Marketplace Opportunities
Integration of Biobased & Conventional Plastics Forum

Project Partners: MN Corn Growers Assoc., MN Soybean Growers Assoc., Jim Lunt & Associates LLC

Agricultural Utilization Research Institute
About AURI

The Agricultural Utilization Research Institute (AURI) helps develop new uses for agricultural products through science and technology, partnering with businesses and entrepreneurs to bring ideas to reality. We work in four core industry areas:

- Food
- Renewable energy
- Biobased products
- Coproduct utilization

Agricultural Utilization Research Institute
From Idea to Reality

At AURI, we believe that implementing innovation takes:

- good ideas, generated through applied research with our partners,
- hands-on scientific technical assistance, and
- a strong resource network.

In the end, this all works together to generate economic impact.
Why We’re Here Today

So, today we have some idea-generating research that we want to share with you.
Why We’re Here Today

Purpose-Outcomes

- Present an accurate portrayal of the plastics industry and opportunities for additional development of biobased materials/plastics.
- The potential market for biobased materials offers opportunity for agricultural commodities and coproducts and to create economic impact for MN.

Agricultural Utilization Research Institute
Introductions

• Over 40+ years in the plastic’s industry.
• One of the founding members of NatureWorks LLC.
• A recipient of the Green Chemistry Award in 2002.
• Managing Director of Jim Lunt & Associates LLC., specializing in the emerging bioplastics industry.
Marketplace Opportunities for the Integration of Biobased and Conventional Plastics

Sponsors:
- Agricultural Utilization Research Institute (AURI).
- Minnesota Corn Research & Promotion Council.
- Minnesota Soybean Research & Promotion Council.
Presentation Outline

- The Oil Based Plastics Industry.
- Evolution and Drivers for Bioplastics.
- Bioplastics Definitions and Classification.
- First and Second Generation Bioplastics.
- Bioplastics Growth Projections and Market Trends.
- Developments in Feedstocks.
- Conclusions.
Conventional Oil Based Plastics

Thermoplastics
(270 million tonnes in 2014)

- PP 25%
- LLDPE 11%
- LDPE 9%
- HDPE 17%
- PET 7%
- PVC 18%
- ABS 4%
- PS 5%
- Other 5%

Thermosets
(90 million tonnes in 2016)

- PF 21%
- UF 26%
- PU 34%
- UP 9%
- Epoxy 5%
- PC 1%
- Nylon 3%
- Other 5%
The Bioplastics Opportunity

Bioplastics Opportunity
Evolution of Bio plastics Drivers


2010. Durable biobased equivalents to oil based plastics.

Today's Drivers for Bioplastics

Renewable resource versus oil based.

Reduced environmental impact.

Concerns about human health.

End-of-Life disposal issues – Landfill.

Legislative initiatives.
Definitions for Bio Plastics

**Biodegradable or Compostable Bioplastics**
Meet all scientifically recognized standards for biodegradability and compostability of plastics and plastic products.

Independent of carbon origin-(i.e. Ecoflex, PBS, PLA ). Focus is on end-of-life or disposability.

**Biobased Products**
Must be organic and contain some percentage of recently fixed (new) carbon found in biological resources or crops.

Focus on renewable resource based origin. Uses C$^{14}$ content measurement.
**Classification of Bioplastics**

- **Biobased**
  - Are biobased
  - Bioplastics e.g. biobased PE, PET, PA, PTT

- **Biodegradable and biobased**
  - Bioplastics e.g. PLA, PHA, PBS, starch blends

- **Non Biodegradable**
  - Conventional plastics
    - Nearly all conventional plastics e.g. PE, PP, PET

- **Biodegradable**
  - Bioplastics e.g. PBAT, PCL

- **Fossil based**
  - Are biodegradable

- **Eu. Bioplastics**
First Generation Bioplastics

Starch/PLA/ECOFLEX

Compounded, Biobased & Compostable

Polylactic Acid (PLA)

100% Renewable & Compostable

L-Lactic Acid

D-Lactic Acid (0.5%)
First Generation PHA’s
Compostable, biodegradable and renewable

PHA picture courtesy of Telles
Target Plastics and Applications for First Generation Bioplastics

Polystyrene.
Single use food serviceware- Rigid trays, containers, cutlery, cups, packaging.

PVC.
Gift cards and cash cards.

PET.
Food trays, containers, film and fibers.

ABS.
3D printing (Emerging application PLA/starch blends)
### Polymer Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>PLA</th>
<th>PS</th>
<th>PET</th>
<th>PVC*</th>
<th>PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tens. St.</td>
<td>MPa.</td>
<td>53.1</td>
<td>45.5</td>
<td>58.6</td>
<td>49</td>
<td>35.9</td>
</tr>
<tr>
<td>Elong. To Break</td>
<td>%</td>
<td>4.1</td>
<td>1.4</td>
<td>5.5</td>
<td>25-45</td>
<td>350</td>
</tr>
<tr>
<td>Tens. Mod</td>
<td>GPa.</td>
<td>3.45</td>
<td>3.03</td>
<td>3.45</td>
<td>2.83</td>
<td>1.31</td>
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<tr>
<td>Izod Impact</td>
<td>J/M</td>
<td>16</td>
<td>21.4</td>
<td>26.7</td>
<td>80</td>
<td>48.1</td>
</tr>
<tr>
<td>Glass Transition</td>
<td>ºC</td>
<td>58</td>
<td>98</td>
<td>74</td>
<td>74</td>
<td>-20</td>
</tr>
<tr>
<td>Melting Point</td>
<td>ºC</td>
<td>130-170</td>
<td>none</td>
<td>270</td>
<td>none</td>
<td>165</td>
</tr>
<tr>
<td>S.G.</td>
<td></td>
<td>1.25</td>
<td>1.05</td>
<td>1.34</td>
<td>1.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* General purpose PVC.
## Areas of Concern

<table>
<thead>
<tr>
<th><strong>Starch Blends</strong></th>
<th><strong>PLA</strong></th>
<th><strong>PHA’S</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolytic stability</td>
<td>Hydrolytic Stability</td>
<td>Hydrolytic Stability</td>
</tr>
<tr>
<td>Distortion Temp</td>
<td>Distortion Temp (amorphous)</td>
<td>✓</td>
</tr>
<tr>
<td>Vapor Transmission</td>
<td>Vapor Transmission</td>
<td>✓</td>
</tr>
<tr>
<td>Shelf Life</td>
<td>Shelf Life</td>
<td>Shelf Life</td>
</tr>
<tr>
<td></td>
<td>Impact Resistance</td>
<td>Processability</td>
</tr>
<tr>
<td></td>
<td>Melt Strength</td>
<td>Melt Strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Economics</td>
</tr>
</tbody>
</table>
PLA Property Modification Technologies

- Improved stiffness - fillers, fibers, nucleating agents.
- Improved impact or flexibility - impact modifiers, plasticizers, copolymers.
- Flammability - non halogenated flame retardants, blends.
- Temperature resistance - blends, nucleating agents, stereocomplex, copolymers.
- Extensional viscosity - peroxides, epoxy branching agents.
- Barrier properties - plasma, silicone dioxide, aluminum coatings.
- Lower color - blue tone.
- Reduced hydrolysis - carbodimide.
Second Generation Bioplastics.
## Commercial Biobased Non Compostable Plastics

<table>
<thead>
<tr>
<th>MAJOR SUPPLIER</th>
<th>BIOBASED PRODUCT.</th>
<th>% RENEWABLE CARBON.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Braskem</td>
<td>HDPE, LDPE.</td>
<td>89-100</td>
</tr>
<tr>
<td>FENC/ Teijin/ Indorama</td>
<td>Bio PET</td>
<td>20</td>
</tr>
<tr>
<td>DuPont</td>
<td>PTT, nylon 6.12</td>
<td>28</td>
</tr>
<tr>
<td>Arkema</td>
<td>Nylon 11, Pebax Rnew ®.</td>
<td>50-100</td>
</tr>
<tr>
<td>Dow, Cargill</td>
<td>Soy-based urethanes</td>
<td>22-70</td>
</tr>
<tr>
<td>Ashland, Reichhold</td>
<td>Bio unsat.Polyesters</td>
<td>8-35</td>
</tr>
<tr>
<td>Ecopoxy, Entropy</td>
<td>Bio epoxies.</td>
<td>17-25</td>
</tr>
</tbody>
</table>
Biobased carbon in PET

\[
\text{ROOC} - \begin{array}{c}\text{COOR} \\ \text{Diacid}\end{array} + \begin{array}{c}\text{OH} - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ \text{Diol}\end{array} \\
\downarrow \\
\begin{array}{c}\text{C} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} \\ \text{PET} \end{array} \\
\text{C} - \text{O} \\
\text{n}
\]

Acid component = 8C; glycol component = 2C; Acid component = 68.75%; glycol component = 31.25% on mass basis
Bio (carbon) content is 20% if two petro carbons substituted by bio carbons – by using the glycol (diol) component from bio(plant sources)

Contains 31% renewable resource (20%\text{C}) based on bio ethylene glycol.
## New Biobased Plastics

<table>
<thead>
<tr>
<th>Company</th>
<th>Product</th>
<th>Bio component(s)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segetis</td>
<td>Polyketals</td>
<td>Levulinic acid</td>
<td>Early stage Commercialization</td>
</tr>
<tr>
<td>Avantium</td>
<td>Polyethylene furanoate</td>
<td>Furan dicarboxylic acid</td>
<td>Development</td>
</tr>
<tr>
<td>Novomer</td>
<td>Polypropylene carbonate</td>
<td>Carbon dioxide</td>
<td>Commercial</td>
</tr>
<tr>
<td>Newlight technologies</td>
<td>PHA</td>
<td>Carbon dioxide. Methane</td>
<td>Development</td>
</tr>
<tr>
<td>DSM, Arkema, BASF, DuPont, Evonik</td>
<td>Polyamides</td>
<td>Castor oil/ amino undecanoic acid</td>
<td>Commercial.</td>
</tr>
</tbody>
</table>
## Key Bio Monomers for Thermoplastics

### Ethylene/ethylene glycol
Braskem, India Glycols.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Companies</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA</td>
<td>Gevo, Anellotech, Amyris, Genomatica, UOP, Global Bioenergies, Sabic, Virent, Chemtex.</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>PTT, DSM, BASF, Bioamber, Roquette, Mitsubishi Chem., Myriant, Purac.</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>Rennovia, Verdezyne, Genomatica.</td>
</tr>
<tr>
<td>Butane diol</td>
<td>Genomatica, Myriant, BioAmber.</td>
</tr>
<tr>
<td>FDCA</td>
<td>Avantium.</td>
</tr>
<tr>
<td>Ketals</td>
<td>Segetis, XLTerra/Reluceo.</td>
</tr>
<tr>
<td>Caprolactam</td>
<td>Amyris.</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>Ceres, Dow/OPX.</td>
</tr>
<tr>
<td>Isosorbide</td>
<td>ADM, Roquette.</td>
</tr>
<tr>
<td>Propylene</td>
<td>Braskem.</td>
</tr>
<tr>
<td>Propane 1,3 diol</td>
<td>DuPont / Tate &amp; Lyle.</td>
</tr>
</tbody>
</table>
# Key Bio Monomers for Thermosets

<table>
<thead>
<tr>
<th>Category</th>
<th>Monomers</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethanes.</td>
<td>Soy based polyols</td>
<td>Cargill, Dow</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unsat. Polyesters.</td>
<td>Glycerol</td>
<td>Ashland, Cargill, ADM, Dow Chemicals, BASF</td>
</tr>
<tr>
<td></td>
<td>Propylene glycol</td>
<td></td>
</tr>
<tr>
<td>Epoxies.</td>
<td>Epichlorohydrin</td>
<td>Solvay</td>
</tr>
</tbody>
</table>
Bioplastics are still less than 1% of the approximate 270 million tonnes of plastics in use today.

Projected 19% AGR
<table>
<thead>
<tr>
<th>Study</th>
<th>Report Date</th>
<th>Projected Global Capacity End of Period (tonnes)</th>
<th>Projected Global Demand End of Period (tonnes)</th>
<th>Time Period Covered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nova Institute</td>
<td>2013</td>
<td>12 million</td>
<td>12 million</td>
<td>2020</td>
</tr>
<tr>
<td>Eu. Bioplastics</td>
<td>2013</td>
<td>6.2 million</td>
<td>Not given</td>
<td>2017</td>
</tr>
<tr>
<td>Freedonia</td>
<td>2011</td>
<td></td>
<td>1.0 million</td>
<td>2015</td>
</tr>
<tr>
<td>World bioplastics</td>
<td>2009</td>
<td></td>
<td>0.9 million</td>
<td>2013</td>
</tr>
<tr>
<td>Freedonia</td>
<td>2008</td>
<td></td>
<td>0.816 million</td>
<td>2013</td>
</tr>
<tr>
<td>PRNewswire</td>
<td>2010</td>
<td></td>
<td>0.138 million*</td>
<td>2014</td>
</tr>
<tr>
<td>Eu Bioplastics</td>
<td>2007</td>
<td>1.36 million</td>
<td></td>
<td>2011</td>
</tr>
<tr>
<td>PROBIP</td>
<td>2009</td>
<td>2.94 million</td>
<td></td>
<td>2020</td>
</tr>
<tr>
<td>SRI</td>
<td>2010</td>
<td></td>
<td>0.281 million*</td>
<td>2014</td>
</tr>
<tr>
<td>SPE</td>
<td>2010</td>
<td></td>
<td>0.75 million</td>
<td>2014</td>
</tr>
<tr>
<td>BCC Research</td>
<td>2010</td>
<td></td>
<td>3.231 million</td>
<td>2015</td>
</tr>
<tr>
<td>PIRA</td>
<td></td>
<td></td>
<td>0.884 million**</td>
<td>2015-2020</td>
</tr>
</tbody>
</table>

*Biodegradable plastics only  **Biodegradable packaging only
## 2013 Sales Estimate for Bioplastics

<table>
<thead>
<tr>
<th>Product</th>
<th>2013 Bioplastics Manufacturing Capacity (million tonnes)</th>
<th>2013 Sales Estimates. (million tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Green” Polyethylene</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>Bio PET</td>
<td>0.66*</td>
<td>0.66*</td>
</tr>
<tr>
<td>PLA</td>
<td>0.26</td>
<td>0.2</td>
</tr>
<tr>
<td>Starch Blends</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>PHA’s</td>
<td>0.02</td>
<td>0.005</td>
</tr>
<tr>
<td>Others</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Totals</td>
<td>1.31</td>
<td>1.095</td>
</tr>
</tbody>
</table>

* Contains only 30% renewable resource (20%C) based on bio ethylene glycol.

Jim Lunt & Associates LLC. Estimates
Increasing demand for biobased, durable products in electronics and automotive applications.

By 2015 durables are expected to account for almost 70% of bioplastics capacity – compared with 7% in 2009.
Why The Change?

- “Compostables” performance v durables.
- Continuing lack of infrastructure for use and disposal of compostable plastics.
- Increasing demand for biobased, semi-durable and durable products for household goods, electronics and automotive applications.
- Increasing interest and developments in existing and new monomers from renewable resources.
Key Bio Monomer Activities.
Bio Ethylene Glycol (MEG)

India Glycols, GTC, FENC, JBF

- Ethylene glycol
- Ethylene oxide
- Ethylene

Fermentation of sugar cane molasses leads to ethanol, which is then oxidized to ethylene glycol and ethylene oxide.
Bio Terephthalic Acid (TPA)

Gevo
- biobutanol

Global Bioenergies
- isobutylene
- isoctene

Amyris
- t,t muconic acid

Genomatica
- d limonene
- p cymene

Toray/UOP
- p-xylene

SABIC
- dimethyl furan

BP
- fdca
- TPA
Biobased p-Xylene (PX)

Virent Process.
Anellotech Process- Bio BTX

BTX=benzene, toluene, xylenes mixture.
Bio Succinic Acid and Derivatives

Biobased Succinic Acid

Butane diol
- Genomatica

Adipic acid
- Rennovia
- Verdezyne

Succinic acid/PBS
- BioAmber
- PTT
- MCC
- DSM/Roquette
- BASF/Purac

Butane
Maleic Anhydride
CO₂

C5 or C6 Sugars
Sugars / Biomass
CO₂

Petroleum

Succinic Acid

Replace Adipic Acid & Phthalic Anhydride
Urethanes
Engineering Plastics
Phthalates
Plasticizers

Butanediol Market

Total Market Size
90 M lb
1.4 BN lb
6.0 BN lb

Pharma
PBS
Pigments

Existing Succinic Acid Market

Courtesy Myrian
Bio Butane Diol

Same Chemical:
- pure product (99.7% BDO)
- no color
- no reformulation
- positive customer conversion testing
  - PBT, TPU, PTMEG, PVP
Bio FDCA (furan 2,5 dicarboxylic acid) - Avantium
Key Biobased Polymer Activities.
Braskem “Green Polyethylene” from Sugar Cane

- Sugar cane molasses
- Ethanol
- Ethylene
- HDPE polyethylene
Bio PET

Plant-based polyethylene terephthalate (PET) Synthesis/Production

- Green PET production

![Diagram showing the synthesis of Bio-PET](image-url)
Nylon 6,6

Rennovia Bio-Based Adipic Acid and HMD for Nylon-6,6

Glucose

Adipic Acid

HMD

100% Bio-Based Nylon-6,6
Sorona™-PTT

Bio-PDO™ Manufacturing

Combined in a Single Biocatalyst

*Bio-PDO™ process consumes 40% less energy than the chemical PDO process it replaces.*

1,3-propanediol (PDO) + DMT / TPA

- Unique polymer with versatile properties
- 37% renewably sourced ingredients by weight

Sorona® polymer
Today's Bioplastic Feedstocks

- Corn
- Cassava
- Sugarcane
- Sugarcane
- Sorghum in Europe
- Sugar beet
- Sorghum in Asia
- Sorghum in Latin America

All refined sugars - dextrose, glucose, sucrose.
Concerns with Existing Feedstocks from Food Crops

The Food versus Fuel debate:

- Food Crops Diversion to Fuels/Plastics
- Land Use
- Fertilizer Use
- Pesticide Use
- The “Ripple Effect “

Use of GMO's
More “Sustainable” Biomass Feedstocks

**Lignocellulose**
(wood, corn stover, other agricultural residues)

**Oil seeds**
(soy, rape/canola, palm, coconut, Jatropha)

**Microalgae**

**Macroalgae**
(kelp)

**Waste:**
- MSW, food processing (cellulosic)
- Used fats and oils
- Animal processing wastes (rendering, feathers, hair, manure)
Leading Biomass Source – Lignocellulosics

- Corn stover
- Sugar cane bagasse
- Wood chips
- Rice straw
- Wheat straw
- Tall grasses

Source: Virent –”The Future For Bioplastics Feedstocks”
## Extracting Sugars From Cellulosics

### Most Common Approaches

<table>
<thead>
<tr>
<th>Dilute acid and enzyme hydrolysis</th>
<th>Concentrated acid extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet oxidation and enzyme hydrolysis</td>
<td>Catalytic biomass deconstruction</td>
</tr>
</tbody>
</table>
Commercially Proven Technology

Virdia (Stora Enso) Process (c1938)

Loblolly Pine

Preparation
Sizing
Tall Oil Removal

HCL

Concentrated HCL
Deconstruction

HCL

Lignin Deacidification

HCL

Sugar Recovery
HCL Recycle

Final Purification

Soluble
C5/C6 Sugars

Tall Oil

Lignin

HCL
Extracting Sugars From Cellulosics

Pilot Scale

- Renmatix
- Chemtex/M&G- Beta Renewables
- American Science and Technology (AST)
Green House Gases as Feedstocks

Newlight Technologies PHA’s

Novomer PPC

Air + GHG → Propylene Oxide → CO₂ + Novomer catalyst → Polypropylene Carbonate (PPC)
propylene, butadiene and aromatics yields cut by as much as 55%.

Ethylene/polyethylene costs decreased.
Challenges/Opportunities for Bio Materials

- Oil pricing continuing to increase.
- Improved performance/ reduced cost for compostables.
- Composting/recycling infrastructure developments.
- Expanding from single-use compostable to durable applications.
- Moving to non-food source feedstocks.
- Competition from carbon dioxide based plastics.
- Natural gas dynamics on polyolefin/ aromatics pricing.
Thank You

Jim Lunt & Associates LLC
www.jimluntllc.com
Bioplastic Products In The Marketplace

Extra Slides
<table>
<thead>
<tr>
<th>PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rigids</strong></td>
</tr>
<tr>
<td><img src="image1.jpg" alt="Images" /></td>
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<tr>
<td><strong>Nonwovens / Fibers</strong></td>
</tr>
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<td><img src="image4.jpg" alt="Images" /></td>
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<tr>
<td><strong>Bus. Dev.</strong></td>
</tr>
</tbody>
</table>

PLA: innovative materials from plants, not oil.
Cellulose Acetate
Compounded PLA/Starch Blends
Bio PET
Sorona
Avantium PEF

T-shirts -100% recycled PEF bottles

Made from 100% Recycled PEF

Conventional polyester spinning technology

Conventional polyester dyeing technology