Novel clean and selective processes for starch modification

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Pristine starch: a semi-crystalline polymer

- Lipids
- Amylose: MW $2 \times 10^5 - 10^6$ g.mol$^{-1}$
- Amylopectin double helix: MW $5 \times 10^7 - 5 \times 10^8$ g.mol$^{-1}$
- Crystallinity: 20-45%
- Anhydroglucose unit (AGU)
- ?(1? 4) ; 6 AGU per pitch
- Ca. 6% of ?(1? 6) linkage
<table>
<thead>
<tr>
<th>Food additives (16 %)</th>
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<tbody>
<tr>
<td>✐ Sweeteners</td>
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<tr>
<td>✐ Thickeners</td>
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<tr>
<td>✐ Stabilizers</td>
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<td>✐ Humectants</td>
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<tr>
<th>Major non-food applications (84 %)</th>
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<tbody>
<tr>
<td>✐ Paper making industry (60%)</td>
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<tr>
<td>✐ Construction Plaster wallboards</td>
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<tr>
<td>✐ Adhesives</td>
</tr>
<tr>
<td>✐ Pharmaceutical, galenics</td>
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<tr>
<td>✐ Textile sizing, Fabric finishing,</td>
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<tr>
<td>✐ Printing industry (anti-set-off powder)</td>
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<td>✐ Flocculating agents</td>
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Applications of starch

Foreseen market expansion or radically new applications

- Textiles - for weaving production lines and printing cloth plastics
- Construction: binders, antifreeze, retarding agents for concrete (gluconic ac.)
- Lubricants - in association with vegetable oils for manufacture of biolubricants
- Agrochemicals - binder for fertilizers, controlled release by encapsulation, seed coatings
- Super-absorbent products - grafted starches disposable nappies, root coating
- Thermoplastic material
Clean processes for starch modification

Vegetal origin + Clean processing = Greener chemistry

Processing

- Reactive extrusion
- High-energy radiation

Chemical modification of starch

1. Cationization (quaternary ammonium)
2. Enzymatic hydrolysis
3. Radiation grafting of thermoplastic starch
1 - Cationization of starch

<table>
<thead>
<tr>
<th>Papermaking industry</th>
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<tbody>
<tr>
<td>- Different types of starches</td>
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<tr>
<td>- Up to 10 wt-% of starch in some papersheets</td>
</tr>
<tr>
<td>- Cationic starch for binding cellulose fibers</td>
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</tbody>
</table>

![Starch molecule](image1)

![Papermill](image2)
Cationization of starch

Etherification of AGU by trimethylammonium reagents

1,2-epoxypropyl trimethylammonium chloride

3-chloro-2-hydroxypropyl trimethylammonium chloride

+ some elimination products
$^1$H NMR analysis of starch cationization

Consistent values of the degree of substitution (DS):
NMR, elemental analysis, Kjeldhal, Cl$^-$ exchange $0.005 < DS < 0.2$
Influence of [reactant] to [AGU] ratio on DS

DS increases when [co-reactant] increases, but reaction yield decreases.
Influence of glycerol content on DS

5 min @ 120°C
[reactant] / [AGU] = 0.05
[reactant] / [NaOH] = 1

DS decreases when plasticizer content increases.
Factors influencing cationization efficiency

Some other selected results

- Modeling of cationization reaction
- Distribution of cationic functions
- Competing side reactions
- Relation between molecular structure and functional properties

A. Ayoub et al. Starch/Stärke (2004), 55 (7), 297-303
A. Ayoub et al. Starch/Stärke (2004), 56 (11), 513-519.
2 - Dextrinisation of starch

Conventional methods

- Acidic hydrolysis
- Enzymatic
  - ?- or ?-amylase
  - liquefying or saccharifying enzymes

Drawback of current processes

- batch operations
- wet chemistry
- long reaction time

glucose syrup, dextrines.....
Dextrinisation of starch by reactive extrusion

- native starch
- co-reactant (water)
- catalyst (enzyme)

- hydration and destructurization
- hydrolysis

- hydrolysis is faster
- process is continuous
- products are obtained as a concentrate
Dextrinisation of starch by reactive extrusion

SEC profiles of obtained oligosaccharides

Reactive extrusion sample

Reference wet-technology
Dextrinisation of starch by reactive extrusion

Points under study

- Search for new thermally-mechanically resistant enzymes
- Multiparameter control of starch hydrolysis
  (T°, power, water content, enzyme concentration)
- Oriented hydrolysis towards target distributions

Confirmed advantages

- Low energy consumption
- Single step process
- Continuous production
- Easy drying
3 – Radiation grafting of starch

Potentialities of thermoplastic starch (TPS)

- High MW polymer with interesting mechanical properties
- Biodegradable thermoplastic material
- Cheap, from renewable resources

Some limitations to be overcome

- Retrogradation (recrystallization)
- High hydrophilicity (poor properties when wet)
- Limited compatibility between starch and organic additives
- Migration or phase separation of plasticizer upon ageing
Lignins as additives for TPS

- A broad family of polyphenolic compounds biodegradables and hydrophobic

- Constituent of wood, second in abundance after cellulose

- Large variety of structures depending on botanical origin and industrial extraction process

- By-products of the pulp and paper industry to be valorized
Radiation processing for improving the properties of thermoplastic starch

Concept
Use high energy irradiation to create covalent linkages between amorphized starch and organic additives (low to high MW compounds, natural or synthetic)

- Structural defects impeding starch retrogradation
- Forced compatibility between blends constituents
  No phase separation, absence of migration

Objectives
Evaluate the scope and limits of ionizing radiation for improving the existing materials and processes
Radiation processing of starch-AU blends

Electron beam accelerator
High voltage : 175 kV
5-800 kGy - in air

- Physical stabilization effective
- Multiple grafting demonstrated
- MALDI TOF mass spectrometry for the analysis of model blends

A. Olivier, C. Gors, F. Cazaux, X. Coqueret, Biomacromolecules 2000, 1, 282-289
A. Olivier, F. Cazaux, and X. Coqueret, Biomacromolecules 2001, 2, 1260-1266
Properties of starch-lignin blends

Starch 70 wt-parts + Glycerol 30 wt-parts + Lignins 10-30 wt-parts:
  lignosulfonates (LS)
  wheat lignins (WL)
  bagasse lignins (BagL)

• Reduction of hydrophilicity

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<th></th>
<th>Water sorption at 73 %RH</th>
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<tr>
<td>Starch-Glycerol (no lignin)</td>
<td>21-23 %</td>
</tr>
<tr>
<td>Starch-Glycerol-Bagasse lignins (20 phr)</td>
<td>13-16 %</td>
</tr>
<tr>
<td>Starch-Glycerol-Wheat lignins (20 phr)</td>
<td>14-18 %</td>
</tr>
<tr>
<td>Starch-Glycerol-Lignosulfonate (20-30 phr)</td>
<td>19-23 %</td>
</tr>
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</table>

• Protective effect against radiation
Properties of starch-lignin blends

- Modification of wettability by water
Maldi-ToF MS of maltodextrine Glucidex 19

**Model for starch**: $n = 16$

$m/z = (n \times 162) + 18 + 23$

**2,5-dihydroxybenzoic acid**

DHB$^*$ matrix

Flight tube
Models for lignins
Models for lignins

- **Phenols**
- **Benzyl alcohols**
- **Cinnamic derivatives and lignin monomers**
Reactivity of p-methoxybenzyl alcohol with maltodextrine Glucidex 19

\[
\begin{align*}
\text{observed adduct} &= 1133 \text{ Da} \\
\text{m}_{\text{hexamer}} &= 1013 \text{ Da} \\
\text{m}_{\text{alcohol}} &= 138 \text{ Da} \\
\text{m}_{\text{Na}^+} &= 23 \text{ Da} \\
\text{Sum} &= 1154 \text{ Da}
\end{align*}
\]
Reactivity of various benzyl alcohols with maltodextrine Glucidex 19

Hypothesis of a common mechanism for the various benzylic derivatives

The benzyl alcohol function seems to be involved in the condensation process
Quantification of p-methoxybenzyl alcohol reactivity by $^{13}$C NMR analysis

- Maltodextrine G19 + p-methoxybenzyl alcohol (20 phr)
- $^{13}$C NMR (gated decoupling): integral of $-{\text{CH}}_2$-OH to AGU $\text{CH}$-OH

![Graph showing conversion (%) vs. dose (kGy)]
Formation of multiple adducts

Maltodextrine G19 + p-methoxybenzyl alcohol - 400 kGy

- High grafting yield, and multiple grafting
- Confirmation of free radical mechanism for grafting since there is only a single site for acetalization per molecule
Coupling mechanism for benzyl alcohols

- **Radiolysis of constituents**
  - UAG-UAG-UAG $\overset{\rightleftharpoons}{\longrightarrow}$ [UAG-UAG-UAG(-H)]° + H°
  - H₂O $\overset{\rightleftharpoons}{\longrightarrow}$ H° + HO°
  - Ar-CR₂-OH $\overset{\rightleftharpoons}{\longrightarrow}$ Ar-CR₂° + HO°

- **Secondary activation of polysaccharide by transfer**
  - UAG-UAG-UAG + Rad° $\overset{\rightleftharpoons}{\longrightarrow}$ [UAG-UAG-UAG(-H)]° + Rad-H

- **Coupling by combination of free radical species**
  - [UAG-UAG-UAG(-H)]° + Ar-CR₂° $\overset{\rightleftharpoons}{\longrightarrow}$ [UAG-UAG-UAG(-H)(+CR₂-Ar)]
Grafting of Cinnamyl alcohol onto maltotriose (200 kGy dose)
Grafting of cinnamyl alcohol onto maltodextrine Glucidex 19 (400 kGy dose)

Composition: G19 63%, H2O 16%, CML 5%, MeOH 16% - 400 kGy
Quantification of cinnamyl alcohol reactivity by $^1$H NMR analysis

$$\text{[CinOH]}_0 = 0.08, 0.36, 0.68, 1.21 \text{ mol.kg}^{-1}$$

Fractional conversion exceeds 50% at 200 kGy
Conclusion

Tailored structure and properties of starch derivatives are obtained by applying appropriate treatment: chemical, enzymatic or radiation processing with better respect of green chemistry principles.

Physical limitation to chemical reactivity: lack of mobility

High energy irradiation induces selective chemistry, is not so complex and can be well-controlled

LignoStarch project (ANR 2007)