Industrial Products from Starch

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Lecture content

- Industrial (non-food) uses of starch
  - Starch production/consumption in the EU (2002/2003) (2)
  - Starch properties
  - Technical requirements for renewable raw materials (starch)
  - Starch based detergent products (4)
  - Starch based binders (3)
  - Starch in biodegradable polymers (3)
  - Starch based products for pharma and cosmetics (3)
  - Starch hydrolysates for fermentation (3)
  - Versatility of starch
  - Economic evaluation
  - Product possibilities
  - Future R&D requirements
  - Outlook
European Starch Production/Market - 2002

► Total raw materials processed: 20.5 mio t

► Total starch produced: 8.6 mio t (8.9 mio t in 2003; Giract)

► Consumption of starch and starch derivatives (excl. feed): 7.9 mio t

Source: AAC
Starch & Starch Derivatives
EU Market by Sector - 2002

Confectionery & Drinks 29%
Processed Food 24%
Feed 1%
Corrugating & Paper Making 4%
Pharma. & Chemicals 13%
Other non-food 4%

Total Market: 7.9 mio tons
Non food: 47%  Food: 53%

Source: AAC
Industrial Uses of Starch

- Cereals / Tubers
- Starch
  - Modified Starches
    - Hydrolysed
    - Oxidised
    - Esters
    - Ethers
    - Crossbonded
    - Dextrins
  - Maltodextrins
  - Hydrolysates
  - Derivatives
  - Fibers, hemicellulose, bran
  - Germ oil
  - Gluten
  - Steepwater
  - Paper & corrugating (27%)
  - Thickeners
  - Binders
  - Cobuilders
  - Thermoplastics
  - Complexing agents
  - Flocculating agents
  - Coatings
  - Latex copolymers
  - Fermentation feedstocks
  - Polyols
  - Surfactants
  - Pharma & Cosmetic aids
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<th>Starch Properties</th>
<th>Applications</th>
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<td>Viscosity (Rheology)</td>
<td>Foodstuffs</td>
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<td>Gel strength</td>
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<td>Water binding</td>
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<td>Adhesive power</td>
<td>Paper/Corrugating</td>
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<td>Film forming</td>
<td>Textile processing</td>
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<td>Biodegradability</td>
<td>Biodegradable products</td>
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<td>Protective colloid</td>
<td>Emulsion polymerisation</td>
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# Technical Requirements for Renewable Raw Materials (Starch)

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<th>General</th>
<th>Specific</th>
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<tr>
<td>Availability</td>
<td>(Bio)compatibility</td>
</tr>
<tr>
<td>Uniformity</td>
<td>Biodegradability</td>
</tr>
<tr>
<td>Purity</td>
<td>Non-toxicity</td>
</tr>
<tr>
<td>Workability</td>
<td>Molecular structure e.g. chirality</td>
</tr>
<tr>
<td>Economy</td>
<td>Reactivity</td>
</tr>
<tr>
<td>Ecology</td>
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Starch Based Detergent Products

Potential (partial) replacement of oil/gas based (petrochemical) products (surfactants, builder/cobuilder and bleach activators)

Advantages

- Use of renewable raw materials (starch, fats and oils)
- Environmental friendly (sustainable) processes
- Products are biodegradable, non toxic and non allergenic
- No eutrophication of stagnant waters
- No nitrosamine formation
- "Natural/green products"

Critical: price/performance of « green » products compared to petrochemical products
Starch Based Detergent Products

**Surfactants**

Alkyl poly glucosides (APG)

**Builder/Cobuilder**

Oxidised Starch

**Bleach activators**

Hexaacetyl sorbitol/mannitol

**Glucamides**

Citric Acid

Hexaacetyl sorbitol/mannitol
Starch Based Detergent Products/Barriers

► Alkylpolyglucosides (APG) Global
  ■ 60-70 ktpy
  ■ Strong initial growth, now leveled off
    • Used as cosurfactants (functional properties)
    • Further market penetration depends on price/performance in comparison to alternative cosurfactants
    • Superior skin compatibility

► Builder/cobuilder systems for powder detergents
  ■ Efficient builder/cobuilder systems (zeolite/acrylic acid (co)polymers) established since a long time
  ■ No sustainable and economic industrial process for C-6 oxidized starch (DS=1) (polyglucuronic) established
  ■ Polyglucuronic acid is biodegradable (adaptation)
  ■ Ca complexation is comparable to established systems
Hexaacetyl sorbitol/mannitol as bleach activator

- TAED is produced in written off plants at low costs
- TAED is biodegradable
- Due to recent results, there is no concern about “toxic” metabolites of TAED anymore
- Peracetylated polyol mixture performance as perborate or percarbonate bleaching booster is comparable to TAED (washing tests)
Starch Based Binders

- Use of native and modified starches as binders for compacting of powders and dust to pellets, bars, briquettes for further processing

- Replacement of cheap binders like sulphite black liquors, bitumen and pitch to reduce the burden on the environment

- Replacement of urea/formaldehyde and phenol/formaldehyde binders, due to difficult environmental control

- Construction materials (i.e. plaster board, mineral fibre board, concrete retarders, plaster, glass and mineral wool.....)
Starch Based Binders

- Powder:
  - e.g. ceramic powder
  - aluminium dust
  - coal powder
  - filter dust

- Dough:
  - e.g. Pellets

- Pieces:
  - bars
  - briquettes
  - cylinders
  - sheets

- Drying:
  - ambient temp.
  - about 200°C
  - about 300°C

- Effect:
  - green bonding
  - hot bonding
  - carbonisation
Starch Based Binders/Barriers

► Market for construction materials (e.g. plaster board, plaster, tiles adhesives…) is very fragmented. Western European market is mature, exciting growth potential in Eastern Europe.

► Pricing of binders is critical in relation to special functionality

► Starchy products can only partially replace oil based binders
More than 100 million tonnes of solid municipal waste (SMW) per year are produced in Western Europe, which contains 25-30 volume % (5-10 weight %) of plastic materials, predominantly packaging material.

Landfill space is running short, and incineration has an acceptance problem in the public.

Development of biodegradable (compostable) materials for applications, where long term stability is not required, seems to be logical, e.g. one-way packaging for fast food items, containers for pralines and ampoules, mulch foils and planting pots for agriculture, hygiene articles (e.g. disposable diapers), and loose fill (chips).

EU legislation (order) for waste management 1. Prevention, 2. Reuse, 3. Controlled incineration, 4. Disposal in landfills, 5. Composting of renewable raw materials into biomass, water and CO$_2$ is seen as biological recycling.
## Starch in Thermoplastic Polymers

| Biopolymers based on fermentation products (PHB, Polylactic acid) | Polyester | 100% based on starch | Molds, films, fibres, medical implants |
| Extruded plastified starch | Thermoplastic starch | > 90% starch | Molds, films, expanded products with lower water resistance / mechanical properties |
| Disintegrated reactive starch | Composite material with different synthetic polymers | > 50% starch | Molds, films, expanded products (loose fill) |
| Granular native starch | Filler for polyethylene polypropylene | 6-20% starch | Molds and films but not biodegradable |
Starch in Thermoplastic Polymers/Barriers

► Overproportional growth can only be achieved by new applications

► Material properties have to be improved, e.g. stability at changing climate conditions

► Infrastructure for separate collection, transport and composting has to be established. Spores from compost installations, giving allergic reactions, are now controlled

► Public acceptance for premium (for biodegradability) is not given

► Legislation and taxation have to be the drivers
Starch based Products for Pharma and Cosmetics

Pharma

► Excipients for tabletting, binders for coatings, desintegrating agents, carriers, lubricants, matrices for controlled release

► Conformity with Pharmacopeia (US, EU, Jpn)

Cosmetics

► Emollients, humectants, thickeners, film forming agents, emulsifiers

► Skin compatibility, skin protection, tactile characteristics, non critical impurities, environmental compatibility, stability, processibility, no colour, no odour, plant derived (natural) raw materials

natural-compatible-non-toxic-functional-controlled release-nutritional-chiral
## Starch based Products for Pharma and Cosmetics

<table>
<thead>
<tr>
<th>Native starches</th>
<th>Maltodextrins</th>
<th>Polyols (liquids &amp; powders)</th>
<th>Polyol Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified starches</td>
<td>Glucose syrups</td>
<td>Sorbitol</td>
<td>Anhydropolyols</td>
</tr>
<tr>
<td>• Esters</td>
<td>Dextrose</td>
<td>Maltitol</td>
<td>Chiral building blocks</td>
</tr>
<tr>
<td>• Ethers</td>
<td>Maltose syrups</td>
<td>Mannitol</td>
<td>Citric acid/Citrates</td>
</tr>
<tr>
<td>Physical mod. starches</td>
<td>Dextrins</td>
<td>Xylitol</td>
<td>Gluconolactone</td>
</tr>
<tr>
<td></td>
<td>Cyclodextrins</td>
<td>Erythritol</td>
<td>Vitamin C/Erythrobate</td>
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<table>
<thead>
<tr>
<th>Formulation aids</th>
<th>Excipients</th>
<th>Pharma</th>
<th>Cosmetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cough syrups</td>
<td>• diluents</td>
<td></td>
<td>- natural - compatible - non-toxic - functional</td>
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<tr>
<td></td>
<td>• desintegrating agents</td>
<td></td>
<td>- controlled release - nutritional - chiral</td>
</tr>
<tr>
<td></td>
<td>• binders</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• bulking agents / carriers</td>
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<td></td>
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<td></td>
<td>• lubricants</td>
<td></td>
<td></td>
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<tr>
<td>Parenteral / enteral nutrition</td>
<td>Acidulants / Antiacidulants</td>
<td></td>
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<tr>
<td>Intermediates</td>
<td>Infusion solutions</td>
<td></td>
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<td></td>
<td>Synthons for drugs</td>
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</tbody>
</table>

| Skin care | Fragrances | Decorative cosmetics | Hair care | Oral / dental hygiene | Deodorants |
Starch based Products for Pharma and Cosmetics/Barriers

► Value added specialities

► Scientific marketing and special technical service is precondition

► Special manufacturing requirements (cGMP); apyrogenicity.

► Regulatory requirements (excipients/actives)
  ■ Approval
  ■ Pharmacopoeia compliance
  ■ Certificate of suitability/DMF
Starch Hydrolysates for Fermentation

► Low cost sugar beet- and cane molasses are traditionally used by the fermentation industry as cheap carbon sources, causing high costs during refining and purification of end products. Melanoidins and sulphate in waste waters and solid by-products like gypsum have to be treated and to be disposed of.

► Increasing environmental consciousness, legislation and the necessity to control investment and operating costs, force the fermentation industry to use new technologies with pure raw materials.

► The starch industry is offering a broad range of carbohydrate feedstocks, e.g. cryst.dextrose, glucose syrups, maltose syrups, starches, maltodextrins….. in high purity and adapted composition.

► Advantages to use pure adapted raw materials: lower capital investment per unit of installed fermenter capacity, lower energy consumption at higher d.s., higher space/time yield.
Starch Hydrolysates for Fermentation

- **WHEAT**: Dry milling & Separation → Vital Gluten
- **POTATO**: Liquefaction → Refining
- **TAPIOCA**: Steeping → Refining
- **CORN**: Wet milling & Separation → Corn Steep Liquor

**STARCH**

- **Dry milling & Separation**: Vital Gluten
- **Liquefaction**: Very High Maltose Syrup, High Maltose Syrup, 90 DE Syrup, 97 DE Syrup, 99% Dextrose Syrup
- **Refining**: Crystalline Dextrose

**Ingredients**
- Corn Oil
- Maize Proteins
- Maltodextrins
Starch Hydrolysates for Fermentation

- Competition with low cost molasses on basis of fermentable carbohydrates, but advantage in overall wastewater treatment costs and significant reduced downstream processing costs

- Very high flexibility for feedstock composition in nutritive media

- Competition with low cost sugar is increasing due to change in European sugar regime and WTO ruling
VERSATILITY OF STARCH

**DEXTRINS**
- White
- Yellow
- Gums

**MALTODEXTRINS**
- Block-Copolymers
- Solutions
- Emulsions
- Trehalose
- Polycarboxylates
- Maltitol
- Alkyl glucosides

**MALTOSE**
- 1,5-Anhydro D-fructose
- Cyclodextrins

**SYRUPS**
- Liquefacts
- Organic acids
- Citric acid
- Lactic acid/PLA
- Itaconic acid

**MOD. STARCHES**
- Graft Polymers
- SAP
- Hydrolysed
- Oxidised
- Esters
- Ethers

**SYRUPS**
- Amino Acids
- Lysine
- Glutamate
- Tryptophane

**GLUCOSE**
- APG’s
- Gluconates
- Glucarates
- Glucosamine

**SORBITOL**
- Aminosorbitols
- Glucamides
- Dibenzyldiene Sorbitol

**MANNOSE**
- 2-KGA
- DAS
- Mannitol
- Isosorbide Esters
- Polyester
- HMF

**FRUCTOSE**
- Xylitol
- xylose
- Sorbitan Esters
- “Sorman”

**VERSATILITY OF STARCH**
- Glucoside esters
- TPS Composites
- Biopolyls
- Antibiotics
- Vitamins
- Enzymes
- Antibiotics
- Vitamins
- Enzymes

**XYLOSE**
- Ethanol
- Butanol
- Propane diol

**VERSATILITY OF STARCH**
- Xylitol

**VERSATILITY OF STARCH**
- Polyesters
- Covellite
- Glycerol
Economic Evaluation of Renewable Raw Materials (Starch)

► Sufficient quantities for non-food applications will be available in the EU (old: set aside, new: subsidies will be independent from volumes – single farm payments (2005) will be linked to market needs: environment, food safety, animal welfare

► Reformation of the EU agronomical system will ensure availability at world market prices

► Basic chemicals can be cheaper produced from petrochemical resources (if price is at >40 USD/barrel !!!)

► Renewable resources cannot serve as cheap fillers: functionality is a prerequisite to their utilisation

► Intermediate products can be more economic on the basis of renewable resources

► Finished products with higher added value are favoured when based on renewable resources
Product Possibilities for Renewable Raw Materials (Starch)

- Regain traditional application areas where synthetic products have replaced natural materials through:
  - Combination
  - Complementary effects
  - Synergistic effects

- Make use of special functionalities like:
  - Biodegradability
  - Biocompatibility
  - Non-toxicity

- Make use of structural elements (synthesis power of nature) e.g.
  - Molecular recognition
  - Chirality effects

- Benefit from environmental requirements for new systems like:
  - Solventless inks, paints, glues
  - Biodegradable detergents
  - Biodegradable packaging materials
  - Controlled release agrochemicals
Future R&D Requirements for Renewable Raw Materials (Starch)

► **Agricultural products:**
- Classical breeding and plant biotechnology for new or improved plants with:
  - Better separability
  - Resistance against diseases and pests
  - Higher yields
  - Uniform composition / monocomposition
  - New functionalities

► **Technical processing:**
- Better separation technologies as well as enrichment & purification techniques:
  - Microfiltration, ultrafiltration & nanofiltration
  - Chromatographic separation
  - Electrodialysis
  - Ultrasound, High pressure, Pulsed electrical fields

► **Modification and derivatisation:**
- New technologies for the incorporation of interesting functionalities, e.g.:
  - Chemoenzymatic modification
  - Biotransformation

- Application development:
  - Simplified model systems for easier products screening
  - Combination with petrochemical products for achieving complementary or synergistic effects
Outlook – Starch non food

► Further developments can be expected in

■ Fermentation products
  • Chemicals/Monomers for polymers
  • Biofuel

■ Bioplastics
Outlook – Starch non food

- Fermentation products, e.g. monomers for polymers (from DOE top 10 (12) list of platform chemicals)
  - Di-carboxylic acids
    - Fumaric acid, malic acid
    - Succinic acid
    - Itaconic acid
    - Glucaric acid
    - Furan-2,5-dicarboxylic acid (from HMF)
  - Hydroxymonocarboxylic acids
    - 3-OH propionic acid
    - 3-OH-butyrolactone
  - Amino acids
    - aspartic, glutamic acid
  - Polyols
    - Sorbitol, xylitol, arabinitol, glycerol