Collaborative Research to Advance Bioplastics

Developing Higher Value Bioplastic Applications
Overview

• NatureWorks Overview
• The value of Ingeo™ biopolymers
• Growth in durable applications
• Opportunity to differentiate
• Injection molding with Ingeo™ biopolymers
  – Ingeo™ 3251D
  – Ingeo™ 3801X
• Development through collaboration
NatureWorks LLC

- Established in 1997
- Wholly owned by Cargill
- Major investment in technology and infrastructure
- Capacity expansion completed in July 2009 (300 million pound annual capacity)
- Ingeo™ the leading biopolymer in the market place
What are Bioplastics?

- Some are of bio-based / agricultural origin.
- Some are compostable.

Bioplastics
What are Bioplastics?

Some are of bio-based / agricultural origin.

Both Bio-based and Compostable

Giving retailers and brand owners a dual value proposition around sustainability.
Foundation of the Ingeo™ Value Proposition

**Environmental**
- Reduced footprint
  - 68% less fossil energy use
  - 80-90% less greenhouse gases
  - Made from plants – not oil
  - Environmental leadership
  - Validated LCA, eco profile
  - New after-use options

**Performance**
- Clarity and optics
- Form and stiffness
- UV Stable
- Non-allergenic
- Printability
- Ability to light-weight

**Emotional**
- All natural origins
- Annually renewable
- Pure innovation
- Brand differentiator
- Enables consumer choice
- Feels right
- Supports consumer values and beliefs
Improving Eco-Profile:

Greenhouse Gases

Non-renewable energy use

Continuous improvement process

Ingeo 2005 ➔ Ingeo 2009 ➔ Ingeo target
Vision for end markets

- **Disposables**
  - Sun Chips

- **Semi-durables**
  - Tomatoes
  - Flowers
  - Magazine

- **Durables**
  - Car
  - Laptop

Ingenious materials from plants not oil
iTunes Gift Cards from Ingeo™
And Brands are responding to the challenge…

• Mako – Desk top accessories
• Cargo – Lipstick
• Leoplast – Lipstick & compacts
• Quickpoint – Promotional mugs
• BIC – Razor handles
• Stilolinea - Pens
Performance in new durables applications

Ingeo™ in Cargo Cosmetics

Toyota Prius Ingeo™ Floor mats

Samsung Ingeo™ Cell Phone Casing

Telecom Italia Ingeo™ housing for Cordless phone
......in even more demanding products

- Fujitsu – Laptop
- Sony – Walkman, DVD player
- Sony- Erickson – Cell phone
- Toyota – Prius spare tire, mat
- Toyota - Floor mat for third-generation Prius
- NEC- Mobile phone housing
- Nokia – Mobile phone housing
Ingeo™ innovations transform injection molded parts from a functional commodity cost item to a **differentiable marketing feature**

Critical to message appropriately and responsibly. Claims need to be well founded on good science around recognized standards
Disposables
Neat Ingeo™ Resins

*Durables*
Ingeo™ Blends

- 3251D (High Flow)
- GPPS
- HIPS
- SAN
- ABS
- PC/ABS
- PC

Value
Performance

- 3801D Formulation (High Heat, High Impact)
- 3251D (High Flow)
- PP comp
- PET
- SAN
- HIPS
- GPPS
Challenges to meet demanding semi-durable and durable injection molding applications for PLA

- Heat resistance of amorphous PLA is not high enough for sea container, auto interior or trunk environments (~65°C required)
  - Solution space 1: Blends of Ingeo with other thermoplastics offers biocontent advantages, and property versatility of second polymer
  - Solution space 2: Heat resistance of crystalline PLA can be high enough for shipping and storage, but production cycle time is historically very slow

- PLA demonstrates limited shear-thinning behavior and is shear-sensitive
Challenges continued...

- Toughness / impact resistance of un-oriented, injection molded PLA is low

- Useful life of product must be demonstrated

- Complex mixtures of additives can lead to chemical and / or physical interactions

- Additional product requirements (e.g. color, flame resistance, mold release) demand further ingredients
Ingeo™ 3251D Injection Molding Grade

- Neat IM grade
- Compostable – ASTM 6400, BPI Certified
- Good processability
- For clear or opaque semi durable applications
- Where heat requirements are no more than 120-130°F (55°C)
- Replacing incumbent styrenics (GPPS, HIPS, SAN);
  - Impact somewhat better than GPPS – can be improved with impact modifiers
  - Use of low shrinkage molds (PS, SAN, ABS – 0.004 in/in)
  - Potential to down gage GPPS or SAN
- Replacing PP
  - PP density difference
  - PP molds might require modifications
  - Could potentially down gauge due to higher stiffness
- Higher flow allows for better mold-fill characteristics
Collaboration leads to rapid development with 3801X

- Additive Suppliers
- Compounders
- Academia
- NatureWorks
- Converters
- Brand-owners
NatureWorks’ motivation and approach

• Understand the performance of additives in crystalline PLA solution space for injection molding
  – Make recommendations
  – Enable new applications and volume growth

• Demonstrate a set of target properties
  – Notched Izod impact of > 2.0 ft*lb/in
  – HDT targets
    • 65°C = No distortion in shipping, auto interiors or trunks
    • 100°C = Demonstration of high temp usefulness
  – Injection molding cycle time of < 60 seconds

• Use technology as a starting point to help spring board innovation and market penetration into semi-durables
Two examples of compounded formulations for injection molding of semi-durable goods with high bio-content

<table>
<thead>
<tr>
<th>Example</th>
<th>HHIM 670-82-01</th>
<th>Ingeo™ 3801X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat resistance</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Impact strength</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Cycle time</td>
<td>Fast</td>
<td>Mod. Fast</td>
</tr>
<tr>
<td>Appearance</td>
<td>Opaque</td>
<td>Opaque</td>
</tr>
</tbody>
</table>
Formulation and source of components
Example 1: High heat sample

Ingeo HHIM weight fraction of components

- Base Resin: 79%
- Accelerant: 10%
- Reinforcing Agent: 10%
- Nucleating Agent: 1%

Ingeo HHIM weight fraction of component source

- Bio content: 79%
- Petrol content: 11%
- Natural mineral content: 10%
## Ingeo™ HHIM components

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial name</th>
<th>Supplier</th>
<th>Chemical</th>
<th>Formula weight fraction</th>
<th>25°C density [g/ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Ingeo™ 3251D</td>
<td>NatureWorks LLC</td>
<td>PLA</td>
<td>0.79</td>
<td>1.24</td>
</tr>
<tr>
<td>Crystal accelerant</td>
<td>Plasthall® DOA</td>
<td>The HallStar Company</td>
<td>Dioctyl adipate</td>
<td>0.10</td>
<td>0.98</td>
</tr>
<tr>
<td>Reinforcing Agent</td>
<td>ULTRATALC® 609</td>
<td>Specialty Minerals Inc.</td>
<td>&lt;0.9 μm particle 3MgO·4SiO₂·H₂O</td>
<td>0.10</td>
<td>2.80</td>
</tr>
<tr>
<td>Nucleating Agent</td>
<td>LAK-301</td>
<td>Takemoto Oil &amp; Fat Co., LTD</td>
<td>Aromatic Sulfonate Derivative</td>
<td>0.01</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Formulation and source of components
Example 2: High impact and high heat sample

Ingeo 3801X weight fraction of components

- Base Resin: 71%
- Impact Modifier: 10%
- Accelerant: 9%
- Reinforcing Agent: 9%
- Nucleating Agent: 1%

Ingeo 3801X weight fraction of component source

- Bio content: 71%
- Petrol content: 20%
- Natural mineral content: 9%
## Ingeo™ 3801X components

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial name</th>
<th>Supplier</th>
<th>Chemical</th>
<th>Formula weight fraction</th>
<th>25°C density [g/ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Ingeo™ 3001D</td>
<td>NatureWorks LLC</td>
<td>PLA</td>
<td>0.711</td>
<td>1.24</td>
</tr>
<tr>
<td>Impact Modifier</td>
<td>Biostrength® 150</td>
<td>Arkema Inc.</td>
<td>Proprietary core-shell copolymer</td>
<td>0.100</td>
<td>1.00</td>
</tr>
<tr>
<td>Crystal accelerator</td>
<td>Plasthall® DOA</td>
<td>The HallStar Company</td>
<td>Dioctyl adipate</td>
<td>0.090</td>
<td>0.98</td>
</tr>
<tr>
<td>Reinforcing Agent</td>
<td>ULTRATALC® 609</td>
<td>Specialty Minerals Inc.</td>
<td>$&lt;0.9 , \mu m , \text{particle} , 3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$</td>
<td>0.090</td>
<td>2.80</td>
</tr>
<tr>
<td>Nucleating Agent</td>
<td>LAK-301</td>
<td>Takemoto Oil &amp; Fat Co., LTD</td>
<td>Aromatic Sulfonate Derivative</td>
<td>0.009</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Injection Molding of Ingeo™ 3801X

- Successful molding of ASTM test specimens using cold runner, cold sprue
- Sumitomo 100 ton press
- Tested with both water and oil mold coolant media
- Optimized melt temperatures and mold temperatures for minimum cycle time and best properties
Optimizing Processing Conditions

- Finding an optimum mold coolant temperature is recommended in order to get the best quality parts and the shortest cooling times

- Izod impact strength is sensitive to mold temperature

- Ingeo™ 3801X, ASTM test bar tooling, barrel temperature = 190°C
**Main differences between examples**

<table>
<thead>
<tr>
<th>Example</th>
<th>HHIM 670-82-01</th>
<th>Ingeo™ 3801X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base resin</td>
<td>3251D Low RV, Low %D</td>
<td>3001D Med RV, Low %D</td>
</tr>
<tr>
<td>Impact modifier</td>
<td>None</td>
<td>Biostrength 150</td>
</tr>
<tr>
<td>Bio + natural mineral content</td>
<td>89%</td>
<td>80%</td>
</tr>
</tbody>
</table>
Ingeo™ 3801X – Launched in Jan 2010

- Compounded solution for injection molding
  - High Bio Content (70% Ingeo™)
  - For non food, opaque, semi-durable, non compostable applications

- Property Improvements
  - High crystallinity → Good thermal dimensional stability
  - High impact strength → Similar to HIPS and ABS
  - High modulus

- Processing Improvements
  - Rapid crystallization rate → Fast cycle times
  - Higher linear shrinkage → Easier part ejection
<table>
<thead>
<tr>
<th><strong>Physical Properties</strong></th>
<th>ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.33</td>
</tr>
<tr>
<td>Melt Index, g/10 min (190°C/2.16K)</td>
<td>8.0</td>
</tr>
<tr>
<td>Relative Viscosity</td>
<td>3.1</td>
</tr>
<tr>
<td>Crystalline Melt Temperature (°C)</td>
<td>160-170</td>
</tr>
<tr>
<td>Glass Transition Temperature (°C)</td>
<td>45</td>
</tr>
<tr>
<td>Clarity</td>
<td>Opaque</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Mechanical Properties</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Modulus, psi (MPa)</td>
<td>432,000 (2,980)</td>
</tr>
<tr>
<td>Tensile Yield Strength, psi (MPa)</td>
<td>3,750 (25.9)</td>
</tr>
<tr>
<td>Tensile Elongation at Break, %</td>
<td>8.1</td>
</tr>
<tr>
<td>Notched Izod Impact, ft-lb/in (J/m)</td>
<td>2.7 (144)</td>
</tr>
<tr>
<td>Flexural Strength, psi (MPa)</td>
<td>6,400 (44)</td>
</tr>
<tr>
<td>Flexural Modulus, psi (MPa)</td>
<td>413,000 (2,850)</td>
</tr>
<tr>
<td>HDT B at 66 psi / 0.45 MPa (°C)</td>
<td>65</td>
</tr>
<tr>
<td>HDT at 16.5 psi* / 0.114 MPa (°C)</td>
<td>140</td>
</tr>
</tbody>
</table>

* Modified version of E2092 to simulate "light" load
Injection Molding of Ingeo™ 3801X at Hennepin Technical College

- Successful molding of coat hanger using heated sprue, polypropylene tooling
- Toshiba 114 ton press
- Water coolant medium at 90°C
- Cycle time = 45 seconds
Visual demonstration of the deformation of Ingeo 3801X with common thermoplastics

- Heating rate of 0.5°C/min from 25 to 118°C
- At 118°C, PP, PS and amorphous Ingeo™ 3251D have all softened and bent
- Ingeo™ 3801X retains enough stiffness to hold distortion to a minimum
Collaboration leads to rapid development of 3801X

- **Additive suppliers:**
  - Takemoto Oil & Fat/Goulston – Nucleating agent
  - Specialty Minerals – Reinforcing agent
  - HallStar – Crystallization accelerator
  - Arkema – Impact modifier

- **Academia:**
  - Hennepin technical college – injection molding

- **NatureWorks:**
  - Formulation and compounding, material science, analysis

- **Compounders and brand-owners:** Now evaluating formulation and product performance. Targeted development tailored towards specific applications
Conference Stats

- 324 Attendees
- 200 Companies
- 30 Countries
- 50 Speakers
- 31 Exhibitors
- 14 Sponsors
Acknowledgements

3801X and High Heat Injection Molding information:
Jed Randall, Krag Anderson, both of NatureWorks LLC

Market Drivers information:
Dr. Marc Verbruggen, NatureWorks LLC

Eco-profile information:
Erwin Vink, NatureWorks BV
We invite you to collaborate to develop more Ingeo™ innovations with NatureWorks, partners and customers!

Thank You