Sustainable Material Technology
Bio-Polymer Technology

Stephen P. McCarthy
University of Massachusetts Lowell
Department of Plastics Engineering
Lowell, MA 01854
Biodegradable Polymer Research Center (1990-2007)

3M
ICI
Dow
BASF
Cargill
Morflex
Eastman
Metabolix
Union Carbide
National Starch
Warner Lambert
Johnson & Johnson
Bristol Meyers / Squibb
US Army Natick Labs
National Science Foundation
Bio-Based Polymers

1. Polymer Blends

2. Block Copolymers
BIOBASED POLYMERS
Polysaccharides

Cellulose

Starch
Konjac
Pullulan
Chitin
BIOBASED POLYMERS
Modified Polysaccharides

Cellulose Acetate

Starch Acetate

Chitosan
BIOBASED POLYESTERS

- Poly Lactic Acid
- Poly Hydroxy Butyrate
- Poly Hydroxy Alkanoates
Poly Lactic Acid

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\quad & \quad \\
-\text{C} - \text{C} - \text{O} - \\
\quad & \quad \\
\text{CH}_3
\end{align*}
\]

L - Lactic Acid  Crystalline
D - Lactic Acid  Crystalline
D,L - Lactic Acid  Amorphous

\[T_g = 60^\circ C\]
\[T_m = 185^\circ C\]
Slower Hydrolysis
Melting Points ($T_m$) and Heats of Fusion ($\Delta H_f$) Determined by DSC for PLA Stereoisomers of Variable Stereochemical Composition
Tensile Stress – Strain Curve
Tensile Stress-strain of Polylactic Acid
PLA Physical Aging

- Densification / Packing
  - in the Amorphous Region
- Excess Enthalpy Relaxation
- Endothermic Peak at Tg

- BRITTLE FRACTURE
DSC curves of PLA aged at room temperature for various times
Poly L-Lactic Acid

- Brittle after physical aging
- Increase ductility by
  - Miscible blend to lower Tg
  - Immiscible, co-continuous blend
  - Thin multilayer coextrusion
Plasticizers

- Lower Tg to room temp or below
- Miscibility (Solubility Parameters)
- Eliminates Physical Aging
- High elongation, but Low Modulus
# Biobased Citric Acid Esters

![Chemical structure of biobased citric acid esters](image)

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Citroflex</th>
<th>R’</th>
<th>R’’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethly Citrate</td>
<td>C1</td>
<td>H</td>
<td>Methyl</td>
</tr>
<tr>
<td>Triethly Citrate</td>
<td>C2</td>
<td>H</td>
<td>Ethyl</td>
</tr>
<tr>
<td>Acetyltriethyl Citrate</td>
<td>A2</td>
<td>OAc</td>
<td>Ethyl</td>
</tr>
<tr>
<td>Tri-n-butyl Citrate</td>
<td>C4</td>
<td>H</td>
<td>Butyl</td>
</tr>
<tr>
<td>Acetyltri-n-butyl C.</td>
<td>A4</td>
<td>OAc</td>
<td>Butyl</td>
</tr>
<tr>
<td>Acetyltri-n-hexyl C.</td>
<td>A6</td>
<td>OAc</td>
<td>Hexyl</td>
</tr>
</tbody>
</table>
DSC Evaluation of Tg vs. % plasticizer of the extruded films aged one day
Polymer Blends

PLA with

- Biobased Polymers
- Synthetic Polymers
Biobased Polymer Blends

- PLA with
- Starch
- Thermoplastic Starch
- Wood Flour
- Natural Fibers

- LOWER COST / COMPROMISE PROPERTIES
BIODEGRADABLE POLYMERS
Synthetic

Poly Caprolactone

Poly Ethylene Oxide

Poly Vinyl Alcohol

Poly Succinates / Adipates

Poly Succinates / Adipates / Terephthalate
Miscible Polymer Blends

PLA with:

- Poly Ethylene Oxide
- Poly Propylene Glycol
- Poly Vinyl Acetate
The Stress Strain Curve for PLA/PPG-e Blends
Polymer Blends

- PLA with
- Bionolle
  (Poly Ethylene Butylene Succinate)
- or Ecoflex
  (Poly Ethylene Butylene Succinate Terephthalate)

Low Tg compatible biodegradable polyester
Blending Conditions

1. Melt Blending - Single or Twin Screw Extruder

2.a. Injection Molding

2.b. Compression Molding

2.c. Cast Film

2.d. Blown Film
Tensile Stress-strain curves of Polylactic acid and Bionolle Blends
Tensile Stress-strain curves of Polylactic acid and Bionolle Blends
Tensile Modulus of Polylactic acid and Bionolle Blends
Elongation at yield and break of Polylactic acid, Bionolle#3000 and their blends
Polymer Blends

- **PLA and Bionolle --- WHY?**

Appear Compatible – Miscible?

Dynamic Mechanical Analysis

To determine Miscibility
Dynamic Spectra of PLA, Bionolle and their blends
Polymer Blends

- PLA and Bionolle - WHY?

Are Immiscible!

Selective Solubility of PLA

To determine Morphology
SEM Micrographs of the A30B70 extrusion sample
SEM Micrographs of the A50B50 extrusion sample after extracting PLA
SEM micrographs of the A70B30 extrusion sample after extracting PLA
Brittle / Ductile Transition

- Plane Strain to Plane Stress
- Immiscible Co-Continuous Blends
- Match Melt Viscosities
- Second Phase is Ductile
- Confirmed with Co-extruded PLA/PCL
Elongation at break of Polylactic acid, Bionolle and their blends as a function of aging
Nanocomposites Preparation

2 Different matrices:

   PLA4031D

   PLA4060D

4 Different Masterbatch Carriers:

   PLA4031D (used as MB for PLA4031)

   PLA4060D

   Ecoflex

   Eastar Bio

2 Different clays:

   Cloisite 25A

   NC174
Material

Southern Clay Cloisite® 25A

- **Montmorillonite (MMT)**

- **Ammonium cation:**

  \[(C_{18-H_{37}}-N-(CH_3)_2-CH_2-CH(C_2H_5)-C_4H_9\]

- **Organic fraction in wt:** 26.9%
Conclusions

- Most significant improvements in PLLA with Cloisite 25A via PLLA masterbatch
- Cast films are quenched
- Oxygen transmission rate decreased by 33%
- Tensile modulus increased by 37%
- Elongation at break increased 48%
- Tensile strength - no significant changes
- Toughening and OTR Indicates some degree of exfoliation
Biodegradation / Weight Loss

PLA Hydrolytic Degradation (Water)

Heterogeneous Degradation for Thick Samples (> 2 mm)

Inside Degrades before Outside due to build up of acid (autocatalytic)
Water absorption of PLA$_{50}$ plates during degradation at 37°C and pH = 3.7
Weight Loss of PLA\textsubscript{50} plates during degradation at 37°C and pH = 3.7
Molecular weight of PLA_{50} plates during degradation at 37°C and pH = 3.7
DSC (first run) of PLA$_{50}$ plates after 0, 98, & 126 days degradation at 37°C and pH = 3.7
X-ray diffraction spectra of PLA$_{50}$ after 128 days degradation at 37°C and pH = 3.7
Water absorption of PLA$_{50}$ plates during degradation at 60°C and pH= 7.4
Weight Loss of PLA$_{50}$ plates during degradation at 60°C and pH = 7.4
Molecular weight changes of PLA$_{50}$ plates during degradation at 60°C and pH = 7.4
DSC (first run) of PLA_{50} plates after 0, 21, & 57 days degradation at 60°C and pH = 7.4
X-ray diffraction spectra of PLA 50 after 0, 28, & 38 days at 60°C and pH = 7.4
Normalization weight loss of PLA/Bio#3000 blends in composting conditions
Molecular weight (Mn) change with testing time in composting conditions for PLA/Bio#3000 blends at 55°C
Poly Hydroxy Alkanoates

Polyesters synthesized by Bacteria

Poly 3-hydroxy butyrate
Poly 4-hydroxy butyrate
Poly 3-hydroxy valerate
Poly 3-hydroxy hexanate
Poly 3-hydroxy heptanoate
Poly 3-hydroxy octanoate, etc

Copolymer combinations of above
Blends of above and copolymers
Poly Hydroxy Alkanoates
Bacterial Polyesters

**Manufacturing method:** Microbial Fermentation

**Timing:** Now

**Projected price (50 kton):** approx $2.00/lb

- Fully developed for range of plastics
- High productivity and yields
- Demonstrated at industrial scale

Sugar or veg oil → Co-feed → Plastic Granules Inside Bacteria

Recovery

\[
\text{PHB - co - HX}
\]
Metabolix-UMass Lowell Partnership

- Significant work on PHA polymer formulation and conversion
- Pilot manufacturing in ‘06, ADM JV for full-scale in ’08
- Metabolix and UMass-Lowell (UML)
- Worked with UML for over 8 years
- Knowledge base for PHA processing established at UML
- New Leistritz MAXX TSE Facility
- Telles Headquartered in Lowell
BLOWN FILM LINE OF PHA
Specimens with Flashing
Rheological Study and Mold Flow Predictions

- The rheological behavior is being modified to incorporate the reduction in viscosity with time and temperature due to degradation.

- The freeze temperature is being modified to incorporate the crystallization rate differences due to temperature, wall thickness and nucleation rate.
Thank You

PRESENTED BY

Stephen P. McCarthy
Professor
University of Massachusetts Lowell
Department of Plastics Engineering
stephen_mccarthy@uml.edu

Please remember to turn in your evaluation sheet...