Polysaccharides in the foods industry

“Happy families are all alike, but each unhappy family is unhappy in its own way” – Anna Karenina

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The emulsion clock

Most foods are emulsions. Both water and oil phases are usually structured.
History of emulsions

Industrial revolution

Increasing population

Population shifts from countryside to cities

Ongoing warfare in Europe (Crimean war, Franco-Prussian war)

Desire for cheaper alternatives to butter

Napoleon III offers prize for substitute for butter

Mège-Mouriés makes margarine from palm oil

Sells the patent to the Dutch company Jurgens

18th Century

19th Century

1869

1871
History of emulsions II

1929
- Merger of Margarine Unie and Lever Brothers

1939
- Second world war
- Fortification of margarine with vitamins
- Drive to cost reduction with lower fat (75%)
- Low fat spread (40%)

1969
- Fat reduction seen as important for health reasons

1980
- Very low fat spreads (25%)

1998
- Cholesterol lowering spreads
How to fill the water phase?

For a margarine, we have 75% of the volume taken up by water.

- Full fat margarine
- Very low fat margarine

For a mayonnaise, the same issue arises, but phase inverted.

- Full fat mayonnaise
- Low fat mayonnaise
Composition of emulsions

- Droplets (created by homogenisation)
- Surfactants to keep emulsion stable against Ostwald ripening, coalescence, creaming (small amphiphilic molecules, HLB ratios etc, proteins, but also: small polysaccharides)
- Structuring water phases helps to keep emulsions more stable and obtain texture/mouthfeel by structurants that strongly increase viscosity or provide gelation

Emulsions:

**Creaming:** density difference dispersed phase/continuous phase

**Ostwald ripening:** solubility gradient between large and small droplets. Large droplets grow at expense of small

**(partial) coalescence:** attractive force between particles/droplets of dispersed phase

**Flocculation:** droplet aggregation through weak attractive forces (DLVO- theory), droplet structure conserved

**Phase inversion:** mediated by coalescence
Structuring water phases: Starch fits all?

A traditional polymer to use in these applications is starch:

Starch granules are a mixture of:

- **Linear amylose polymers:**
  - Produce brittle, hard gels, but vulnerable to retrogradation

- **Branched amylopectin polymers:**
  - Weak gel / viscosifier

**Positives:**
- Can produce viscosity or gelation
- Uncharged polysaccharide, so not sensitive to presence of salt
- Amylose attached by amylase in mouth: so some “melting” like fat

**Negatives:**
- Amylose is vulnerable to retrogradation
- Will hydrolyse in acidic environments
Considerations for Starch in food applications

If you are looking for a polymer, here are a few things to think about:

Is it a thickener or a gelling agent (starch can be both)

If used as a gelling agent, what is the trigger for gelation (temperature or the presence of an ion)? Is it reversible? What is the viscosity when it is not gelled? All these are important for processing.

How sensitive is the polymer to its environment? Salt, temperature certain ions (particularly Ca$^{2+}$ and pH are most important for foods). Charged polymers are more sensitive.

Details of the rheology: starch has a “sticky” mouthfeel, other rheologies may give “sliminess”

Is it transparent / opaque or clear? Is it coloured? (starch can be opaque, translucent or clear, depending on source & processing)

Starch is not the only possibility!
Alternative: Specific solutions by biopolymers

In all similar cases, we structure with polymer solutions or polymer dispersions – usually polysaccharides.

Polysaccharides in solution are either:

**Thickeners:**

Gelling agents:

Semi-dilute solutions (above entanglement concentration $c^*$). Rheology is shear thinning.

Chain interactions (e.g. junction zones) lead to an elastic solid (gel).
Salad dressings provide an example where we have very different requirements:

For a clear salad dressing, you may want to suspend herbs and other pieces.

- Must be transparent
- Not degrade at low pH
- Low shear rate viscosity must be very high (or gel-like)
- At moderate shear rates must have low viscosity

This focuses attention on the details of the rheological profile: we want a very steeply shear-thinning material.
Suspending particles - Technology

Typical solution is to use xanthan:

Steeply shear thinning behaviour, with very high zero shear-rate viscosity

The polymer is very stable to a wide range of pH (although because it is charged, need to use different levels at different pH)

Also transparent.
**Gelling polysaccharides**

For many applications, more solid food structures are preferred, and again there are some options, depending on what properties you want, e.g.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trigger for gelation</th>
<th>Is it reversible?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate</td>
<td>Ca(^{2+}) ions</td>
<td>No</td>
</tr>
<tr>
<td>Agar</td>
<td>(Low) temperature</td>
<td>Yes</td>
</tr>
<tr>
<td>CMC</td>
<td>(High) temperature</td>
<td>Yes</td>
</tr>
<tr>
<td>HM Pectin</td>
<td>High sugar concentration</td>
<td>No</td>
</tr>
<tr>
<td>LM Pectin</td>
<td>Low pH or Ca(^{2+}) ions</td>
<td></td>
</tr>
<tr>
<td>Starch</td>
<td>Temperature / dissolution</td>
<td>No</td>
</tr>
<tr>
<td>(\kappa)-carrageenan</td>
<td>Low temperature and K ions</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Each of the gels when formed has its own textural properties (e.g. brittleness, amount of syneresis, transparency, firmness)

Choosing the right polymer is somewhat like a crossword puzzle!
Example: Alginate

Polyanion produced by seaweed: a co-polymer of mannuronic and guluronic acid

\[
\text{G-blocks (mainly) responsible for gelling properties}
\]

Sodium alginate is soluble, but in the presence of Ca\(^{2+}\) ions, it forms an irreversible gel (“egg-box” junction zones)

Mixed with fruit juice or pureé and then gelled, this has been used since the 1970’s to make pie fillings, pimento fillings for olives etc..
Biopolymer toolbox for water structuring

- Starches
- Polysaccharides
- Proteins: Gelatin/collagen

→ Relatively limited to a few ingredients
→ Further options for tailoring functionalities?
In foods, chemical modification is much less widespread than in non-food applications – but a few examples are allowed as food additives.

- Enzymatic degradation: e.g. maltodextrins from starch
- Chemically cross-linked starch granules
- Hydrophobized starch
- Cellulose modified for higher solubility: CMC & HPMC

Getting anything else approved is a long process (5+ years)!

→ Process or temperature tweaks modifying biopolymers (‘physical modifications’) are thus preferred.
Physical modifications I: Shear gels

So: it looks perfect! However, xanthan comes from bacterial fermentation of a plant pathogen (*Xanthomonas campestris*) – it’s not seen as a “natural” ingredient – and it has some textural issues (sliminess).

An alternative approach is to think harder about the rheological requirements: we want a something which is an elastic gel when at rest, but a thin liquid when it flows – and the change must be reversible.

If you take a material which forms a solid gel, and shear it while it is gelling, then you end up with many tiny gel particles.

The resulting particle dispersion will (if it is close packed) be a gel – but it will break down (reversibly) to a liquid under applied shear.
Physical modifications II

• Pre-processed starch (making use of gelatinization, tempering etc.)

• More unconventional: Processing routes on raw ingredients → contain gelling/structuring agents
The most common polysaccharide particles encountered in foods are plant tissues, cells & cell fragments.

Cell walls are cellulose microfibrils bound together with hemicelluloses.

The middle lamella is made of pectins and cements neighbouring cells.
Controlling the particles

When you process plant material, you end up with a particle gel.

The properties of that gel depend upon the particle concentration, shape, size & interactions – and you can control these through processing.

Heating can leach calcium & pectins from the middle lamella and weaken it.

Heat then shear, then...
Controlling the particles

Shear then heat

Raw plant material → Broken clusters & cell fragments

High pressure homogenization

Raw plant material → Cell fragments

Carrot, sheared then heated

Carrot, HPH

Data from Patricia Lopez-Sanchez
Controlling the particles

HPH produces cell fragments with lower effective phase volume than rounded cells – which lowers the gel modulus.

However the high aspect ratio of the fragments tends to make “longer” (more elastic) gels – with a larger strain at failure.

Changing process conditions and blending different streams can give high degree of control over gel properties and the texture experienced by consumers.

Data from Patricia Lopez-Sanchez
Real world application: Ice Cream

→ Ingredient interactions need to be taken into account
Frozen desserts have been made for thousands of years, principally for the aristocracy, using ice stored in ice houses, mixed, for example with honey and nuts or fruit.

Notable patrons of the confection were Alexander the Great & Nero.

Ice cream was from freezing using ice + salt
Large-scale commercial manufacture became possible with refrigeration.

Ammonia refrigeration, still used today, invented by Carl von Linde in 1872.

Unilever (as Lever Brothers) entered the ice cream market in 1922 with its purchase of Walls Ice Cream.
Outline of commercial process

1. Mixing of ingredients
2. Homogenization
3. Pasteurization
4. Freezing and aeration in a scraped surface heat exchanger
5. Hardening at -35°C
6. Storage and distribution at -25°C
7. Ageing at 5°C

... however, this hides a wealth of physical chemistry ...
Basic structure of ice cream

As a first approximation, ice cream is composed of four phases:

- Air bubbles (around 50μm)
- Ice crystals (around 50μm)
- Small fat droplets visible in the matrix and on air / matrix interface (around 2μm)
- Unfrozen matrix

Scanning Electron Micrograph of Magnum ice cream
The unfrozen matrix phase

Main peculiarity is freeze-concentration, which affects the viscosity & phase behaviour of the unfrozen matrix.

We want the ice cream to be thick and creamy when it has melted in mouth, to give it a rich texture.

We thus want to structure the matrix phase.

Home-made ice cream has very high levels of fat – but (for health, cost and storage stability), we use polysaccharides with lower levels of fat, e.g.

- Locust Bean Gum
- Guar gum
- \( \kappa \)-Carrageenan
- Alginate

- Gelatin
- Pectin
- Xanthan

But ... this can lead to problems!
Staining with Nile blue and imaging the fluorescence shows up the phases:

- Air bubble
- Matrix is phase separated protein / polysaccharide gel, with included emulsion drops (not visible).
- Ice crystals produce concentration water phase and contribute structure.

(image from Dudley Ferdinando)
Phase separation

Many biopolymers are thermodynamically incompatible and phase separate segregatively.

It is usually slightly energetically favourable for similar monomers to be close, rather than dissimilar ones (unless there is a specific interaction).

As you move to higher DP, the enthalpic cost of demixing falls (cost is \( \propto n_{\text{molecules}} k_B T \)), so for high DP, high conc & low T, demixing wins.
Phase separation

This is even more pronounced in the ice cream matrix, where all polymers are more concentrated and the temperature is lower (so entropy cost of demixing is lowered).
This kind of micro-phase separation is not much of a problem.

However, the phases can coarsen during the ageing step of the pre-mix, leading to bulk phase separation, which is a problem.

Coarsening of micro-phase separated structure is driven by water-water interfacial energy and retarded by rheology of the phases.

Macroscopic phase separation is driven by gravity (density differences) and controlled by the coarseness of the structure and the rheology of the phases.
Preventing bulk phase separation

**Interaction of κ-carrageenan and κ-casein**

This specific interaction is used to thicken many milk products, not just ice cream.

κ-carrageenan also forms a weak gel of helices on cooling.

This high viscosity / weak gel prevents bulk phase separation (same issue as with salad dressings).

Other polyanions, such as pectins will also associate with proteins.
Cryo-gelation of LBG

LBG molecules consist of smooth regions of just mannose, and hairy regions with galactose side-branches. The smooth regions lead to chain-chain interactions (giving higher viscosity than expected for non-interacting chains), and can lead to gel formation at sub-zero temperatures.

For example, LBG forms cryo-gels in 60% sucrose at >1% concentration, which remelt at >40°C.

This helps to stabilize the ice cream on storage, and gives a thicker mouthfeel on melting (due to thermal hysteresis).
Conclusions

• Extensive toolbox of biopolymers for structuring water phases available
• Clever processing routes (‘physical modifications’) can even increase the size of your water structuring toolbox
• Of key importance in food product design: Ingredient interactions need to be taken into account!