BIO-BASED Nano/Micro COMPOSITE MATERIALS: CHALLENGES and OPPORTUNITIES

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BioPolymers come from...

Sugar → Fermentation → Lactic Acid → Monomer Production → Lactide → Polymer Production → PLA

Future:

Ref.: B. S. Glasbrenner (Natureworks) Antec 2005
Bio-Based Polymers

- Commercial Products

- Poly(lactic acid) ‘Natureworks’ (Cargill) & Mitsui Chemicals
- Starch plastics Novamont, National Starch
- Cellulosic Plastic Eastman Chemical
- Bacterial polyester ‘Telles’ Metabolix-ADM

- Aliphatic / aliphatic-aromatic copolyester
  - Easter Bio Eastman
  - Biomax DuPont
  - Ecoflex BASF
  - BAK Bayer
  - Bionolle Showa High Polymer

- Petroleum blend with Renewable Resources
  - Sorona (DuPont)
  - Bio-based polyurethanes
  - Bio-based Epoxy/Polyester

Bio-Based Structural Polymer Composites are the Materials for the 21st Century!

• Advantages of Bio-Based Polymers:
  - Biodegradable, made from renewable, sustainable Resources
  - Very Good processability, Good mechanical properties
  - Eco-friendly

• Shortcomings:
  - Biodegradable, Brittle, Water Sensitive, Low HDT
  - Thermally Degradable, inherent variability in composition, properties, quality
  - primarily for textiles, packaging and disposables

• Bio-based Structural polymer composite materials have both properties and performance:
  - Bio-Composite Materials
    • Addition of reinforcing fibers or nanoparticles to improve mechanical, thermal properties and durability
  - Control of reinforcement orientation and concentration ‘optimizes’ properties
  - Adding biobased reinforcing fibers reduces cost
REINFORCEMENTS

![Diagram showing specific tensile strength and modulus for various materials including Graphite, SiC, Asbestos, Kevlar, Cellulose crystallite, Ramie, E glass, Spruce, Al, Steel, Cast iron, Linerboard, Filled PET, Nylon, PET, LDPE, HDPE, PP, and PET.](image-url)
Motivation for BioFibers

**Cost comparison**

<table>
<thead>
<tr>
<th></th>
<th>Glass</th>
<th>Biofiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S. Cents/lb.</td>
<td>70</td>
<td>25</td>
</tr>
</tbody>
</table>

**Weight savings**

<table>
<thead>
<tr>
<th></th>
<th>Glass</th>
<th>Biofiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>2.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Energy savings**

<table>
<thead>
<tr>
<th></th>
<th>Glass</th>
<th>Kenaf</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (BTU's)/1 lb fiber</td>
<td>23,500</td>
<td>6,500</td>
</tr>
</tbody>
</table>

- Mechanical PERFORMANCE
- Biodegradable and Recyclable
- CO₂ Neutral & Sequesterization

Biodegradable Materials

Photosynthesis

Sunlight + H₂O → CO₂ + Energy

Biodegradation

Use & discard → Processing → Innovation: Polymer production → Natural resources

Biodegradable Materials
BIOFIBER REINFORCEMENTS from PLANTS

Straw BioFibers
- Corn, Wheat, Rice Straw

Non-wood BioFibers
- Kenaf, Flax, Jute, Hemp, Grasses

Cellulose Nano-whiskers
- Sisal, Henequen, Pineapple Leaf Fiber

Wood BioFibers
- Wood & Non-wood Fibers Through AFEX

LEAF
- Cotton, Coir

SEED/FRUIT
- Coniferous Deciduous
Hierarchical Structure-Bast Fiber

Bio-FIBERS

BioComposite Manufacturing Process Requirements

- Preserve BioFiber Mechanical Properties
- minmize attrition
- minimize mixing degradation
- Processing temperature < 200°C

- High Degree of BioFiber Dispersion and Wettability
- Maximize BioFiber Volume Fraction
- Control BioFiber Orientation
- High Speed
- Low Cost
- Environmentally Benign
- No organic solvent
- Water process or Dry process
- Low energy consumption
Kenaf Plant Fiber/Soy Plastic Biocomposites

A = 30% kenaf 6mm fiber/soy composites injection molding
B = 33% Kenaf 6mm fiber/soy compression molding
C = 55% Kenaf 2mm fiber/soy compression molding
D = 56% Kenaf 6mm fiber/soy compression molding
E = 57% Kenaf 2 inch fiber/soy compression molding
F = 54% Kenaf long fiber/soy compression molding
Microfibrillated Cellulose (MFC)
Cellulose Nanowhiskers (CNW)

A schematic of wood cell wall ultrastructure *

The fringe-micelle model of cellulose microfibrils **

Disintegrated cellulose microfibrils - MFC

Extracted cellulose crystals - CNWs

Crystalline region

Paracrystalline region

Advantages of MFC and CNW

- Raw materials are abundant, cheap, and renewable
- Biodegradable
- High aspect ratio. Diameter from 3 to 20 nm; Length can be several hundreds of nanometers.
- Large relative surface area
- Less energy required in production compared with glass and carbon fibers
- High modulus, high strength and low density

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Tensile strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E glass fiber [1]</td>
<td>2.54 - 2.62</td>
<td>~3.4 at 21 °C</td>
<td>~72.4 at 21 °C</td>
</tr>
<tr>
<td>Jute fiber [2]</td>
<td>1.3 - 1.45</td>
<td>0.39 - 0.77</td>
<td>13 - 26</td>
</tr>
<tr>
<td>SiC whisker [3]</td>
<td>3.2</td>
<td>21.0 (max)</td>
<td>700 (max)</td>
</tr>
<tr>
<td>Cellulose nanowhisker [4]</td>
<td>1.5</td>
<td>~10</td>
<td>~150</td>
</tr>
</tbody>
</table>

Cellulose Micro+Nanowhiskers - Wheat Straw

- **Availability of wheat straw**
  - 1.3-1.4 lb of straw per lb of wheat grain*
  - 58.7 million tons of wheat were produced in the US in 2004**
  - 627.1 million tons produced worldwide
  - Partial removal of straw does not hurt soil fertility

- **Straw as a low-cost feedstock for cellulose**
  - Contains about 35-40 % cellulose
  - Is being used for cellulosic ethanol production

- **MFC and CNW extraction strategy in our lab**
  - Peracetic acid and alkali treatments
  - High pressure homogenization (MFC)
  - Acid hydrolysis, dialysis and ultrasonication (CNW)


Microfibrillated Cellulose (MFC) extracted from wheat straw

- The web-like structure of the MFC
- The width of the individual microfibrils is about 15 nm.
Cellulose Nanowhiskers (CNW) extracted from wheat straw

- The length and width of the extracted nanowhiskers are in the range of 100-200nm and 5-10nm respectively.
- Aspect ratio: 20+, Modulus ~130 GPa, Strength ~10 GPa
Polyvinyl Alcohol (PVOH) Composites

- Advantages:
  - PVOH is water soluble
  - PVOH is biodegradable
  - Easy to process

- Disadvantages
  - Hygroscopic. Material properties affected by moisture content.
  - Difficult to make bulk samples
Polyvinyl Alcohol (PVOH) Composites

A simple solution - film casting method was used:

- CNW suspension
- PVOH water solution

Mixing → Sonication → Film-casting

Advantages:
- PVOH is water soluble
- PVOH is biodegradable
- Easy to process

Disadvantages
- Hygroscopic. Material properties affected by moisture content.
- Difficult to make bulk samples

The thickness of the films was controlled to be approximately 100 micrometers.
The films were conditioned in 20% relative humidity.
All films reinforced with cellulose nanowhiskers were transparent.

The 5wt% and 10wt% MFC/PVOH films were a little opaque.
Well-Dispersed MFC in composites

1 wt% MFC/PVOH

3 wt% MFC/PVOH

5 wt% MFC/PVOH

10 wt% MFC/PVOH
Excellent Dispersion of CNW in Composites

1 wt% CNW/PVOH

3 wt% CNW/PVOH

5 wt% CNW/PVOH

10 wt% CNW/PVOH
CNW/PVOH and MFC/PVOH 
Plasma etched surfaces

With the polymer etched away by Oxygen Plasma, the fillers are exposed ...

- Notice the network structure formed by the MFC in the polymer matrix.
- The white dots - CNWs.
Wheat Straw MFC/PVOH Composites - Dynamic Mechanical Analysis

- The reinforcement effect became more significant above the Tg of the polymer.

Wheat Straw CNW/PVOH Composites - Dynamic Mechanical Analysis

- The improvement of the storage modulus was much greater for the MFC filled PVOH than for the CNW filled PVOH films.
Comparison of the storage moduli at 20 °C + 85 °C

Wheat Straw MFC / PVOH

Wheat Straw CNW / PVOH

Neat PVOH
1wt% WS-MFC/PVOH
3wt% WS-MFC/PVOH
5wt% WS-MFC/PVOH
10wt% WS-MFC/PVOH

Neat PVOH
1wt% WS-CNW/PVOH
3wt% WS-CNW/PVOH
5wt% WS-CNW/PVOH
10wt% WS-CNW/PVOH

Storage modulus at 20 °C

Storage modulus at 85 °C

240% increase
96% increase
BioBased Materials are a Value Added Product of a BIOREFINERY

<table>
<thead>
<tr>
<th>Origin</th>
<th>Processing</th>
<th>Refining</th>
<th>Intermediates</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstocks</td>
<td>Carbohydrate</td>
<td>Modified starches</td>
<td>Citric acid, Itaconate, Lactic acid, Ethanol, Isosorbide</td>
<td>Lubricants, Coatings, Polyols, Plasticizers, Thermoplastics, Urethanes, Polyesters, Plastic intermediates, BioComposites</td>
</tr>
<tr>
<td>Corn, Soy, Wheat, Canola, Sugar, Flax, Sunflower, Grasses, Biomass</td>
<td>Fermentation feedstocks</td>
<td>Glucose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oils</td>
<td>Fatty acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glycerol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BioFibers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MFC &amp; CNW</td>
<td></td>
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</table>
Wheat Straw Ethanol Production Residue

- Cellulosic Ethanol from Wheat Straw
  - Fuel from a waste instead of from food
  - Ammonia Fiber Expansion (AFEX) pretreatment at MBI and MSU
  - At 50-60% glucan conversion, what can we do with the rest of the cellulose in the residue?

- Possible applications of the fermentation residue
  - Burnt to produce thermal energy
  - Pyrolysed to produce organic acids and other chemicals
  - Processed into fertilizer or animal feed, etc.
  - A possible cheap feedstock for MFC and CNWs?

- Ongoing effort of extracting MFC and CNW from the residue in our lab
  - Characterization of the residue (morphological and chemical)
  - MFC and CNW extraction from the residue
  - Composite preparation and characterization
After being used for ethanol production, the cellular structure of the wheat straw is still largely preserved. But the surface of the cell wall has become rougher and more heterogeneous.
MFC extracted from the residue
Surface Chemistry Changes

- The peak at 1731 cm\(^{-1}\), which is characteristic of hemicellulose, disappeared.

- More prominent peaks at 1420 cm\(^{-1}\), 1458 cm\(^{-1}\), 1505 cm\(^{-1}\) and 1593 cm\(^{-1}\), which are all characteristic peaks of lignin.

- The theoretical values of O/C ratios for cellulose, hemicellulose, lignin and extractives are 0.83, 0.80, 0.33 and 0.04-0.12 respectively.*

- The untreated wheat straw is covered by extractives on the surface, while the AFEX+SSF residue has high concentration of lignin on the surface.

<table>
<thead>
<tr>
<th></th>
<th>O/C</th>
<th>C1 %</th>
<th>C2 %</th>
<th>C3 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wheat straw</td>
<td>0.17</td>
<td>81.8</td>
<td>13.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Residue</td>
<td>0.30</td>
<td>62.7</td>
<td>32.6</td>
<td>4.7</td>
</tr>
</tbody>
</table>

*These values are approximate and subject to experimental variation.
Opportunities...

- Plant Derived Fiber and Crop Derived Plastics
  - Biopolymer growth is expected to exceed ~+25% per year over the next 3 years
  - Global demand for biopolymers is forecast ~338,000 tons by 2012 with U.S. market ~$845 million
  - Structural composites (consumer) ~2-3 million tons by 2008
  - Market demand for bio-based composites is being driven by:
    - Replace/Substitute Petroleum Based Composites
    - Compete on a modulus, strength and impact basis
    - Require less energy to produce and process
    - Renewability, Biodegradable, Recyclability
    - More competitive price structure
    - Government / legislative traction
    - Consumer education & adoption
    - Expanded Market - Agricultural Industry
Summary:
✓ Cellulose Fibers from Plant have potential to replace Glass Fibers as Reinforcements in Polymer Composites
✓ Microfibrillated Cellulose (MFC) and Cellulose Nanowhiskers (CNW) from Wheat Straw have excellent mechanical properties
  ✓ Stiffness, Strength Impact, Transparency

Challenges:
✓ Properties of MFC and CNW after AFEX Pretreatment
✓ Cost Effective Process for MCF and CNW Fibers
✓ Modification of Manufacturing Technology