High-Value Bioproducts

Dean C. Webster
Coatings and Polymeric Materials
North Dakota State University
Fargo, North Dakota, USA
Materials and the F-E-W Nexus

• **Food**
  - Packaging
  - Agricultural equipment
  - Timed-release fertilizers
  - Food additives

• **Energy**
  - Wire and cable insulation
  - Fracking fluids
  - Battery technology
  - Wind turbines
  - Photovoltaics

• **Water**
  - Anticorrosion coatings for pipelines, tanks
  - Membrane filtration systems
What are high value bioproducts?

- **High Value**
  - Utilization beyond use as a fuel
  - Use waste
- **Bioproducts**
  - Materials made from agricultural products
- **To be successful**
  - Meet or exceed properties of petrochemical materials
  - Cost effective
Center for Sustainable Materials Science

Objective: Provide a transformative approach to the development of sustainable materials derived from agricultural raw materials

Scientific Elements:
1. New Monomer Synthesis
2. Sustainable Methods
3. Polymers and Composites
4. Design 4 Degradation

Opportunities: (1) collaborative projects; (2) Research experiences for undergraduates; (3) Graduate assistantship program; (4) Seed grants for PUIs / TC investigators as a collaborative effort

Center Core-Researchers:
1. Prof. Dean Webster
2. Prof. Mukund Sibi
3. Prof. Sivaguru Jayaraman
4. Prof. Chad Ulven
5. Prof. Bret Chishlom
6. Prof. Qualani Chu
7. Prof. Guodong Du
8. Prof. Alex Parent

www.csms-ndsu.org
DakotaBioCon

Dakota Bioprocessing Consortium

Vision: Become the intellectual leader for lignin bioprocessing.

North Dakota State University
University of North Dakota

South Dakota State University
South Dakota School of Mines

Lignin

Bioprocessing

Separations

Chemicals

Polymers

NDSU | Coatings and Polymeric Materials
Thermoplastics
Thermoset Polymer Applications
Agricultural Sources of Chemicals

- Cellulose
- Hemi-cellulose
- Starch
- Lignin
- Rosin
- Tall Oil FA
- Terpenes

Drying Oils
Semi-Drying Oils
Glycerol
Fatty Acids
Chemicals from Biomass

Drop-In Replacements

- Direct substitution
  - Known Markets
  - Known Performance

Biomass

New Chemicals

- New Properties
  - Unknown Performance
  - Unknown Markets
Some Important Issues

- Supply chain
- Funding
- Non-food crops
- Non-food parts of crops
ESE Resins: A Platform Technology

- Polyols
- Crosslinking
- (Meth)acrylates
- Thermal Crosslinking - Blocked Acids
- Thermal Crosslinking - Anhydrides
- Photo-polymerization

NDSU | Coatings and Polymeric Materials
Anhydride Curing

Catalyst, heat

- Strong base, metal catalysts
- Thermally activated
- Forms a polyester
- Some polyetherification

Initial studies:
Curing: 80°C, 12 Hrs
Catalyst: DBU
### Tensile Properties

<table>
<thead>
<tr>
<th>Epoxy compound</th>
<th>Modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile toughness (J) X 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESL</td>
<td>1395 ± 191</td>
<td>45.8 ± 5.4</td>
<td>5.7 ± 2.6</td>
<td>8.44 ± 3.5</td>
</tr>
<tr>
<td>ESSF</td>
<td>909 ± 179</td>
<td>31.5 ± 3.2</td>
<td>8.5 ± 2.7</td>
<td>11.5 ± 6.3</td>
</tr>
<tr>
<td>ESS</td>
<td>497 ± 38</td>
<td>20.3 ± 4.3</td>
<td>21.7 ± 7.8</td>
<td>29.4 ± 9.2</td>
</tr>
<tr>
<td>ESSB6</td>
<td>1002 ± 52</td>
<td>35.1 ± 3.6</td>
<td>5.4 ± 0.7</td>
<td>9.1 ± 3.8</td>
</tr>
<tr>
<td>ESO (Control)</td>
<td>65 ± 10</td>
<td>10.2 ± 2.5</td>
<td>167 ± 19</td>
<td>97 ± 13.8</td>
</tr>
</tbody>
</table>

Remarkable tensile modulus for a VO based system

Composites with Natural Fibers

Biobased resin gives equivalent or better performance than petrochemical resin

Reinforcement: Loose flax fibers

<table>
<thead>
<tr>
<th>Category</th>
<th>Untreated Fiber</th>
<th>NaOH Treated Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Araldite</td>
<td>ESS F1</td>
</tr>
<tr>
<td>Tens. Str. MPa</td>
<td>158.09 ± 21.69</td>
<td>154.16 ± 6.77</td>
</tr>
<tr>
<td>Flex. Str. MPa</td>
<td>195.65 ± 24.64</td>
<td>252.42 ± 24.20</td>
</tr>
<tr>
<td>Sht. Beam Str. MPa</td>
<td>12.65 ± 1.56</td>
<td>22.32 ± 3.16</td>
</tr>
</tbody>
</table>

Data courtesy of C. Taylor, T. Krosbakken, Chad Ulven, NDSU Mechanical Engineering
Methacrylated ESS for Composites

Cure Catalysts: Luperox P, Luperox 10M75
Cure Schedule:
150 °C for 1 hour, 175 °C for 1 hour, and 200 °C for five hours
Glass Fiber Composites

MESS Resin System Comparable or Better Than Vinyl Ester (VE)

Data from: Nassibeh Hosseini, Chad Ulven, NDSU Mechanical Engineering
Plastic Waste

This is not the solution
Concept: Product Dissassembly

Polymers can play an important role in this concept.
Bio-based, zero VOC, degradable thermoset

- Excellent physical and mechanical properties
  - Hardness, flexibility, adhesion, etc.
- Degradable using base (NaOH)

Epoxidized sucrose soyate (ESS)

Chemical structures:
- Citric acid \( pK_a = 3.13, pK_{a2} = 4.76, pK_{a3} = 6.39 \)
- Tartaric acid \( pK_a = 2.98, pK_{a2} = 4.34 \)
- Malic acid \( pK_a = 3.40, pK_{a2} = 5.11 \)
- Oxalic acid \( pK_a = 1.25, pK_{a2} = 4.14 \)
- Malonic acid \( pK_a = 2.83, pK_{a2} = 5.69 \)
- Glutaric acid \( pK_a = 4.34, pK_{a2} = 5.22 \)
Proof of Concept

Summary

- Renewables can be used to create new types of polymers
- High functionality resins can be derived from sucrose esters of vegetable oils
- High functionality leads to high crosslink density in thermosets
  - High modulus
  - High hardness
  - Good solvent resistance
- Properties are comparable to petrochemical counterparts
- It is possible to design polymers for their eventual degradation
Coatings can prevent the settlement of mussels in waterways.
Thank You!