FiberTech Seminar-
Cellulose super material

Prof. Ali Harlin, 19.9.2018 Savonlinna
Cellulose properties

- Cellulose is unique renewable material
- Recycleble multipurpose fiber
- Highly performing nano structure
- Most abundant polymer on the planet

![Diagram of cellulose properties](image)
In the past decade we have learned together more of cellulose than century before.
Cellulose challenges

- Current pulp mill concepts and their challenges
  - Wet-dry processes have a high capital cost leading to large production units.
  - Heterogeneous composition of biomass leads to complicated biorefinery concepts.
  - Reduction of CO$_2$ emission by means of improved carbon yield and later capturing to products.

- Cellulose inherent properties
  - Cellulose pulp fibres are short compared with many structural fibres.
  - Pure cellulose is not thermoplastic. Only chemically modified cellulose can be melt-processed.
  - Native cellulose adsorbs water because it is hygroscopic, unlike synthetic plastics.
# Cellulose inherent properties

## Molecular level interactions

- Giant Crystal Microscopy (GCM) and Surface Phonon Resonance (SPR)
  - Monitoring of molecular transferring between cellulose and material surface and in response to a material on varying conditions
- **IOM-1**: acoustic method recording of noise
  - A compression and adiabatic rarefaction is in constant state
- **IRM**: optical method recording of refractive index
  - Observation of internal microstructures
- **OS**: detection of molecular interactions in solid-water and solid-gas interfaces [1–4]
  - Molecular scale information on adsorbed, dispersed, and adhered behavior on surfaces [1–5]
  - Phase transitions of material surfaces by adsorption, chemical treatments, physical treatments at internal surfaces [5–8]
- **Raman**: common measurement for material characterization [9–14]

## Interfacial chemistry

- Contact angle goniometry: surface behavior/pore topography and optical treatment
  - Determination of adhesion, porosity, surface free energy and roughness, surface/tension interactions, and interfacial rheology
- Contact angle measurements with solid drop captive bubble and meniscus method, dynamic contact angles with pendant or fixed drop
- Adsorption, desorption, surface free energy and roughness
- Surface tensile and interfacial rheology at liquid/gas or liquid/liquid interfaces

## Nanoscale surface topography

- Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM)
  - AFM is based on interaction between a scanning probe and the surface
  - 3D information on topography and resolution (visually smooth-1 pm nanoscale surfaces)
- **AFM**: force of attraction and interaction of different materials

## Model surfaces for interaction analyses

- **SEM**: based on interaction between scansion probe and the surface
  - High-resolution topography imaging of rough surfaces
- **SEM**/ **ESEM**: energy dispersive X-ray (EDS) analysis
  - 3D information on chemical and elemental analyses performed in the sample
- **SEM**: elemental analysis based on light ion beam and chemical reactions
  - X-ray excited X-ray emitted from the sample

---

**Possible deposition methods for preparation**
- Lamination/layering
- Electrospinning
- Layer-by-layer deposition
- Langmuir-Schaefer deposition

---

**References**

1. [1–4]: Molecular scale information on adsorbed, dispersed, and adhered behavior on surfaces [1–5]
2. [5–8]: Phase transitions of material surfaces by adsorption, chemical treatments, physical treatments at internal surfaces [5–8]
3. [9–14]: Common measurement for material characterization [9–14]
CNF-bike

Team:
Kim-Niklas Antin, Design and manufacturing Aalto/ENG
Tiina Härkäsalmi, Nanocellulose tubes Aalto/ARTS
Tuomas Pärnänen, Composites fabrication and finishing Aalto/ENG

Photo: Eeva Suorlahti
Game-changer technologies

- Ionic liquids and deep eutectic solvents
- Enzyme-assisted modification
- High consistency processing
- Foam forming
- 3D printing and personalized production

Thermoplastic cellulose

New plastic

Inherent cellulose

Ground break
MMCC – Thermoplastic cellulose for plastic replacement

**CHALLENGE**
- Increase oil price independency and obtain thermoplastic cellulose-based products

**SOLUTION**
- MMCC to reduce chemical consumption and make thermoplastic cellulose which is processable with existing plastic converting equipment

**BENEFIT**
- A considerable reduction of chemicals and additives used for cellulose upgrading and processing
- Non-food replacement of plastic films and composites
- Comes in granulate and/or filament form
- Water vapor resistant
- Heat-selable
- 100% bio-based

**PATENTS**
- WO2016193542 A1

**PUBLICATIONS**
- *Carbohydrate Polymers* (2016), 151, 988-995
- *Cellulose* (2017), 24, 505-517
- *Carbohydrate Polymers* (2017), 170, 160-165

**CONTACTS**
- **Jarmo Ropponen**, Research Team Leader
  +358 400 215 951, jarmo.ropponen@vtt.fi
- **Jouni Lattu**, Key Account Manager
  +358 40 728 8519, jouni.lattu@vtt.fi
- **Jonas Hartman**, Key Account Manager
  +358 40 845 3150, jonas.hartman@vtt.fi
Ellen MacArthur material challenge winner
VTT biobased material solution

- Novel
- 100 % biobased
- Renewable
- Can be made from multiple raw materials – Local resources
- Customizable
- Compostable
- Increased shelf life
3D Printing cellulose

- Future promise
- High flexibility
- Complicated shapes
- Spare parts
Future cellulose-based high-value applications – Strategy 2025-2030

Novel value added cellulose-based concepts

VTT goal
- Performance solutions for existing and new applications

Industry needs based VTT research opportunities
- Creating product performance (additional/novel) by exploiting inherent cellulose structure and properties
- Novel manufacturing methods
- Recyclability, safety & reduced carbon footprint
- Brand image with no increased cost, need to develop new business areas

Possible game changers
- Legislation
CAPTURING THE UNCATCHABLE
From Research Topic to Research Area
Research on feasible processes to produce controlled nanostructures
Orienting nanocellulose with shear alignment

Flow field + electrophoretic deposition: experimental setup successfully constructed
- Initial tests with water complete
- Flow field verification with optical coherence tomography (OCT)
  → extensional flow field with orientating effect achieved
Examples of new products

- Packaging materials, with improved barrier properties and moldability that can be used instead of plastics, e.g., packaging films.
- Textiles that are able to replace cotton especially in clothing. Alternatively, textiles that replace oil-based synthetic fibres in hygienic and technical textiles, e.g., filaments, yarns, and nonwovens.
- Composites that are environmentally acceptable and affordable compared to conventional materials, especially in short service-life applications that have medium performance requirements.
- Novel application of cellulose like cellulosic substrates for electronics and sensors that are easier to recycle and thus have better environmental acceptance.
Efficiency, speed and lower risks to development with piloting and demonstrations

Piloting
- Efficiency
- Speed
- Lower risk
- Technology testing

Challenges in commercialisation
- Market uptake
- Market entry strategy
- Strategic partners and value chains
- Standardisation

PILOT PRODUCTION
Combining product, manufacturing, organization and market

Uncertainty
Economic risk
Cumulative investments

Piloting

VALLEY OF DEATH
Foam forming in a nutshell

- Fibres and other furnish components are mixed with foam instead of water.
- Foam consists of water, foaming agent and air. Typical air content 30-70%.
- Air bubbles prevent flocculation of fibres in the headbox.
- Important to have a “right type of foam”.

Foam Technology at VTT pilot machine

- Foam forming start-up in September 2012
- Press dry roll samples & off-line drying
- Foam generation technologies
  - Tank mixing
  - On-line generation
- Speed up to 1000 m/min in roll production
3D Forming & Formability of paper

- Sliding blank
  - Deep-drawing
  - Stampin g
- Fixed blank or web
  - Air forming/Vacuum forming
  - Hydroforming
  - Hot pressing

Formability = frequency of compression folds (appearance)
- Requirements for good formability vary in accordance with process!
- For the fixed blank process: Formability = extensibility of paper!
Novel packaging materials

Totally new possibilities enabled by:
- Very high bulk (middle layers)
- Controlled bonding (moldable web)
- Long synthetic fibers (specialty papers)
- Fiber molded

Steady growth of packaging will continue:
- i-Commerce sales continues to grow
- New packaging types like pouches. MAP
- Service packaging
Among 10 most attractive start-ups.

Talouselämä 2017

Paptic

VTT:n spinoff makes bags for consumer brands.
Production 2018.
Solutions for hygienic products
Foam-laid nonwovens from cellulosic fibres

- Brilliant formation in the case of long fibres, even though high forming consistency applied
- Mechanical bonding instead of chemical bonding → aspect for sustainability
- Widening of raw material combinations → process simplifying

Mechanical bonding of foam laid nonwovens (MECBO), VTT internal project, 2014
Scale up: SAMPO pilot at VTT Jyväskylä

1. Making foam & mixing fibres
2. Removing foam with vacuum
3. Drying
Base Material
Architecture:
Foam Filled Grid Structure
Laminated structures for interior

Interior element structures from cellulose and nanocellulose. Chip board strength with half of its thickness*. Easy to form in shapes when wet. Excellent machineability. Researched by Vesa Kunnari, Jaakko Pere (VTT), and Heidi Turunen (design, Aalto university).

*Bending strength of this novel structure is $28 \text{ N/mm}^2$, which is higher than the strength of the tested reference materials chip board ($8 \text{ N/mm}^2$), gypsum board (EH, $10 \text{ N/mm}^2$), MDF ($26 \text{ N/mm}^2$) and softwood plywood ($22 \text{ N/mm}^2$).

Photos by Kirsi Kataja and Eeva Suorlahti.
Foam-formed Layered Samples
Multi-ply products with one headbox
### Material and structure combinations

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Description</th>
<th>Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random fiber network</td>
<td>EPS particles randomly in fiber network</td>
<td><img src="image1.png" alt="Image" /> <img src="image2.png" alt="Image" /> <img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Density gradient in fiber network</td>
<td>EPS particles in the middle layer</td>
<td><img src="image4.png" alt="Image" /> <img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>Mimicked pomelo structure</td>
<td></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- **Coated random fiber network**
- **Bio-PLA particles in outer layer**
- **Coated top ply**
- **Manufacturing in Sept. 2016**
Intro to sound and noise management

- Acoustic control: controlling absorption, reflection and transmission of sound
- Sound absorption: in air pockets inside flexible open cell structures
- Acoustic materials are needed in:
  - automotive and vehicles
  - construction and partitioning walls
  - industrial equipment and machinery
  - appliances and consumer products
  - aerospace and marine
Benchmarking results:
Shoddy product in automotives

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
<th>Density</th>
<th>Grammage</th>
<th>Flow resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoddy</td>
<td>29</td>
<td>58</td>
<td>1655</td>
<td>19500</td>
</tr>
<tr>
<td>Foamsound 1</td>
<td>30</td>
<td>36</td>
<td>1074</td>
<td>25000</td>
</tr>
<tr>
<td>Foamsound 2</td>
<td>30</td>
<td>42</td>
<td>1260</td>
<td>23600</td>
</tr>
</tbody>
</table>

Foamsound solution:
- Clearly lighter at similar performance

Absorption coefficient measured with ACUPRO impedance tube with 0 mm air gap
Fiber yarn

- Method saving 99 % of water

Spinnova

Regenerated Cellulose Fibre Processes
Many fibers for different uses

Dissolved pulp
Or
Recycled Cotton

Pretreat
Derivatization
Dissolve
Spinning/ regeneration
Fibres

CS₂ → xanthate
NaOH → Wet → Viscose
NMNO → Dry-Wet → Lyocell
Urea → carbamate
NaOH → Wet → Carbamate
Enzymes
ZnO/NaOH + Freezing → Wet → Biocellos
Ionic liquid → Dry-jet-wet → Ioncell

Commercial
Emerging
<table>
<thead>
<tr>
<th>Fiber</th>
<th>Linear density (dtx)</th>
<th>Young's modulus (cN/dtx)</th>
<th>Tenacity (cN/dtx)</th>
<th>Elongation (%)</th>
<th>Flexibility (nM m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.68 ± 0.48</td>
<td>32.4 ± 17.8</td>
<td>2.54 ± 1.08</td>
<td>8.31 ± 2.61</td>
<td>12.3 ± 5.5</td>
</tr>
<tr>
<td>CV</td>
<td>1.80 ± 0.12</td>
<td>42.5 ± 5.16</td>
<td>2.11 ± 0.14</td>
<td>17.4 ± 1.2</td>
<td>29.0 ± 7.6</td>
</tr>
<tr>
<td>PLA</td>
<td>1.70 ± 0.23</td>
<td>25.0 ± 10.1</td>
<td>1.90 ± 0.72</td>
<td>33.8 ± 10.7</td>
<td>16.0 ± 5.4</td>
</tr>
<tr>
<td>BCS</td>
<td>2.04 ± 0.33</td>
<td>38.3 ± 4.4</td>
<td>1.14 ± 0.18</td>
<td>15.9 ± 3.9</td>
<td>38.2 ± 17.8</td>
</tr>
<tr>
<td>CCA</td>
<td>1.71 ± 0.21</td>
<td>48.4 ± 5.3</td>
<td>1.70 ± 0.20</td>
<td>15.9 ± 3.9</td>
<td>29.8 ± 17.6</td>
</tr>
<tr>
<td>ION</td>
<td>1.63 ± 0.23</td>
<td>107 ± 13</td>
<td>4.46 ± 0.56</td>
<td>7.25 ± 1.19</td>
<td>20.3 ± 21.9</td>
</tr>
</tbody>
</table>
Cellulose carbamate – from R&D project to pilot and startup

The Relooping Fashion Initiative

The Relooping Fashion Initiative received a Highly Commended status in the Awards Program’s public sector category in The Circularsardi Awards Ceremony held at the WEF Meeting in Davos on 19 January. The Circulars is the world’s premier circular economy award programme, whose judging panel includes the circular economy pioneers such as Ellen MacArthur and William McDonough, as well as representatives from global business and university sector.

CLIMATE SOLVER 2016 HONOREE

Creating new ways to produce cellulose fibers
Developed by: THE INFINITED FIBER COMPANY
Sustainable regenerated fiber

Inﬁnited Fiber Company

New normal collection

Helsinki Fashion Week 2018
New Normal Collection
Fabriks: Infinited Fiber Company
All-cellulose shoes

UPPER:
- NON-WOVEN FROM PULP & PULP YARN (DES) & VISCOSE, PRODUCED BY FOAM FORMING
- CELLULOSE DERIVATIVE 3D PRINTED ON SURFACE (ORANGE MATERIAL)
  - LEATHER-LIKE TEXTURE
  - SUPPORTS THE MATERIAL
HEEL:
- VENEER GLUED WITH CATLIGNIN
OUTSOLE:
- THERMOFORMABLE CELLULOSE DERIVATIVE
Finland as a future textile country

- By 2030 Finland may have
  - 2-3 dissolving pulp units: 900M€
  - 2-3 recycling units: 150M€
  - 1-2 spinning units: 100M€
  - 5-10 users of the fibers: 250M€

Total (without pull through): 1400M€
Net total: 2000-3000 M€ pa
Doubling the value-add of forest bioeconomy in Finland with new innovative products

Source: VTT "BiolowC" publication - release imminent
Cellulose goes digital

- Digitally assisted business ecosystems between industries will develop value-added cellulose products and revolutionize bio-based material markets
- Agile wood fractionation processes
  - Reduction of carbon dioxide emissions will make kraft biorefineries the material refineries of the future
  - Alternative fractionation: Mini-refineries will become business ecosystem cores (Agile and resource-efficient close to the biomass source)

- Cellulose-based materials as service
  - Added value and high performance materials
  - Materials are customized close to end-user
    - Improved disposable products: Hygiene, personal care
    - Thermoplasticity of cellulose films makes replacement easier
    - Cellulose composites can also be applied in medical, home, sports and leisure applications