Microfibrillated Celluloses (MFCs) are generally considered to be fibrils with diameters in the range of 10-100 nm liberated from larger plant-based cellulose fibers. MFCs have garnered much attention for the use in composites, coatings, and films because of high specific surface areas, renewability, and unique mechanical properties. Many of the recent studies of MFC generated from wood pulp have focused on fully bleached chemical pulps; however, these materials must be further modified to be incorporated in hydrophobic matrices for composite reinforcement. The production of MFCs containing hydrophobic lignin may reduce the need for surface modifications and generate MFCs with new properties for use in other applications. To investigate, wood pulps of different chemical compositions were used to produce MFCs to determine the effect of lignin on microfibril and film properties.

The energy requirement of the processing of these materials is a major drawback for industrial scale-up. Chemical pretreatments can be implemented to reduce the energy consumption, but further analysis of the processing equipment has not been preformed. This study will investigate the differences in MFC characteristics as well as the energy consumption of the three common processing methods, homogenization, microfluidization, and micro-grinding.

Pulp samples were used as received from pulp mills in the southeastern United States. These samples included bleached hardwood, bleached softwood, unbleached hardwood, two unbleached softwoods, and thermo-mechanical pulp. Pulps were subjected to a refining pretreatment with a Valley beater in order to shorten the fibers and reduce equipment plugging. The pretreated pulps were then processed with a homogenizer, a microfluidizer, or a micro-grinder. Films were generated using a casting-evaporation technique and were tested using TAPPI standard methods. Film characterization included thickness, roughness, optical properties such as opacity, brightness, and scattering coefficient, mechanical properties, and water interaction properties such as water vapor transmission rate and water adsorption. The MFC slurries were evaluated using water retention value, hard-to-remove water content, and the Congo red specific surface area method.

It was found, after homogenization, that the presence of lignin significantly increased film toughness, tensile index, and elastic modulus, contrary to physical properties of paper, Figure 1. It was also found that MFC films had similar surface roughness values to the surface upon which casting occurred. Unexpectedly, the lignin-containing films had higher water vapor transmission rates than the bleached samples, even though the initial contact angle of these materials was higher. This can be explained by the internal hydrophobic pore structures likely formed in the materials containing lignin; this structure allows for the water vapor to rapidly pass through the film.

Further, three different types of mechanical processing equipment were used to generate MFCs from the bleached and unbleached hardwood samples. Film densities were approximately 900 kg/m³ for all samples and specific surface area of the processed materials ranged from approximately 30 to 70 m²/g for bleached hardwood and from 70 to 200 m²/g for unbleached hardwood. Preliminary results show that the microfluidizer resulted in significantly tougher films than both micro-grinding and homogenization and required less energy to obtain these properties, offering great promise for producing MFC materials with lower energy input, Figure 2. Analysis of the processing methods further allow for process optimization
with regards to energy consumption. Unexpectedly, increasing processing pressure and number of passes with the microfluidizer did not improve mechanical properties, suggesting that the optimum processing conditions may be less than 10,000 psi and 5 passes. The refining pretreatment was found to reduce the minimum number of homogenizer passes required to approximately 8 passes from the standard 20 passes, and processing with the grinder was found to eliminate the need for the pretreatment.

These results show that it is possible to produce MFCs containing lignin with properties similar to MFCs made from purified cellulose. The ability to produce MFCs containing lignin could potentially provide new markets for MFC such as composite reinforcements in hydrophobic matrices without surface modification while production with the microfluidizer and the micro-grinder could provide a more economically feasible production method as compared to the homogenizer.
Aspects of Raw Materials and Processing Conditions on the Production and Utilization of Microfibrillated Cellulose

Kelley Spence, Richard Venditti, Orlando Rojas

Department of Forest Biomaterials
North Carolina State University
1. Effect of chemical composition on MFC and film properties

2. Effect of Processing method on MFC and Film properties
Where do plastic bottles go??

- Americans throw out 2.5 million plastic bottles EVERY HOUR
- Americans make enough plastic wrap ANNUALLY to shrink-wrap the state of Texas (696,241 km²)
- ANNUAL world consumption of plastic is almost 100 million tons

http://www.cleanair.org/Waste/wasteFacts.html
http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.htm
www.greergoods.com
• Petroleum
  o Cheap
  o Widely produced
  o Non-renewable
  o Lifespan of 100 years in a landfill
  o Variable market price

• Cellulosic
  o Renewable
  o Tunable properties
  o Compostable
  o Hydrophilic & dispersion in non-polar media
  o Energy consumption
  o Production costs
  o Production scalability
  o $
Overall Goal

• Develop plastic alternatives using cellulose from wood pulps
  – Minimize waste in landfills
  – Reduce dependence on petroleum

http://www.cleanair.org/Waste/wasteFacts.html
1. EFFECT OF CHEMICAL COMPOSITION ON MFC AND FILM PROPERTIES


Pulps obtained from local pulp mills

<table>
<thead>
<tr>
<th>Pulp Type</th>
<th>Extractives (%)</th>
<th>Hemicellulose (%)</th>
<th>Cellulose (%)</th>
<th>Total Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSW</td>
<td>0.0</td>
<td>20.0</td>
<td>79.2</td>
<td>0.8</td>
</tr>
<tr>
<td>BHW</td>
<td>0.5</td>
<td>20.3</td>
<td>78.0</td>
<td>1.3</td>
</tr>
<tr>
<td>UBHW</td>
<td>0.3</td>
<td>19.3</td>
<td>78.0</td>
<td>2.4</td>
</tr>
<tr>
<td>UBSwLoK</td>
<td>0.2</td>
<td>22.0</td>
<td>69.0</td>
<td>8.8</td>
</tr>
<tr>
<td>UBSwHiK</td>
<td>0.8</td>
<td>20.1</td>
<td>65.2</td>
<td>13.8</td>
</tr>
<tr>
<td>TMP</td>
<td>1.9</td>
<td>29.2</td>
<td>37.7</td>
<td>31.2</td>
</tr>
</tbody>
</table>
MFC Production

Hornification:
- Refined to ~ 300 CSF
- Dried completely at 105 °C
- Dispersed with TAPPI disintegrator
- Refined to total refining time

Chemical pulps:
- Cast at 1% K
- Dried at 25°C, 50% RH

TMP:
- Cast at 1%K in Teflon dish
- Dried at 50 °C
MFC Production (Cont’d)

- Physical Properties
- Optical Properties
- Mechanical Properties
- Water Vapor Transmission
- Water Pick-up
- Dynamic Contact Angle
- SEM Imaging
- X-Ray Diffraction

- Water Retention Value
- Microscope Imaging
- Hard-to-Remove Water
- Specific Surface Area
- Viscosity
Specific Surface Area

Direct Dye 28 (Congo Red)
- Monolayer adsorption
- Langmuir Isotherm

\[
y = 2.36533 \times 10^{-4} x + 2.21968 \times 10^{-2}
\]

\[
R^2 = 9.99657 \times 10^{-1}
\]
Film Optical Properties

UBSWloK  BSW

UBSWhiK  Hornified BSW
Film Density

<table>
<thead>
<tr>
<th></th>
<th>BSW</th>
<th>BHW</th>
<th>UBHW</th>
<th>UBSWloK</th>
<th>UBSWhiK</th>
<th>TMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>210 ± 12</td>
<td>273 ± 14</td>
<td>228 ± 10</td>
<td>165 ± 8</td>
<td>142 ± 7</td>
<td>134 ± 15</td>
</tr>
<tr>
<td>Pretreated</td>
<td>637 ± 75</td>
<td>697 ± 87</td>
<td>717 ± 87</td>
<td>622 ± 48</td>
<td>465 ± 26</td>
<td>455 ± 16</td>
</tr>
<tr>
<td>Homogenized</td>
<td>860 ± 74</td>
<td>903 ± 44</td>
<td>972 ± 36</td>
<td>784 ± 58</td>
<td>792 ± 32</td>
<td>514 ± 25</td>
</tr>
</tbody>
</table>
Mechanical Properties & Lignin Content

\[ R^2 = 0.8089 \]
\[ R^2 = 0.1982 \]
\[ R^2 = 0.4932 \]

Cellulose, 17, 835 (2010)
## Comparison to Other Polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regenerated cellulose film</td>
<td>170.3(^a)</td>
</tr>
<tr>
<td>Regenerated cellulose/MCC composite film</td>
<td>215.1–242.8(^a)</td>
</tr>
<tr>
<td>Cellophane</td>
<td>50–120(^b)</td>
</tr>
<tr>
<td>30 g/m(^2) MFC films, prepared by free drying</td>
<td>136(^c)</td>
</tr>
<tr>
<td><strong>Original pulp handsheets</strong></td>
<td>2.2–5.9</td>
</tr>
<tr>
<td><strong>MFC films</strong></td>
<td>82.2–90.3</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>75.9(^d)</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>8.3–31.4(^d)</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>22.1–31.0(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Gindl and Keckes (2005).  
\(^b\) Mark et al. (1968).  
\(^c\) Syverud and Stenius (2009).  
\(^d\) Callister (2003).
Water Vapor Transmission Rate (WVTR)

- **Untreated**, **Pretreated**, and **Homogenized** materials are compared in terms of WVTR.

**Graph 1:**
- Bars representing WVTR for different materials.
- Untreated materials show higher WVTR compared to pretreated and homogenized.

**Graph 2:**
- Plot of Film Density (g/m³) vs. WVTR (g/m²•day)/(m).
- Correlation between density and WVTR is shown.

**Graph 3:**
- Plot of Initial Contact Angle (°) vs. Lignin Content (%).
- Lignin content does not correlate strongly to contact angle.

**Graph 4:**
- Scatter plot of Initial Contact Angle (°) vs. WVTR (g/m²•day)/(m).
- Contact angle does not correlate well with WVTR.

**Graph 5:**
- Scatter plot of Film Density (g/m³) vs. WVTR (g/m²•day)/(m).
- There is a strong correlation between film density and WVTR.

**Legend:**
- BSW, hBSW, BHW, hBHW, UBSWloK, UBSWhiK, TMP, Polyethylene.
2. EFFECT OF PROCESSING METHOD ON MFC AND FILM PROPERTIES

Spence et al., Applied Physics, Submitted
<table>
<thead>
<tr>
<th>Pulp Type</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Extractives (%)</th>
<th>Total Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleached Hardwood</td>
<td>78.0</td>
<td>20.3</td>
<td>0.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Unbleached Hardwood</td>
<td>78.0</td>
<td>19.3</td>
<td>0.3</td>
<td>2.4</td>
</tr>
</tbody>
</table>
MFC Production

- Homogenization
- Microfluidization
- Micro-grinding

- Cast at ~1% K
- Dried at 23°C and 50% RH
- 30g/m²
Homogenization
Manton-Gaulin 15MR
0.7% K, 550 bar
3940 kJ/kg (per pass)
Scale-ability
Continuous operation
Energy intensive
Clogging

Grinding
Masuko Super Masscolloider
0.7% K, 25 Hz
620 kJ/kg (per pass)
*Operates by friction between disks*
No clogging
Batch operation
Energy intensive

Microfluidization
Microfluidics, Inc
0.7% K, 10, 20, 30 kpsi
200, 390, 630 kJ/kg (per pass)
*Operates by rapid pressure drop*
No moving parts
Changeable chambers
Continuous operation
Energy intensive
Clogging
Specific Surface Area

- Bleached Hardwood
- Unbleached Hardwood

- Original Pretreated Homogenizer + Pretreatment
- Microfluidizer + Pretreatment
- Grinder + Pretreatment
- Grinder

Specific Surface Area (m²/g)

0 50 100 150 200 250
Film Optical Properties
Film Mechanical Properties

Load (N) vs. Extension (mm) graph showing different pretreatment methods:
- Homogenizer
- Microfluidizer
- Grinder (no pret)
- Pretreat
- Original
Energy Consumption

Homogenizer

Grinder

Microfluidizer

Energy consumption (kJ/Kg)

Tensile index (N/mm²)

Tensile Index
Toughness

Increasing pressure

Increasing passes

Energy consumption (kJ/Kg)
## “Rough” Economics

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>Energy Cost per Ton</th>
<th>Cost per Ton</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bleached Hardwood (BHW)</strong></td>
<td>Homogenizer 8 Pass + Pre</td>
<td>$650</td>
<td>$1,300</td>
</tr>
<tr>
<td></td>
<td>Microfluidizer 5 pass + Pre</td>
<td>$140</td>
<td>$790</td>
</tr>
<tr>
<td></td>
<td>Grinder 9 Pass + Pre</td>
<td>$210</td>
<td>$860</td>
</tr>
<tr>
<td></td>
<td>Grinder 9 Pass</td>
<td>$95</td>
<td>$745</td>
</tr>
<tr>
<td></td>
<td>Homogenizer 20 Pass</td>
<td>$1,310</td>
<td>$1,960</td>
</tr>
<tr>
<td><strong>Unbleached Hardwood (UBHW)</strong></td>
<td>Homogenizer 8 Pass + Pre</td>
<td>$650</td>
<td>$1,000</td>
</tr>
<tr>
<td></td>
<td>Microfluidizer 5 pass + Pre</td>
<td>$140</td>
<td>$490</td>
</tr>
<tr>
<td></td>
<td>Grinder 9 Pass + Pre</td>
<td>$210</td>
<td>$560</td>
</tr>
<tr>
<td></td>
<td>Grinder 9 Pass</td>
<td>$95</td>
<td>$445</td>
</tr>
<tr>
<td></td>
<td>Homogenizer 20 Pass</td>
<td>$1,310</td>
<td>$1,660</td>
</tr>
<tr>
<td><strong>Recycled Fiber</strong></td>
<td>Grinder 9 Pass</td>
<td>$95</td>
<td>$195</td>
</tr>
<tr>
<td><strong>Sludge</strong></td>
<td>Grinder 9 Pass</td>
<td>$95</td>
<td>$115</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Market Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE*</td>
<td>$1,500</td>
</tr>
<tr>
<td>HDPE*</td>
<td>$1,400</td>
</tr>
<tr>
<td>PP*</td>
<td>$1,840</td>
</tr>
<tr>
<td>PS*</td>
<td>$1,600</td>
</tr>
<tr>
<td>PLA**</td>
<td>$1,900</td>
</tr>
</tbody>
</table>

* www.ptonline.com/pricing
**Biopolymers strive to meet price/performance challenge. www.thefreelibrary.com

- Energy assumption: $60/ MWh
- Pulp assumption: $350/ton
UBHW, $650/ton BHW, $100/ton recycled, and $20/ton sludge
Final Remarks

• Lignin-containing fiber: significant mechanical property improvement with pretreatment and homogenization

• Hornification did not significantly impact final film properties

• Production method has significant impact on film properties
  – Microfluidizer – highest toughness and tensile index
  – Homogenizer – highest specific surface area (SSA)
  – Micro-grinder – lowest scattering coefficient
Acknowledgements

• Support for this student training project was provided by USDA National Needs Graduate Fellowship Competitive Grant No. 2007-38420-17772 from the National Institute of Food and Agriculture.

• Microfluidics, Inc.

• Kevin Daniel for assistance in film testing

• Linda McMurray, Ricardo Santos, and Ewellyn Capanema for assistance in pulp chemical composition analysis.
Film Physical Properties

- Processing resulted in similar densities for both (bleached and unbleached) samples

- All films resulted in similar final densities, regardless of processing method
Tensile Index

Tensile Index (TI) = \frac{\text{Tensile Strength (N/m)}}{\text{Basis Weight (g/m}^2\text{)}}

Tensile Strength (TS) = \frac{\text{Max Load (N)}}{\text{Sample Width (m)}}

- Microfluidization (10kpsi) resulted in significantly higher T.I.
- Grinder sample without pretreatment was similar to pretreated sample
Water Retention Value (WRV)

- TAPPI Useful Method 256 (modified)
  - 900 G (2400 rpm)
  - 30 minutes
  - 700 g/m² pulp pad
  - Oven dried overnight at 105°C
Water Vapor Transmission Rate (WVTR)

• Measured with Dynamic Wetting Apparatus in TAPPI standard conditions (23°C and 50% RH)
• 3.9 cm diameter circle
• 50 ml of water
Water Retention Value (WRV)
Film Physical Properties

- Microfluidizer resulted in smallest surface roughness, suggesting smaller particle size
- Unbleached samples had a larger reduction of surface roughness
Film Mechanical Properties

- Tensile index (N/m/g) vs. Density (kg/m³)
- R² values for each category (SW, HW, TMP)

- Density (kg/m³) vs. Diameter (μm)
- R² values for each category (SW, HW, TMP)
Energy Consumption: Microfluidizer

Unbleached Hardwood

Increasing passes
5P 10 kpsi
5P 20 kpsi
5P 30 kpsi
20P 10 kpsi

Increasing pressure

Energy Consumption (kJ/kg)

Tensile Index ((N·m)/g)

Toughness (kJ/m³)

NC STATE UNIVERSITY

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Energy Consumption: Homogenizer

Unbleached Hardwood

Tensile Index (N*m/g)

Energy Consumption (kJ/kg)

Toughness (kJ/m^3)

1P 4P 8P 16P 20P

Tensile Index
Toughness

NC STATE UNIVERSITY
Energy Consumption: Grinder

![Graph showing energy consumption versus tensile index for different pretreatment levels. The graph compares 'No Pretreatment' (red squares) and 'Pretreatment' (blue diamonds) with pretreatment levels 1P, 3P, 6P, and 9P.](image-url)
Potential Uses of Microfibrillated Cellulose

- Emulsifiers\(^1\)
- Thickening agents\(^1\)
- Food additives\(^1\):
  - Soups
  - Gravies
  - Mayonnaise
- Cosmetics\(^1\)
- Paints and coatings\(^1\)

- Films/coatings for packaging\(^2\):
  - Dry food products
  - Frozen foods and beverages
  - Fresh foods
- Composite reinforcements\(^3\):
  - Shipping crates and pallets
  - Toys
  - Storage bins
  - Outdoor furniture

\(^1\)Turbak, Snyder et al. 1983
\(^2\)Kirwan and Strawbridge 2003
\(^3\)Kokta, Chen, et al. 1983
Objectives

• Produce microfibrillated cellulose from fibers with different chemical compositions

• Determine the effects of fiber type, lignin content, and harsh drying on MFC film properties
Film Properties

- Thickness – L&W Micrometer 51
- Roughness – L&W Parker Print Surf
  - Clamp pressure 0.5 psi
- Density – calculated from basis weight and thickness
- Optical – Technidyne Spectrophotometer
- Tensile strength
  - Instron
  - Sample width: 15mm
  - Gap width: 25.4 mm
  - Crosshead speed: 4 mm/min
Production of Microfibrillated Cellulose

• Homogenization
  – Operates by rapid pressure drop and shearing
  – Manton-Gaulin 15MR
  – 3940 kJ/kg (per pass)
  – Advantages:
    • Scale-ability
    • Continuous operation
  – Disadvantages:
    • Energy intensive
    • Clogging
Equipment Comparison

• Homogenizer:
  – Friction losses: elbows, valves
  – Issues: plugging at ball valve, large $\Delta P$
  – Pretreatment reduced required passes to 8 from 20

• Microfluidizer:
  – Friction losses: elbows, chamber walls
  – Issues: plugging in chamber, large $\Delta P$
  – Increasing $P$ resulted in T.I. decrease
  – Increasing no. passes from 5 to 20 did not significantly improve props

• Micro-grinder:
  – Friction losses: disk-disk interactions
  – Pretreatment not required
Processability of Fibers

• Unbleached pulps:
  – 0.7% K
  – Plugged constantly – some passed without having to stop and clean out machine

• Bleached pulps:
  – Initial plugging (1st several passes)

• Hornified bleached pulps:
  – No plugging

• TMP:
  – Initial plugging (1st several passes)
Introduction to Microfibrillated Cellulose

Introduction to Microfibrillated Cellulose

• Gel-like properties at 2%K
• Have diameters ranging from 25-100 nm
• Advantages of these materials:
  – Renewability
  – Abundant fiber precursor
  – High surface area
  – Mechanical properties
    • More hydrogen bonding
    • More distributed defects
    • Crack stopping mechanism
• Typically purified cellulose
Film Mechanical Properties

Tensile Index (N*m)/g

Lignin Content (%)

original pulps (□), pretreated materials (Δ), and homogenized samples (◊).

R² = 0.8089

R² = 0.4932

R² = 0.1982