Starch as a Hydrocolloid
Why is starch the most important food thickener?

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The starch granule

Gelatinisation and gelation: What is the difference?

Modified starches

What is the difference between starch and hydrocolloid solutions at the same viscosity
Size shape and morphology of the granules is characteristic of the botanical source.

- Wheat
- Lentil
- Shoti
- Potato
- Rice
- Avocado
- Maize
- Rye
- Green pea

Each sample is labeled with the corresponding botanical source and the scale is 10 μm.
## Amylose / amylopectin contents

<table>
<thead>
<tr>
<th>Starch Source</th>
<th>% amylose</th>
<th>% amylopectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize</td>
<td>26</td>
<td>76</td>
</tr>
<tr>
<td>Wheat</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>Potato</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>Tapioca</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Rice</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>&lt;1</td>
<td>&gt;99</td>
</tr>
<tr>
<td>High amylose</td>
<td>50 / 75</td>
<td>50 / 25</td>
</tr>
</tbody>
</table>
Amylose and Amylopectin

Starch normally contains two polysaccharides amylose and amylopectin

Amylose
- Almost entirely linear ($\alpha 1$-$4$ linked)
- Molecular size $\sim 5 \times 10^5$ g mol$^{-1}$

Amylopectin
- Highly branched ($\alpha 1$-$4$ and $\alpha 1$-$4$ linkages)
- Molecular size $\sim 10^8$ g mol$^{-1}$
Amylopectin

Glucose units linked 1-4\(\alpha\) and some \(\alpha\) 1-6 linkage

70-99% by weight

Mol weight \(\approx 10^8\) g mol\(^{-1}\)

branch chains ~20 glucose units

only one reducing end
Diagram of the starch polymer organisation
Packing of the molecules to form a starch granule

Jenkins and Donald, 1995
Gelatinisation vs Gelation
Gelatinisation

- Description of structural transformation which occurs when starch granules are heated in excess water
  - Swelling of starch granules
  - Increase in viscosity
  - Loss of birefringence (maltese cross pattern seen under polarising microscope)
  - Accompanied by heat adsorption as seen by endotherm in differential scanning calorimetry
  - Occurs in temperature range ~55-75 °C as measured by loss of birefringence (high amylose starches higher)
Gelation

- Formation of crosslinked network on cooling as a result of formation of amylose double helices
- Individual polysaccharides
  - Amylose forms “strong gels rapidly at minimum concentrations (~2%).
  - Amylopectin forms weak gels slowly, much higher concentrations required (~20%)
Electron Micrograph Showing Structure of an Amylose Gel

Representative area of amylose gels prepared by the fast-freeze, deep-etch rotary-shadowed replica method.

Leloup et al., Carbohydrate Polymers (1992) 18 189-197
Modified Starches
Modified starch e numbers

- E 1404 oxidised starch
- E 1410 monostarch phosphate
- E 1412 distarch phosphate
- E 1413 phosphated distarch phosphate
- E 1414 acetylated distarch phosphate
- E 1420 acetylated starch
- E 1422 acetylated distarch adipate
- E 1440 hydroxypropyl starch
- E 1442 hydroxypropyl distarch phosphate
- E 1451 acetylated oxidised starch
- E 1450 Starch sodium octenyl succinate

Acid thinned starches like unmodified starches are deemed to be ingredients NOT additives
## Properties of native starches

<table>
<thead>
<tr>
<th>Starch Source</th>
<th>Granule Size μ.</th>
<th>Gel Temp °C</th>
<th>Solution Clarity</th>
<th>Gel Texture</th>
<th>Stability to retrogradn.</th>
<th>Resistance to shear</th>
<th>Freeze / thaw stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize</td>
<td>10 - 20</td>
<td>62 - 74</td>
<td>Opaque</td>
<td>Short</td>
<td>Poor</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>Wheat</td>
<td>A 25 – 35 B 2 -5</td>
<td>52 – 64</td>
<td>Opaque</td>
<td>Short</td>
<td>Poor</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>Rice</td>
<td>3 - 8</td>
<td>61 – 78</td>
<td>Opaque</td>
<td>Short</td>
<td>Poor</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>Potato</td>
<td>15 - 100</td>
<td>56 – 69</td>
<td>Clear</td>
<td>Very Cohesive</td>
<td>Fair</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Sago</td>
<td>15 - 25</td>
<td>52 – 64</td>
<td>Clear</td>
<td>Soft</td>
<td>Fair</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Waxy Maize</td>
<td>6 - 30</td>
<td>63 - 72</td>
<td>Clear</td>
<td>Cohesive</td>
<td>Good</td>
<td>Poor</td>
<td>Fair</td>
</tr>
</tbody>
</table>
## Chemical Modification

<table>
<thead>
<tr>
<th>Modification</th>
<th>Reagent</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Thinning</td>
<td>Hydrochloric acid</td>
<td>Acid thinned starch</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Sodium hypochlorite</td>
<td>Oxidised starch</td>
</tr>
<tr>
<td>Cross linking</td>
<td>Phosphorus oxychloride</td>
<td>Distarch phosphate</td>
</tr>
<tr>
<td></td>
<td>Sod. Tri meta phosphate</td>
<td>Distarch phosphate</td>
</tr>
<tr>
<td></td>
<td>Adipic anhydride</td>
<td>Distarch adipate</td>
</tr>
<tr>
<td></td>
<td>Epichlorohydrin</td>
<td>Distarch glycerol</td>
</tr>
<tr>
<td>Esterification</td>
<td>Acetic anhydride</td>
<td>Starch acetate</td>
</tr>
<tr>
<td>Etherification</td>
<td>Propylene oxide</td>
<td>PO starch ester</td>
</tr>
</tbody>
</table>
Effect of Cross linking on Brabender Viscosity

Viscosity

Temperature °C

0.03% POCl₃
0.05% POCl₃
0.075% POCl₃
Control
0.15% POCl₃
What is the difference between starch and hydrocolloid “solutions” at the same viscosity?
Solutions can be thickened with swollen particles or polymers in solution

Swollen starch granules
Plant cells
Gel particles

Guar gum
Pectin
Hydroxypropylcellulose
The next slide shows the appearance of a predominantly particulate suspension (wheat starch) and a polymer solution (hydroxypropylmethylcellulose (HPMC)) which have been stained with a red food dye and gently hand mixed with water. Prior to mixing the viscosity of the stained suspension/solution was 380 mPa.s at ambient temperature and a 50s\(^{-1}\).

In contrast to wheat, waxy maize starch which contains no amylose will disrupt on gelatinisation behaving more like a polymer solution than a suspension of particles. The modified waxy maize starch maintains the particulate structure.
Five Minutes After Mixing

Native Waxy Maize Starch

HPMC

Wheat Starch

Modified Waxy Maize Starch
Consequence of Good Mixing of Solutions Thickened by Swollen Starches

- Good taste perception
- Short non-stringy texture
- Longer gastric emptying time
Perceived Flavour Plotted Against Kokini Shear Stress

log (mean flavour)

log (Kokini shear stress (Pa))
Mouthfeel of Hydrocolloid Solutions (Szcznesniak and Farkas (1962), Mitchell (1979))

Slimy material thick, coats the mouth and is difficult to swallow
Effects in the stomach

MRI pictures of stomach content following the ingestion of 400g of water and 100g of (a) a crosslinked waxy maize starch and (b) HPMC at an equivalent viscosity of 500mPa.s at 50s$^{-1}$.

• fully mixed
• longer gastric emptying time

(b) some remains unmixed

Acknowledgements: L. Marciani
Consequences of changing microstructure of starch

Origin of Starch

- Waxy maize (100% amylopectin)
- Waxy maize physically treated to prevent granule break up
- Wheat

Salivary amylase
Effect of processing, origin and amylase on microstructure of paste

Processing

Heat shear

Swelling
Polysaccharide released from swollen granule

Granule disruption

Botanical origin
Modified/crosslinked waxy maize
Wheat

Salivary amylase
Native waxy maize starch

Processing Effect of processing, origin and amylase on microstructure of paste

Swelling Polysaccharide released from swollen granule Granule disruption

Botanical origin Modified/crosslinked waxy maize Wheat

Salivary amylase Native waxy maize starch
## Cooked starch Characteristics

<table>
<thead>
<tr>
<th></th>
<th>Undercooked</th>
<th>Optimal cooking</th>
<th>Overcooked</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>Cloudy</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td><strong>Texture</strong></td>
<td>Thin, starchy taste</td>
<td>Heavy bodied, short textured</td>
<td>Cohesive, long texture</td>
</tr>
<tr>
<td><strong>Stability</strong></td>
<td>Poor</td>
<td>Good</td>
<td>Many fragments, few intact granules</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Low</td>
<td>Good</td>
<td>Viscosity drop</td>
</tr>
<tr>
<td><strong>Microscope</strong></td>
<td>Small granules, under swollen, birefingent cross</td>
<td>Well swollen, some fragments</td>
<td>Many fragments, few intact granules</td>
</tr>
</tbody>
</table>
Consequences of changing microstructure of starch
Starch systems – impact of origin

- Wheat – Modified waxy maize give higher mixing efficiency / sodium release / taste perception than non-modified waxy maize.
Starch systems – impact of salivary amylase

- $\alpha$-amylase is an enzyme present in saliva, can cleave $\alpha$ 1-4 bonds between glucose residues in starch molecules
- At the concentrations present in saliva it can halve the viscosity of a starch paste in a few seconds
- Large variation in in-mouth amylase activity between subjects
Starch systems – impact of salivary amylase

Waxy maize starch

Modified waxy maize starch

2-a
<table>
<thead>
<tr>
<th>Thickener type</th>
<th>Saltiness</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMC</td>
<td>0.11ns</td>
<td>0.09ns</td>
</tr>
<tr>
<td>Waxy maize starch</td>
<td>-0.20*</td>
<td>-0.28***</td>
</tr>
<tr>
<td>Modified waxy maize starch</td>
<td>-0.43***</td>
<td>-0.19*</td>
</tr>
<tr>
<td>Wheat starch</td>
<td>-0.25***</td>
<td>-0.14ns</td>
</tr>
</tbody>
</table>
Conclusions from amylase study

- Amylase activity in the mouth releases polymeric material from swollen starch granules reducing mixing efficiency and salt perception.
- Data suggests that consumers who have a high in-mouth amylase activity perceive flavour/taste in starch thickened foods less well.
The Weakest Link?

Microstructure → Rheology

Mixing

Sensory/in body performance
Observation of droplet break up in two fluid systems

- Easy break up of the viscous fluid element will result in good mixing
  - Rheooptics
  - CaBER rheometer
Counter rotating shear cell

- 2 transparent plates rotating in opposite directions
- Gap (h) is 1mm, radius (r) at which the droplet sits 5-10mm
- Droplet is submitted to a known shear rate calculated as follows: \[ \dot{\gamma} = \frac{(\omega_u - \omega_l)^* r}{h} \]

with \( \omega_u \) and \( \omega_l \) the relative velocities of upper and lower plate respectively

- Suspending fluid: high viscosity silicon oil (transparent, inert towards aqueous systems, induces high stresses)

Observed system is static in laboratory reference
HPMC and cross linked waxy maize starch at equivalent shear viscosities

Under the same conditions, HPMC and CLWM behave differently;

- HPMC reaches a steady-state deformation
- CLWM deforms and breaks up.
CaBER Extensional Rheometer
Experimental Conditions

- The sample is placed between two parallel plate (6mm diameter) separated by a 3mm gap.
- The fluid is then exposed to a rapid extensional step strain by moving the upper plate upwards (final gap 11.3mm, linear strike, 50ms), thereby forming a fluid filament.
- A laser micrometer measures the midpoint diameter of the gradually thinning fluid filament, after the upper plate has reached its final position, until its break-up.
Filament break-up times for good mixers

- Processed xanthan
- Waxy maize
- Wheat
- Modified waxy maize

Break-up time (s.) vs. Viscosity 50s$^{-1}$ (Pa.s)
Perceived Flavour Plotted Against Kokini Shear Stress

![Graph showing perceived flavour plotted against log (Kokini shear stress (Pa)) with different markers for waxy maize (crosslinked), w heat, waxy maize native, HPMC (Anne-Laure), and HPMC (Dave Cook).]
Conclusion

- As a thickener for foods starch has a fundamental advantage over most other polysaccharide hydrocolloids due to its more efficient mixing with bodily fluids.
References


Thanks

- Ann-Laure Ferry (Nestlé, DEFRA Food Link)
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- Andy Taylor
- Dave Cook
- Dave Howling
- Margaret Hill