Cellulose Fibers From Nanometers to Millimeter
New Applications and Opportunities

Arthur J. Ragauskas
Institute of Paper Science and Technology
Georgia Institute of Technology
Current Nanotechnologies in Modern Pulp Mill

Printing speeds continue to increase

Consumer demands more/sharper colors

- Silica nanoparticles for high-performance retention/drainage providing better formation

  - Silica sol 1\textsuperscript{st} generation 1980s
  - 350 paper machines/25 countries

- Silica nanoparticles yielding a favorable open sheet structure for select bag applications
Current Generation of Nanotechnologies in Modern Pulp Mill

New nano-sizing technologies to improve surface sizing

Nanoparticles
  – Improved coating hold out
  – Improved print quality
Nano-Enhanced Paper

New Product Platform Applications
Fiber-Fiber Bonding Improvement

- Common method: Refining is one of the common methods for improving fiber-fiber bonding in papers.
- Our approach: Bond nano/micro-fibrils onto fiber surface to enhance the fiber-fiber bonding.
Nano-Enhanced Paper: Product Platform Studies

SEM of Unmodified Fiber

Surfaces are relatively smooth

Fibrils was generated by refining
Nano-Enhanced Paper

5% Precipitated cellulose

SEM of Nano-fibril and Micro-fibril Fibers
Nano-Enhanced Paper: Tensile Strength Improvement

![Graph showing tensile strength improvement](image-url)
Nano-Enhanced Paper:

Folding Strength Improvement

3.5 time increases in the folding strength
Nano-Enhanced Paper:

ZDT Strength Improvement

33% increase in ZDT
Nano-Enhanced Paper: Coatings

Application of Polyelectrolyte Coating Technologies

Layer-by-Layer Self-Assembly

General Considerations:

• Assembly via electrostatic and H-bond interactions
• Aqueous Processing
• Process Parameters:
  • pH; salt concentration
  • Polymer charge/DP
• Wide range of materials can be employed
Nano-Enhanced Paper: Coatings

Current Studies

\[ \text{PAH} : \text{NH}_3^+ \text{Cl}^- \]

\[ \text{PDDA} : \text{N}^+ \text{Cl}^- \]

Montmorillonite K10

Kaolin InFilm 9
Nano-Enhanced Paper: Coatings

Current Studies

\[ \text{NH}_3^+ \text{Cl}^- \]

\[ \text{PAH} \]

\[ \text{PDDA} \]

Montmorillonite

Kaolin
Nano-Enhanced Paper: Coatings

8 Bilayers PDDA/Montmorillonite

8 Bilayers of PDDA/Kaolin

PAH

\[ \text{PAH} \]

\[ \text{N} \]

\[ \text{NH}_3^+ \]

\[ \text{Cl}^- \]

PDDA

\[ \text{N} \]

\[ \text{Cl}^- \]

Montmorillonite

Kaolin

Graph showing absorbance vs. wavelength (nm) for different number of bilayers.
Nano-Enhanced Paper: Coatings

PAH

\[ \text{PAH} \]

PDDA

\[ \text{PDDA} \]

Kaolin
Nano-Enhanced Paper: Coatings

Current Studies

Initial Fibers

8 Bilayers of PAH
Kaolin
Nano-Enhanced Paper: Coatings

Current Studies

Bilayers of PAH/Kaolin

Ongoing Studies

- Enhance hydrophobic effect
- Utilize select nanoclay
- Examine optical properties
- Alternative barrier properties
Nano/Self Assembly Program

Clay

Charge

Polymer

Charge

Polymer

Charge

Polymer

Control

Coated clay

Tensile Index vs. Percentage clay

5% 10% 15% 20% 9 layer

26 28 30 32 34 36

Charge Charge Charge

Polymer Polymer Polymer

Clay
Nano Clays for Barriers/Coatings

• Numerous patents/differing materials
• Impact of differing alkylammonium nanoclays as fillers/coatings
  • Barrier
  • Printability

The thickness of nanoclay in the composite is about 1nm.
Polymer-Nanoclay Composites

The thickness of nanoclay in the composite is about 1nm.

Barrier coating for food containers and paper packages

- Water and vapor resistance
- Fatty and oil resistance
- Paper-board strength
Polymer-Nanoclay Composites
Paper Application

Relationship between barrier properties (WVTR and COBB) of waxed liner paper and nanoclay content.
Wax used: Paraffin wax.

- 3% nanoclay in wax can increase water-barrier by 50%, and gas barrier by 100%, target for wax-coated paper container.
Nano-Enhanced Paper and Board Composites

Nanocellulose Additives for Innovative Composites

1. Disperse Plastic Resin

2. Heat Press - Resin Coat Fiber
   Resins: PLA, Starch, PMMA
Nano-Enhanced Paper and Board Composites

Nanocellulose Additives for Innovative Composites

1. Disperse Plastic Resin

2. Heat Press – PMMA
   Polymethyl methacrylate

Fiber
10% PMMA
30% PMMA
ECF SW Kraft

Contact Angle (degrees)

- Micro-sized PMMA
- Nano-sized PMMA
- 60 nm PMMA
- 5-100 micron PMMA

0% PMMA   10% PMMA   30% PMMA
SEM

ECF Pulp Fines
SEM

Course PMMA, 10%

Nano PMMA, 10%
Polystyrene-ECF Kraft Composite

Nano-polystyrene sheets being characterized
Anticipate Benefits According to nano PMMA
NanoCellulosic Structures

Surface Area m²/g
- E-Glass Fibers: approx. 1
- Paper Fibers: 4
- Graphite: 25 - 300
- Fumed Silica: 100 - 400
- Fully Exfoliated Clay: approx. 500
- Nanocellulose Whiskers: 400 - 700
- Carbon Nanotubes: approx. 100
Nano-Enhanced Cellulosics

- Acid Hydrolysis Technique
  - Bleached softwood kraft pulp
  - *Strong Acid*
  - Stirred at 45 C, 45 min ~ 1 hour
  - Dilute with water
  - Centrifuged, wash and neutralize
  - Allowed to stand over a mixed bed resin for 48 h
  - The mixture was centrifuged and the supernatant was filter through filter paper. The filtrate was colloidal nanowhisker suspension

*Over 50% of yield could be achieved by this method.*
Nano-Enhanced Cellulosics

- Nanocellulose Whisker:Polystyrene Composite Film

- Polystyrene /whisker film

### Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>TEA*, J/m²</th>
<th>Elongation, %</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>8.9</td>
<td>1.3</td>
<td>46.5</td>
</tr>
<tr>
<td>Polystyrene/NC whisker</td>
<td>+70%</td>
<td>+ 11%</td>
<td>+ 23%</td>
</tr>
</tbody>
</table>

*: Tensile energy absorption.

- Mechanical tests were carried out on an Instron 4400R
- 4.5 inch length * 15 mm width
Nano-Enhanced Composites:

- Nanocellulose Whisker
- Acrylic Acid Composite Film

Experimental Method

- Dow acrylic latex, solids 50%
- Add cellulose whiskers or hardwood bleached kraft pulp
- Mixture cured at RT
- Initial film dried 50 °C for 2 days.
Nanocellulose Whisker:Acrylic Acid Composite Film

- **Tensile strength, MPa**
  - Curve for Whisker:
    - Increases sharply from 0 to 10%
    - Peaks at around 10%
  - Curve for Pulp Fiber:
    - Stays relatively constant

- **TEA, J/m²**
  - Curve for Whisker:
    - Increases sharply from 0 to 10%
    - Peaks at around 10%
  - Curve for Pulp Fiber:
    - Increases and then plateaus

- **Strain, %**
  - Curve for Whisker:
    - Decreases sharply from 0 to 10%
    - Peaks at around 10%
  - Curve for Pulp Fiber:
    - Decreases and then plateaus
Nanocellulose Whisker:Acrylic Acid Composite Film

Latex Film

Contact angle

Whisker content, %
Nanocellulose Balls

- SW ECF bleached kraft pulp
- Refined to 20-mesh
- Swell fibers with 5M NaOH followed by DMSO
- Sonicate cellulose with HCl – H₂SO₄ 75 °C
- Wash with water, purify by centrifugation
- Sonicate cellulose with HCl – H₂SO₄ 75 °C
- Wash with water, purify by centrifugation
## Nanocellulose Balls

<table>
<thead>
<tr>
<th>Initial Cellulose Length (nm)</th>
<th>Yield (%)</th>
<th>Average Cellulose Particle Diameter (nm) with Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.465</td>
<td>62</td>
<td>505 ± 100 (29%) and 190 ± 100 (33%)</td>
</tr>
<tr>
<td>0.452</td>
<td>65</td>
<td>495 ± 100 (29%) and 185 ± 100 (36%)</td>
</tr>
<tr>
<td>0.347</td>
<td>71</td>
<td>485 ± 100 (31%) and 175 ± 100 (40%)</td>
</tr>
<tr>
<td>0.237</td>
<td>74</td>
<td>460 ± 100 (31%) and 170 ± 100 (43%)</td>
</tr>
</tbody>
</table>
Nanocellulose Balls

First nanocellulose procedure able to provide practical control of particle sphere dimensions!!
Nanocellulose Balls – 76 nm AFM Images
Nanocellulose Balls

180 nm balls

76 nm balls
Nanocellulose Crystallinity Results

13C-CP/MAS NMR Analysis

| Crystallinity index |  
|---------------------|---|
| Original pulp – Cellulose 1 | 0.61 |
| 300 – 500 nm Nanocellulose Balls Cellulose II | 0.65 |
| 50 – 100 nm Nanocellulose Balls Cellulose II | 0.70 |
NanoCellulosic Structures

Nanocellulose Whisker-Balls: Acrylic Acid Composite Film

5% Cellulose Balls: Latex Film

5% Cellulose Whiskers: Latex Film

Latex Film

Bar chart:

- Latex
- Nanoball
- Whisker
- Acacia

Graphs:
Pathforward

- Nanocellulose balls
  - Derivatives to be used for superabsorbers – viscosity modifiers
  - Artificial blood/drug delivery
  - Cosmetics
  - Template for Nanospheres

- Nanocellulose whiskers
  - Composites with plastics
  - Composites with natural polymers
  - In-situ polymerization
Cellulose Superabsorbents
Tying Cellulose Together

\[
\text{PMA} + \text{PEG}_n \rightarrow \text{Cellulose}
\]

US Patent 5049235
**SW Kraft Pulp**

**Water Absorbed**

Tea bag method, 0.1 g in water for 8 h

**Water Retained**

Centrifuge for 10 min at 770 rpm

**ECF Pine Kraft Fibers**
- 2.499 mm
- 0.455 mm
Crosslinked Pulps – ECF Pine Kraft

Water absorption and retention value (g/g)

<table>
<thead>
<tr>
<th>Fiber length (mm)</th>
<th>Uncrosslinked</th>
<th>Crosslinked</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.406</td>
<td>4.97</td>
<td>86.5</td>
</tr>
<tr>
<td>0.974</td>
<td>4.72</td>
<td>137.9</td>
</tr>
<tr>
<td>0.499</td>
<td>3.82</td>
<td>189.2</td>
</tr>
</tbody>
</table>

Water absorption and retention value (WAARV) of SW
Crosslinked Whisker Sample Preparation

- Whiskers + PMVEMA + PEG $\rightarrow$ film
  - Vary percentage (weight) of whiskers
    - 0, 25%, 50%, 75% 100% whisker films
  - Air dry in oven
- Cure at 135°C for 6.5 min
- Stored in humidity controlled desiccators for further testing
  - 2%, 54%, 92% relative humidity
Crosslinked Cellulose Whisker Films
Behavior of Crosslinked Materials in Water

- Crosslinked pulp fibers $\rightarrow$ dry, then wetted...

- Crosslinked whisker films $\rightarrow$ dry, then wetted...

0.5 g SA Pulp + 8.5 ml
21.5 ml
136.5 ml
Mechanical Properties of Crosslinked Whiskers

- Tensile (Stress-Strain)
  - Measured with 500 N Load Cell, on Instron 4411
  - A rectangular shaped strip (60 mm long x 8 mm wide) with a 25 mm distance between the two heads, with a 5 mm/min load rate

54% Relative Humidity
Water Sorption of Crosslinked Whiskers

- Timed absorption
Surface Morphology

25% CNW Film – Cut

25% CNW Film – Tensile Test Fractured
Surface Morphology
After Water Absorption

25CNW

50CNW

75CNW
Conclusions

• First example of crosslinked cellulose whisker films that exhibit unique hydrogel properties
  – Tailorable physical properties

• Future applications for managing water/humidity in packaging and for medical devices
Nanotechnology at IPST@GT

• Georgia Tech to be Part of 13-University National Nanotechnology Infrastructure Network Funded by National Science Foundation

• National and International Investigators

• Current Nano forest product studies include:
  – Nanoclay coatings/barriers
  – Nanoclays for UF composite wood products
  – Nanocellulose super absorbers
  – Nanocellulose self-assembly
  – Nanolignocellulosic composites
  – Cationic Polymeric Nanoparticle Retention Systems
Fiber - Challenge

Innovative Products

Petroleum Costs

Fiber engineering:
The key to industry change

Imagine major benefits in our industry's efficiency, economics, and product quality without changing the basic papermaking process. Fiber modification can make it possible.

g Doug Mills could improve their operations if they had a way to modify fibers so that any given fiber could be used effectively in the production of any grade. While this may not be a realistic goal, the ability to modify the bulk or surface properties of fibers, so that they provide new or enhanced benefits at reduced costs, is a very worthwhile objective.

Since papermaking unit operations also create unwanted (and harmful) changes in the cell wall structure, it is
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arthur.ragauskas@ipst.gatech.edu