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Understanding the role of processing and formulation on RBW oleogel microstructure

Vincenzo di Bari



1. World innovation trends for lipids
2. Oil structuring strategies:
 - TAGs: Fats
 - Non-TAGs: Oleogels
3. Formulation of RBW oleogels:
 - Understanding the thermomechanical behaviour
 - Engineering RBW oleogels
4. Key features of wax oleogels research

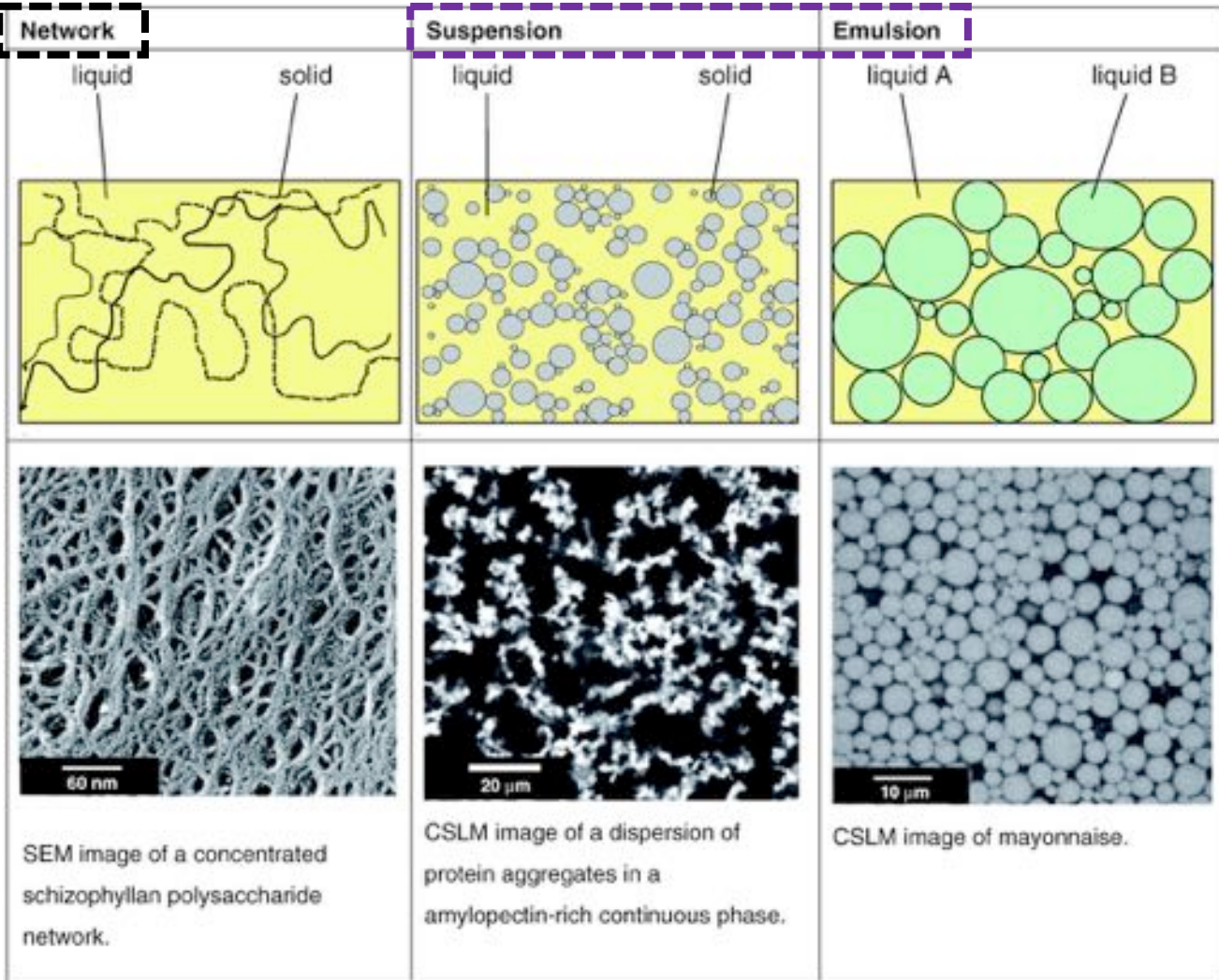
1. World innovation trends for lipids

Trend	Driver
Reduction in <i>trans</i> - & saturated ($\leq 10\%$) fats	Nutrition – health
Reduction in chemically modified oils	Nutrition – health Natural
Reduction in animal fats	Nutrition – health Choices Sustainability
Reduction in palm oil and fats in general	Sustainability Nutrition – health
Increase in PUFA content	Nutrition – health Natural

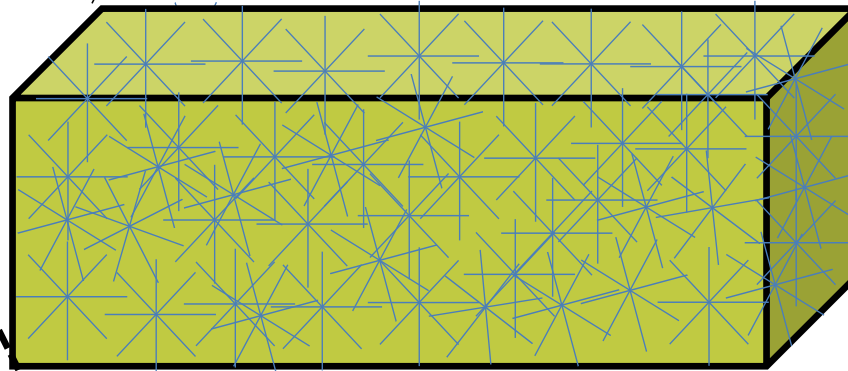
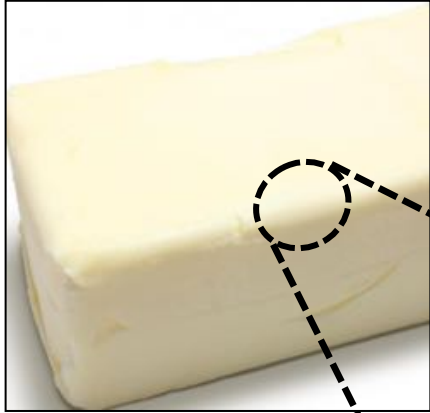


2. Edible oil structuring strategies

Molecular mechanisms



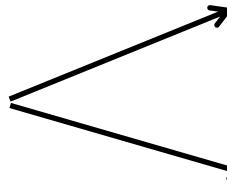
Particles dispersion



Traditional: TAGs
Fats

Novel: Non-TAGs
Oleogels

Solid structure = $f(\text{building blocks})$



Fats: complex hierarchical structure of TAGs

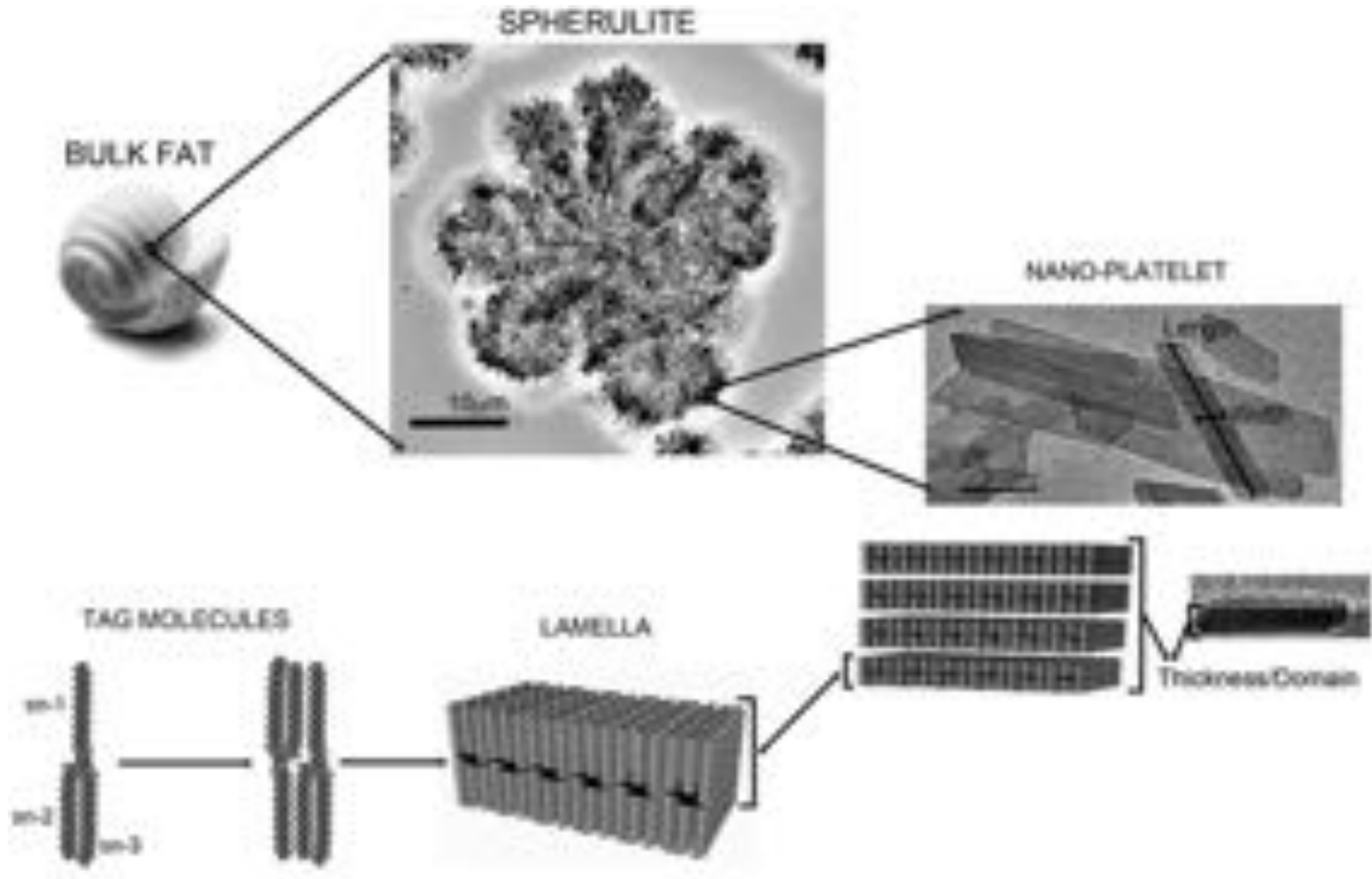


Image taken from “Structure and functionality of edible fats”, Marangoni *et al.* *Soft Matter*, 2012, 8, 1275.



Non-TAGs: Oleogels*

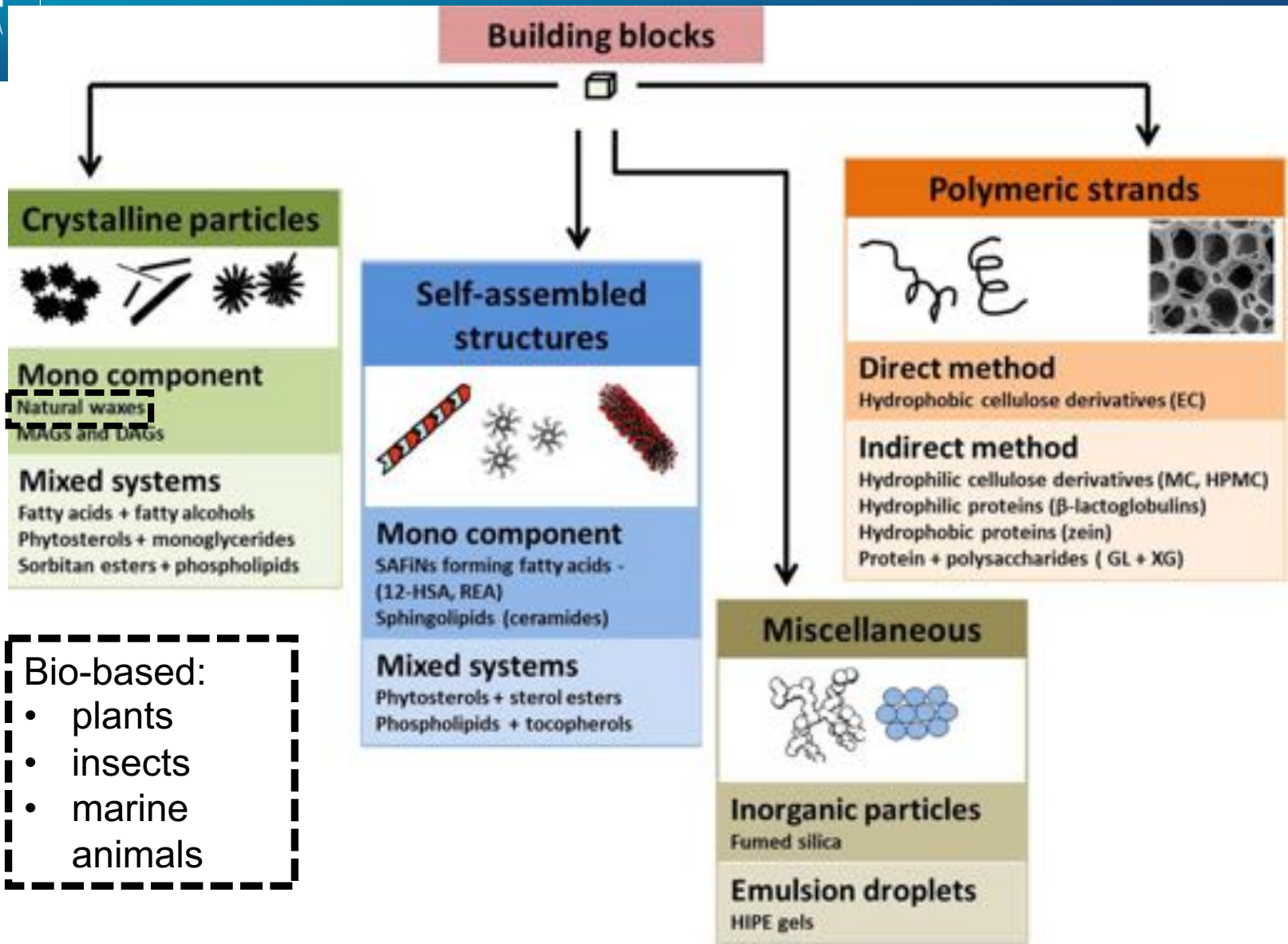


Novel routes to structure edible oils



Mechanisms & Functionality = $f(\text{building block})$

*Organogels are called “Oleogels” when structuring to edible oils



² Image taken from: Patel, A, and Dewettinck, K (2015). Comparative evaluation of structured oil systems: Shellac oleogel, HPMC oleogel, and HIPE gel. Eur. J. Lipid Sci. Technol. 117, 000-000.



- Natural plant hydrophobic compounds deposited outside the epidermal cells
- Complex mixture of fatty alcohols and acids, their esters, hydrocarbons, ketones, etc
- Considered to be among the most promising oleogelators^{6,7}



Plant wax based oleogels

Wax

- Candelilla
- Carnauba
- Sunflower
- Rice Bran
- Berry
- Bee
- Fruit

Oil

- Olive
- Sunflower
- Rice bran
- Rapeseed
- Vegetable
- Salad



Plant wax based oleogels

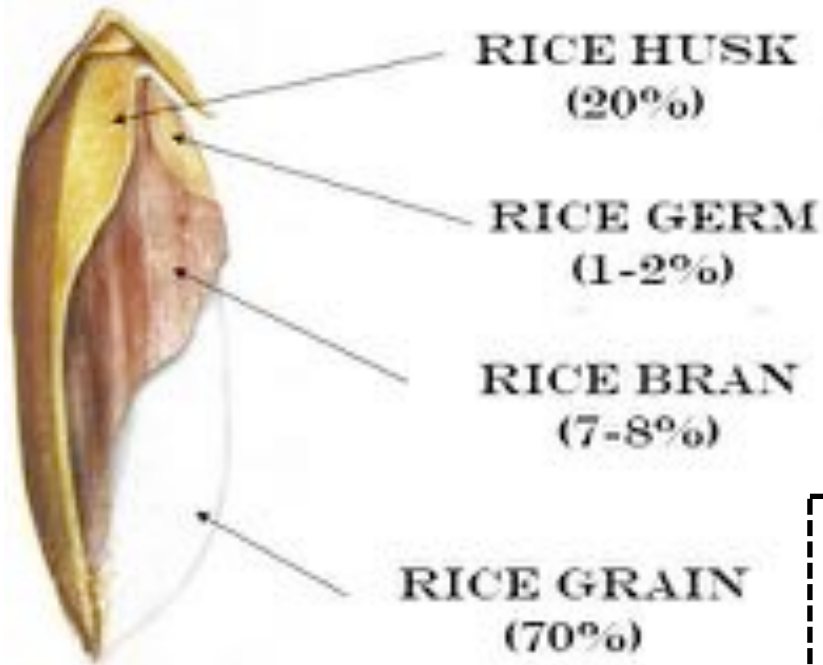
Wax

- Candelilla
- Carnauba
- Sunflower
- **Rice Bran**
- Berry
- Bee
- Fruit

Oil

- Olive
- **Sunflower**
- Rice bran
- **Rapeseed**
- Vegetable
- Salad

Rice bran wax (RBW)



Rice Bran (7.6×10^7 tons/year)¹

Extraction / Hexane

Crude Rice Bran Oil

Degumming

Dewaxing

RBW (5-8%)
~700,000 tons

Neutralisation

Bleaching
De-odorisation

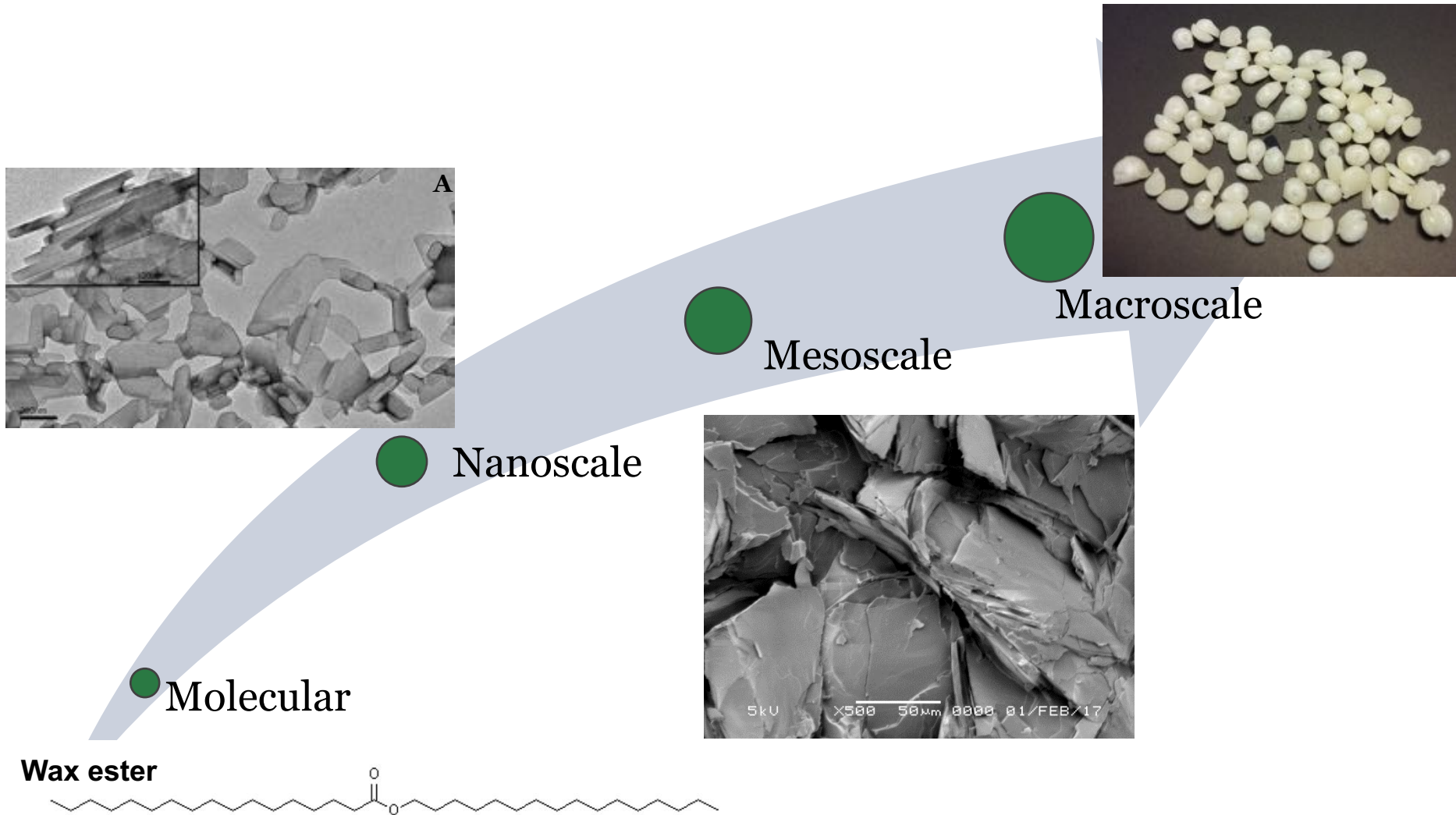
Rice Bran Oil

Rice bran wax (RBW)

- By-product
- Available in large volumes
- Promising gelling agent
- Temperature of phase transition compatible with pasteurisation
- In food applications Rice Bran Wax is EU regulated as a food additive E908.



RBW: structural levels



^A Image taken from reference 8: Characterization of the Nanoscale in Triacylglycerol Crystal Networks



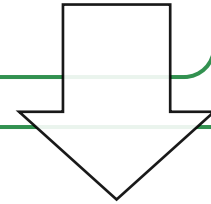
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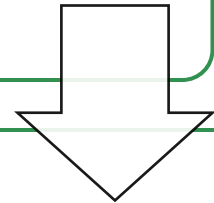
Formulation of RBW oleogels



Characterisation



Functionalisation



**Application:
cakes & SCP**

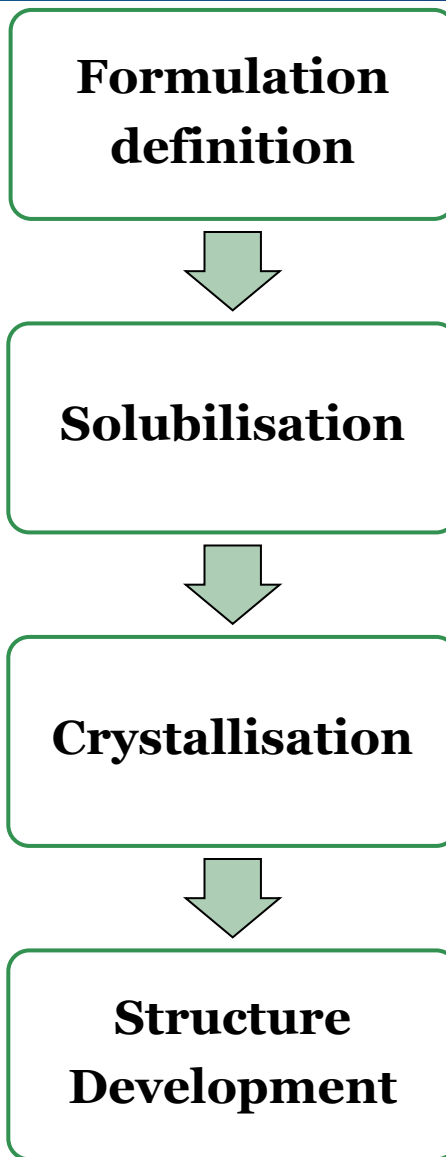


(LMWO) Oleogels: Definition

- Organic liquid entrapped within a thermo-reversible, three-dimensional gel network³
- Network: Thermo-reversible 3D supramolecular structure formed *via* self-assembly of small molecules in an organic solvent at low concentration⁴.

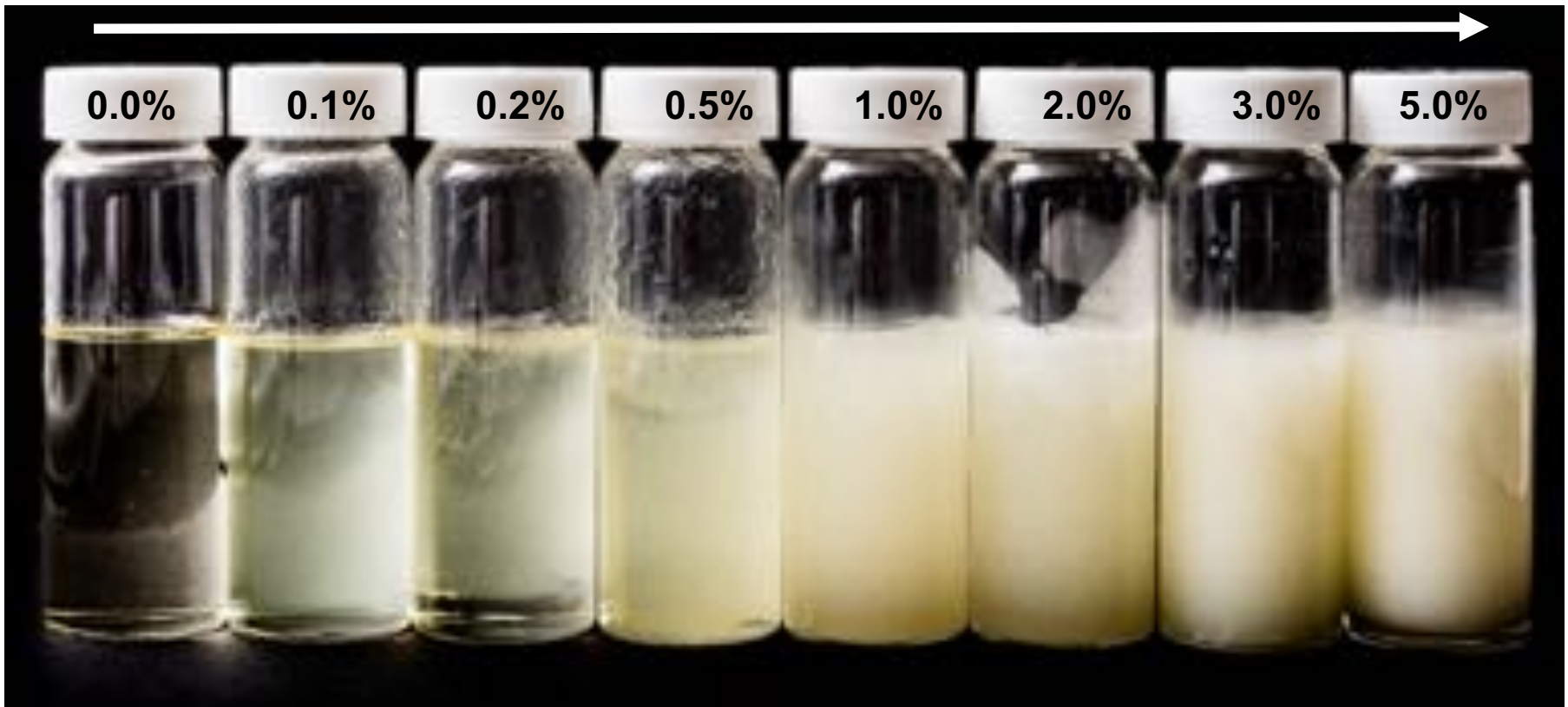


RBW Oleogels: preparation



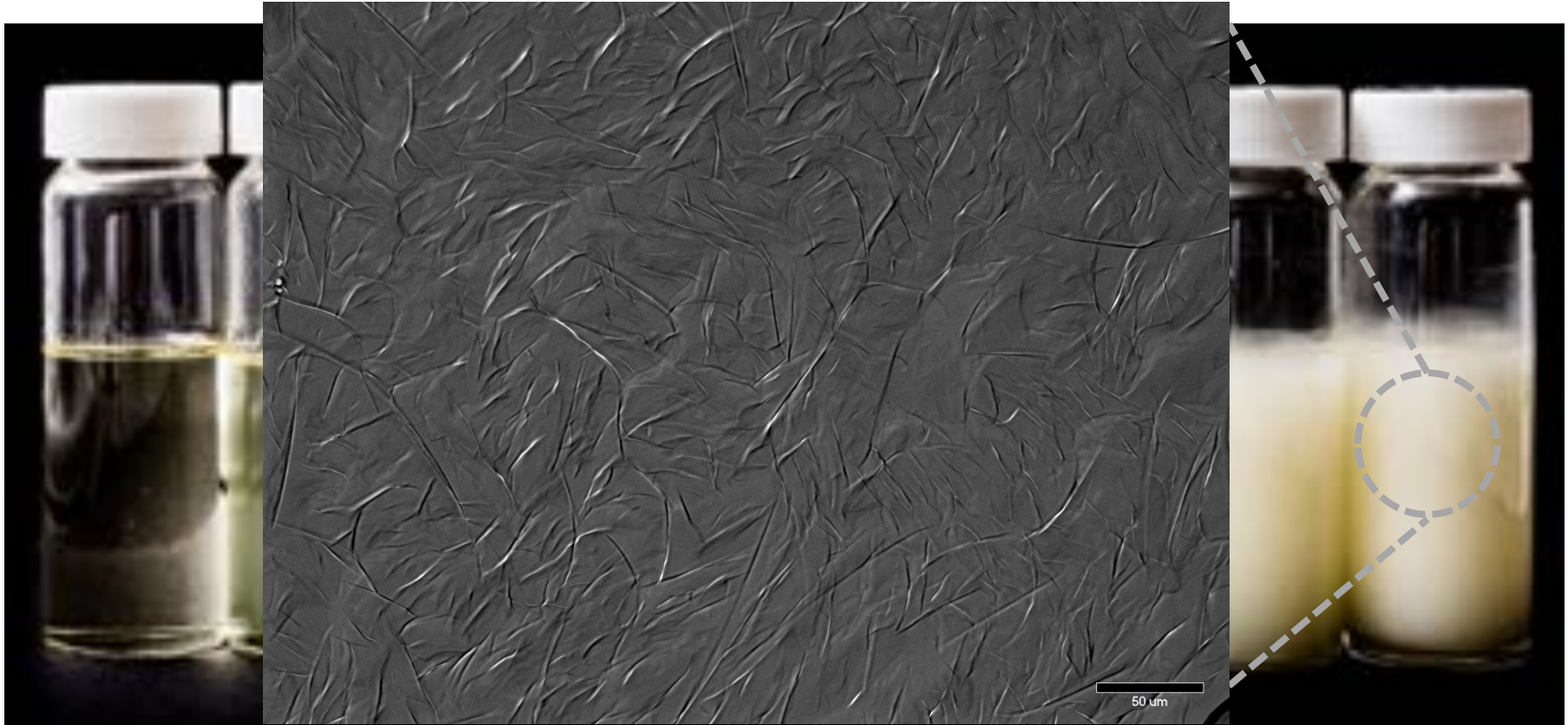
RBW oleogels: Appearance

RBW concentration (%)



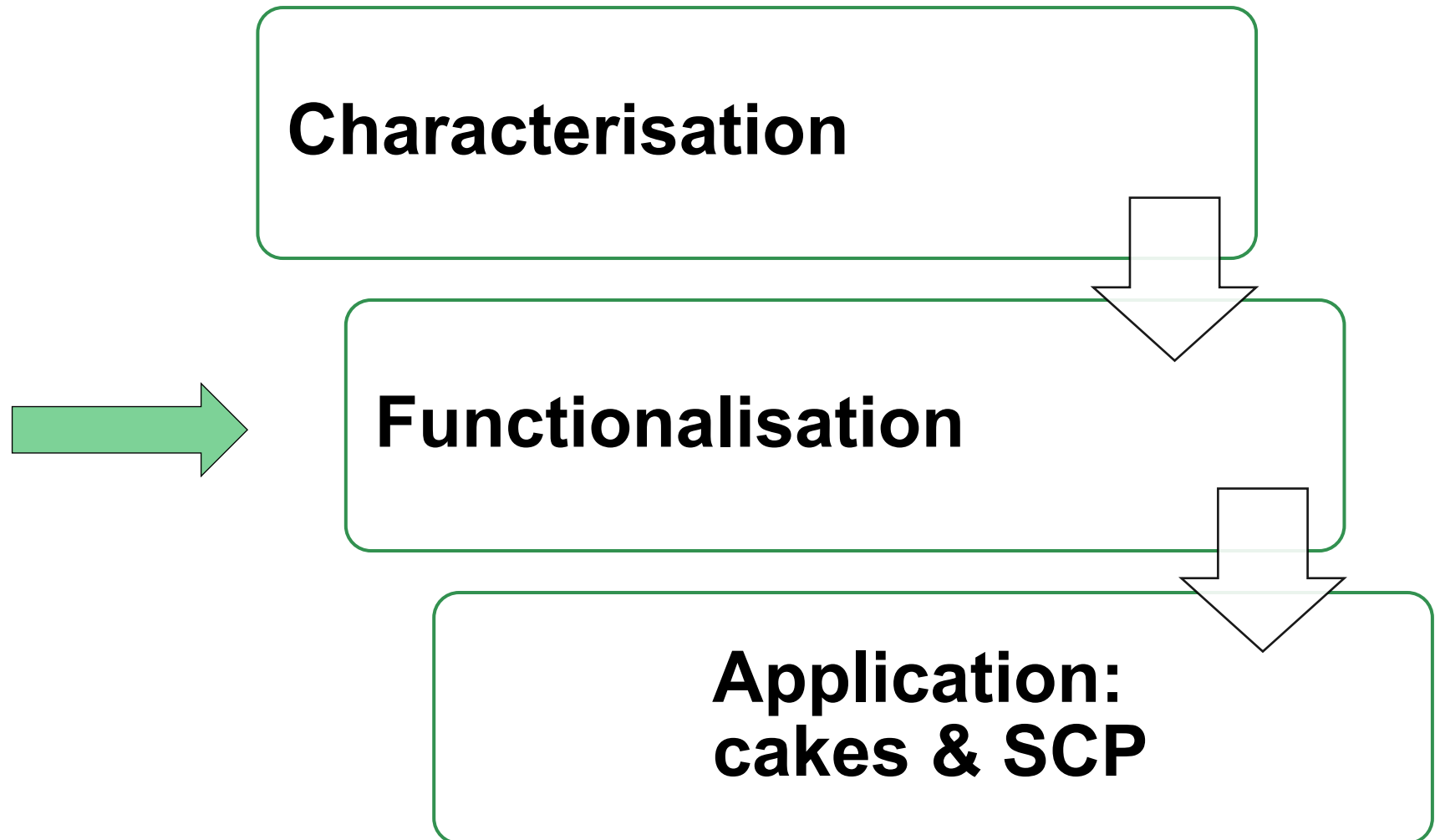


RBW oleogels: microstructure



RBW oleogels: microstructure





Microstructure functionalisation: Understanding the thermo-mechanical behaviour



Formulation

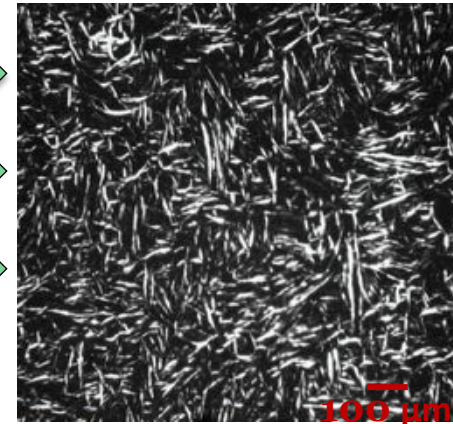
**[RBW]
Additives**

Processing

**Cooling
rate
Shear**

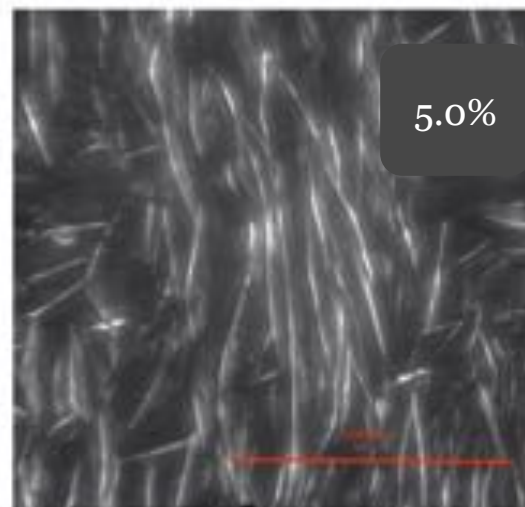
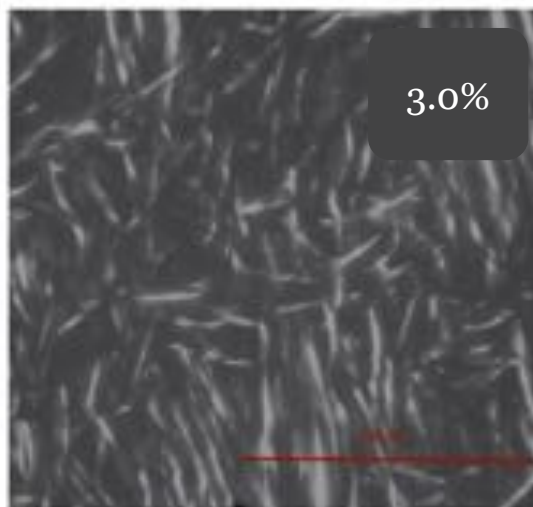
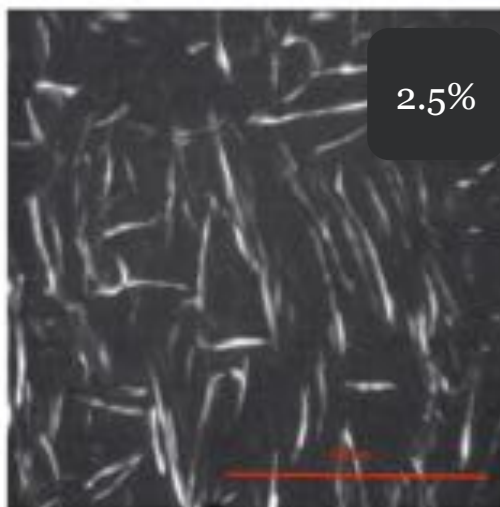
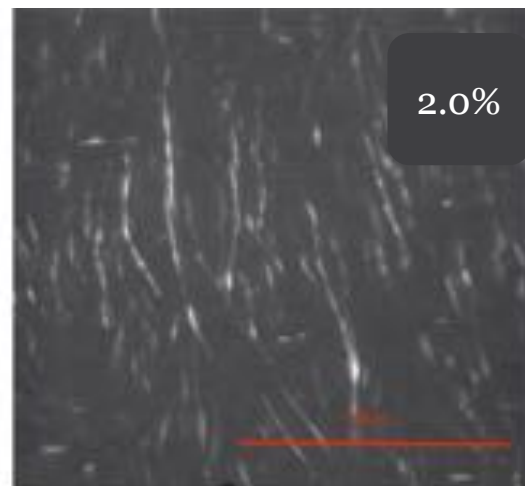
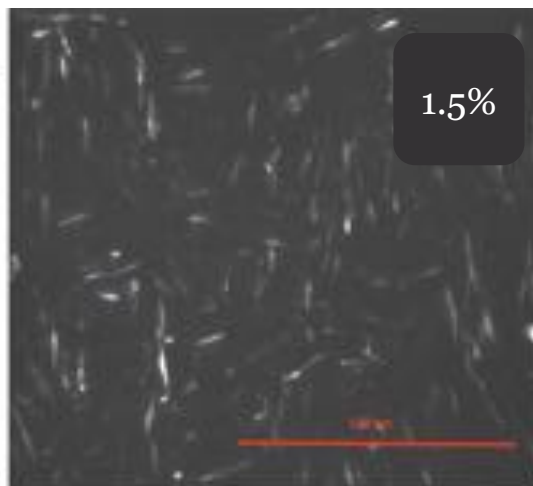
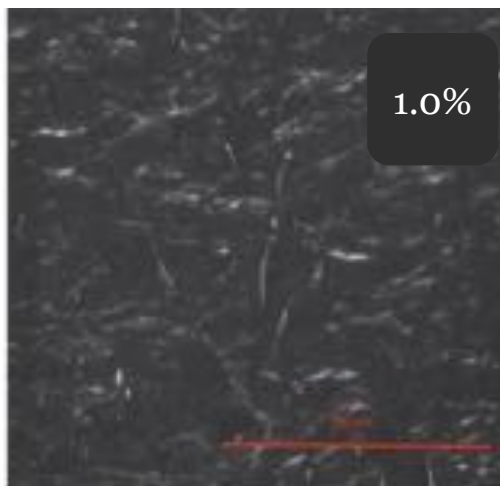
Thermodynamic/kinetics

Temperature



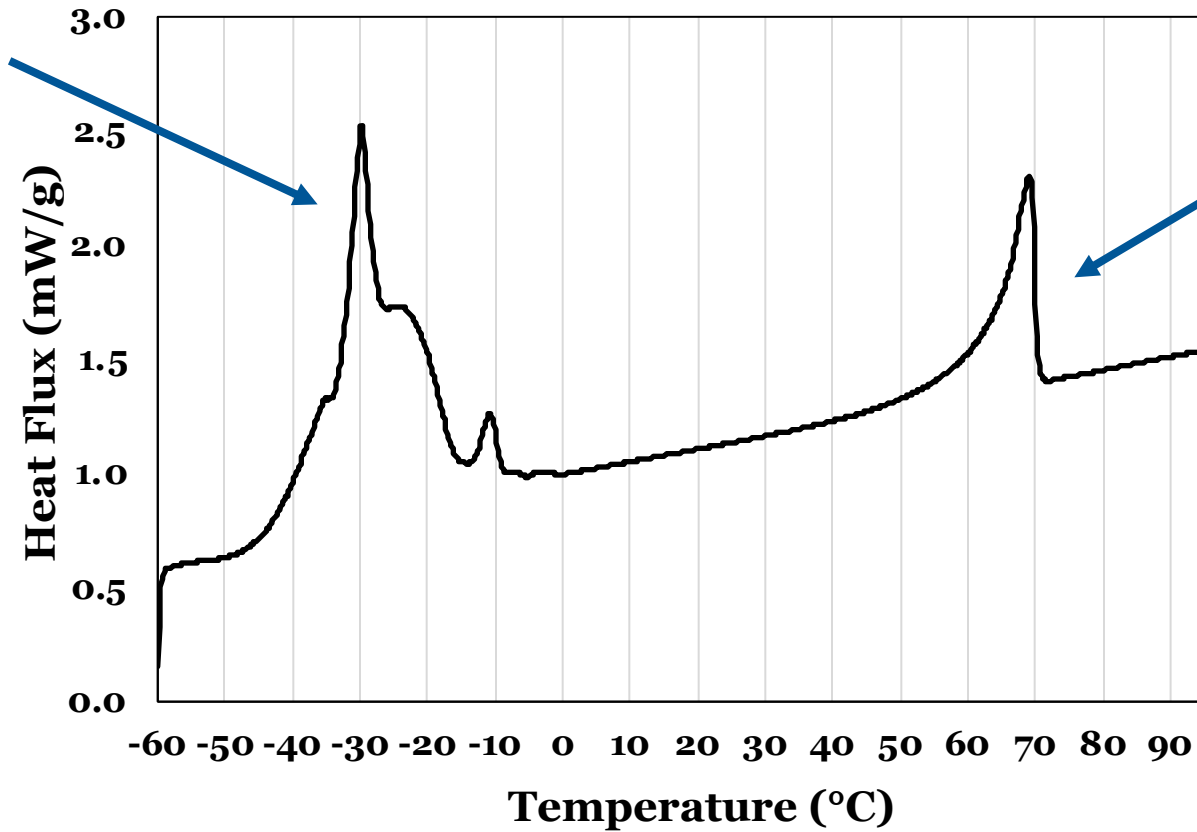


Microstructure = f ([RBW])



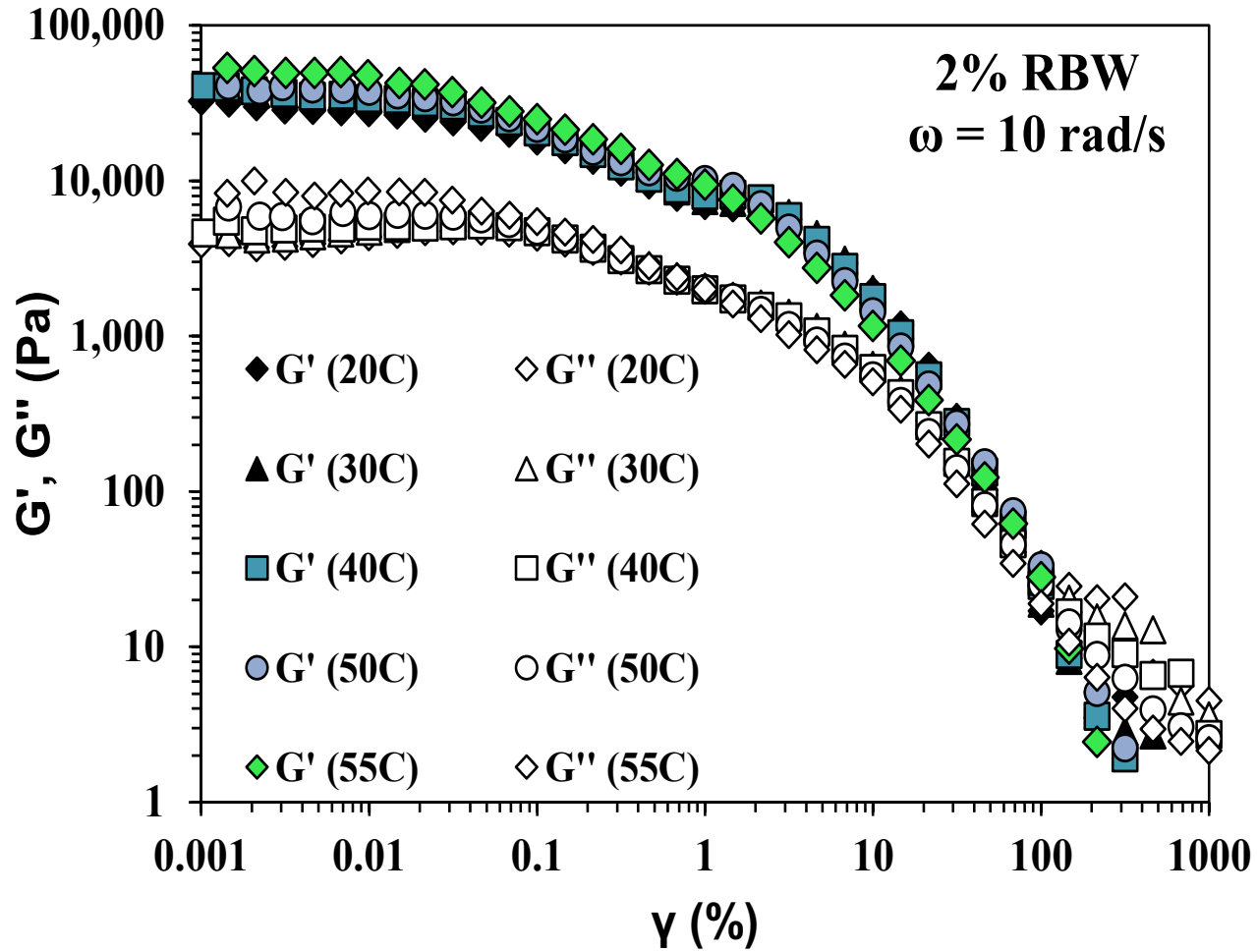
RBW oleogels thermal properties

Liquid oil



Oleogel

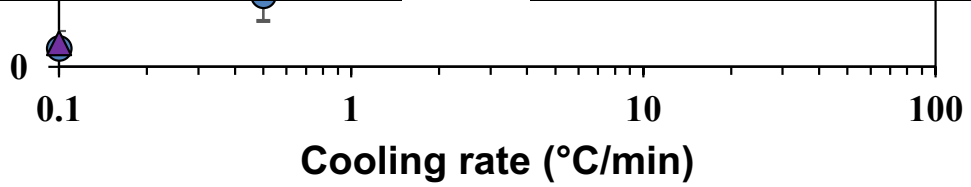
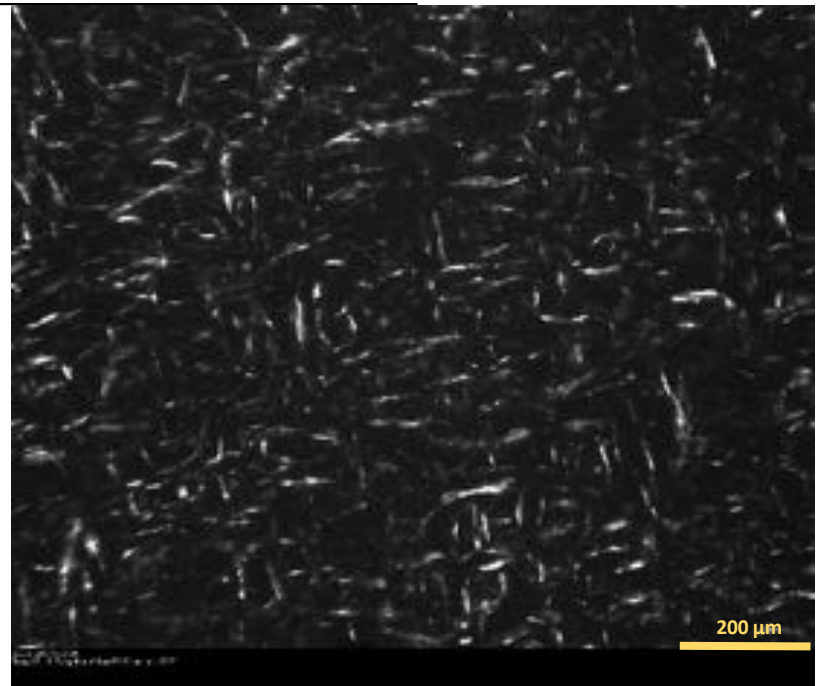
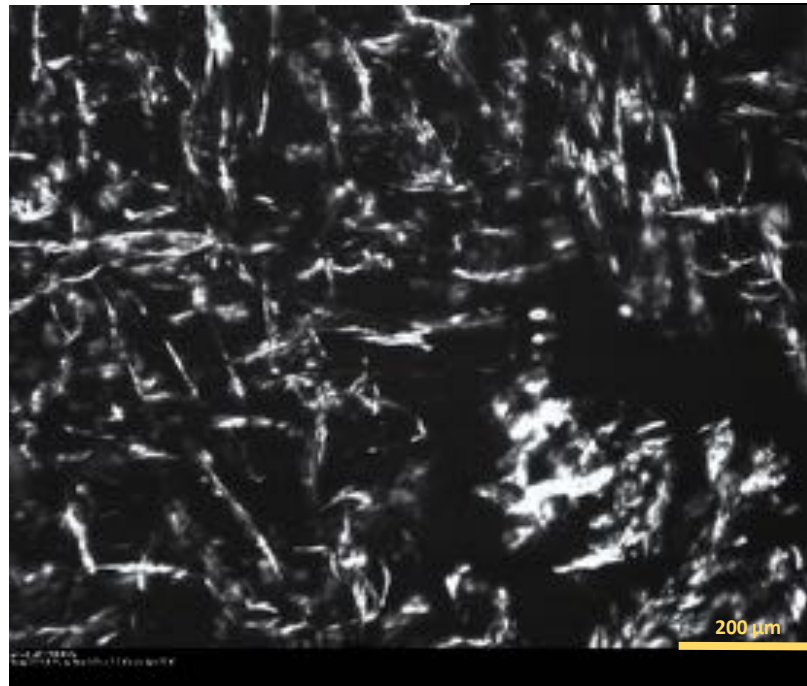
Gel strength = $f(\text{Temperature})$



Engineering the mechanical behaviour = f ([RBW], cooling rate)

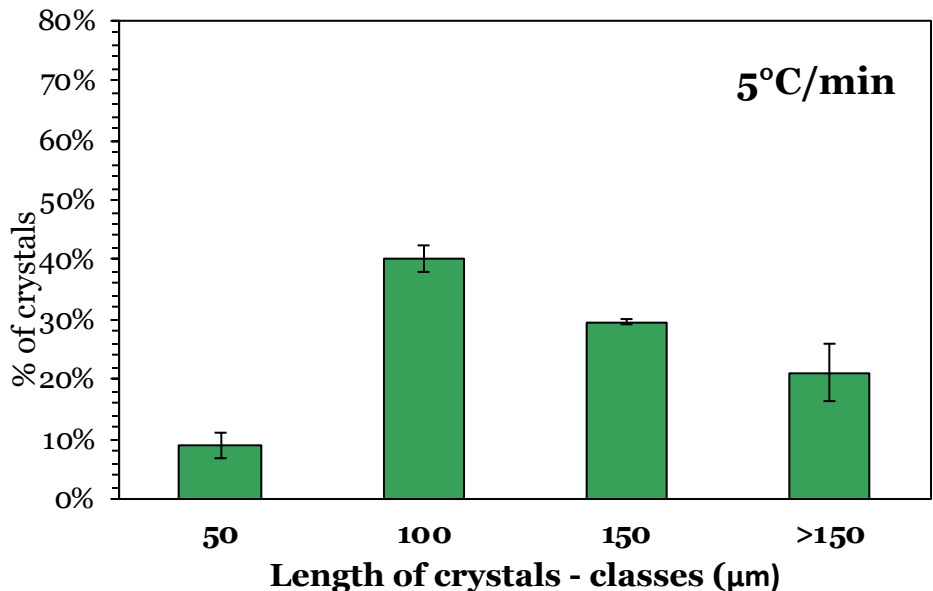
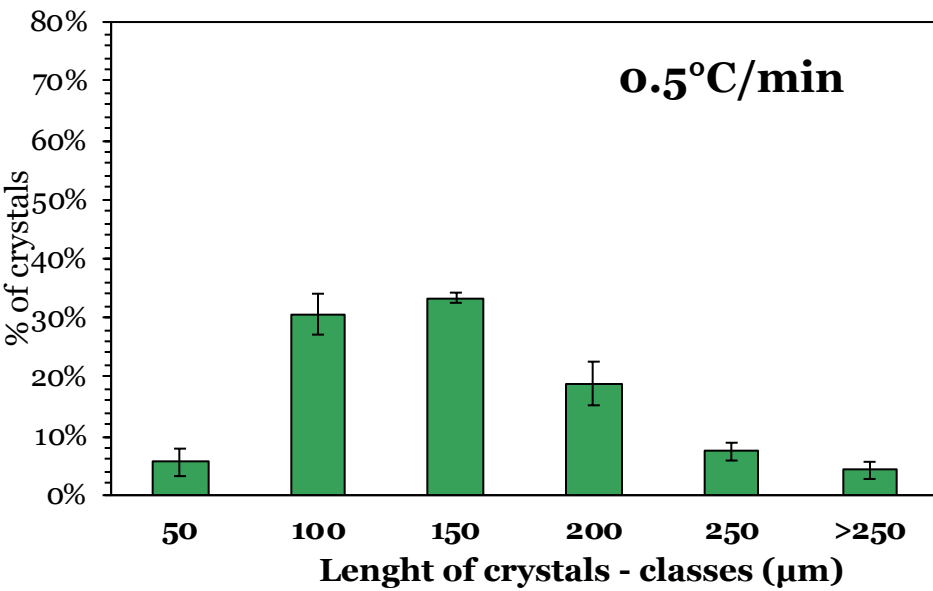
0.5 °C/min

50 °C/min

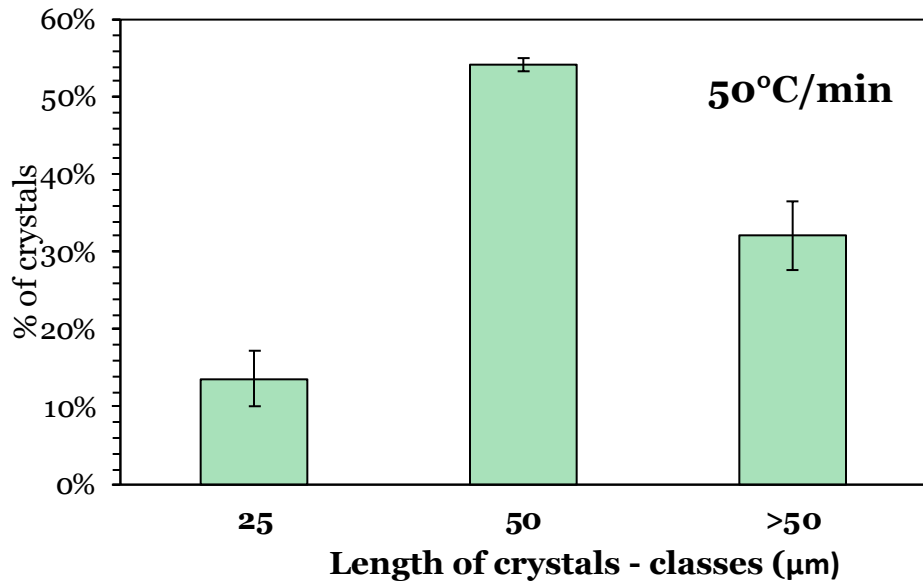


PP50 Sandblasted, $\omega = 10$ rad/s, 40 °C, 0.5 mm gap

Engineering the mechanical behaviour = f ([RBW], cooling rate)



Average number (%) of crystals in each length class after cooling, at 27°C (1%RBW)





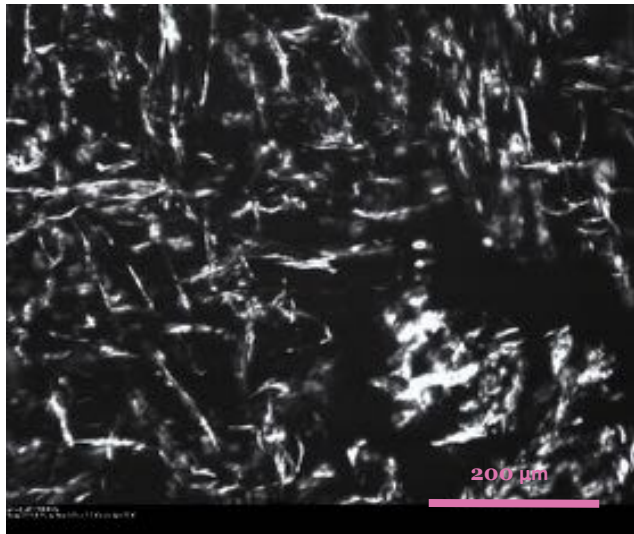
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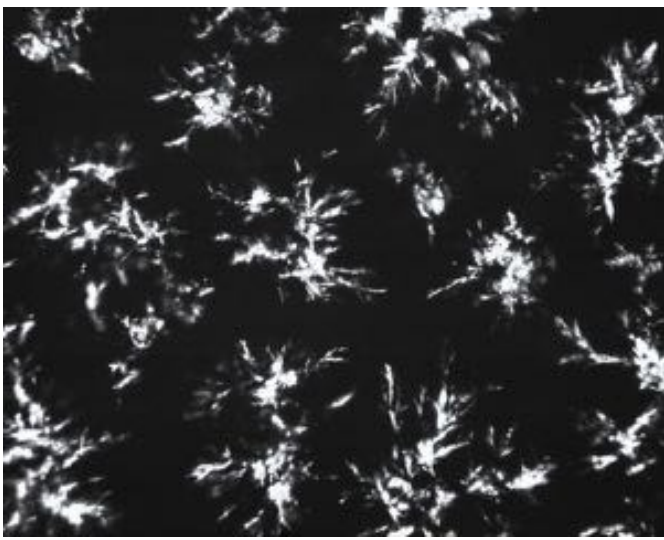
Role of additives on RBW oleogels



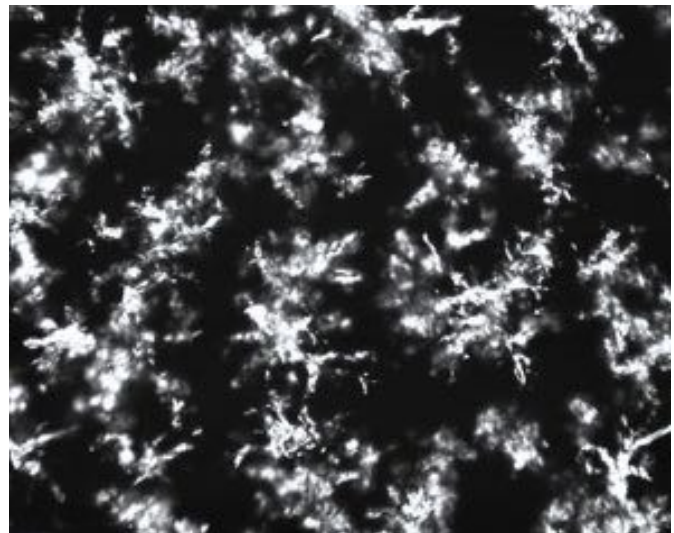
Control (0% Emulsifier)



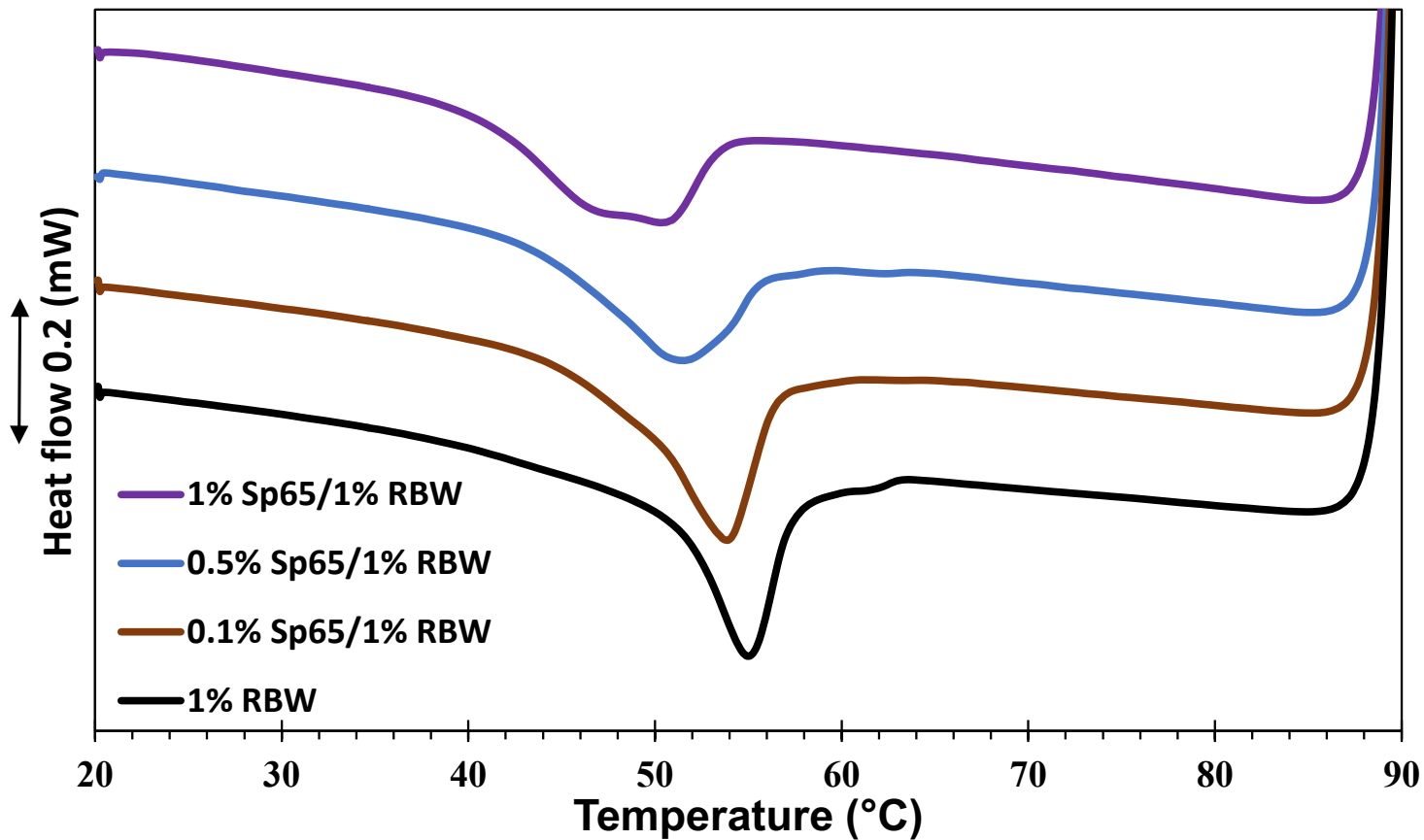
1% Span 60



1% Span 65



Crystallisation profile of RBW + Additive (Span 65)





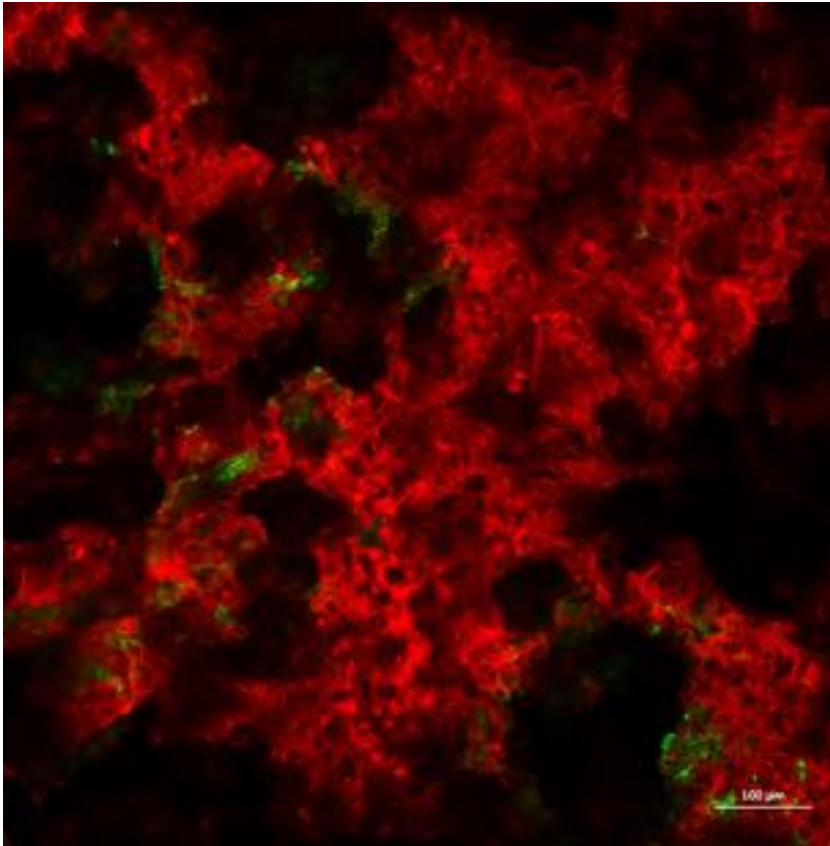
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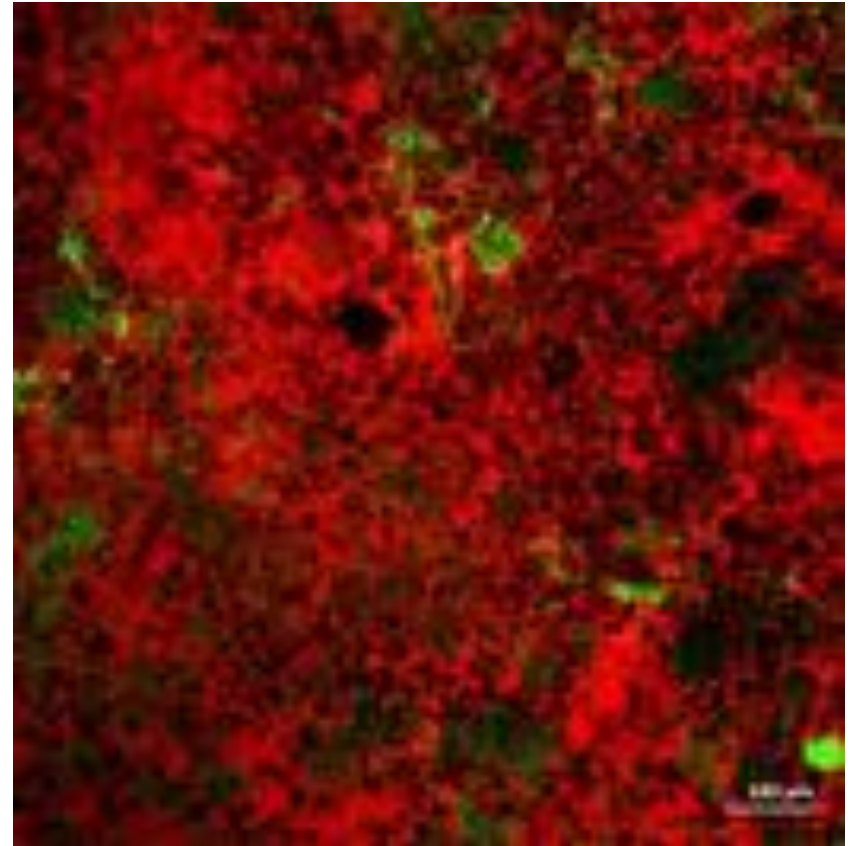
Application

Pastry re-formulation

Palm oil

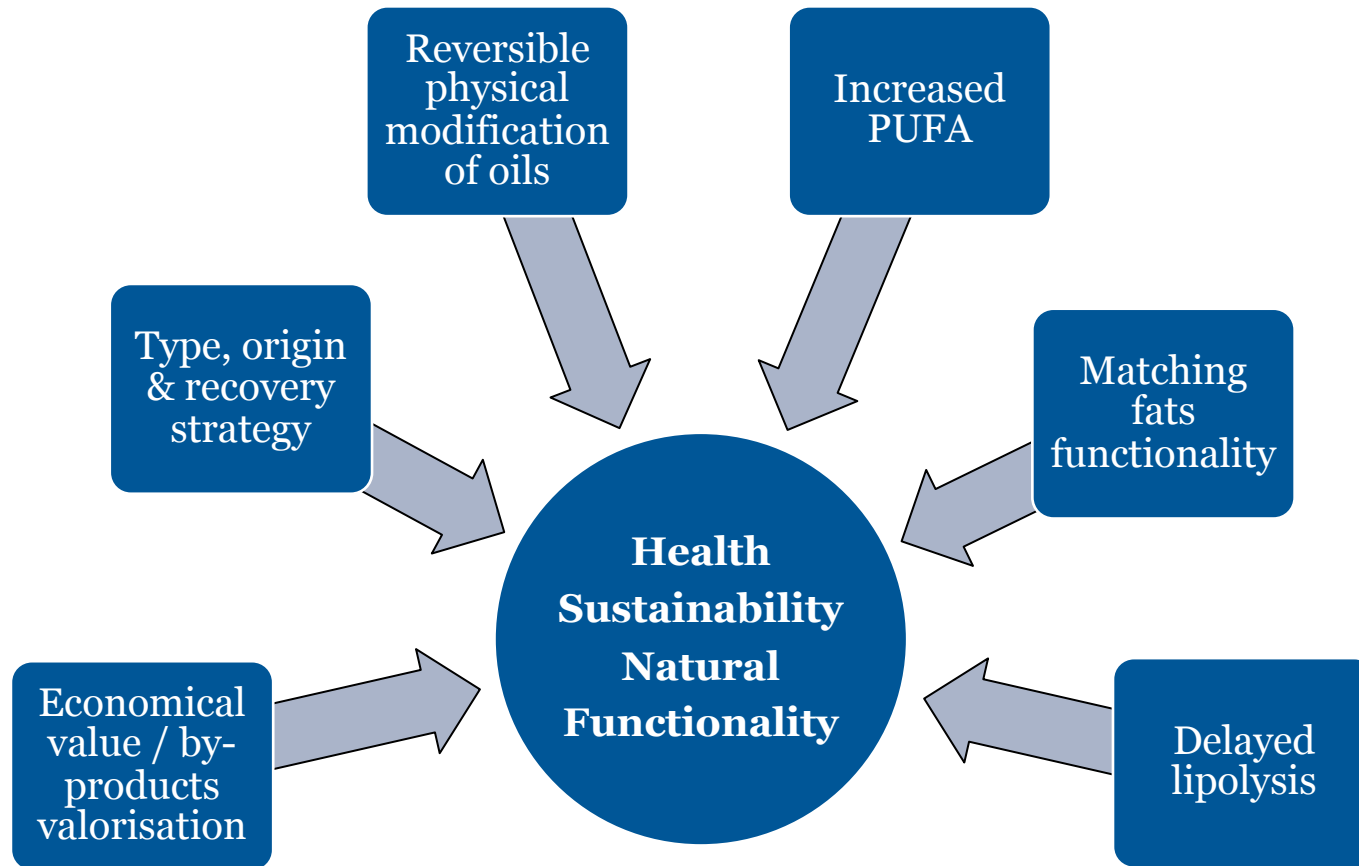


20% Replacement with 3% RBW



Images taken by Khatija Nawaz Husain (CIM Nottingham)

4. Key features of wax oleogels research



- Low molecular weight gelators
- Unidirectional molecular packing leading to anisotropic platelet shaped crystals with β' sub-cell structure
- Long range intermolecular interactions
- Self-arrange to form a dispersion of crystals sintered to form an oil-structuring continuous network
- The addition of additives promotes new microstructural arrangement mirrored by different crystallisation profile



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**Many thanks
for your
attention**

Any Questions?