Nanofibrillated Cellulose Fibers: Where Size Matters in Opening New Markets to Nanofiber Usage

Presentation to 2008 TAPPI Nanotechnology Conference

June 25-27, 2008
St Louis, MO

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Nanofibrillated Cellulose Fibers: Opening New Markets to Nanofiber Usage

- Introduction
- Regenerated / Natural Cellulose - Structure and Nanofibrillation
- Commercial Production of Cellulose Nanofibrillated Fibers
- Applications / Performance of Nanofibrillated Fibers
- Summary
Conventional Nanofiber
Definition /
Polymeric Fibers

- Fibers with Diameters less than About 0.5 microns
  *(Consensus Not Universal with Definitions Down to < 10 Nanometers and Up to 1 Micron)*

- Typical Polymeric Nanofibers Currently Produced
  Have Diameters Between 50 and 300 Nanometers

- Presentation Focused on Cellulosic Nanofibers
  Created By Nanofibrillation Technology and
  Produced on Commercial Scale

- Alternative “Low Cost” Nanofibers for Range of
  Paper Making and Other Engineered Applications
Relative Size of Nanofibers Compared to Human Hair
(20,000 to 30,000 nm)
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Nanofibrillation of Cellulosic Fibers (1)

- **Natural Cellulosic Fibers**
  - **Wood / Non-Wood**
    - Grow with Microfibrillar Structure
    - Micro / Nano Fibrils Can be Generated Under Special Fibrillation Processing
  
- **Regenerated Cellulose**
  - **Rayon / Viscose**
    - More Amorphous Structure – Generally Abrades into short lengths
    - Higher Modulus Polynosic Rayon (Tufcel) had High Fibrillation Levels
  
  - **Lyocell**
    - High Crystallinity with microfibrillar structure / similar to lyotropic rods – low lateral bonding between crystalline regions
Production of Regenerated Cellulose Fibers

Lyocell Technology

N-Methylmorpholin-N-oxid

Dissolving

Spinning

Washing

Finishing Drying

Lyocell-Fibre

Waste Water
Production of Lyocell Fibers

Physical vs. Chemical Process

- Purified Dissolving Wood Pulp
- Amine Oxide Solvent
- Extruded (Spun) Through Spinnerets
- Continuous Filaments / Circular Cross-Section (Cut to Short - 0.5 to 8 mm-Lengths)
- Long Chain Molecules / Highly Crystalline ( > 60 % ) Structure
Lyocell Fiber - As Spun
Proposed Structure at Different Dimensional Levels of Lyocell Fiber

Fibre, diameter 10 to 30 µm

Skin, ca. 100 nm dry, can swell very widely.

Macrofibril, ca. 0.5 .. 1 µm

Mainly the disintegration on the macrofibril level is relevant for fibrillation!

Macrofibril, made up of microfibrils

Cellulose structure with amorphous & crystalline regions, pores and voids

Cellulose molecular structure (crystal lattice)
Lyocell Fiber Morphology (3) - The Ultimate “Islands in the Sea”

<table>
<thead>
<tr>
<th>Structure Element</th>
<th>Size</th>
<th>Approximate number of fibrils per fibre cross-section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofibril</td>
<td>10 nm</td>
<td>1,330,000</td>
</tr>
<tr>
<td>Microfibril</td>
<td>0.15 μm</td>
<td>5902</td>
</tr>
<tr>
<td>Macrofibril</td>
<td>0.75 μm</td>
<td>236</td>
</tr>
<tr>
<td>Complete fibre</td>
<td>13 μm</td>
<td>(1)</td>
</tr>
<tr>
<td>diameter</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fibrillation / Splitting Mechanism to Create Lyocell Nanofibers

- Initial peeling of fibrils (macro bundles) along the fiber length of individual fibers, induced by mechanical stress, special processing / treatments
Fibrillation / Splitting Mechanism to Create Lyocell Nanofibers

- Continued Splitting Into Microfibrils / With Final Nanofibrillated Fiber Exhibiting Range of Fibril Diameters
- High Aspect Ratio Fibrils (Est. > 1000:1)
Lyocell Nanofibrillated Fiber Structure

- Large majority (number average) of fibril diameters are between 0.05 and 0.5 microns, with typical average of about 0.3 micron

- Very small number fraction of 2-5 micron diameters
  - Effective as a “bridge or scaffold fiber” in coating applications
  - < Other Typical Fibers In Paper Formulation
Nanofibrillated Lyocell Fibril Diameter Distribution

Fraction (%)

Diameter (nm)
Nanofibrillated Lyocell Exhibits Very High Aspect Ratio Fibrils
Other Wood / Non-Wood Nanofibrillation Process Developments

Cotton

Wood Pulp
Synthetic Nanofibrillated Fiber Developments

- Acrylic/PAN Conventional
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Production of Lyocell Nanofibrillated Fibers

- Various Processes Described for Fibrillation In Literature Using Short-Cut Fibers

- EFT Proprietary Process Developed for Nanofibrillation

  - Fiber / Fibril Length Controlled by Length of Starting Short-Cut Fiber

  - Nanofibrillation Process Less Energy Intensive / Very High Number Average Submicron Fibril Diameters

  - Commercial Scale

  - Economic Alternative to Other Sources of Nanofibers
Processes Being Developed for Nanofiber Production

<table>
<thead>
<tr>
<th>Technique</th>
<th>Fiber Size (nm)</th>
<th>Throughput</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrospinning</td>
<td>~100-300</td>
<td>0.3 g/ hole/ hour</td>
</tr>
<tr>
<td>Meltblowing</td>
<td>300+</td>
<td>0.5 g/ hole/ hour</td>
</tr>
<tr>
<td>Bicomponent spinning/ separation</td>
<td>300+</td>
<td>0.5 g/ hole/ min with multiple rows of holes</td>
</tr>
<tr>
<td>Nanofibrillation</td>
<td>50-500</td>
<td>+1500 g/ min/ reactor</td>
</tr>
</tbody>
</table>

- Nanofibrillation Process Provides a 1000X Improvement in Throughput Compared to Other Processes
New Process Lyocell
Nanofibrillated Fiber - Production
Features of New Process Nanofibrillated Fibers

- Wide Range of Nanofibrillation Level (CSF) and Fiber Length Possible
  - CSF 200 to Zero \((and\ Much\ Less)\)
  - Fiber Length 1 to 8 mm

- Products Provided In Various Forms
  - Wet Slurry \((2-3\%\ Consistency)\)
  - Dewatered \((\sim10\%\ Solids)\)
  - Wet Lap / Crumb \((\sim20\%\ Solids)\)
  - Dry Lap \((\sim80\%\ Solids)\) Developmental
Features of Cellulosic Nanofibrillated Fibers

- Cellulose Nanofibrillated Fiber Supply
  - Renewable / Sustainable Sources
  - Biodegradable
  - FDA Approved Fiber Grades

- Low Cost/ High Value Compared with Other Nanofiber Technologies

- Current Development Scale & Commercial-Scale Production In Place (tonnes/ day production scale)
Features of New Nanofibrillated Fiber Technology

- Hydrophillic and Hydrophobic Chemistry
  - Manmade and Natural Cellulose
  - Cellulose Blends
  - Acrylic (PAN)

- Compatible with High Speed Papermaking / Wet Laid Nonwoven Technology
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Current Applications of Nanofibers / Wet-Laid Papers

- Air Filtration
- Water / Liquid Filtration
- Protective Clothing
- Medical Barriers
- Clean Room Wipes

*Cost and Low Productivity Limiting Development / Use in These and Other Applications*
Cellulosic Nanofibrillated Fibers

In Papermaking / Filtration / Nonwoven Applications

- 100% Nanofibrillated Fiber Wet-Laid Papers / Microporous Structure
  (Mean Pore Size < 1 Micron)

- High Efficiency Binder Fiber for Other Fibers / Active Particulates
  (Without Blinding Absorptive Particles/ Fibers)

- Coatings
Nanofiber Papers with Microbial Barrier Properties

Nanofibrillated Lyocell Added to Wood Pulp - Compared with Commercial Papers

<table>
<thead>
<tr>
<th></th>
<th>100%</th>
<th>50%</th>
<th>10%</th>
<th>1%</th>
<th>Medical Paper A</th>
<th>Medical Paper B</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM F1608 Log Reduction Value</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
Nanofiber Papers with Microbial Barrier Properties

ASTM F1608 Spore Penetration (%)

Nanofibrillated Lyocell Added to Wood Pulp - Compared with Commercial Papers

Medical Paper A: 0.01%
Medical Paper B: 2.01%
## Comparison of Nanofibrillated Fiber and Other Filtration Media (5)

<table>
<thead>
<tr>
<th>Paper Construction</th>
<th>Mean Pore Diameter (microns)</th>
<th>Air Permeability@ 1 psi (L/psi/cm²/min)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofibrillated Fiber</td>
<td>0.35</td>
<td>2.3</td>
<td>0.85</td>
</tr>
<tr>
<td>Microglass Fiber</td>
<td>3.25</td>
<td>30</td>
<td>0.85</td>
</tr>
<tr>
<td>Meltspun Web</td>
<td>10</td>
<td>105</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Nanofibrillated Fiber Coated Webs

- Coating Weights of 0.5 - 5 g/m² Typically Applied
- Slurry Coated
- Dual Headbox
- Other
Effect of Nanofibrillated Coatings on Filtration Efficiency of Automotive Air Filter

- 1.6 g/m² Lyocell Nanofiber Coating Level on Resin Bonded Cellulose Filter

- Relative performance can be compared using Figure of Merit (FOM)

\[ FOM = -\log(1 - \text{efficiency}) \frac{\Delta P}{P} \]

- Can be thought of as benefit to cost ratio

- Tested using 0.18 μm DOP aerosol at 32 l/m airflow
Nanofibrillated Fibers for Paper Coating Applications

Advantages of Nanocellulose Coatings:

- Extremely light weight additions (down to 0.005g/ sq. meter)
- Increase smoothness of paper surface
- Do not have rheology issues with other additives
- Enhance pigment application in printing processes / brighter colors / greater clarity of print
- Can be charged to enhance pigment attraction to print surface.
Potential Benefits of Nanofibrillated Fibers / Wet-laid Papers

- Better Filtration Efficiency
- High Level of Particle / Fiber Retention
- Higher Wet / Dry Strength
- Lower Basis Weight
- Higher Absorbency
- Better Surface Smoothness
- Increased Barrier Properties
- Better Printing Quality
- FDA Approval / Biodegradable
Other Potential Applications
EFTec™ Nanofibrillated Fibers

- Structural Reinforcements
- Surface Modifiers
- Print Clarity Coatings
- Wet / Dry Strength Enhancers
- Processing Aids
- Particle Binders
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Summary

- EFTec Nanofibrillated Cellulosic Fibers Offer New Products for New Applications
- Production Capabilities in Place for EFTec Nanofibrillated Fibers
- Various Product Forms Can Be Supplied to Meet Specific Requirements of Papermakers
- Customer Specific EFT Cellulosic Nanofibrillated Fibers Can be Produced
Acknowledgements

The Assistance of A. Slater and C. Mechtler, Lenzing Fibers, in Preparing this Presentation is Greatly Appreciated.
References


