NatureWorks Ingeo™ Polylactide: Past, Present and Future

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NatureWorks LLC
Minnetonka, MN

IOWA STATE UNIVERSITY
BIOPOLYMERS & BIOCOMPOSITES WORKSHOP

August 14, 2012
Agenda

• NatureWorks: Who we are and what we do
• Early History
• Bioplastics Value Proposition
• Ingeo EOL Value Proposition
• Further Look into the Future
Who We Are . . .

- 1st world-scale biopolymer producer
- Economies of scale to compete in traditional plastics markets (140,000 MT capacity)
- Peer reviewed eco-profile (LCA)
- Global plastics & fibers customer base
- Ingeo applications breadth across many markets, geographies, and retail applications
- Privately owned by Cargill Inc and PTT Global Chemical
Where it comes from…natural plastic from plants, not oil
Polylactide Synthesis

Starch $\xrightarrow{\text{Fermentation}}$ Dextrose (Glucose) $\xrightarrow{\text{Hydrolysis}}$ Lactic Acid $\xrightarrow{\text{Chemical Processing}}$ PLA
Creating a Family of Polymers

D-Lactic Unit  L-Lactic Unit
Early History of Polylactide Polymers

- Lactide monomer production described in 1912
- Polylactide production described in 1932 (W.H. Carothers et al.)
  - Technology developed further by DuPont, with high molecular weight polymers in 1955, but technology appears to have been shelved
  - First commercial application c.1972, with Ethicon Inc. development of resorbable sutures (poly-lactide-co-glycolide)
- Resurgence of interest in 1980’s
- Cargill project started in 1989
- Commercial production in Blair, Nebraska Dec. 2001
By 1996 the field was heating up....

<table>
<thead>
<tr>
<th>Company</th>
<th>PLA capacity (MM lb/yr)</th>
<th>Patent activity</th>
<th>PLA approach</th>
<th>Purity/ mol wt control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cargill (U.S.)</td>
<td>10 (100 MM lb/yr in preliminary design phase, not announced)</td>
<td>10</td>
<td>Ring opening polymerization</td>
<td>Lactide distillation</td>
</tr>
<tr>
<td>Chronopol (US)</td>
<td>2 planned (1996)</td>
<td>56</td>
<td>Ring opening polymerization</td>
<td>Crystallization/ melt crystallization</td>
</tr>
<tr>
<td>Shimadzu (Japan)</td>
<td>0.2</td>
<td>22</td>
<td>Ring opening polymerization</td>
<td>Lactide crystallization, solid state polymerization</td>
</tr>
<tr>
<td>Mitsui Toatsu (Japan)</td>
<td>2-20 planned</td>
<td>97</td>
<td>Direct condensation</td>
<td>Solvent with water removal</td>
</tr>
<tr>
<td>Neste OY (Finland)</td>
<td>Not available</td>
<td>1</td>
<td>Direct condensation</td>
<td>Reactive coupling</td>
</tr>
</tbody>
</table>

Capacity based on published news reports. Patent activity is worldwide published applications. Chronopol patents assumed to include Battelle, EcoChem, Ecopol, and DuPont.

It has been a complex journey…..

Project begins at Cargill

Polysar JDA

JDA Dow Chemical

Cargill Dow Polymers, LLC (JV)

NatureWorks LLC (Stand Alone JV)

NatureWorks jointly owned by Cargill and Teijin

Cargill acquires Dow’s interest in NatureWorks

Wholly owned by Cargill

'89 '90 '91 '92 '93 '94 '95 '96 '97 '98 '99 '00 '01 '02 '03 '04 '05 '06 '07 '08 '09 '10 '11 '12

Pilot plant (5 lb/hr)

Semi-works plant (1,000 lb/hr)

Blair, NE (20,000 lb/hr)

Blair, NE (40,000 lb/hr)

'AmberWorks JV w/ BioAmber
A Cycle of Innovation

Innovation:
People implementing new ideas to create value.

Requires:
People using new knowledge and understanding to experiment with new possibilities in order to implement new concepts that create new value.

Adapted from Joyce Wycoff, Innovation Network, Thinksmart.com
Cycle 1.

Project begins in Cargill

Semiworks plant (1,000 lb/hr)

JDA Dow Chemical

Blair, NE (20,000 lb/hr)

Blair, NE (40,000 lb/hr)

'89 '90 '91 '92 '93 '94 '95 '96 '97 '98 '99 '00 '01 '02 '03 '04 '05 '06 '07 '08 '09 '10

Development of basic monomer properties, polymer properties, technology to purify lactide and to control polymer molecular weight, melt point, and stability.

Process technology developed.

Culminates in products available for market development.

Development of processes has initial peak in 1993-1996, NatureWorks is actively filing at same time.

Market development quantities of Ingeo™ are available. Polymer is processed on commercial scale lines. Process control and manufacturing strategy are refined. Culminates in design and construction of full scale manufacturing plant at Blair, Nebraska.

Development of end use applications expands explosively, peaking in 2000-2002.
Cycle 3.

Cycle 3. (2003-2010)
Ingeo™ available in standard grades. End products are developed and moved into retail. New compositions, copolymers, flow additives, color packages, nucleants, inhibitors, etc. being developed worldwide. New investments in processing equipment opens bigger markets* and achieves economy of scale.

*Historically, new polymers have averaged 11 yrs to reach 300 MMlb/yr sales from when commercial plant was operational. C. Musso, Ph.D. (McKinsey)
Cycle 4. A Quick Look at What’s New & What’s Next

Our collective journey to a sustainable future.

<table>
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<th>'08</th>
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<th>'27</th>
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</table>

New players enter PLA field
Production becomes global
Full complement of biobased additives/ modifiers
Stereocomplex available in market development quantities
Pilot development of 2nd generation biopolymers and biobased chemicals
Recycle infrastructure developed and organics collection/ composting becomes widespread

Cellulosic feedstock in use at commercial scale
Biorefinery campus, with multiple ventures. On-site cogeneration, minimal waste.

Children today are in college and in the workforce, innovating even better ways to a sustainable future.
Value Drivers for the Industry

Even in these extraordinarily difficult economic times, the STRATEGIC and ENVIRONMENTAL value drivers remain strong

“A SIGN OF THE TIMES”
Ingeo™ Technology Credentials

**Review process for new Eco-Profile**

1. **Publication in the Industrial Biotechnology Journal, August 2010.**
   - Manuscript reviewed by several reviewers
   - Update of our 2007 publication

2. **Peer review by Dr. Ian Boustead of Boustead Consulting.**
   - Final report now available

3. **Review by Dr. Alberta Carpenter of NREL followed by uploading the eco-profile as well as a process description into the US LCI database**

   ![www.nrel.gov/lci](www.nrel.gov/lci)

**Download:**
- Spreadsheets with the data files
- Report giving description of Ingeo production process
**Value drivers:**

- **Environmental**
- **Economic**
- **Strategic**

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**Greenhouse Gases**

<table>
<thead>
<tr>
<th>Material</th>
<th>Ingeo Current</th>
<th>Ingeo 2005</th>
<th>PVC (suspension)</th>
<th>Polypropylene</th>
<th>LD Polyethylene</th>
<th>PET (amorphous)</th>
<th>PET (SSP)</th>
<th>Polystyrene (HIPS/GPPS Avg)</th>
<th>Polycarbonate</th>
<th>Nylon 6</th>
<th>Nylon 66</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>From cradle to polymer factory gate</strong> [kg CO2 eq. / kg polymer]</td>
<td>-60%</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</table>

- **Non-renewable energy use**

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<th>Nylon 66</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>From cradle to polymer factory gate</strong> [MJ / kg polymer]</td>
<td>-50%</td>
<td></td>
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</table>

- **Continuous improvement process**

Ingeo 2005 ➞ Ingeo Current ➞ Ingeo Target
“The world is shifting to an innovation economy and nobody does innovation better than America.”
—President Obama, December 6, 2011

“Decades of life-sciences research and the development of increasingly powerful tools for obtaining and using biological data have brought us closer to the threshold of a previously unimaginable future: “ready to burn” liquid fuels produced directly from CO2, ... plastics made not from oil but from renewable biomass...”
National Biomass Strategy 2020: New wealth creation for Malaysia’s palm oil industry

The Biobased Economy: The state of the art in The Netherlands
2012 & Beyond: NatureWorks Looking Forward

- Globalizing the Manufacturing Platform
- Broadening Products & Applications
- Monetizing the EOL Value Proposition
- Cellulosic Feedstocks
2015 target: Ingeo bioresin structurally less expensive than PS (and PET)

In 2015 NatureWorks will have 2 Ingeo plants operational
- Supported by 3 feedstock sources (corn, sugar cane, cassava)
- Stronger global commercial organization
NatureWorks

Broadening from

A comprehensive platform of polymer grades with world scale economies

NatureWorks

Ingeo Polylactides

Ingeo Lactides

Now offering polymer grade Ingeo lactides to support further global growth of the industry

Broadening Products & Applications

8000 Series - foam
7000 Series – ISBM Bottles
6000 Series – fibers/nonwovens
4000 Series - films
3000 Series – Injection Molding
2000 Series - Thermoforming

Cost effective Ingeo production is via the Ingeo lactide intermediate

Lactic Acid → Lactide → Ingeo Polylactide
<table>
<thead>
<tr>
<th>Products</th>
<th>Where we are in the Market</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid materials</td>
<td></td>
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<tr>
<td>Food serviceware</td>
<td></td>
</tr>
<tr>
<td>Films</td>
<td></td>
</tr>
<tr>
<td>Nonwovens/Fibers</td>
<td></td>
</tr>
<tr>
<td>Durables</td>
<td></td>
</tr>
<tr>
<td>Lactides</td>
<td></td>
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<tr>
<td>Incubator</td>
<td></td>
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Where we are in the Market:
- **Rigid materials**
- **Food serviceware**
- **Films**
- **Nonwovens/Fibers**
- **Durables**
- **Lactides**
- **Incubator**
Ingeo™ High-Heat Technologies - Food Service-Ware

High-Heat Ingeo™ Hot Cup Lids

StalkMarket

International Paper

High-Heat Ingeo™ Cutlery

StalkMarket

US Biopolymers
Biaxially Oriented Films Growth

- Taghleef Industries successfully starts production of NATIVIA™

- NATIVIA™ is based on Ingeo™, and is 100% made from renewable resources

- NATIVIA™ is a compostable film that complies with EN13432
Ingeo™ Based Card Technology

DaiNippon, Mitsubishi Plastics and Sony

iTunes

Sony Bank, Inc.

REI
Injection Stretch Blow Molded Technology

Bormioli

Vedat

Extrusion Blow Molded Technology

Shiseido Shampoo Bottle

Polenghi Lemon Juice Bottle
Fibers / Nonwovens

GroVia

Ahlstrom

Huggies

Elements Naturals
Apparel

FASHION SUMMIT
DECEMBER 9, 2009
THE COPENHAGEN OPERA HOUSE DENMARK

Hernandez Cornet  Max Jenny  Dave Andersen
Ingeo in Japan
Ingeo in Korea

LG Hausys zea® Wall Paper

Structure

0.2(T) x 1,060(W) × 15M(L)

Print

Ingeo

Backing Paper

Roll type

Application

- Residential
- Commercial
Ingeo in Korea
LG Hausys, zea® Flooring, “Prestige” line

Structure

9.0(T) x 75(W) x 900(L)

- Ingeo Laminate
- Water Resistant Plywood

Application

- Residential

Eco-friendly

Dent, scratch resistant

No color change by environmental
NatureWorks LLC

Agenda

• NatureWorks: Who we are and what we do

• Early History

• Bioplastics Value Proposition

• Ingeo EOL Value Proposition

• Further Look into the Future
Progressing New After-Use Options

End of Life Options | Incumbent Plastics | Ingeo™
--- | --- | ---
Landfill | X | X
Recycle | X | X
Incineration | X | X
Compost | | Food waste diversion: From landfill to composting facility
Anaerobic Digestion | | X
Feedstock Recovery | | X

Total US MSW Generation (by material), 2008
250 Million tons (before recycling)

- Yard trimmings: 13.2%
- Food Scraps: 12.7%
- Other: 3.5%
- Paper: 31.0%
- Wood: 6.6%
- Rubber, leather & textiles: 7.6%
- Plastics: 12.0%
- Metals: 8.4%
- Glass: 4.9%

31.8 MM tons/year
Methane (x23 CO₂) release in landfill

Source: Municipal Solid Waste in the US: 2008 Facts & Figures
Total US MSW Generation (by material), 2008
250 Million tons (before recycling)

Source: Municipal Solid Waste in the US: 2008 Facts & Figures

A Credible Closed Loop Solution Exists Today In Seattle…

End-of-Life Options And Opportunities
Progressing New After-Use Options

Total US MSW Generation (by material), 2008
250 Million tons (before recycling)

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- Plastics 12.0%
- Metals 8.4%
- Glass 4.9%
- Other 3.5%

30 MM tons/year < 10% recycled (some PET bottles only)

End of Life Options

- Landfill
- Recycle
- Incineration
- Compost
- Anaerobic Digestion
- Feedstock Recovery

Incumbent Plastics

Ingeo™

Closed loop recycling vs. today’s bottle ► package ► landfill
A new paradigm for Cradle-to-Cradle materials recycle . . . “Feedstock Recovery”

*Ingeo is a bio-polymer made from lactic acid*
• COP 15 main conference area: Ingeo™ used in main hall carpeting and Food Serviceware

• New Company, BIOCOR LLC, launched with a business model founded on trading post consumer PLA in any format...
Agenda

• Who we are and what we do
• Early History
• Bioplastics Value Proposition
• Ingeo in the Market Today
• Ingeo 3801X
• Ingeo EOL Value Proposition

• Further Look into the Future
Latest Ingeo Business & Product Developments

• Extending the Ingeo Product / Applications Range

1. Ingeo Lactides

2. New High % L (> 0.3%D) Performance Grades


4. Arkema’s Rnew – Partnering to produce bio-based (& improved) Plexiglas
Ingeo Platform Extension

Family of Monomers

L-100 Lactide
L-300 Lactide
M-3000 Lactide

Lactide monomer platform

Ingeo Platform: “Performance materials from renewable resources”
**Ingeo Platform Extension**

<table>
<thead>
<tr>
<th>Family of Monomers</th>
<th>Family of Polymers</th>
<th>Family of High % L Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-3000 Lactide</td>
<td>8 series Foam</td>
<td>6100 D</td>
</tr>
<tr>
<td>L-800 Lactide</td>
<td>7 series ISBM – bottles, BM</td>
<td>6260 D</td>
</tr>
<tr>
<td>L-300 Lactide</td>
<td>6 series Fibers, Nonwovens</td>
<td>3100 HP</td>
</tr>
<tr>
<td>L-100 Lactide</td>
<td>4 series Films, cPLA</td>
<td>3260 HP</td>
</tr>
<tr>
<td></td>
<td>3 series Injection Molding</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 series Thermoforming</td>
<td></td>
</tr>
</tbody>
</table>

**Ingeo Platform: “Performance materials from renewable resources”**
Improved Nonwovens
- Reduced shrinkage and improved dimensional stability
- Increased hydrolysis resistance
- Capable of higher heat set temperatures
- Higher $T_m$ creates advantages in bi-component systems
- Larger processing windows

Improved Durables
- Faster cycle times & higher production rates for lower molded part cost
- 3-4x increase in bulk crystallization rate
- $15^\circ$C improvement in heat deformation temperature vs traditional Ingeo grades
- ~30% higher modulus above $T_g$
- Increased hydrolysis resistance
New compounded Ingeo grades combining properties of succinic and lactic acid polymer platforms.
The Joint Venture combines the best of both companies into an entity tasked with developing a new family of bio-based compounded Ingeo polymers.
New Developmental Grades Resulting from the JV

- Thermoforming Grade
  - Ingeo AW 240D

- Injection Molding Grade
  - Ingeo AW 300D
Arkema’s Ingeo-based Plexiglas® Rnew resins

- Compounded alloys of Arkema / Altuglas International’s PMMA and NatureWorks’ Ingeo (durable product focus)
  - Provide step change in impact performance (≈ PETG, PC)
  - Significant increase in chemical resistance ( > PC)
  - Drastic increase in processability
  - Reduced carbon footprint & cost

- All whilst incorporating bio-sourced materials … without compromising optics, scratch resistance, color acceptance or surface aesthetics
Arkema’s Ingeo based Plexiglas® Rnew resins

Multi-axial impact

Synergistic Impact Modification Effect

- Formulation design allows for tailored solutions
- Extraordinary improvements in impact strength while maintaining modulus and strength
- Impact performance comparable to PETG and PC

Source: Altuglas International a subsidiary of Arkema International
Our footprint is small: At full capacity, Ingeo™ represents:
- < 0.2 % of 2007 US corn production (< 0.05 % of global corn production)
- Ingeo technology is feedstock Agnostic. 2nd plant will use most abundant local industrial sugar or starch source
- 2nd Generation is becoming an industrial reality
Swapping from 1\textsuperscript{st} to 2\textsuperscript{nd} generation feedstock will be as much an \textbf{economic} as an \textbf{environmental} decision.

- US government strongly supports cellulosic bio-refinery concept
- Various feedstocks being evaluated
- Questions:
  - Timing of first bio-refineries?
  - Economics of bio-refineries?
Biopolymers are here to stay . . .
• Meet a strategic need to shed our oil addiction
• Meet a strategic need to lower our carbon footprint
• Meet global consumer expectation for sustainability without sacrifice

Biopolymers are no longer “embryonic”
(Translation: hard to get, hard to use, very expensive)

Let the journey continue . . .
• New entries into the market place (partially Bio PET, Bio PE, PHA)
• Feedstock diversification
• Economies of scale (resin, converters)
• Recycling infrastructure

Summarizing Comments:
Acknowledgements:

- Dr. Jeff Kolstad
- Steve Davies
- Andrea Ziadi
- Lisa Moore
- Julie Sobon
You don’t have to leave your mark on the world in order to make one.
Thank you!

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