Bio-based Polymers and Composites for Container Production Materials

Samy Madbouly, James Schrader, Gowrishanker Srinivasan, Kyle Haubric, Kunwei Liu, David Grewell, William Graves, Michael Kessler

Iowa State University
August 15, 2012
Contents

• Bio-plastic, origin, advantages and disadvantages.
• Bio-based PLA blends and composites.
• Bio-based PHA and lignin-cellulose fiber composites.
• Bio-based PA and lignin-cellulose fiber composites.
• Bio-based dip coatings (PUD, PLA, and PA).
• Summary
Bio-plastics

Biodegradable plastics produced from nonrenewable recourses: Polycaprolactone (PCL), Poly (butylene succinate) (PBS), pol(ethylene succinate), etc.

Bio-based plastics produced from renewable resources: Polylactide (PLA), poly (hydroxybutyrate), soy protein, etc.
Why bio-based plastics?

1. Petrochemical-based polymers make up about 20% by volume waste per year.

2. The increase of oil prices.

3. Natural resources are inexpensive and readily available.

4. Reduction in CO₂ emissions.

5. Renewable biological origin and biodegradable at the end of its life.
Origin and Description

Biobased Polymers

Directly extracted from biomass
1. Polysaccharides: (starch, potato, rice, wheat, etc.)
2. Lignocellulose: (wood, straws, stover, etc.)
3. Proteins: animals (casein, collagen) or plant (soy)
4. Lipids: cross linked triglyceride

Starch, soy protein, lignin corn stover, and DDGS

Synthesized from bio-derived monomers
1. Polylactate
2. Other polyesters

PLA and PA

Produced by microorganisms
1. Polyhydroxyalkanoates
2. Bacterial cellulose

Mirel (PHA)
Some drawbacks of bio-based polymers

- Relatively high cost compared to petroleum-based polymer (PLA, PA, and PHA).
- Unsatisfactory mechanical properties coupled with strong moisture and temperature sensitivity (SP and starch).

Some possible routes to improve the properties of bio-based polymers

- Bio-based polymer blends.
- Bio-based polymer composites.
- Bio-based dip coatings.
Reasons for Blending

- Dilute high-cost of some polymers with low-cost one.
- Improve mechanical and physical properties.
- Control the biodegradation rate.
- Decrease processing temperature.
- Adjust the composition for suit application.
Bio-based polymer composites

- Fillers are often added to polymers to decrease cost and increase dimensional stability, strength, toughness, and environmental resistance.

- Natural resource fillers are abundant, inexpensive, renewable, and biodegradable.

  DDGS, corn stover, lignin-cellulose fiber, and nanoclay.
## Bio-based materials & prices

<table>
<thead>
<tr>
<th>Materials</th>
<th>Source</th>
<th>$/ lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>NatureWorks LLC</td>
<td>2.50</td>
</tr>
<tr>
<td>PHA</td>
<td>Metabolix®</td>
<td>2.80</td>
</tr>
<tr>
<td>PA (Uni-Rez 2930)</td>
<td>Arizona Chemical</td>
<td>2.55</td>
</tr>
<tr>
<td>PA (Uni-Rez 2651)</td>
<td>Arizona Chemical</td>
<td>3.90</td>
</tr>
<tr>
<td>SPI</td>
<td>Solae Company</td>
<td>2.36</td>
</tr>
<tr>
<td>SPF</td>
<td>Solae Company</td>
<td>0.28</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>Sigma Aldrich</td>
<td>1.10</td>
</tr>
<tr>
<td>Glycerin</td>
<td>Fisher Scientific</td>
<td>0.10</td>
</tr>
<tr>
<td>Lignin fiber</td>
<td>NPS</td>
<td>0.35</td>
</tr>
<tr>
<td>DDGS</td>
<td>Ethanol plants</td>
<td>0.08</td>
</tr>
<tr>
<td>Corn stover</td>
<td>SMEC</td>
<td>0.027</td>
</tr>
<tr>
<td>Nanoclay (Cloisite 30B)</td>
<td>South. Clay Products</td>
<td>3.99</td>
</tr>
<tr>
<td>Tung oil</td>
<td>Welch, Holme &amp; Clark</td>
<td>2.80</td>
</tr>
<tr>
<td>PUD</td>
<td>Alberdingk Boley, Inc</td>
<td>2.70</td>
</tr>
</tbody>
</table>
Project aim

- Develop and evaluate commercially feasible bioplastic cropping containers that will fulfill all of the functions of petroleum-based plastic containers without their drawbacks.

- Many biorenewable polymers such as, PLA, PHA, PA, SP, starch, etc. and their blends and composites with other natural materials will be used for the production process.

- Recently developed natural oil-based coatings will be also used to enhance mechanical properties and water resistance containers constructed from proteins, natural oils, carbohydrates, and other composites.
Poly(lactic acid) or polylactide (PLA) is a thermoplastic aliphatic polyester produced from renewable resources, such as corn starch through fermentation process.

PLA is the most widely used bio-based and biodegradable polyesters.

PLA has good mechanical properties but is still more expensive than the conventional plastics.

PLA can be easily degraded by enzymes, but its rate of degradation in soil is slow.
Bio-based PLA Blends and Composites

PLA

Blends
- SPA
- SP

Composites
- Clay
- DDGS
- Corn Stover

A means 5 wt.% adipic acid
Soy protein is a protein that is isolated from soybean.

- Natural polymers that can form amorphous three-dimensional.
- Three kinds of high protein commercial products: soy flour (SPF), concentrates (SPC), and isolates (SPI).
- SPI and SPF obtained from Solae Company, St. Louis, MO will be used in bio-container production.
### Flower pot formulation

<table>
<thead>
<tr>
<th>Parts</th>
<th>Fraction</th>
<th>%</th>
<th>$/lbs</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPI</td>
<td>50</td>
<td>0.26</td>
<td>26.1</td>
<td>$2.36</td>
</tr>
<tr>
<td>Soy flour/meal</td>
<td>50</td>
<td>0.26</td>
<td>26.1</td>
<td>$0.28</td>
</tr>
<tr>
<td>Glycerin</td>
<td>22.5</td>
<td>0.12</td>
<td>11.7</td>
<td>0.1</td>
</tr>
<tr>
<td>PA</td>
<td>7.5</td>
<td>0.04</td>
<td>3.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Water</td>
<td>60</td>
<td>0.31</td>
<td>31.3</td>
<td>0</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>1</td>
<td>0.01</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Potassium sorbate</td>
<td>0.5</td>
<td>0.00</td>
<td>0.3</td>
<td>0.31</td>
</tr>
<tr>
<td>Total</td>
<td>191.5</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Problems:

Poor mechanical properties and high water sensitivity.
Bio-based PLA/SP blends

PLA/SP (5% PA) = 50/50

- Pure PLA
- PLA-SP

---

$E'/\text{MPa}$ vs. $T/\text{°C}$

$\tan \delta$ vs. $T/\text{°C}$
Bio-based PLA/SP (5% adipic acid) blends

PLA/SP (5% PA+5%AA) = 50/50
DDGS (Dried Distillers Grains with Solubles)

- DDGS is a by-product of the ethanol production process.
- DDGS contains about 26.8–33.7% protein (dry weight basis), 39.2–61.9% carbohydrates (including fibers), 3.5–12.8% oils, and 2.0–9.8% ash.

$ 0.08/lb
Bio-based PLA/DDGS composites
Corn Stover

- Corn stover is the largest quantity of biomass residue in the United States.
- Around 120 million tons of biomass residue is available annually.
- Corn stover is composed of about 70 percent cellulose and hemicellulose, and 15 to 20 percent lignin.

$ 0.027/lb
Bio-based PLA/corn stover composites
PLA/Clay composites

Structure of layered silicate

One Clay Platelet
L: 100 – 200 nm in case of MMT
Polymer-Clay Nanocomposites

Clay composed of platelets

- Immiscible
- Intercalated
- Exfoliated

Challenge
Bio-based PLA/clay composites
Polyhydroxyalkanoates (PHAs)

- PHAs are linear polyesters produced in nature by bacterial fermentation of sugar or lipids.
- PHAs accumulate as granules within cell cytoplasm.
- PHAs are thermoplastic polyesters with m.p. 50–180 °C.
- They are certified to biodegrade in soil and water environments
- Mirel™ can be obtained from Metabolix®
Bio-based PHA

PHA = Mirel 1008 (10 wt.% starch)
PHA = Mirel P4010 (30 % starch)
Lignin-cellulose fiber

- NeroPlast® it is a mixture of long chain cellulose and lignin, the hemicellulose (hydrophilic part has been removed).
- It is a specially engineered, water resistant (non-swelling) fiber designed to improve stiffness for engineering resins, and biopolymers.
- NeroPlast® has been awarded USDA BioPreferred designation.

Molecules 2010, 15(12), 8641-8688

$0.35/lb
Bio-based PHA/lignin-cellulose fiber composites

PHA = Mirel 1008 (10 wt.% starch)
Bio-based PHA/lignin composites

PHA = Mirel 1008 (10 wt.% starch)
Tall oil can be obtained from pine trees and as a by-product of the pulp and paper industry.

PA is normally used as bio-based polymer binder in ink industry.

Arizona Chemical is the leading producer and bio-refiner of pine chemicals. PA derived from dimerized tall oil fatty acid.
Bio-based PA/lignin-cellulose composites

- Tan Delta
  - Temperature (°C)
  - 0% 1% 5% 10% 20% 30%

- Storage Modulus (MPa)
  - Temperature (°C)
  - 0% 1% 5% 10% 20% 30%

- Young's Modulus (MPa)
  - Lignin Content

- Weight (%)
  - Temperature (°C)
  - 0% 1% 5% 10% 20% 30% 100%
### Commercially available bio-based pots

<table>
<thead>
<tr>
<th>Pot Type</th>
<th>Wholesale per unit (¢)</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Round pot 4.5&quot; (Injection mold Petroleum Plastic)</td>
<td>12</td>
<td>655</td>
</tr>
<tr>
<td>Thermoformed Standard 4.5&quot; (Petroleum Plastic)</td>
<td>8</td>
<td>653</td>
</tr>
<tr>
<td>Coir Fiber pots 4.5&quot; round</td>
<td>23</td>
<td>610</td>
</tr>
<tr>
<td>Paper Fiber pots 4.5&quot; round</td>
<td>14</td>
<td>600</td>
</tr>
<tr>
<td>Jiffy Pots (Peat Pot) 5&quot;</td>
<td>18</td>
<td>760</td>
</tr>
<tr>
<td>Wood Fiber (FertilPots) 4&quot; x 4&quot; round</td>
<td>20</td>
<td>440</td>
</tr>
<tr>
<td>Standard Round pot 4.&quot; (Injection mold Petroleum Plastic)</td>
<td>10</td>
<td>480</td>
</tr>
<tr>
<td>Ball / Summit, TerraShell Wheat Pot (10 cm) (Thermoformed)</td>
<td>9</td>
<td>473</td>
</tr>
<tr>
<td>Ball / Summit TerraShell Wheat Pot (15 cm) (Thermoformed)</td>
<td>16</td>
<td>1240</td>
</tr>
<tr>
<td>Bioplastic Injection Molded (our project)</td>
<td></td>
<td>680</td>
</tr>
</tbody>
</table>

- **Coir Pots**
- **Paper Fiber Pot**
- **Wood Fiber Pots**
- **Wheat polymer Pot**
Coir Pots
- Environmentally-friendly (100% biodegradable).
- Renewable alternative to plastic pots.
- Moisture is maintained in the soil.
- Easy to be transplanted into ground

Paper Fiber Pot

Wood Fiber Pots

Poor mechanical properties and high water sensitivity.
Bio-based deep coatings

- **Castor oil**: + DIC, DMPA, TEA, Water → PUD
- **Tung oil**: + Chloroform, Cationic polymerization → Coating
- **PLA or PA**: + Chloroform → Coatings
Castor oil

- Castor plant has high content of castor oil
- Not a food plant
- Not competing with food crops
- Grown in semi arid areas (India, China, Brazil)

PUD (dip coating)
Bio-based aqueous PUD

Advantages

- Outstanding adhesion to numerous synthetic materials
- Wide range of flexibility combined with toughness
- High chemical resistance
- Resistance to discoloration
- Excellent weatherability
- Health and environmental safety
Diisocyanate (IPDI)

Dimethylol propionic acid

Cator oil polyol

Adding $\text{H}_2\text{O}$

Apply to substrate (wood, metal, glass, plastic ...)

PUDs

Numerous applications ... but,

Many variables affect film formation
Castor oil-based waterborne PUD

Xia et al. Macrom. Mat. Eng., 2011 296, 703-709
Mechanism of film formation

1. Polymer dispersion
2. Water loss and shrinkage
3. Coalescence and inter diffusion
4. Homogenous film
Dip coating

The coating thickness can be controlled by the solid content and coating viscosity.

The coating thickness can be calculated by the Landau-Levich equation [1] (eq 1).

\[ h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}} \]

- \( h \) = coating thickness
- \( \eta \) = viscosity
- \( \gamma_{LV} \) = liquid-vapour surface tension
- \( \rho \) = density
- \( g \) = gravity
DMA and DSC of PU film

Xia et al. Macrom. Mat. Eng., 2011 296, 703-709
Tung oil

- Tung oil can be extracted from the seeds of tung tree.
- It consists primarily of the glycerides of the fatty acids linoleic acid and oleic acid.
- An acre of tung trees will produce one hundred gallons of raw tung oil annually.

Cationic polymerization

Dip coating
Tung oil thermoset for dip coating

Tung oil in chloroform

Cationic polymerization

![Chemical structure of tung oil](image1)

![Graph showing gel time vs. tung oil content](image2)

![Graph showing tan delta and storage modulus vs. temperature](image3)
Effect of different coatings on the water uptake of wood fiber pot

\[
\text{water uptake(\%)} = \frac{\text{Wet weight} - \text{original weight}}{\text{original weight}} \times 100
\]
Summary

- Novel biopolymers, blends and composites with prescribed macromolecular properties have been successfully prepared from PLA, PA, PHA, SP, starch, and others natural fillers for production of environmentally-friendly bio-based containers.

- These bio-based materials have excellent thermal and mechanical properties as well as good dimensional stability.

- The water resistance of some commercially available bio-based containers was dramatically enhanced using recently developed bio-based coatings.
Questions?