Nanotechnology Applications in Forest Products: Current Trends

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Advanced Wood Processing II Session
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Overview

• What is nanotechnology?
• Brief history of nanotechnology
• Nanotechnology Research Initiatives
• Past Applications
• Current Trends
• Low Hanging Fruit
• Challenges!
What is Nanotechnology?

• Nanotechnology is science of
  • A nanometer (nm) is one billionth of a meter (10^-9 m) about 4 times the diameter of an atom
  • Creating uniquely designed materials or systems through the control of matter on the nanometer (atomic) scale
  • The exploitation of novel properties and phenomena developed at that length scale

Why is This Length Scale So Important?

- Interactions are influenced by material variations on the nm scale
  - Control fundamental properties of materials without changing the materials’ chemical composition
  - New, high-performance products and technologies that were not possible before
  - Use of nanoparticles and nanolayers with very high surface-to-volume ratios for use in polymeric materials
Brief History of Nanotechnology

Wikipedia filtered by Gardner

- Richard Zsigmondy 1914 Gold Sols
- Interface and colloid science (20th Century)
  - “colloids, heterogeneous systems consisting of a mechanical mixture of particles between 1 nm and 1000 nm dispersed in a continuous medium.”
- Langmuir-Blodgett films “monolayers”
- Richard Feynman 1959 “There’s Plenty of Room at the Bottom”
- Norio Taniguchi 1974 first to coin the term “nanotechnology”

Milk is an emulsified colloid of liquid butterfat globules dispersed within a water-based liquid.
Brief History of Nanotechnology

Wikipedia filtered by Gardner

- Eric Drexler 1980s “Molecular Nanotechnology”
- Fullerenes 1985
- Carbon Nanotubes late 1980s
- Richard Jones 2004 “Biomimetic nanotechnology”

Experimental Advancements
- Scanning tunneling microscope (STM)
- Atomic force microscope (AFM)
- Nanoindentation
- Nanolithography
Nanotechnology and Forest Products

- Apply nanotechnology to forest products
  - Coatings
  - Biocides
  - Modified resins
- Obtain nanomaterials from forest products
  - Cellulose nanofibrils
  - Lignin nanoparticles
  - Extractives
Collaborative, Multi-agency, Cross-cut Program Among 25 Federal agencies, 15 of which have specific nanotechnology budgets

Funds R&D to advance understanding and control of matter at nanoscale toward:
- National economic benefit
- National and homeland security
- Improved quality of life
U.S. Forest Products Nanotechnology Research Roadmaps - Needs

2005

2006

2010

www.nanotechforest.org

www.agenda2020.org

International Forest Products Nanotechnology

- FP Innovations Canada
  - Nanotech. Applications in the forest sector (McCrank 2009)
- Nanoforest – Innventia, Europe
- Japan
- New Zealand
- Etc.
Nanotechnology for the Forest Products Industry R&D Focus Areas

- Polymer Composites and Nanoreinforced Materials
- Self-Assembly and Biomimetics
- Cell Wall Nanostructure
- Nanotechnology on Sensors, Processing and Process Control
- Analytical Methods for Nanostructure Characterization
Nanotech is 3rd Industrial Revolution
Renewable Forest-based Materials: Maine’s Niche to Compete in Nanotech

“From the Sawmill to the Nanomill?”
Size Scale of Lignocellulosics

Forest products, biomass → Wood cells → Cell wall layers → Cellulose microfibrils

CNC’s consist of organized stacks of $I_\alpha$, $I_\beta$ cellulose chains

AFM image of a cellulose Nanocrystal (CNC)

Chemical treatment releases crystalline phase
Wood-Orders of Scale (Powers of 10)

FRP Laminate
1 meter

Glulam-FRP
10 centimeters

Shear specimen
1 centimeter

Microdroplet on Fiber, 1 millimeter

Bond line micrograph
100 microns

Bordered Pit
10 microns

UF Resin on loblolly fiber
(2 micron scan)

Cellulose nanocrystals
200 nm long, 10 nm wide

Valonia
10 nanometers

1 nanometer
Past Applications in Forest Products

• Colloids in Paper Manufacture
  • Fines retention
  • Filler retention
  • Modifying zeta potential
  • Rosin Sizing (100 to 1000 nm particle size)
• Going back more than 50 years
• “Nano” Terminology becomes important

Clay coated by cationic polystyrene Latex (130 nm diameter)
Source: van de Ven 2009

Nanosilicate sol as flocculants
Current Applications in Forest Products

• High Profile Nanotechnology applications in forest products
  • Optically transparent nanofiber paper
  • Optically transparent cellulose nanocomposite for flexible LED display

Yano research group (Japan 2009)
Wood Protection Applications
(Clausen 2007)

- **Nanobiocides**
  - Preservative penetration in commercial lumber species
  - Treatability of refractory species
  - Durability of engineered composites
  - Non-leachable treatments
- **Nanocarrier delivery systems**
  - Delivery and placement of biocides
  - Slow release of biocide
  - Release under specific environmental conditions
  - Protection of heat labile biocides during treatment of composite fabrication

![Image of copper carbonate nanoparticles](image)

Evans et al. 2008

![SEM micrograph of untreated and treated southern pine](image)

Figure 1. SEM micrograph of (a) untreated sample of southern pine, and (b) southern pine treated with tebuconazole in a PVPy matrix.

Laks and Heiden, 2001
Wood Coating Applications

• Improve
  • Scratch resistance
  • Abrasion resistance
  • Gloss/matting
  • UV blocking without loss of clarity
  • Hydrophobicity
  • Oleophobicity
  • Dust free surfaces?
Carbon nanostructures formed from the wood cell wall

- Formation of unique carbon nanostructures via carbonization of wood.
- Does this provide an explanation for the quality of Damascus steel?

Significant research activity in cellulose nanomaterials

In 2010-2011, 6 comprehensive reviews

1. Cellulose
2. Journal of Materials
3. Polymers
4. Chemical Reviews
6. Angewandte Chemie

Cellulose nanomaterials
NNI Signature Research Initiative (Jul 2010)

Siro and Plackett, Cellulose 17, 459 (2010)
Types of Cellulose Nanofibrils (CNF)

- Bacterial cellulose nanofibers 5000X
- Nanofibrillated cellulose
- Electrospun cellulose nanofibers
- Cellulose nanocrystals (whiskers)
Applications of Cellulose nanofibrils

- Opportunities for renewable nanomaterials from wood
  - Batteries
  - Super-Capacitors
  - Bio Plastics
  - Nano Coatings
  - Reinforced Polymers
  - Smart Sensors
  - High Efficiency Filters
  - Light Weight Nano Composites
  - Nano Membranes
  - Photonic Devices

Can be produced in tens of millions of ton quantities
Brief history of cellulose nanofibrils

• Rånby 1951 colloidal properties of cellulose micelles
• Turbak 1983 microfibrillated cellulose
• Revol et al. 1992 self-ordering of cellulose microfibrils
• Daicel, JRS, EFTech mid to late 2000s
• Scale up in Sweden
  • Innventia 2010
• Scale up in Canada
  • 2010 Domtar $32M facility 1-tonne per day
  • 2011 Bio Vision Technology pilot plant
• Scale up in U.S.
  • FPL 2012 CNC and TEMPO
  • UMaine 2012 NFC
• Are we there yet?
Close to Commercial Applications?

1. the fruit that grows low on a tree and is therefore easy to reach
2. a course of action that can be undertaken quickly and easily as part of a wider range of changes or solutions to a problem: *first pick the low-hanging fruit*
3. a suitable product to exploit as a straightforward investment opportunity

Disclaimer: The thoughts expressed are based on the author’s world view.
Cellulose Nanopaper

- High strength (4 times Kraft, 8 times newsprint)
- High Toughness exceeding plant fibers
- Large strain to failures

Henrikson et al. 2008 Biomacromolecules 9(6)1579-1585.
Paper or Board Coatings

E-SEM micrographs of uncoated and NFC-coated papers Aulin et al. 2010 Cellulose 17,559-574
NFC Aerogels/Foams

Low mag. SEM micrographs

Freeze-dried NFC aerogels

Bacterial Cellulose Applications

• Long established food in Southeast Asia – Nata De Coco
• Clothing – Suzanne Lee, TED seminar
• Artificial veins
Spray Dried Cellulose Nanofibrils as Novel Tablet Excipient

- CNF particles less prone to permanent deformation and less ductility
- Slightly faster drug release from CNF compared to MCC
- Assuming NFC?

“Nanodiapers”

- Current disposable diapers are a composite of air-laid paper and superabsorbent polymers (hydrogels)
- Could CNF hydrogels replace “petroleum-based” acrylate hydrogels?

<table>
<thead>
<tr>
<th>Country</th>
<th>Billion Units/Yr. Potential</th>
<th>Billion Units/Yr. Current</th>
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<tbody>
<tr>
<td>United States</td>
<td>22.4</td>
<td>21.3</td>
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<tr>
<td>China</td>
<td>75.7</td>
<td>12.1</td>
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<tr>
<td>Brazil</td>
<td>15.7</td>
<td>7.7</td>
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<tr>
<td>Mexico</td>
<td>10.4</td>
<td>6.8</td>
</tr>
<tr>
<td>Japan</td>
<td>5.8</td>
<td>5.7</td>
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Richter 2012 Nonwovens Industry
**CNF Commercialization Barriers**

- Only modest investment in scale up processes - development of production technology – from lab scale to pilot scale and further to mill scale.

- Lack of product line growth due to “no supply” of large quantity samples.

- Difficulty in cost estimation due to lack of scale up data and overly concerned for a potential initial high price.

- Lack of coordinated approach between research institutes (university and research organizations) and potential customers.

- Lots of uncertainties and risks (safety issues/regulations).

Mohini Sain, OECD Nanocellulose Workshop, 2009
Timo M. Koskinen, TAPPI Nanotechnology Conference, 2010
Cellulose Nanomaterial Standards

- Standardize “Nano-cellulose” terminology
- TAPPI and ISO Technical Committee (TC) 229
- “Nanocellulose” task group established in June 2011
- Proposed TAPPI Standard
- **Standard Terms and Their Definition for Cellulose Nanomaterial WI 3021**
Future Needs of Nanotechnology in Forest Products

• Ability to have scalable nano-manufacturing
  • Adapt conventional manufacturing processes
  • Develop novel processing equipment
• “Papermaking is self assembly of wood cells at 60 mph (100 kph)”
• Novel composite manufacturing processes for ballistics, automobiles, coatings, adhesives, biomedical applications, drug delivery
Concerns, Challenges and Opportunities of Nanotechnology in Forest Products

• Consumer perception issues
  • Sustainability
  • Risks and unknowns

• Regulation issues
  • Health and Safety (Is cellulose non toxic? What about Brown Lung?)
  • “regulating nanotechnology will be a process not an event”

• Market opportunities
  • Improve existing products
    • Do you have nano?
    • Nano diapers?
  • Intelligent packaging
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