NEW PERSPECTIVES FOR BIOMASS-BASED FUNCTIONAL MATERIALS

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ÅBO AKADEMI UNIVERSITY

- Founded 1918
- Swedish-language university
- Multi-faculty university, seven faculties
- Today 7,000 students, over 600 international students
- Two campuses: Åbo and Vasa
- Small and personal university

- www.abo.fi
- www.abo.fi/fa/ie/indexeng.htm
Faculty of Technology

- Two departments:
  - chemical engineering
  - information technologies
- Founded in 1920 as Faculty of Chemical Engineering, named changed in 2006
- Main specialisation areas: computer science, information systems, process chemistry, process system engineering and pulp and paper technology
- The faculty has two centres of excellence in scientific research appointed by the Academy of Finland: Process Chemistry Centre (PCC) and Center for Functional Materials (FUNMAT).
- The faculty offers master’s of science degrees in Technology, Science and Economics and Business Administration.
Our Research and Education Areas

- Fibre Technology
- Cellulose Technology
- Nano-analysis
- Biomass Pre-treatment & Fractionation
- Topochemistry
- High-added value fibres
- New concepts For Fiberlines

Methods:
- SIMS
- XPS
- AFM
- EM
- Fluorescence
- Nanoparticles
- Beads
- Films
NEW PERSPECTIVES FOR BIOMASS-BASED FUNCTIONAL MATERIALS
Polysaccharides

- Natural polymers such as starch, cellulose, chitin, carrageenan
- Produced by plants and animals

- Chitin
- Starch
- Cellulose

- crab
- corn
- bacteria
- tree
- wheat
- cotton
- coconut
- hemp
- alga
- alga
From biomass to functional materials

- **Biomass collection**
- **Biomass disassembly**
- **Fractionation and isolation**
- **Functionalisation**
- **Re-assembly**
- **Incorporation into products**

**Advanced characterisation and nano-analysis**

**Multifunctionalisation**
From wood to polysaccharides

Wood

Disassembly

Lignin

Cellulose
Hemicelluloses

Extractives

pulp

nanocellulose

cellulose solution

hemicellulose solution
Pulp fibres: Functional Material?

- Pulp: 350 million ton worldwide
- Used in paper, packaging, tissue, composites
- Available value chain (collection - recycling)
- Tailored optical and mechanical properties
- Other functionalities unexplored
Fibre Technology at FCT

Fibre separation

Wood
- Mechanical
- Chemimechanical
- Chemical

Fibre functionalisation

- Bleaching
- LC-refining
- Papermaking
SMART FIBRE CONCEPT

- Thermoplastics
  - Cellulose biopolymer plastics
  - Cellulose nanoparticle plastics
- Fabrics and insulation materials
  - Self-cleaning cellulose coatings
  - Antistatic insulations or plastics
- Electric devices
  - Intelligent paper
  - Cellulose polyelectrolyte films
- Chemical resistant packages
  - Ultrahydrophobic coatings for packages
  - Cellulose nanoparticle composites
- Coatings and device for medicine
  - Cellulose drug coatings
  - Diagnostic paper strips
  - Bioresponsive sensors
  - Biodegradable cellulosic implants
Challenges and opportunities for functional pulps

• Conditions of functionalisation compatible with current processes/technology
• Functionality is transferred to final product
• Sustainable, low energy intensive, recyclable
• Availability of value chains
• Opportunity to replace oil-based materials
Cellulose

- 50 % of biomass on earth
- 100-150 billion-ton per year
- One tree: ~14 g of cellulose per day
- Vegetal (plants)
- Seaweed (valonia, microphycon)
- Biosynthesised by bacteria (acetobacter xylonium)
Cellulose

Other (14%)

Wood (86%)

softwood (51%)

hardwood (35%)

Pulp & paper (80%)

Dissolving pulp (20%)

Regenerated cellulose

Cellulose derivatives
Chemical modification of cellulose

- Homogeneous reaction medium (HM)
  - one phase, requires dissolution

- Heterogeneous reaction medium (HT)
  - two phase
Cellulose dissolution

- Raw material (availability, costs, pretreatment)
- Choice of solvent system
  - Viscose (xanthate)
  - NMMO (N-methylmorpholine N-oxide)
  - NaOH-water (urea, ZnO)
  - Ionic Liquids (ILs)
  - Others (several derivative and non-derivative)
- Environmental aspects
- Is the solvent inert?
Cellulose based materials

- Microfibrillar or nanocellulose (HT)
- Cellulose nanorods or crystals (HT)
- Regenerated cellulose from solution (HM) (fibres, particles, films, aerocellulose)
- Cellulose derivatives (HT or HM)
Nanocellulose and nanocrystals

SEM and AFM of MFC

SEM (40000x)  
Lindström and Winter, 1988

AFM  
Notley, 2003

Microfibrils

+ Acid

Nanocrystals
Cellulose Technology at FCT

- Beads
  - Drug release
- Biomaterials
- Aerocellulose
- Medical applications
- Cellulose
  - Chemical sorbents
- Chemicals
- Functional coating
- Rheology
  -Modifiers in coating, food, cosmetics
- Composites
- Bioplastics
Bead-making process

Frozen viscose
→ Defrosting
→ Deaeration

Bead reactor

Drop formation
→ Regeneration

→ Washing
→ Drying
→ Cellulosic beads

2 Cellulose-OCS₂Na + H₂SO₄
→ 2 Cellulose-OH + Na₂SO₄ + 2 CS₂

Cell I → Cell II (irreversible)
Form factor

Selluloosapitoisuus, %

Form Factor

Graph showing the relationship between form factor and selluloosapitoisuus (cellulose content) with data points and error bars.
Beads of regenerated cellulose

x100

x1000

x5000

x10000

100 μm

10 μm

5 μm

1 μm
Cellulose chemistry: opportunity to tailor functionality of materials
Table 5. Conditions and results of the acetylation of cellulose (2.9%, w/v) dissolved in dimethylsulfoxide/tetrabutylammonium fluoride trihydrate (16.6%, w/w) with vinyl acetate at 40 °C for 70 h.

<table>
<thead>
<tr>
<th>Molar ratio$^a$</th>
<th>Catalyst$^b$ [mg]</th>
<th>Partial DS</th>
<th>DS$^c$</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at O-6$^c$</td>
<td>O-2/3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:2.3</td>
<td>—</td>
<td>0.49</td>
<td>0.55</td>
<td>1.04</td>
</tr>
<tr>
<td>1:2.3</td>
<td>20</td>
<td>0.52</td>
<td>0.55</td>
<td>1.07</td>
</tr>
<tr>
<td>1:1.5</td>
<td>20</td>
<td>0.39</td>
<td>0.24</td>
<td>0.63</td>
</tr>
<tr>
<td>1:10.0</td>
<td>20</td>
<td>0.98</td>
<td>1.74</td>
<td>2.72</td>
</tr>
</tbody>
</table>

$^a$ Molar ratio of vinyl acetate to anhydroglucose unit (mole/mole).
$^b$ Mixture of KH$_2$PO$_4$ and Na$_2$HPO$_4$.
$^c$ Degree of substitution calculated from $^1$H-NMR spectra.
Aerocellulose (with tailored porosity)

1x

4x

1250 µm
600 µm
250 µm
Challenges and opportunities for functional cellulose

• Challenges:
  – Dissolution in inert solvents and purity of raw materials
  – Evenness of functionalisation, stabilization of suspension in heterogeneous conditions

• Opportunities
  – Renewable resource with high availability
  – Excellent possibilities for chemical and physical functionalisation. New functional materials
What are hemicelluloses?

• Biopolymers present in different biomass materials (wood, plants, cereals)
• A moderate low DP in comparison with cellulose (50-300 vs 3000-10000)
• A multitude of combinations of sugar units as backbone and side groups
• Interesting properties: bioactive, biodegradable, water soluble
POLYSMART consortium

Suomen Akatemia
Finlands Akademi • Academy of Finland

Centro de Biotecnología
Universidad de Concepción
Región del Bio-Bio

FCT
ABO AKADEMI e Technology

POLYSMART consortium
Polysmart overview

Wood → Pulping → (E) Fibre and sheet properties → Paper making / Converting → (D) Bioactive paper

(A) Disassembly of wood matrix

Hemicelluloses

(B) Bioconversion

(C) Chemical modification

Biofuel → Biomaterials → Reassembly
Disassembly of hemicelluloses by hydrothermal treatment
Extraction of hemicelluloses

Wood → pre-hydrolysis (acid or alkaline) → auto-hydrolysis (water) → Hemicelluloses → delignification → lignin → cellulose
Extraction equipment (PHWE)
Extraction equipment (LiqCir)

200 g of wood/biomass

4000 g of wood/biomass
Summary of exploratory experiments

• Time and temperature are main variables in extraction of xylan
• Xylan can be disassembled from wood at different levels up to 95% w/w
• Higher xylan disassembly leads to disassembly of lignin up to 30% w/w
• About 29% of xylan in wood (11% on wood basis) can be disassembled without removal of lignin
Effects of hemicellulose extraction on fibre properties
Refining - SR

SR (°)

Valley beating time (min)

- ▲ Ref
- • 170 °C 10 min
- ○ 170 °C 40 min
Effect of Hemicellulose extraction on Kraft Pulping and Fibre Chemistry

- Extraction of xylan reduces the yield in kraft cooking (about 10% lower)
- Lower dosages of alkali are needed in cooking (33 % reduction in active alkali)
- Only 3% of residual hemicelluloses in birch after water extraction and pulping
- Dissolving pulp grade possible after 40 min pre-treatment + kraft pulping + bleaching
Effects of hemicellulose extraction on fibre properties

• Refining (higher energy consumption)
• Decrease the fibre length
• Slightly increase in bulk of handsheets
• Reduction in tensile index
• Benefitial for tear index after refining
• Positive for light scattering of handsheets
Utilization of hemicelluloses

- Fibre modification
- Paper coatings/converting
- Bioactive packaging
- Bioactive films in tissue healing
- Food and cosmetic additives
- Biofuels
- Pharmaceuticals
Challenges and opportunities for functional hemicelluloses

• Challenges:
  – Disassembly from wood
  – Negative impact on fibre properties using current technology
  – Purity/evenness of biopolymer

• Opportunities
  – Large availability
  – Incorporation into products
  – Few commercial exploitation
Complementary research activities between Finland and Japan

- Fractionation technology
- Cellulose chemistry and technology
- Lignin chemistry and utilization
- Fibre based functional materials
- Nanoscale characterisation
Acknowledgements
CONFERENCE 2009

“Polysaccharides as a Source of Advanced Materials”

Turku, Finland
September 21-24, 2009

Important dates
Last minute abstract submission: March 30, 2009
Early bird registration: June 30, 2009