Emerging and Applied Clean Label Starch Technologies

Technical and Commercial Perspective
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www.skpatilassociates.com

www.GlobalFoodForums.com /CleanLabel
Outline

- Introduction to modified starch
- Brief summary of modified starches current situation
- Properties and applications – modified starches

- Clean label starch technologies (all) a review
- Clean label starch – Physically Modified Starches
- Physically mod. starch – properties & applications

- Clean label starch – Enzyme Modified Starches
- Enzyme mod. starches – properties & applications
- Commercial clean label starches
- Applications tests and evaluation methods
- Opportunities & Summary
Starch

- Natural carbohydrate polymer next to Cellulose
- Polymer packed in a granule
- Granule shape, size, morphology depending on plant species
- Granule organization
- Linear and branched polymer
- Swelling with heat and water - Gelatinization
- Retrograde/crystallize upon cooling
- Numerous food and industrial applications/uses
Starch Composition

Starch is a Mixture of Amylose & Amylopectin

**AMYLOSE**
Linear molecule
Mw- 700-5000 Daltons

**Amylopectin**
Branched molecule
Mw- $10^4$-$10^5$ Daltons

α-1,4-glucosidic linkages

α-1,6-glucosidic linkages

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Brief Introduction to modified starch
Why Chemically Modify Starch?

- Impart Process Stability & Shelf Stability
  - Acid
  - Processing (temperature, shear)
  - Storage
- Impart Selected Functional Characteristics
  - Alter viscosity
  - Alter viscosity development during processing
  - Improve film forming properties
  - Impart selected aesthetic properties
  - Control retrogradation of Amylose and Amylopectin
Chemical Modification for Food
FDA Approved

- Phosphorus Oxychloride
- Propylene Oxide
- Acetic Anhydride
- Certain food grade Acids and alkali
- Hypochlorite
- Octinyl Succinic Anhydride
- Phosphates: STMP and STPP
- Epichlorohydrin – not currently used due to safety concerns
Some Functional Properties Affected by Modification

- Viscosity
- Texture
- Shear / acid / heat stability
- Paste clarity
- Freeze-thaw stability
- Degree of solubility
- Gelatinization temperature
- Retrogradation tendency e.g. syneresis
Example: Cross-linking

Objective and Principle

One of the important chemical modification with Phos. Oxychloride & STMP to Increase Starch Granule Stability After Gelatinization

“Spot Welding”
Effect of Cross-linking

- Stabilizes starch granular integrity
  - Acid
  - Heat/time
  - Shear/time
- Alters paste rheology
  - Cohesive ➔ Short
- Alters viscosity development
  - Decreases initial viscosity ➔ Stabilizes final viscosity
Effect of Cross-linking Level on Waxy Starch

pH 3.0, Temp 195 - 200 F with moderate shear

Paste Mod. Waxy Starch Pastes
Native & Modified

Native

Modified x-link

Clean Label Starch Ingredients
Clean Label Starch Ingredients

Consumer desire to eat healthy and foods with simple non chemical sounding ingredients names on food label, cleaner labels or “pantry friendly” ingredients has created excellent opportunities for non chemically modified starches.

Food manufacturers are responding to this trends by introducing foods with simple/clean label

Starch is one of the major food ingredients that is essential to produce foods with good viscosity, texture and other aesthetic properties

Clean label starch with no chemical modification such a physically modified and enzyme modified or other modifications that do not require chemical modification are growing at faster pace

Functional and physical properties similar to chemically modified starches represent a great opportunity for growth in the starch industry and the food manufacturers.
Selected Clean Label Starch
Two Technologies

I. Physical Modifications:
   - Heat Moisture Treatment (HMT)
   - Annealing (ANN)
   - Dry roasting
   - Spray drying

II. Enzyme modifications
Physically modified Starches
HMT & ANN

- Heat-moisture treatment (HMT) and annealing (ANN) are physical modifications that change the physicochemical properties of starch without destroying its granular structure.

- In HMT, starch is heated to temperatures above the gelatinization temperatures but with insufficient moisture to gelatinize.

- Regardless of the starch’s origin, HMT promotes an increase in the gelatinization transition temperature, a widening of the gelatinization temperature range, a decrease in granular swelling and amylose leaching, and an increase in thermal stability.

- In ANN, starch is exposed to excess water for an extended period of time at a temperature above the glass transition but below the gelatinization temperature.
Heat Moisture Treatment (HMT)

- HMT is a physical modification that involves low moisture levels, usually in a restricted range of 10–30%, and heating at high temperatures (90–120 °C) for a period of time ranging from 15 min to 16
- A temperature above the glass transition temperature but below the gelatinization temperature.

- HMT allows control of molecular mobility at high temperatures by limiting the amount of water. HMT-induced changes in starch structure and properties have been found to vary with starch source and amylose content.
- For instance, tuber starches are more sensitive to HMT than legume or cereal starches
Impact of HMT on starch swelling power and solubility

- HMT influences both the amorphous and crystalline regions of starch granules; thus, this treatment degrades the exterior linear chains of amyllopectin and promotes recrystallization and associations mostly involving amylose chains.

- Reduction in the swelling power of HMT starches. This reduction in swelling power has also been attributed to increased crystallinity, reduced hydration.

- Increased interactions between amylose and amyllopectin molecules, strengthening of intramolecular bonds.

- The formation of amylose–lipid complexes.

- DSC - The onset, peak, and conclusion gelatinization temperatures generally rise as the heat and moisture intensity increase.
Impact of HMT on gel texture

- This treatment increases the gel hardness of starch treated with 15 and 20\% moisture.

- For treatments under 25\% moisture, a possible partial gelatinization, resulting in a less rigid gel due to the partial collapse of the structure of the granules.

- During HMT, increase in gel hardness has been attributed to the increased cross-linking between starch chains in the amylose portion.

- This allows the formation of more junction zone in the continuous phase of the gel, resulting in the increased gel hardness.

- Changes in crystallinity during hydrothermal treatment.

- This behaviour intensified as the moisture content of the HMT increased.
Impact of HMT on the susceptibility of starch to enzymatic hydrolysis

- HMT-induced changes probably occur in the amorphous regions of the starch granules, which are more accessible to hydrolysis.
- These amorphous areas are more rapidly degraded by – amylases than the crystalline areas.
- The crystalline structures also create RS (resistant starch) and SDS (slowly digestible starches)
Effect of heat moisture treatment on potato starch – Brabender Viscosity

Physically Modified Starch Applications

<table>
<thead>
<tr>
<th>Dairy</th>
<th>Baby Foods</th>
<th>Pet Foods</th>
<th>Bakery</th>
<th>Salad Dressings</th>
<th>Soups and sauces</th>
<th>Prepared foods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yogurt</td>
<td>Fruits, vegetables</td>
<td>Canned gravies</td>
<td>Fruit fillings</td>
<td>Pourable</td>
<td>Gravies</td>
<td>Dinners</td>
</tr>
<tr>
<td>Sour cream</td>
<td>Formula</td>
<td>Formed meats</td>
<td>Cream fillings</td>
<td>Spoonable</td>
<td>Frozen</td>
<td>Saucers, gravies</td>
</tr>
<tr>
<td>Cheeses</td>
<td>Toddler meats</td>
<td>Treat or snack</td>
<td>Cake mixes</td>
<td>Hot or Cold process</td>
<td>Dry</td>
<td></td>
</tr>
<tr>
<td>Puddings</td>
<td>Powdered drink</td>
<td></td>
<td></td>
<td></td>
<td>Retorted</td>
<td></td>
</tr>
<tr>
<td>Ice cream</td>
<td>Biscuits</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beverages</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Physically Mod. Starch - Annealing (ANN)
Physically Mod. Starch – Annealing (ANN)

- In ANN, starch is exposed to excess water for an extended period of time at a temperature above the glass transition but below the gelatinization temperature.
- Generally the temp. range is 40 to 60 C in excess water/intermediate water content.
- ANN specifically changes the physicochemical properties of starch by improving its crystalline perfection and facilitating interactions between the starch chains.
- Controls swelling, gelatinization, enhances stability, etc.
Enzyme Modified Starches
Carbohydrate Modifying Enzymes

- Carbohydrate
  - Hydrolases
  - Transferases
Why Use Enzymes?

Enzymes are highly selective catalysts, greatly accelerating both the rate and specificity of biochemical & metabolic reactions.

Modern biotechnology has provided to identify, develop and commercial enzymes for numerous food and industrial applications

- Eliminate undesirable byproducts/improve purity
- Consistent high quality products
- Low costs
- Milder reaction such as hydrolysis conditions
- Replace chemical reactions such as starch modification
Example: Baking Enzymes

Eliminate emulsifiers, plasticizers, etc.

- Amylase - Bread softness and volume, flour adjustment
- Xylanase - Dough conditioning
- Lipase - Dough stability and conditioning (*in situ emulsifier*)
- Phospholipase - Dough stability and conditioning (*in situ emulsifier*)
- Glucose oxidase - Dough strengthening
- Lipoxygenase - Dough strengthening, bread whitening
- Protease - Biscuits, cookies
- Transglutaminase - Laminated dough strengths

Other food segments such as dairy, grain processing, oils, etc. and many others have similar applications
Major Starch Modifying Enzymes

- **Endoamylases** are amylases that attack starch randomly or in the interior of glucose α-1, 4 and α-1, 6 linkages, reducing the viscosity rapidly.

- **Exoamylases** such as β-amylase attack glucose polymer chain from the reducing end group successively removing the glucose or maltose units from the starch polymer.

- **Debranching enzymes**: The third group of starch-converting enzymes is the debranching enzymes that exclusively hydrolyze α-1, 6 glycosidic bonds: isoamylase.

These enzymes exclusively degrade amylopectin, thus leaving long linear polysaccharides.
Major Starch Modifying Enzymes

- **Transferases**: The fourth group of starch-convertsing enzymes is transferases that cleave α-1, 4 glycosidic bond of the donor molecule and transfer part of the donor to a glycosidic acceptor with the formation of a new glycosidic bond. Enzymes such as amylomaltase (EC 2.4.1.25) and cyclodextrin glycosyltransferase.

- For example, Cyclodextrins are produced via an intramolecular transglycosylation reaction in which the enzyme leaves the α-1, 4 glycosidic bond and concomitantly links the reducing to the non-reducing end.
- And SDS (slowly digestible starches) among others.
Major Starch Modifying Enzymes

- **Amylomaltases** are very similar to cyclodextrin glycosyltransferase with respect to the type of enzymatic reaction. The major difference is that amylomaltase performs a transglycosylation reaction resulting in a linear product while cyclodextrin glycosyltransferase gives a cyclic product.

- Starch that has been treated with amylomaltase has thermoreversible gelling characteristics: it can be dissolved numerous times upon heating.

- This behavior is very similar to gelatin
Examples of Selected Starch Modifying Enzymes
Amylomaltase-treated starch (ATS)

- Gelation of ATS is driven by the formation of crystalline regions and depends on the amount of crystalline regions still present after the dissolution step.

- These crystalline regions are likely formed by the elongated linear side chains of the amylopectin in ATS.

- Starch products are under development using amylomaltases will be commercially available and the thermoreversible gel starch will then will follow in not too distant future.

- Entanglement and helix formation of the elongated amylopectin side chains is supposed to be the mechanism behind the thermoreversible gelation of amylomaltase-treated starch (ATS).
Amylomaltase-treated starch (ATS)

Schematic representation of the enzymatic conversion of potato-starch-derived amylose and amylopectin into ATS by amylomaltase.
Source: Food Hydrocolloids 23 (2009) 980–987
Enzyme Mod Potato Starch by amylomaltase-(AM) & 4-a-glucanotransferase (ATS)

Thermoreversibility of ATS

- A unique enzyme, 4--glucanotransferase, possessing not only hydrolyzing activity but also glucan-transferring activity.

- A gelatine-replacing starch designed for use in jelly-type confectionery, vegan alternative to gelatine for soft jellies and wine gum-type confectionery.

- And a starch designed as a fat replacer for use in cakes & dairy which the company says can reduce fat content by 30 per cent.

- Amylomaltase-treated starch (ATS) showed that ATS is a creaminess enhancer in yoghurt.
The 4 GT of Thermus thermophilus is used to convert starch into a thermoreversible gelling derivative that is on the market.

Source: Carbohydrates Polymers, 2012
Starch modifying enzymes
RS, SDS & SDC
Impact of HMT on slowly digestible starch (SDS) and resistant starch (RS)

- Rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) based on the rate of glucose released during starch hydrolysis by digestive enzymes.
- Depending on the temperature and the moisture content of the hydrothermal treatment, the SDS content could be doubled compared to the native starch.
- When corn, pea, and lentil starches are heat-moisture treated at 120 °C.
- The RDS decreased by 10.2%, 14.0%, and 15.1%, the SDS content increased by 2.5%, 2.8% and 4.7%, and the RS content increased by 7.7%, 11.2% and 10.4% respectively.
- Majority of RS and SDS by using branching Enzyme Pullulanase/isoamylase.
RS by Debranching enzyme & Retrogradation (RS 3) US 5,281,276 (1994)

- Starch 40-70% Amylose, 15%DS
- Jet Cook gelatinize 120-175c
- Cool 50—75c
- Add De-branching Enzyme, Isoamylase Incubate 60c, 48h
- Concentrate 60 DS Dry Or Retrograde Remove solubles
- Inactivate enzyme 70c or pH 3
- Basic patent with variations to protect this platform
- RS 30% Or higher 70% if separated

Spray-dried enzyme-treated starch samples significantly differed from the control starch and had an increase in the slow digestion property. The digestion rates of starches treated with amylase and transglucosidase were lower (improved SDS) than those of starches treated with one of the amylases alone.

<table>
<thead>
<tr>
<th>sample</th>
<th>rapidly digested starch</th>
<th>slowly digested starch</th>
<th>resistant starch $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal maize starch</td>
<td>87.3 ± 3.2 a</td>
<td>13.1 ± 1.6 c</td>
<td>-0.4 ± 1.6 b</td>
</tr>
<tr>
<td>BA-starch</td>
<td>72.8 ± 2.2 b</td>
<td>22.1 ± 3.2 bc</td>
<td>5.2 ± 3.2 ab</td>
</tr>
<tr>
<td>BATG-starch</td>
<td>58.3 ± 4.8 cd</td>
<td>32.8 ± 3.1 ab</td>
<td>5.1 ± 3.2 ab</td>
</tr>
<tr>
<td>MA-starch</td>
<td>67.5 ± 1.5 bc</td>
<td>18.8 ± 0.4 bc</td>
<td>13.5 ± 0.4 a</td>
</tr>
<tr>
<td>MATG-starch</td>
<td>56.3 ± 1.6 d</td>
<td>24.1 ± 2.7 ab</td>
<td>11.4 ± 2.7 a</td>
</tr>
</tbody>
</table>

BA-starch (â-amylase treated maize starch, BATG-starch (â-amylase- and transglucosidase treated), MA-starch (maltogenic â-amylase-treated), and MATG-starch (maltogenic â-amylase- and transglucosidase treated). J. Ag. & Food Chem 1997
SDC (slowly digestible carbohydrate) Sweetener
Fructose & gluco-oligosaccharides with alternating $\alpha$-1,3/$\alpha$-1,6 linkages (Alternan Sucrase)

Typical Composition (on dry basis)
- Fructose: 37%
- Leucrose: 13%
- Other DP2: 2%
- Higher saccharides: 48%

Average DP = 10
Total DP1 and DP2 = ~ 50%
Starch Applications Tests
Clean Label Starch Applications and Selection Criteria

- Formulation – other ingredients, market criteria of finished food
- How long is the shelf life of the food
- High Acid or Low Acid
- Processing conditions
  - High heat vs low heat
  - High shear vs low shear
  - Both high heat and high shear
Starch Freeze-Thaw Stability Test

1. In a steam table or on a stove top heat a 5.0% (db) starch slurry to 190 F (88 c) and hold for 10 minutes.
2. When paste is cool enough to handle fill 5 ml polypropylene test tubes at least 80% full to a constant weight (+/- 0.05 gm). Record paste weight. Zero the scale with an empty test tube to compensate for tube weight.
3. Cool to room temperature and cap all test tubes.
4. Remove one test tube as the control and freeze the rest.
5. Centrifuge the control at 5000 rpm for 10 minutes.
6. Tilt the tube slightly and decant the water using a Pasteur pipette. Take care not to remove starch paste.
7. Reweigh test tube.
8. Calculate percent water loss.

\[
\% \text{ water loss} = \frac{\text{Weight of original paste} - \text{weight of decanted paste}}{\text{Weight of original paste}} \times 100
\]
9. Remove a small amount of starch paste. Observe and record paste texture (i.e. Smooth, creamy, firm, etc).

10. For each subsequent F/T cycle remove all the test tubes from the freezer, thaw to room temperature and repeat steps 5 to 9.

11. Once the texture of the starch paste becomes grainy, pulpy or cottony it is no longer considered freeze/thaw stable and testing is completed.

Note: If water and starch separation is not distinct increase rpm rate.
Freeze-thaw Stability

Sample

Cycle A

Cycle B

Water Separated
Starch Paste – Freeze Thaw Cycles

Waxy maize starch at 1 % concentration, boil and observe before and after repeated Freezing and Thawing cycles

Native          Modified

A. Time, temperature and pH effect

1. Brabender 1: Neutral (pH as is)
2. Brabender 2: Acid – adjusted to pH 3.0 with 10% acetic acid (simulates vinegar)
   Starch concentration: 5.5% db
   Method: Rapid heat to 50°C, control to 95°C, hold 30 min,
   control cool to 50°C, hold 30 min

Reported results:
Actual slurry pH
Copy of actual curve
Granular integrity (deg of cook) at the end of the run
Final paste texture: visual or analytical
Final paste clarity: visual or analytical
Effect of Cross-linking Level on Waxy Starch

pH 3.0, Temp 195 -200 F with moderate shear

Swelling Power Test and Solubles

Weigh 400 mg starch \((W, \text{ mg, db})\) into a pre-weighed eppendorf tube \((P1, \text{ mg})\)

↓

Add 10 ml DI water

↓

Allow to stand for 10 min then vortex for 10 sec

↓

Heat on a heating block for 30 min at 85 C

↓

Cool to RT by placing in an ice bath for 5 min

↓

Centrifuged for 5 min at 10,000 g

↓

Transfer supernatant into another pre-weighed eppendorf tube \((R1, \text{ mg})\) by suction with a mechanical pipette
Clean Label Starch Applications Tests

↓

Wipe the tube-with-paste with a paper towel and weigh (P2, mg)

↓

Dry the tube-with-supernatant on the heating block overnight

↓

Cool to room temp (1 h)

↓

Weigh the tube-with-dried-supernate (R2, mg)

*Calculation:*
Swelling Power = \[rac{P2-P1}{W-(R2-R1)}\]

% Soluble Solids = \[(R2-R1)\times100/W\]

*Reference:*
Commercial Clean Label Starches

Examples
Commercial Native Starches that can Replace Modified Starches

US and EU manufacturers
Physically modified and/or enzyme modified
Choices based on formulations, process and shelf stability

- 20 Waxy
- ~ 5 Native Dent (regular maize)
- 10 Potato
- ~ 10 Tapioca
- ~ 5 Rice
- ~ 5 Pea
- ~ 7 to 10 Wheat flours

~15 of above are Enzyme Modified
Choices based on formulations, process and shelf stability
All contain 1.7% potato starch
  • A: no other starch
  • B: 2.9% chemically modified
  • C: 2.9% **pregel pea starch** (clean label)

Pulpiness of the tomato sauce made with Pregel pea starch (C) is similar to that made with chemically modified starch (B).

From Roquette USA
Summary

People can live better with CHO if we give good and strong reasons to choose them. It's up to all of us to bring more, better, healthier and easier-to-use foods and beverages into people's lives.

Opportunities for clean label starch remain very bright as we move forward with new discovery of processes, new enzymes and create cost effective options for consumers.

Thank You

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