MODIFIED STARCH
FOR FOOD:
PRODUCTION, PROPERTIES & APPLICATION
Changes in native starch during processing
(Taggart, 2004)

(1) Gelatinisation
(2) Pasting
(3) Retrogradation

for maize starch

39 g starch, anhydrous starch + H₂O = 450 g.
Heat rapidly to 50 °C then 1.5 °C per minute to 95 °C, hold for 20 minutes.
Cool 1.5 °C per minute to 30 °C.
Why native starch should be modified?

- Processing at high temperature
  - $+100^\circ$C: improved solubility, reduced viscosity
  - $>>150^\circ$C: glycosidic linkage easily hydrolyzed
- Mechanical Shear
  - Starch paste agitation & transport through pipes & pumps increased the viscosity
- Acid Media
  - At low pH, starch easily hydrolyzed
- Salts
  - Electrolytes solution influenced to the viscosity & granule swelling
- Low Temperature
  - Retrogradation during freeze & thawed
Starch Modification (BeMiller, 1997)

- Improving the cooking properties
- Decreasing the retrogradation tendency
- Improving the freeze-thaw stability of paste
- Decreasing the paste and/or gel syneresis properties
- Increasing the paste and/or gel clarity
- Increasing the paste and/or gel textures
- Improving the film forming
- Improving the adhesion properties
- Improving the hydrophobic group (for emulsion stabilization)
Cooking properties: Molecular level: Gelatinization and Retrogradation

Heat → Gelatinization

Retrogradation (Re-crystallization)

Long-term Storage (weeks – months)
Granular level: **Swelling and Pasting properties**

- **Native starch**
- **Swelling and amylose leaching**
- **Starch paste**
- **Gelatinization**

**Granule**

- Amylose chain

**Viscosity increase**
Chemical & Biochemical Modification of Starch
(Taggart, 2004)
Effect of cross-linking & stabilization

(Taggart, 2004)
Terminology in Modified Starch

**Carbon Position** (C-) in anhydroglucose unit

- C-6: primary hydroxyl group
- C-2 & C-3: secondary hydroxyl group
**Degree of Polymerization (DP)**
**Dextrose Equivalent (DE) or Reducing Value**

<table>
<thead>
<tr>
<th>Carbohydrate</th>
<th>DP</th>
<th>DE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dextrose</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Maltose</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>Amylose</td>
<td>100</td>
<td>1</td>
</tr>
</tbody>
</table>

**Alkali Number**
Determining the number of *reducing end group* for starch products (number of terminal aldehydic group)

Cleavages of starch products by alkali on certain condition

Amount of alkali solution (ml of 0.10 N) consumed during degradation of starch per g dried starch

Can not applied for esterified, etherified, and oxidized starches.
**Percent of Substitution**
The level of substitution expressed as weight of the substituent moiety as % of the total starch dry substance

**Degree of Substitution (DS)**
The average number of sites per anhydroglucose unit on which there are substituent group

**Molar Substitution (MS)**
The level of substitution in terms of monomeric units in the substituent per mole of hydroglucose unit
**Beta Amylase Digestibility**

Indication of the extent to which starch, amylose, amylopectin, or modified starch is digested by this enzyme.

An indication of the linearity of the glucose polymer of hydrolyzate (products)
Cross-linking

Chemical modification of starch that results in covalently bonded inter- and intramolecular bridges between starch polymers

Objectives:
1. Strengthen starch granule
2. Delay viscosity development by retard granule swelling

Benefit to user:
1. Improved process tolerance to heat, acid & shear
2. Production efficiency: increased heat penetration allowing shorter process time

Application:
Ambient stable products, bottle sauces, Sterilized soups and sauces.
Chemical reactions for (1) phosphorous oxychloride, (2) sodium trimetaphosphate, (3) a mixed adipic-acetic anhydride reagents crosslinking of starch

1. \( \text{St-OH} + \text{O} = \text{P-Cl} \xrightarrow{\text{NaOH}} \text{St-OPO-St} \)
   - \( \text{NaOH} \)
   - Cl
   - Na\(_3\)P\(_3\)O\(_9\)
   - ONa
   - NaCl
   - Na\(_2\)H\(_2\)P\(_2\)O\(_7\)

2. St-OH + CH\(_3\)COC(CH\(_2\))\(_n\)COCCH\(_3\) \xrightarrow{\text{NaOH, pH 8}} \text{St-O-C(CH\(_2\))\(_n\)C-O-St} + \text{CH}_3\text{CONa}

3. \( \text{St-OH} + \text{CH}_3\text{COC(CH\(_2\))\(_n\)COCCH}_3 \xrightarrow{\text{NaOH}} \text{St-O-C(CH\(_2\))\(_n\)C-O-St} + \text{CH}_3\text{CONa} \)
Effect of crosslinking (%trimetaphosphate treatment) on viscosity profile of starch (Smith, 1982)

- Native starch is normally susceptible to viscosity breakdown.
- Crosslinking tends to inhibit granule swelling during cooking.
- Low-DS starch: tends to show a peak viscosity higher than native starch.
  ➔ Granular stability & improved paste texture
- High-DS starch: no peak viscosity. Increase in viscosity throughout the cooking process
Substitution (Stabilization)

Chemical modification of starch resulting in the addition of a chemical blocking group between starch polymers and involving derivatization with a monofunctional reagent through ester or ether formation.

Objectives:
1. Prevent shrinkage of starch granule & provide stability at low temperature.
2. Lower gelatinization temperature.

Benefit to user:
1. Excellent chill and freeze-thaw stability to extend shelf life.
2. Easy to cook in high solid system

Application:
Refrigerated & frozen foods
High brix fillings & toppings
**Starch Esters**

Starch Acetate containing 0.5-2.5% acetyl group for food applications. 

**Acetylated crosslinked** is used as a thickener because of its stability and clarity.

**Chemical reaction for acetate substitution of starch**

\[
\begin{align*}
\text{CH}_3\text{-C-} & \quad \text{OStOH} \quad \text{OH}^- \\
\text{CH}_3\text{-C-O-St} & \quad + \quad \text{NaOAc} \\
\text{CH}_3\text{-C-O-CH=CH}_2 & \quad \text{StOH} \quad \text{OH}^- \\
\text{CH}_3\text{-C-O-St} & \quad + \quad \text{CH}_3\text{CHO}
\end{align*}
\]
Effect of substitution (acetylation) on the viscosity profile of starch (Rutenberg & Solarek, 1984).

Substitution tends to result in
1. A lowering of gelatinization temperature,
2. An increase in peak viscosity,
3. A decrease in set-back during paste cooling, especially in amylose-containing starch,
4. A stable paste that is resistant to retrogradation during storage
Effect of chemical substitution

- Introduction of chemical blocking groups act to “loosen” polymeric structure of granule ➔ more susceptible to cooking
- Upon cooling, the “blocking action” limits polymer re-association & retrogradation is reduced.
- High DS ➔ extremely freeze-thaw stable
- Clarity of paste is improved ➔ increasing the degree of swelling or hydration capacity, & by reducing retrogradation
Starch Ether

Pastes of **Hydroxypropylated Starch** have improved clarity, greater viscosity, reduced syneresis, and freeze-thaw stability.

Chemical reaction for hydroxypropyl substitution of starch

\[
\text{StOH} + \text{CH}_2 - \text{CH} - \text{CH}_3 \xrightarrow{\text{OH}^-} \text{StOCH}_2\text{CHCH}_3
\]

**Crosslinked-hydroxypropylated starch** ➔ the most commonly used modified starch in food industry
For gravies, dips, sauces, fruit fillings & puddings ➔ A smooth, viscous, clear thickener & freeze-thaw stability
Conversion

Starch → good thickening properties → high molecular weight polymeric component.

Conversion

Starch → reduced MW, viscosity

Properties of converted starch
   ➔ Can vary widely depending upon:
   1. Type of base starch used
   2. Conversion process (time)
   3. The method employed (acid, oxidant, enzyme, heat, or combinations)

Acid Hydrolysis
Oxidation
Pyroconversion
Enzyme conversion
Acid Hydrolysis

~ acid-thinned, thin-boiling & fluidity starches

Differs from dextrinisation ➔ conducted in aqueous conditions

Objectives:

1. Lower viscosity/reduce the hot viscosity
2. Increase gel strength

Benefit to user:

Enhances textural properties at higher usage concentration of starch

Application:

Gum, pastilles, jellies
Acid hydrolysis (2.2 N HCl, 37°C) of granular starches (Srichuwong et al., 2006)

Degree of polymerization of sago starch after acid-alcohol treatment at 45°C for 1 hour (Yiu et al., 2008)
Acid Hydrolysis

Mild, prolonged acid hydrolysis

- Hydrolysis of amorphous regions
- Acid resistant residue = crystallites

Source : Srichuwong et al. (2006)
Viscoamylography of native & lintnerized banana starch

Source: Aparicio –Saguilan et al. (2005)
Method for measuring the extent of hydrolysis

- Molecular weight
- Intrinsic viscosity
- Alkaline number
- Reducing value
- “Water fluidity” (WF)

Water fluidity (WF) scale used to measure the extent (degree) of starch conversion
Oxidation

Objectives:
1. Introduce carbonyl group and carboxyl groups which increases clarity and reduces retrogradation of cooked starch pastes
2. Provide lower viscosity & low temperature stability

Benefit to user
1. Improves adhesion of coatings
2. Creates soft stable gels at higher dosage than parent native starch.

Application:
Battered meat, poultry & fish (crispy texture after frying);
confectionary

Major reaction that occur during oxidation
Oxidation & Bleaching

- **Bleaching agents**: hydrogen peroxide, ammonium persulfate, sodium/calcium hypochlorite, K-permanganate & sodium chlorite.
  
  ➛ To improve the whiteness of starch powder by oxidation the impurities such as carotene

- **Oxidant**: only chlorine (sodium hypochlorite) is permitted

**Permitted doses** for Sodium hypochlorite:
- Oxidant ➔ 0.055 g of active chlorine per g starch
- Bleaching agent ➔ 0.0082 g of active chlorine per g starch
Pyroconversion (dextrinization)

Starch products prepared by dry roasting acidified starch.

Objectives:

Breakdown and rearrange starch molecule providing lower viscosity, increased solubility, and a range of viscosity stability from liquid to gel.

Molecular transformation that occur during pyroconversion.
Pyroconversion (dextrinization)

**Benefit to user:**
1. Easily handled or applied at higher dosage than parent native starch for desired effect
2. Create film-forming properties

**Application:**
Fat replacer in bakery & dairy products, bakery glazes, protective coating in confectionery

**Properties:**
- depending upon the reaction condition (pH, moisture, temperature, length of treatment)
- Products characteristics vary in viscosity, cold water solubility, color, reducing sugar content & stability
## Reaction condition & Properties of white dextrin, yellow dextrin & british gum

<table>
<thead>
<tr>
<th>Condition</th>
<th>White dextrin</th>
<th>Yellow dextrin</th>
<th>British Gum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roasting temp. (°C)</td>
<td>110-130</td>
<td>135-160</td>
<td>150-180</td>
</tr>
<tr>
<td>Roasting time (hr)</td>
<td>3-7</td>
<td>8-14</td>
<td>10-24</td>
</tr>
<tr>
<td>Amount of catalyst</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Solubility</td>
<td>Low to high</td>
<td>High</td>
<td>Low to high</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Low to high</td>
<td>Low</td>
<td>Low to high</td>
</tr>
<tr>
<td>Color</td>
<td>White to cream</td>
<td>Buff to dark tan</td>
<td>Light to dark tan</td>
</tr>
<tr>
<td>Type of reaction</td>
<td>Mainly hydrolysis</td>
<td>Hydrolysis &amp; repolymerization</td>
<td>Mainly repolymerization</td>
</tr>
</tbody>
</table>

Sources: Whistler et al. (1984)
Enzyme Conversion

Selective enzyme hydrolysis is a form of biochemical modification → wide range of functionalities

Enzymatic digestion of amylose & amylopectin by α-amylase, β-amylase & a debranching enzyme
Enzyme Conversion

Objectives:
Produces varied viscosity, gel strength, with thermoreversibility and sweetness.

Benefit to user:
1. Contributes texture & rheology
2. Economic dispersant

Application:
Fat mimetics, flavor carriers, dry mix fillers
Sugar preparation from enzymatic hydrolysis of starch

Maltooligosaccharides

Cyclodextrin

Hydrogenation

Maltitol

Maltose

Coupling sugar

Enzymes:
(1) α-amylase
(2) β-amylase
(3) Glucoamylase
(4) CGT-ase (cyclodextrin glucanotransferase)
(5) Glucose-Fructose Isomerase

Starch Syrup

Special amylase

Acid / (1)

(1) & (3)

Starch Syrup Solid

Glucose

Fructose

Sorbitol

Source: Kainuma (1995)
## Applications of starch hydrolysis products

<table>
<thead>
<tr>
<th>Products of Starch Hydrolysis</th>
<th>DE</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maltodextrin</td>
<td>3-20</td>
<td>Stabilizer, thickener, filler, adhesive &amp; paste</td>
</tr>
<tr>
<td>Maltose Syrup</td>
<td>48-63</td>
<td>Hard candy, prevent hygroscopic, Substrate for fermentation</td>
</tr>
<tr>
<td>Glucose Syrup</td>
<td>96-98</td>
<td>Soft drink, substrate for fermentation</td>
</tr>
<tr>
<td>Fructose Syrup</td>
<td>-</td>
<td>Canned food &amp; drinks industries, soft drink, dairy products</td>
</tr>
<tr>
<td>Mixed syrup</td>
<td>42-63</td>
<td>Soft drink, raw material for food industries</td>
</tr>
</tbody>
</table>

Source: Kennedy et al. (1995)
Lipophilic substitution

The hydrophilicity of starch, its propensity to interact with water, can be transformed into hydrophilic & hydrophobic duality

Objective:
Introduce lipophilic groups

Benefit to user:
1. Emulsion stabilizer which improves quality of any fat/-oil-containing products
2. Reduces rancidity by preventing oxidation

Application:
Beverage, salad dressing
Flavor encapsulating agents
Lipophilic substitution

Stabilizing of emulsions

Hydrophilic Starch Chain

Ester

Carboxylic

Hydrophillic Starch-n-octenyl succinate structure

-O-CO-CH-CH₂-CH=CH-(CH₂)₄-CH₃

n-octenyl chain
Emulsifying starches & their main applications

<table>
<thead>
<tr>
<th>Application</th>
<th>Function</th>
<th>Alternative to:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beverage emulsions</td>
<td>Emulsion stabilizer</td>
<td>Gum Arabic</td>
</tr>
<tr>
<td></td>
<td>Clouding agent</td>
<td></td>
</tr>
<tr>
<td>Oleoresin emulsions</td>
<td>Emulsion stabilizer</td>
<td>Gum Arabic</td>
</tr>
<tr>
<td></td>
<td>Clouding agent</td>
<td></td>
</tr>
<tr>
<td>Encapsulated flavors</td>
<td>Encapsulated agent</td>
<td>Gum Arabic</td>
</tr>
<tr>
<td></td>
<td>Emulsion stabilizer</td>
<td></td>
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<tr>
<td>Salad dressing (cholesterol free)</td>
<td>Viscosity stabilizer</td>
<td>Egg Yolk</td>
</tr>
<tr>
<td></td>
<td>Eliminate cholesterol</td>
<td></td>
</tr>
<tr>
<td>Cheese analogues</td>
<td>Emulsifier-stabilizer-</td>
<td>Calcium caseinates</td>
</tr>
<tr>
<td></td>
<td>texturizer</td>
<td></td>
</tr>
<tr>
<td>Creamers</td>
<td>Emulsifier</td>
<td>Sodium caseinates</td>
</tr>
</tbody>
</table>
Pregelatinized Starch

Pregelatinisation is a physical rather than chemical modification. Certain starch require cooking to develop their function.

Objective:
Pre-cook starch to give cold-water thickening properties

Benefit to user:
Cold-water thickening eliminates need to cook, offers convenience and energy saving.

Application:
Instant soups, sauces, dressing, desserts, bakery mixes. Thickener in food that receive minimal heat processing.
Pregelatinized Starch
~ pregels or instant starch

Methods:
- Drum drying (starch suspension or starch gels) → very widely used.
- Extrusion (semi-dry starch) → rarely used
- Spray drying (starch suspension) → increase in use
**Thermal treatment**

Physical modification of starch without any gelatinization, damage to granular integrity or loss of birefringence.

Methods:

*Heat moisture treatment*: heating the starch at a temperature above its gelatinization point but with insufficient moisture to cause gelatinization.

*Annealing of starch*: heating a slurry of granular starch at a temperature below its gelatinization point for prolonged periods of time.
Thermal treatment

Objectives:
1. Strengthen starch granule
2. Delay viscosity development by retarding granule swelling

Benefit to user:
1. Unique functional native starch
2. Improved process tolerance to heat, acid, and shear
3. Production efficiency: increase heat penetration, allowing shorter process time

Application:
Ambient stable products; bottled sauces; sterilized soups and sauces.
Hydrothermal treatment for rice starch

UR : untreated starch
AR : annealed starch
HR : hydrothermal treated starch

Fig. 2. RVA pasting profiles of rice starches and flours. Samples are indicated as: 1 (UR); 2 (AR); 3 (HR); 4 (fresh flour); 5 (aged flour); 6 (flour + 50 g/100 g UR); 7 (flour + 50 g/100 g AR); and 8 (flour + 50 g/100 g HR).