Vers l'industrialisation des Nanocellulose

Julien BRAS

Journée scientifique organisée Fed3G (FR3345) et l'Institut Carnot PolyNat

« Biomasse végétale matière première d’avenir : rêve ou réalité ? »

Laboratory of paper science & graphic arts
LGP2 - UMR 5518

Ab. 100 employees staff, 40 PhD

T1 : Bio-nano-particules & their use:
Cellulose nanocrystals, starch, chitine ; NFC, Bio-nanocomposites, mechanical reinforcement, characterisation

T2 : New biomaterial : from surface treatments to composites
Biopolymer : Bio-composites ; chemical grafting ; Rheology of enduction sauce ; adhesion & coating ; Multilayer ; Microencapsulation ; Specialty paper, extrusion

T3 : Functional Packaging : 3D process & end-use properties
Cardboard, Core ; Thermoforming ; embossing ; Shelf life & barrier properties ; Mechanical simulation & humidity conditions, RFID, functional material & coating, food contact

Converting Biomaterial Packaging Dpt

20 researchers
(10 PhD, 2 post-doc)
BioNanoPolysaccharides

Issue and misunderstanding (LCA)

Family 1

Family 2

Family 3

Directly extracted from Biomass

Classically synthesised from bio-derived monomers

Polymers produced directly by organisms

Polysaccharides

Proteins

Lipids

Animals
- Casein
- Whey
- Collagen/Gelatine

Plant
- Starch Derivatives
- Cellulose
- Cotton
- Wood
- Other Derivatives

Other Polymers

Animals
- Casein
- Whey
- Collagen/Gelatine

PHA
- Bacterial cellulose
- Xanthan
- Curdlan
- Pullan

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**NanoCellulose**

Families of cellulose

- Cellulose I
- Cellulose II
- Textile: 25 million tons
- Regenerated Cellulose: 3 million tons
- Cellulose Derivatives: 6 million tons
- Cellulose for paper: 175 million tons

**Process:**
- Viscose, parchmentization, etc.
- Extraction, bleaching
- Esterification, etherification

**Source:** Missoum PhD 2012.

**Quantity => Work on Native Cellulose**

**BioNanoPolysaccharides**

- 200 x 10^3 tons/year produced
- But only 6 x 10^3 tons/year used

**Cellulose molecule**
- Glucose
- Cellulose

**Crystalline cellulose**

**Source:** http://genomicsgtl.energy.gov/roadmap/, 2009.
Global Context

Need for Bio-based Solutions

SOLUTION = BIO-NANO-PARTICLES

Enhanced properties at Nano-scale

Le Corre, thèse, 2011

BioNanoPolysaccharides

Nanocellulose

INFO ou INTOX?
AGENDA

1. Nanocellulose Definition

2. Properties and Application

3. Towards industrialization?
NanoCellulose

Microfibrillated cellulose (MFC)
20-60 nm × ab.500-1500 nm

Nanocrystals or whiskers
2-15 nm × av. 100-500 nm

Micro-Macro Nano

PAPER FIBRE MFC NCC Polymer

Thickness= 30-400 µm
Basis weight= 15-400g/m²

L= 0.7-10nm
D= 5-50µm

L= 1000-2000nm
D= 20-70nm

L= 200-500nm
D= 5-10nm

DP=10000
Z= 0.5nm

Zavre et al. submitted, 2012

Pääkkö, et al., Biomacromol. 2007

Wood pulp
Sugar beet pulp
Bagasse pulp.
More than 1 paper every day in 2011

⇒ Obviously THE future of Cellulosic materials

⇒ Lack of industrial application + Lack of clear denomination

NanoFibrillated Cellulose (NFC)

Different processes

Different pre-treatments

MFC enzymes  MFC TEMPO

[M. Ankerfors, 2007]

[Innventia, 2010 - http://innventia.com]
3 main groups:

<table>
<thead>
<tr>
<th></th>
<th>L (nm)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC</td>
<td>&gt;1µm</td>
<td>50</td>
</tr>
<tr>
<td>MFC TEMPO</td>
<td>&gt;1µm</td>
<td>10</td>
</tr>
<tr>
<td>Whiskers (Sisal)</td>
<td>200</td>
<td>5</td>
</tr>
</tbody>
</table>

=> Be Carefull: It is not so simple !!!!

**Project discussion**

**Grenoble INP Pagora Possibilities**

<table>
<thead>
<tr>
<th>Production</th>
<th>Characterization</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whiskers - Nanocrystals</td>
<td>(20 sources – pioneer)</td>
<td>(Mechanical, thermal, rheo, barrier)</td>
</tr>
<tr>
<td>MFC by mechanical treatment</td>
<td>(FCBA collaboration)</td>
<td>(Mechanical, thermal, rheo)</td>
</tr>
<tr>
<td>MFC by Tempo treatment</td>
<td>(1st production in 2010)</td>
<td>(under progress)</td>
</tr>
<tr>
<td>Starch Nanocrystals</td>
<td>(several sources- pioneer) 15</td>
<td>(Mechanical, thermal, barrier, rheo)</td>
</tr>
</tbody>
</table>
AGENDA

1. Nanocellulose Definition

2. Properties and Application

3. Towards industrialization?

Application of Nanopolysaccharides

Several possibilities

- Impregnation
- Impregnation- Composites
- Coating
- Multilayer - Coatings
- Composites
- Standing films & others
NanoCellulose Properties & Application

More and more Applications

Gel

Cosmetics

Films

Aerogels

Paints

Car reinforcement

NanoCellulose NFC Application

- Impact of the making process on barrier properties
  - TEMPO pre-treatment
    » TOCN-COOH (acid pH) ≠ TOCN-COONa (basic pH)

![Graph showing oxygen permeability](image)

*Fukuzumi et al. Carbohydrate Polymers, 2011
NanoCellulose Properties & Application

Several possibilities

- Impregnation
- Impregnation- Composites
- Coating
- Multilayer - Coatings
- Composites
- Standing films & others

NanoCellulose


<table>
<thead>
<tr>
<th>E (GPa)*</th>
<th>10</th>
<th>40</th>
<th>70</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

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<thead>
<tr>
<th>Fibre bundle</th>
<th>Ultimate fibre</th>
<th>Cellulose microfibril</th>
<th>Cellulose nanocrystals</th>
</tr>
</thead>
</table>

- Fibre bundle
- Ultimate fibre
- Cellulose microfibril
- Cellulose nanocrystals

Bundles of fibres
- Ultimate fibres
- 1 µm
- 100 µm
Longitudinal ($E_L$) and transverse ($E_T$) moduli of crystalline cellulose.

![Table of data](image)

**NanoCellulose Properties & Application**

Case 1: Water soluble Polymer

**Conditioning:**
24h 23°C - 50% RH

**Whiskers suspension**: Water soluble matrix

**Nanocomposites**

- No whiskers
- 6 wt% Sisal Whiskers
- 12 wt% Sisal Whiskers

![Diagram of nanocomposites](image)
**NanoCellulose**

**Properties & Application**

NCC composites

Evolution of the Young’s modulus (A), strength (B) and strain at break (C) for PCL-based nanocomposites vs. filler (whisker or MFC) content: unmodified (●) and chemically modified whiskers (○), and MFC (λ).

Siqueira et al. (Biomacromolecules 2009)
INTERESTING PROPERTIES

BUT NO APPLICATION BY EXTRUSION

Because Film like or agglomeration when dried

Chemical grafting

Solutions

Encapsulation

Properties & Application

Processing by Melt Compounding

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Nanoparticle</th>
<th>Source of Cellulose</th>
<th>Processing Aid/ Surface Functionalization</th>
<th>Processing Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPOXENT GP 10802</td>
<td>CNC/MDM</td>
<td>DOPPEL Hydrogel</td>
<td>DOPPEL Process</td>
<td>Extrusion</td>
<td>Lenzik et al., 2011</td>
</tr>
<tr>
<td>NR</td>
<td>CNC</td>
<td>MDC</td>
<td>Water</td>
<td>Mixing Homogenization</td>
<td>(Zuo et al., 2012)</td>
</tr>
<tr>
<td>PCL</td>
<td>CNC</td>
<td>BN</td>
<td>DOPPPEL Casting</td>
<td>Extrusion</td>
<td>(Griffith et al., 2011)</td>
</tr>
<tr>
<td>PE</td>
<td>MFC</td>
<td>Surfactant</td>
<td>Ethylene-acrylic ester coating</td>
<td>Melt Blending</td>
<td>Extrusion</td>
</tr>
<tr>
<td>PE</td>
<td>CNC</td>
<td>DOPPEL Hydrogel</td>
<td>—</td>
<td>Extrusion</td>
<td>(Bakhtiar et al., 2012)</td>
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<tr>
<td>PEO</td>
<td>CNC</td>
<td>BN</td>
<td>—</td>
<td>Extrusion</td>
<td>(Allaire et al., 2011)</td>
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<tr>
<td>PLLA</td>
<td>MFC</td>
<td>Stearic Acid</td>
<td>Ethylene-acrylic ester coating</td>
<td>Extrusion</td>
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<tr>
<td>PBSV</td>
<td>CNC</td>
<td>MDC</td>
<td>PEG</td>
<td>Extrusion Injection</td>
<td>Injection</td>
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<tr>
<td>PLA</td>
<td>CNC</td>
<td>MDC</td>
<td>PEG/Valinol PLA</td>
<td>Extrusion</td>
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<td>PLA</td>
<td>MFC</td>
<td>DCA</td>
<td>—</td>
<td>Extrusion</td>
<td>(Bakhtiar et al., 2012)</td>
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<tr>
<td>PLA</td>
<td>DOPPEL Hydrogel</td>
<td>Extrusion Injection</td>
<td>Injection</td>
<td>(Bakhtiar et al., 2012)</td>
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<tr>
<td>PVA</td>
<td>CNC</td>
<td>BN</td>
<td>PVA</td>
<td>Extrusion</td>
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<tr>
<td>PP</td>
<td>MFC</td>
<td>Surfactant</td>
<td>Ethylene-acrylic ester coating</td>
<td>Extrusion</td>
<td>(Caffarelli et al., 2011)</td>
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<td>CNC</td>
<td>BN</td>
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<td>(Dekker et al., 2008)</td>
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INTERESTING PROPERTIES
BUT NO APPLICATION BY EXTRUSION
Because Film like or agglomeration when dried

Solutions

Chemical grafting

Encapsulation

Nanocellulose Encapsulation
Different Solutions

1. Polymer grafting or adsorption
   ROP, admicellar polymerisation

2. Polymer regeneration/precipitation
   Alginate, PVA, PLA, starch

3. Polymer blending
   Waterbased polymer, NR

ACS Macro Letters (January 2012), Ben Azouz, et al
LeMahieu, Bras et al MME, 2011
Bras et al ISWFPC 2011
Application of Nanopolysaccharides

Several possibilities

- Impregnation
- Coating
- Impregnation - Composites
- Multilayer - Coatings
- Composites
- Standing films & others

Paper & Nanocellulose Examples

MFC & Paper

Hamann, Sunpap Workshop, 2011

Effect of grammage reduction

• 3 sheet grammages tested 80, 60, 40 g/m²
• significant grammage reduction by NFC possible (concerning to tensile)
• example: 60 g/m² without NFC gave same tensile like 41 g/m² with NFC
MFC coatings on paper/board
(a) reference paper, (b) 1 g/m² MFC coat, (c) 1.8 g/m² MFC

=> Coating of low basis weight

Paper & Nanocellulose
Examples

=> Best biomaterial barriers
and also interesting for printing properties

Water vapour permeability * 10^-11 g/(m s Pa)

Oxygen permeability (cm³/m²/day kPa)

• MFC coating => Barrier due to « nanoporosity »

• Expect for High value added materials
=> prolonged release due to « nanoporosity »

BiopackFun Project (2010-2013)

Paper & Nanocellulose
Examples

Barrier properties

MFC
Active molecule

Prolonged Release

Antimicrobial property
AGENDA

1. Nanocellulose Definition
2. Properties and Application
3. Towards industrialization?
Towards Industrialization
Nanocellulose

Figure 8: Nanocellulose production volumes tons per year, all types, forecast to 2017

Source: Future Markets Inc, 2012
Towards Industrialization

Nanocellulose

Industrialization and marketing

Boeregaard (Spring 2011) – 100 kg/day
Inventia (Spring 2011) – 300 kg/day

Towards Industrialization

Nanocellulose

NCC timeline

- 1949: First colloidal cellulose suspension (Råby)
- 1952: Rodlike NCC structure by TEM (Mukherjee et al.)
- 1959: Liquid crystal properties of NCC (Marchessault et al.)
- 1992: NCC first extracted from wood pulp (Revol et al.)
- 1995: First observation of iridescent NCC films (Gray et al.)
  First NCC composite (latex) (France)
  First patent (Paprican, 1997)
- 2006: Launch of the first NCC pilot plant (0.5 kg/day)
- 2007-2011: FPInnovations R&D program (>15 patents filed)
- 2011: Start-up of NCC demonstration plant

Source: Bouchard, Sept 2011
Towards Industrialization
Nanocellulose

NCC Demonstration plant:
• 1 ton/day
• 1st plant in the world

First in the world
CelluForce: Joint venture Domtar - FPInnovations
Support from Québec and Federal governments
Design: Canadian engineering firm
Start-up: Fall 2011

Source Bouchard, Sept 2011

Towards Industrialization
Nanocellulose

Source Bouchard, June 2010
Towards Industrialization

**Nanocellulose**

Ecotoxicological Assessment

FPIinnovations: Acute and chronic testing with fish and fleas

- First Nanomaterial that Canada has added to the Domestic Substance List - J.Bouchard, June 2012

University of Ottawa: Hatching and survival tests with Zebra fish

Environment Canada: Tests with various aquatic species

Kovacs et. al. Nanotoxicology, September, 2010; 4(3):1-16

FPInnovations

Source Bouchard, Sept 2011

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**Towards Industrialization**

**Cellulose Nanocrystals**

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<th>R&amp;D</th>
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<td>-Canada/France: Still the pionneers</td>
<td>FP Innovation (Ca) – 2kg/d</td>
<td>BioVision(Ca) – 80kg/d</td>
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<tr>
<td>-More patents</td>
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<tr>
<td>-New functions</td>
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**Announcement & perspectives**

- Alberta Innovates (Ca) – 100kg/d
- New project in Asia
- Forest prod Lab (USA) – 50kg/d

**NON-TOXIC: Similar to MCC and Table Salt**
Towards Industrialization

Nanocellulose

Pre-treatment (enzymatic, chemical...)

Deintegration-Refining
Homogenization

Chemical treatment

Hydrolysis (H₂SO₄...)

Cellulose nanocrystals (CNC, CRLX)
Cellulose whiskers (CWW)
Nanocrystals of cellulose (NCC)

Mechanical treatment

Mechanical homogenization (Microlizer)

Cellulose microfibers
Nanofibrillated cellulose (NFC)
Microfibrillated cellulose (MFC)
Cellulose nanofibers (CNF)

Industrialization and marketing

Boeregaard (Spring 2011) - 100 kg/day
Inventia (Spring 2011) - 300 kg/day

Situation:

- Less clear situation due to different MFC quality

- Several players:
  - Industrial vs Research center
    - JRS, Boeregaard (Inventia, VTT, CTP/FCBA)
    - Sodra, UPM, Stora, Nippon Paper

- Several European projects
## Towards Industrialization

### Nanocellulose

#### Nanofibrillated Cellulose

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<td>LGP2 (FR) 5kg/d</td>
<td>CTP-FCBA (FR) – 50kg/d</td>
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<tr>
<td>- Research centers &amp; european projects</td>
<td>EMPA (Swi) 15kg/d</td>
<td>Innventia (Sw) – 100kg/d</td>
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<td></td>
<td>VTT (Fi) – 15kg/d</td>
<td>Borregaard (Nor)</td>
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<td></td>
<td>PFI (No) – 15kg/d</td>
<td>Stora (Sw)</td>
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<th>Announcement &amp; perspectives</th>
<th>Alberta Innovates (Ca) – 100kg/d</th>
<th>Nippon Paper</th>
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<tbody>
<tr>
<td>- New industries</td>
<td>University of Maine(USA) – 500kg/d</td>
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<tr>
<td>- New functions</td>
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<td></td>
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<td>- Scale up optimisation</td>
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Source: SUNPAP conf, V.meyer, 2012

## Towards Industrialization

### Nanocellulose

- **GEA - ARIETE**
  - 55kW motor
  - 1500 bar max
  - 1000 L/h
- **Homogenizing conditions**
  - Enzyme treated pulp
    - 2% consistency
    - 1 pass at 500 bar
    - 1 pass at 1000 bar
    - 4 passes at 1500 bar
  - TEMPO treated pulp
    - 2% and 4% consistency
    - 2 passes at 1500 bars

Source: SUNPAP conf, V.meyer, 2012
Objective of SUNPAP

(Scale Up Nanoparticles for Modern Paper Making)

- Develop high performance and functional products with innovative properties based on nanofibrillated cellulose (NFC).
- Develop innovative process & high added value products for paper industry

22 partners, 8 countries

http://sunpap.vtt.fi/
Workshop in Oct 2011 Espoo, Helsinki
AGENDA

1. Nanocellulose Definition

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CONCLUSION & NEXT

---

Nanocellulose

CONCLUSIONS

2007 2010 2012

* Increasing interest
  BUT still issue for application/production

* First review

* First conference on the topic / First european projects

* 2010: change the way of thinking
  => Patent & first plant announcement in North America

* More and more solution
  => need denomination/standardisation

INDUSTRIALIZATION

NEXT STEP:

OPTIMISATION & APPLICATION

⇒ High Value Added = Functionnalization

⇒ Application = Drying/Redispersion; Process adaptability
THANK YOU FOR YOUR ATTENTION

Thank my colleague: A. Dufresne, N. Belgacem, K. Missoum, N. Lavoine, R. Bardet