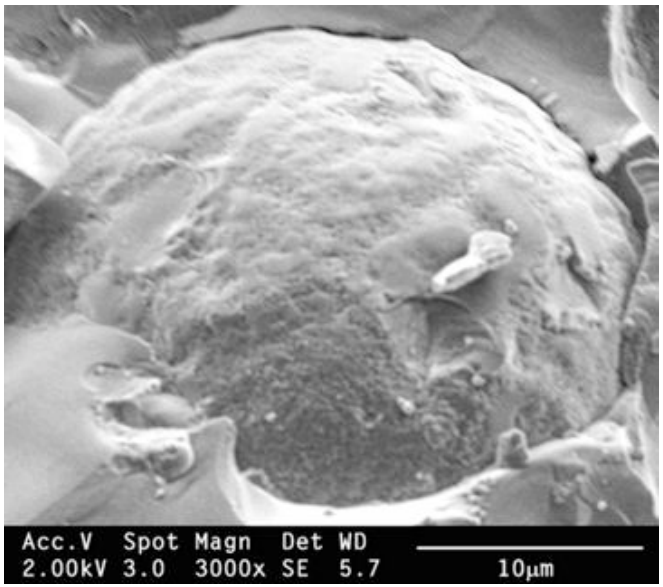
Emulsifier & Particle Stabilised Emulsions



1.5wt% Tween & 1wt% particles



Pichot R., Spyropoulos F., Norton I.T., 2009. *J. Colloid Interface Sci.*, 329, 284-291.

Overview

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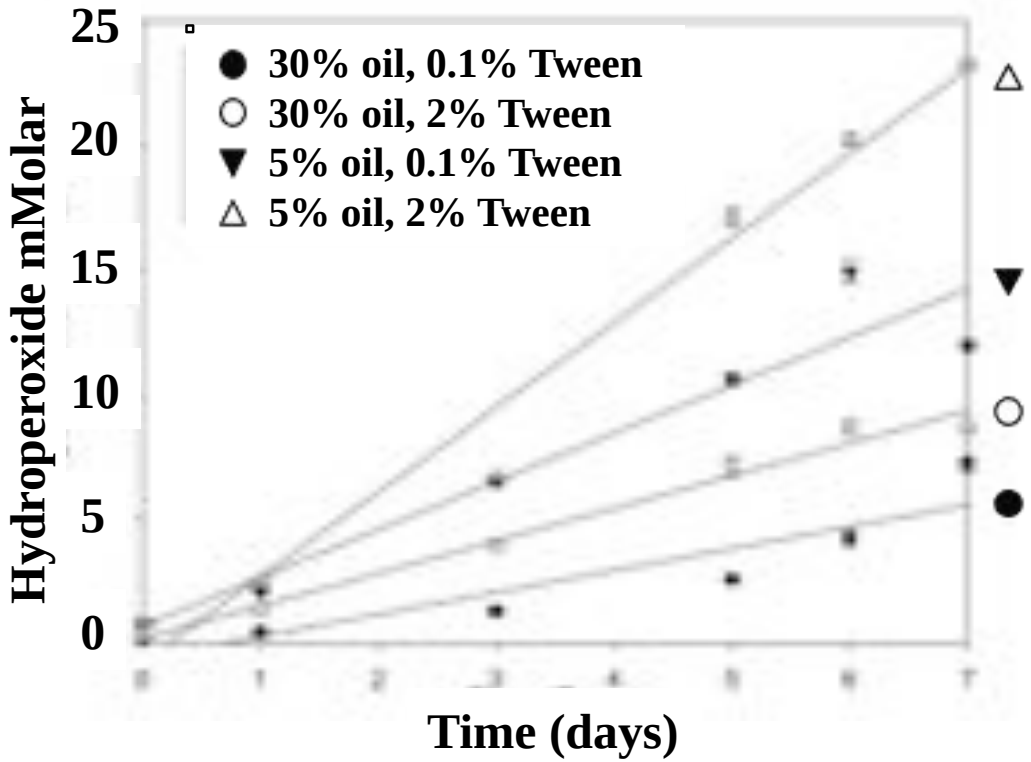
- Potential particles
- Mixed systems
- Applications in foods

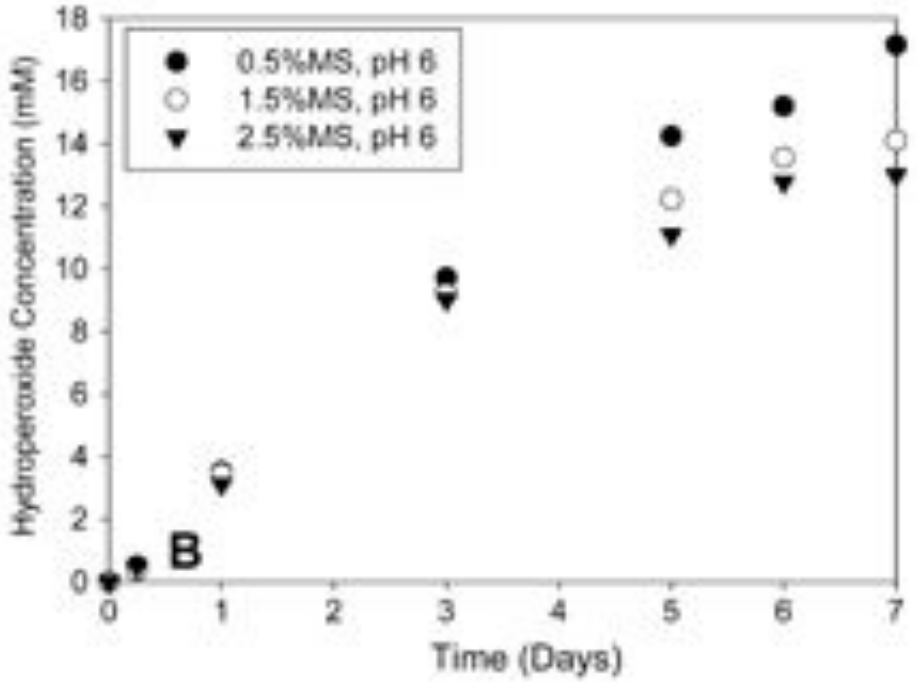
Lipid Oxidation

- Pickering to control oxidation of lipids



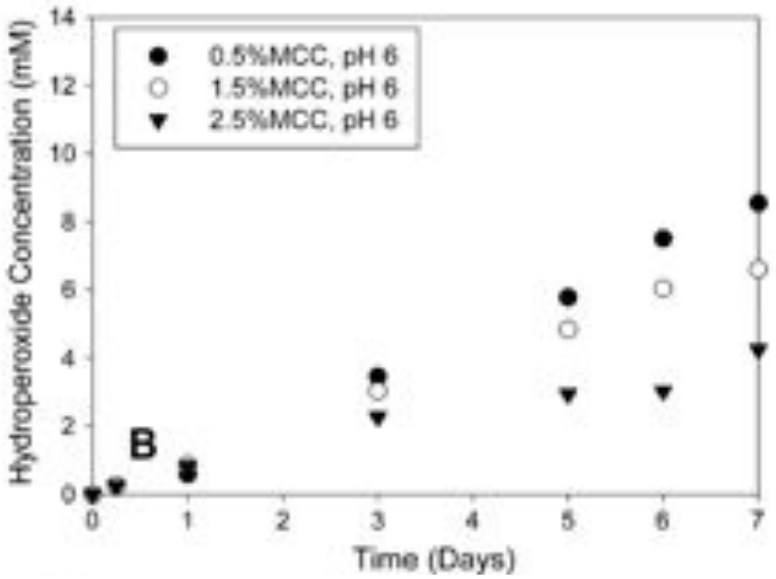
Lipid Oxidation

- Particles can prevent oxidation by forming a physical barrier
  - Modified starch can be used for this purpose



Lipid Oxidation

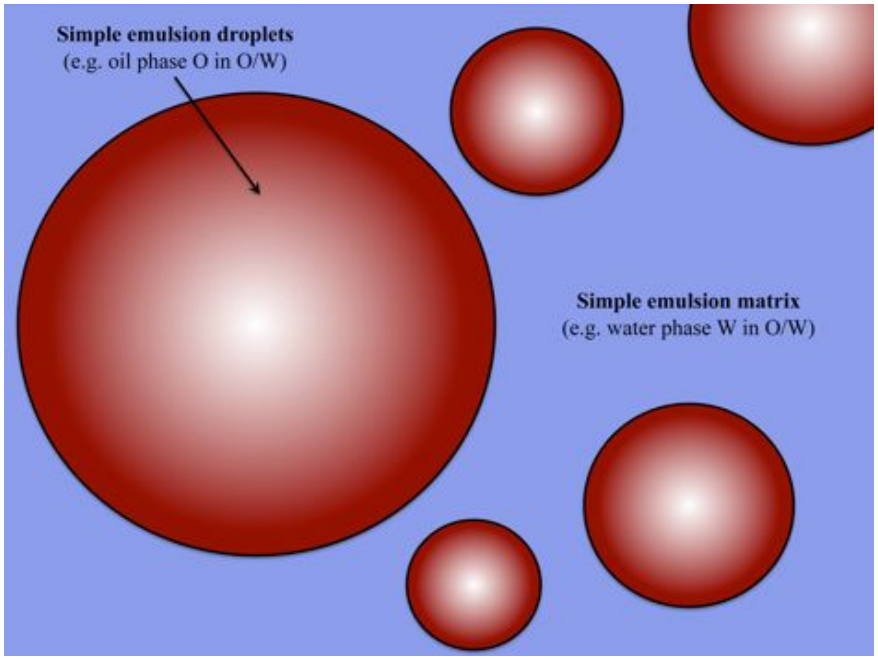
- MCC further prevents oxidation
  - Thicker interfacial layer (415nm particles vs. 120nm for MS)
  - Charged particles scavenge excess free radicals

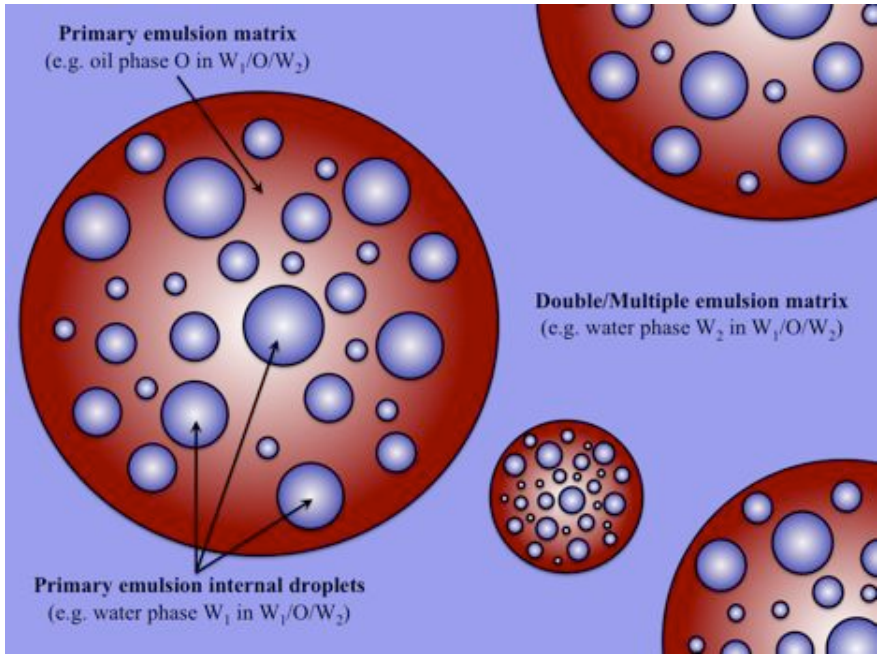


Kargar, M., F. Spyropoulos and I. T. Norton (2011). Procedia Food Science **1**(0): 104-108.

Double Emulsions

- Take mayonnaise: a high fat oil/water emulsion
- Replace some of the fat with water droplets to create a w/o/w, or double emulsion





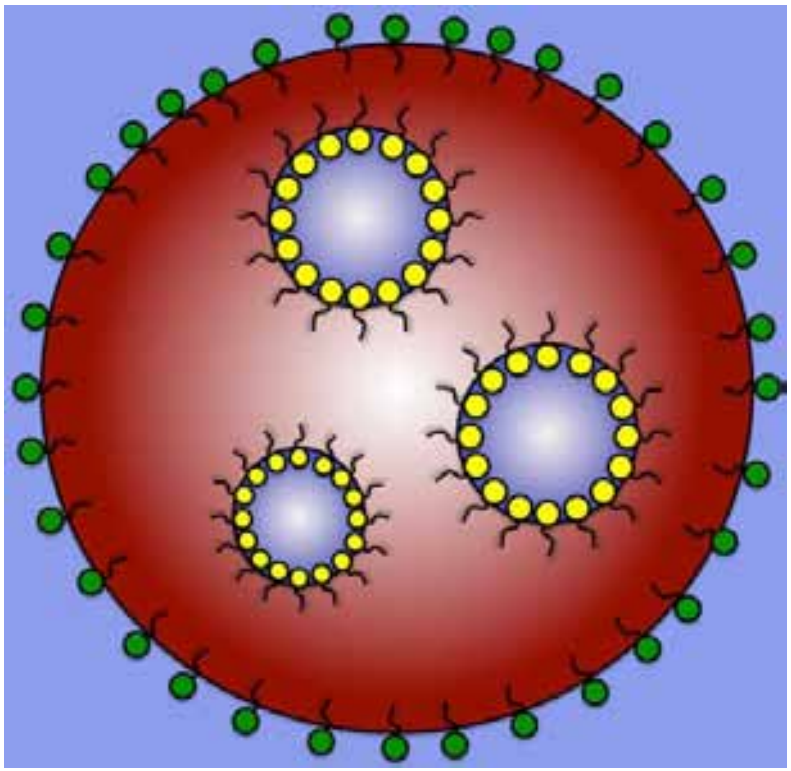
Stability vs. Instability

- Double emulsions are inherently thermodynamically unstable
- The reasons:
  - Physical Instabilities – primarily due to surfactant/emulsifier choice, but also due to production method, properties of oil and/or aqueous phases

Pays *et al.*, 2002; Mezzenga *et al.*, 2004

Stability vs. Instability

- Poor Stability:
  - Two oppositely curved interfaces
  - Two surfactant species (one lipophilic, one hydrophilic)

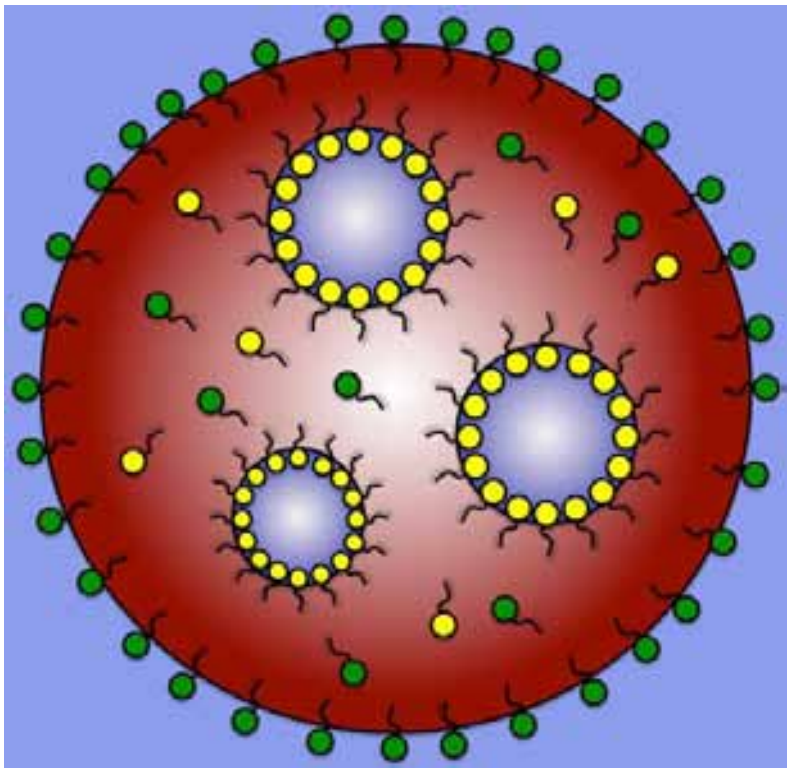


Lipophilic emulsifier

Hydrophilic emulsifier

Stability vs. Instability

- Poor Stability:
  - These tend to diffuse from one to the other

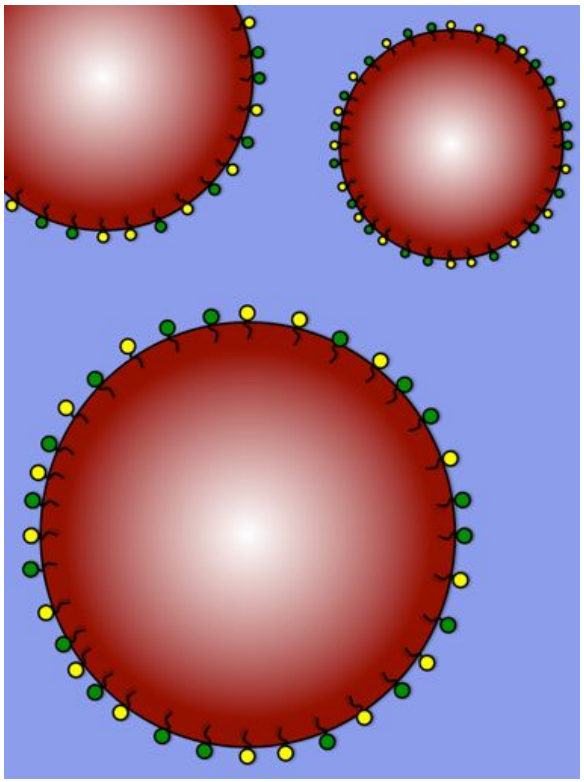


Lipophilic emulsifier

Hydrophilic emulsifier

Stability vs. Instability

- Poor Stability:
  - Double structure collapses



Lipophilic emulsifier

Hydrophilic emulsifier

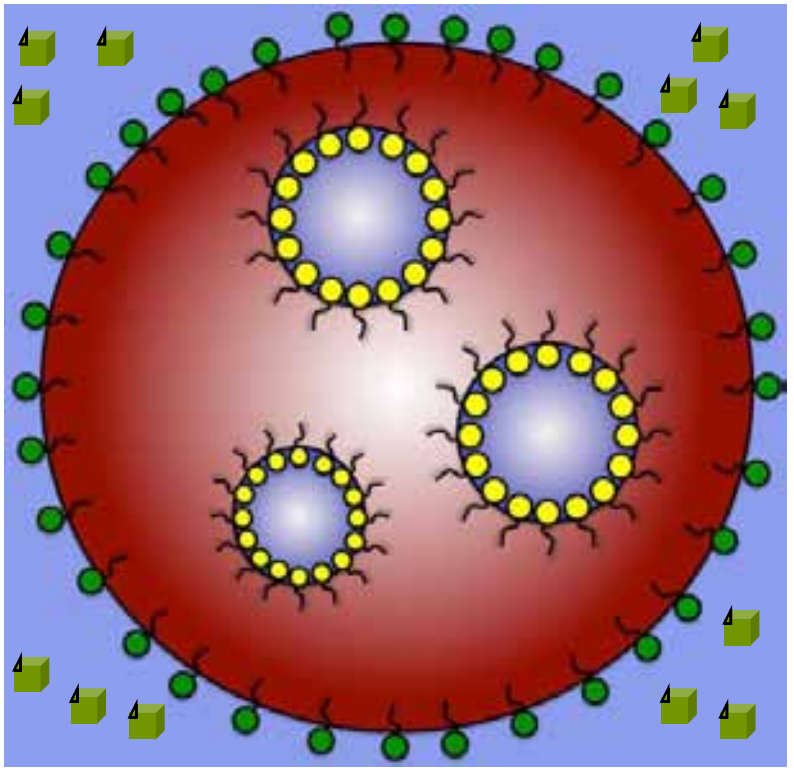
Stability vs. Instability

- Double emulsions are inherently thermodynamically unstable
- The reasons:
  - Physical Instabilities – primarily due to surfactant/emulsifier choice, but also due to production method, properties of oil and/or aqueous phases
  - Osmotic pressure difference between the two aqueous phases (in w/o/w) – due to presence of ionic species

Pays *et al.*, 2002; Mezzenga *et al.*, 2004

Stability vs. Instability

- The presence of small molecular species in one of the two aqueous reservoirs makes stabilisation of these structures even more difficult



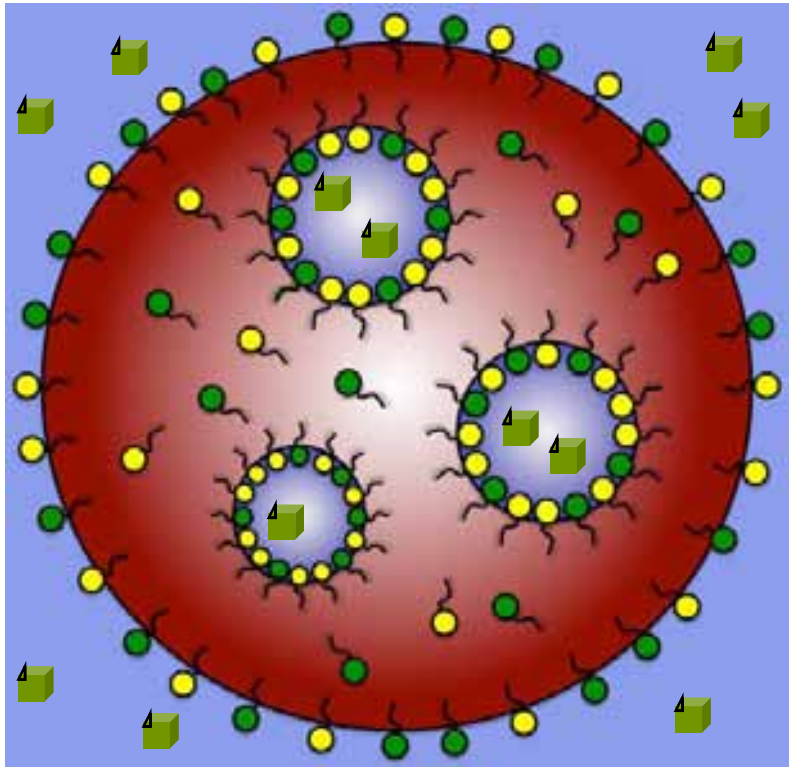
Small molecule (e.g. salt)

Lipophilic emulsifier

Hydrophilic emulsifier

Stability vs. Instability

- Osmotic pressure difference leads to swelling or shrinkage of the internal water droplets.



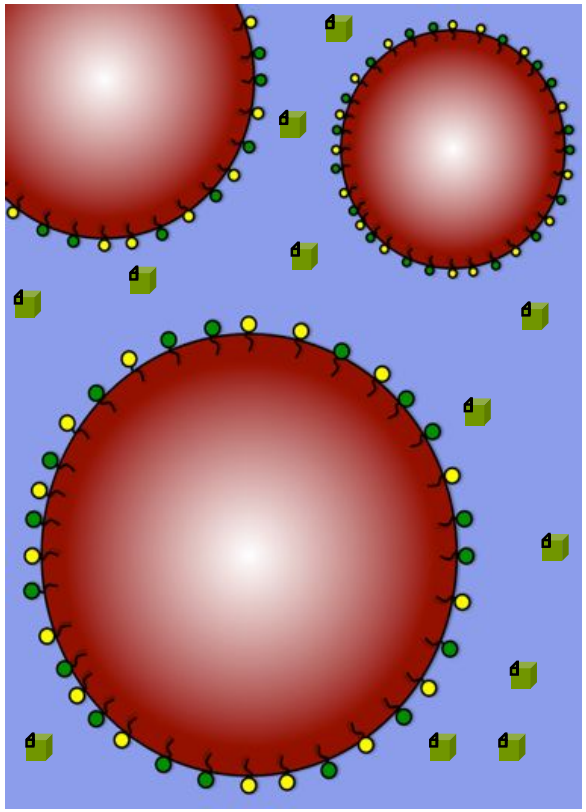
Small molecule (e.g. salt)

Lipophilic emulsifier

Hydrophilic emulsifier

Stability vs. Instability

- Eventually again the structure collapses



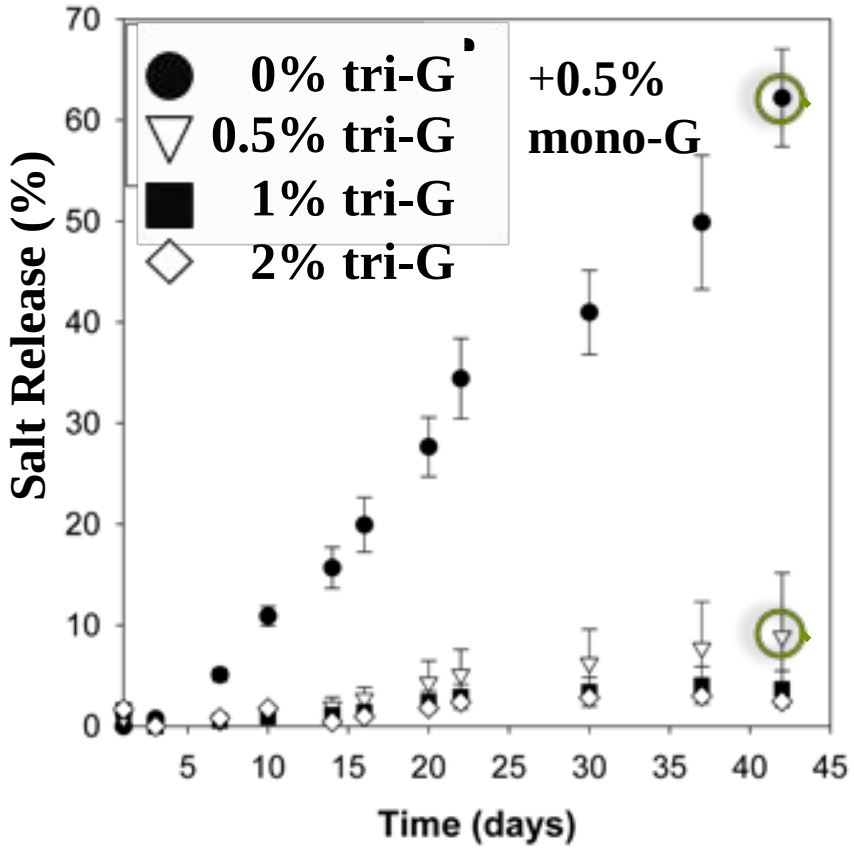
Small molecule (e.g. salt)

Lipophilic emulsifier

Hydrophilic emulsifier

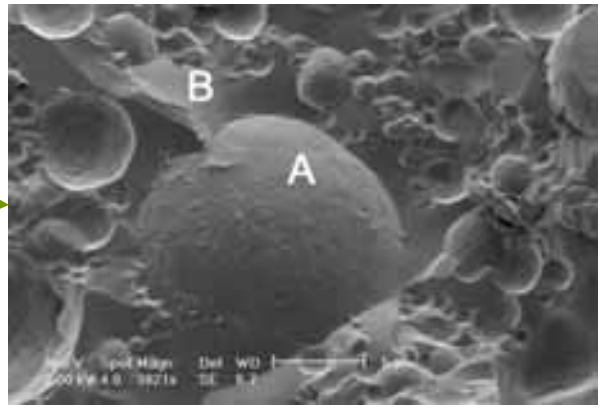
Pickering Stabilised w/o emulsions

@ 22°C



0.5% mono-G only

0.5% mono-G and 1% tri-G



Pickering Stabilised w/o emulsions

- The use of fat crystals can give extremely stable w/o Pickering emulsions
- These fat crystals initially sit at the interface and then sinter into solid shells physically preventing movement of salt
- Salt release can be triggered by temperature if the fat shell is melted

Frasch-Melnik, S., I. T. Norton and F. Spyropoulos (2010). Journal of Food Engineering **98**(4): 437-442.

Double Emulsion Production

Primary Emulsion, 10% containing KCl

+

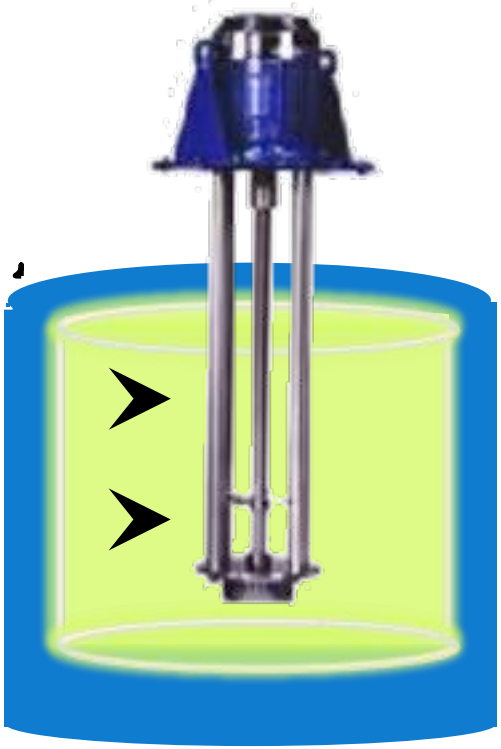
Sunflower Oil, 10%

NaCl or Glucose, Sodium Caseinate or particles (e.g. silica)

+

Aqueous Phase, 80%

High shear mixer



Ice Bath

Stability Against Coalescence

- 1% sodium caseinate as external stabiliser

Oil Droplet size (μm)

Δπ (atm)	Δπ regulated by	After production	6 weeks
5.5	glucose	27.1 ± 9.1	40.7 ± 10.3
0	glucose	23.0 ± 7.9	46.4 ± 14.3
-11	glucose	25.0 ± 8.3	32.4 ± 9.6
5.5	NaCl	31.5 ± 10.3	44.5 ± 13.5
0	NaCl	25.1 ± 8.5	43.8 ± 12.4
-11	NaCl	31.3 ± 9.8	37.3 ± 11.5

Stability Against Coalescence

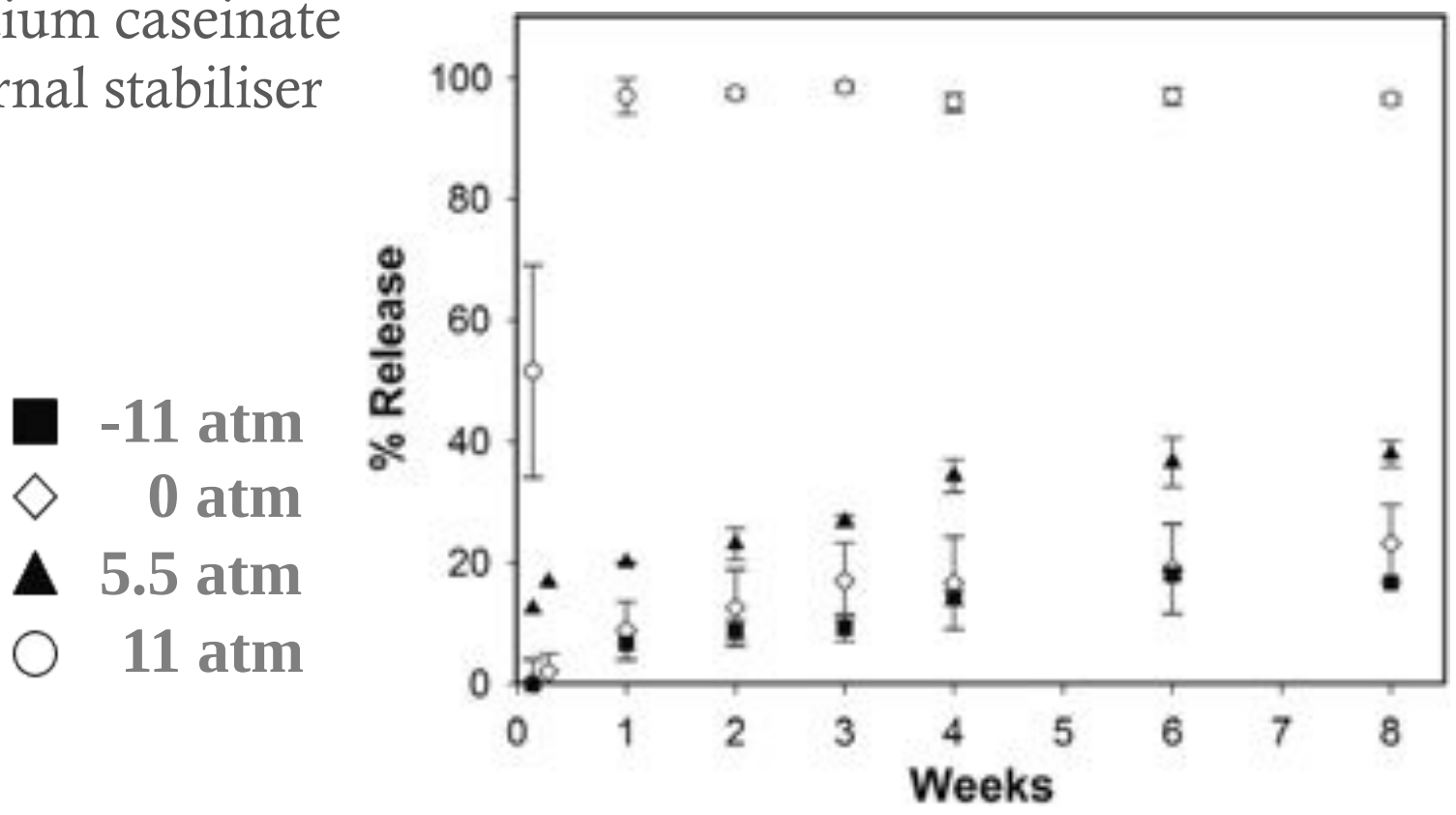
- 1% sodium caseinate as external stabiliser

Internal water droplet size (µm)

Δπ (atm)	Δπ regulated by	After production	6 weeks
11	-	5.7 ± 1.7	12.9 ± 3.2
5.5	glucose	2.8 ± 0.8	9.6 ± 2.1
0	glucose	2.4 ± 0.7	2.2 ± 0.6
-11	glucose	2.1 ± 0.6	2.7 ± 0.7

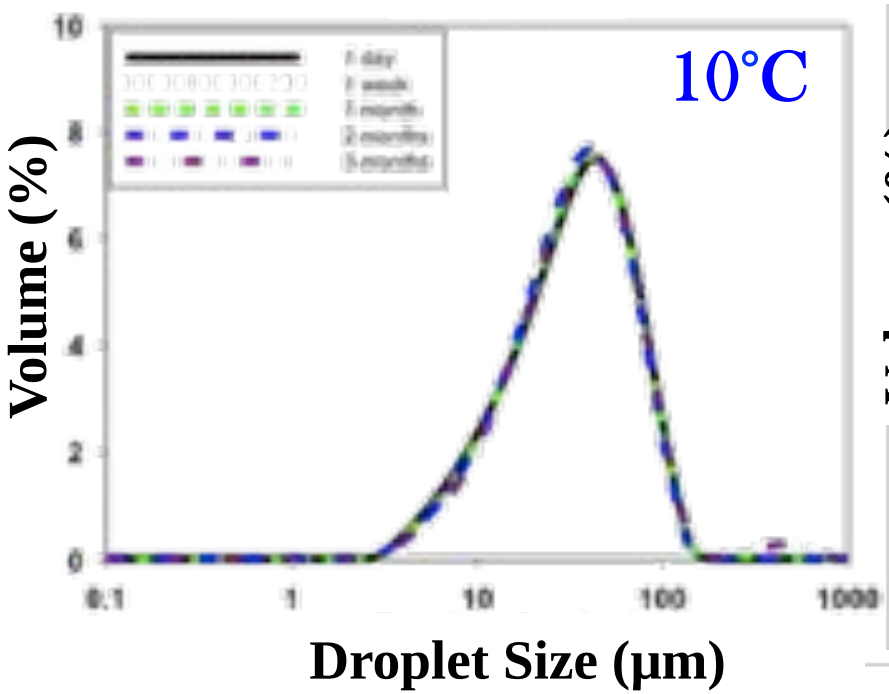
Stability Against Coalescence

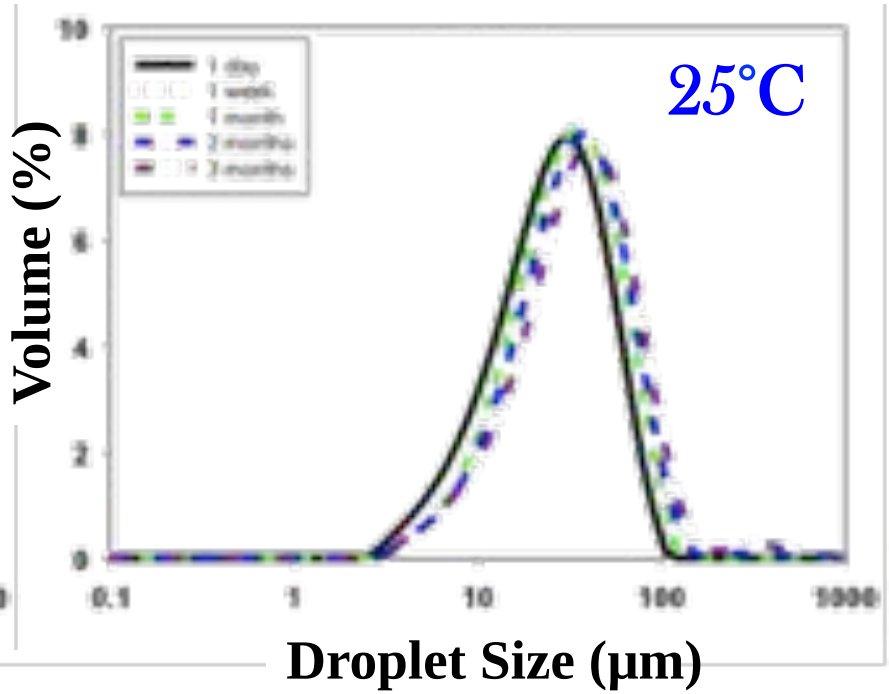
- 1% sodium caseinate as external stabiliser



Stability Against Coalescence

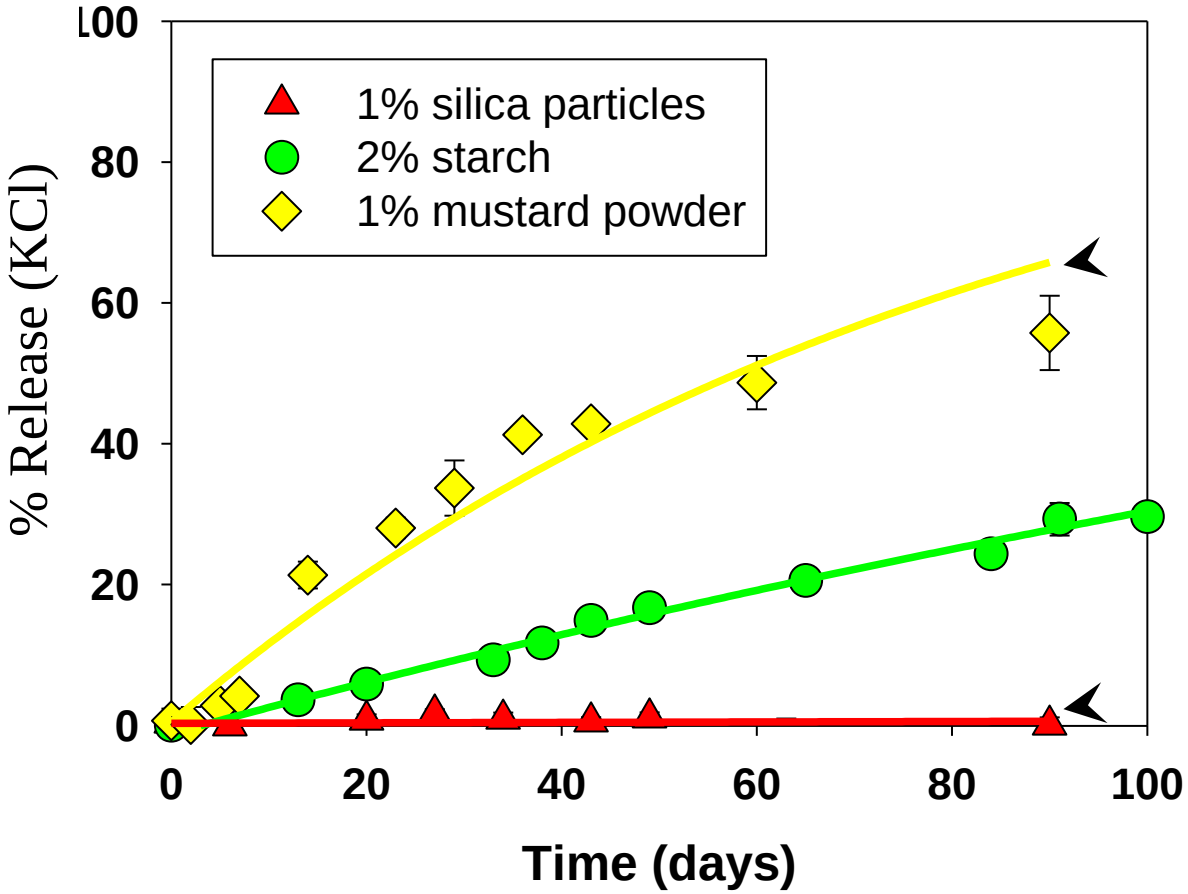
- 1% silica particles as external stabiliser – Oil droplet size





- Stable against coalescence for >3 months at 10°C
- Good stability also at 25°C

Salt Release at 10°C



- Even the least stable formulation retains 50% salt after 2 months storage
- Minimum salt release

Concluding remarks

- Some shells are damaged during the second emulsification step
- When silica particles are placed on the secondary interface, these help to prevent any salt release.
- A “milder” less shear intensive emulsification process is needed for the second emulsification step.
- Designer food grade Pickering particles would be nice as well !

End

- Thank you - Questions