Bioadvantaged Thermoplastic Elastomers at Iowa State University

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Bio-based Thermoplastics
Biopolymers and Bioplastics 2015

Iowa State University
Chemical & Biological Engineering

OMICS International
International Conference and Exhibition on
Biopolymers and Bioplastics
August 10-12, 2015 San Francisco, USA

Argo Genesis Chemical LLC
ADM
USB
United Soybean Board

Iowa Soybean Association

Bio-based Thermoplastics
Biopolymers and Bioplastics 2015
August 10, 2015
1. About my home institution…

2. The partnership…

3. The problem the technology solves…

4. The Technology…

5. Putting the technology to work…
We offer a full suite of polymer synthesis and characterization services.
Bio plastics at ISU
We have a new I/UCRC!

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http://www.cb2.iastate.edu
Bio plastics at ISU
Some key players...
Bio plastics at ISU
Key thrusts

- Feedstock Logistics
- Synthesis and Compounding
- Composites
- Economics, Social Issues and Commercialization
- Performance Evaluation and Engineering Design

Biobased Products
Bio plastics at ISU
USDA-NIFA Critical Agricultural Materials

Feedstock
- Biodiesel Processing → Biodiesel
  - Glycerin
  - ADM Pilot Plant
    - Glycerin + Acrylic Acid
      - Acrylated Glycerin (AGₙ)

Monomer
- Task 1: Cochran
  - RAFT Polymerization
    - ISU Patent
      - 100% Soy-based

Homopolymer
- Task 2-3: Cochran

Products with Future Products of Paints
- Task 4-8: Chen, Grewell, and Madbouly
  - Waterborne Adhesives: Tunable and Contains Initiator
    - Crosslinked with Heat or UV
      - PSA/Soft Adhesives
    - Block Co-polymer (PLA or PMMA): Tunable Hardness
      - Structural Adhesives

- Task 9: Grewell
  - cyclic anhydride amine catalyst
    - heat, 3 hours
      - no solvent, no purification
  - isosorbide
  - 190 °C, 30 minutes
    - no solvent, no purification
      - alkene isomerization (raise $T_g$)
    - methyl esters (lower $T_g$)

Soybean Oil
Biodiesel
Glycerin
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So how did we get here?
(Putting soybean-oil/glycerine based thermoplastic elastomers to work)
Project Team
A partnership in progress...

3M

ARGO GENESIS CHEMICAL LLC

ADM

Kraton
Giving Innovators Their Edge

STATE

Seneca Petroleum Company

Bio-based Thermoplastics

The partnership...

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Project Team

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Thermoplastic elastomers are ordered materials…
(a $14$ bn industry)

An SBS (Kraton®) material

Polymer, 13, 22 (1972)

Poly styrene

Poly styrene

Poly styrene

Poly styrene

Softens at 100°C

Soft and rubbery
...and can be processed into any shape

(1) Ship as Pellets

(2) Extrude

(3) Mold
Thermosets are processed much differently...

Start with liquid resin

Mix

Cure

Mold
A butadiene refinery

Ethylene can be produced from crude oil by *cracking* large oil molecules into smaller pieces.

\[ \text{CH}_2=\text{CH}_2 \]

This is a high-temperature high-pressure catalytic process (high energy consumption)

\[ \text{CH}_2=\text{CH}−\text{CH}=\text{CH}_2 \]

Butadiene and isoprene are produced as byproducts.
The Economics of Triglycerides

Butadiene contract price
Soybean Oil Spot Price (www.indexmundi.com)
Distiller’s Corn Oil

$1000’s/metric ton

Jan ’06, May ’07, Sep ’08, Feb ’10, Jun ’11, Nov ’12, Mar ’14

The problem the technology solves...
Outline

1. About my home institution...
2. The partnership...
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Too much of a good thing…

- A typical triglyceride has up to 6 double bonds.
- The C=C bonds in natural oils are not reactive enough to polymerize.
- The C=C bonds in Acrylated Epoxidized Soybean Oil are very reactive.

Diagram:

- Polymerization process showing the transformation of triglycerides into polymerized forms.
A typical triglyceride has up to 6 double bonds.

The C=C bonds in natural oils are not reactive enough to polymerize.

The C=C bonds in Acrylated Epoxidized Soybean Oil are very reactive.
A small quantity of free radical initiator generates radicals and initiates polymerization.

Chain transfer agent (CTA) scavenges the growing radicals to form a stable intermediate.

The intermediate dissociates briefly to allow polymers to add a few units at a time.

The key difference

Controlled vs. Not

- In a conventional polymerization chain transfer (crosslinking) reactions lead to gelation at low monomer conversion (< 1%)

- With controlled polymerization, we can achieve high molecular weight polymers at 90% conversion and arrest the polymerization prior to gelation.

Molecular weight vs. conversion

- Conventional free radical & cationic
- ATRP/RAFT
- Gel Point

M_n

\( \log_{10} \) Conversion

-4 -3 -2 -1 0
About my home institution…

The partnership…

The problem the technology solves…

The Technology…

Putting the technology to work…
With RAFT/ATRP the path to thermoplastic elastomers is straightforward...in principle

- Formation of elastomeric block copolymers
  - Analogous to, e.g. the PS-polybutadiene-PS (SBS) polymers of the Kraton® family.

Acrylated Epoxidized Soybean Oil (AESO)  Homopolymer

\[
\begin{align*}
\text{Poly(Styrene-b-AESO)} & \quad \text{Poly(Styrene-b-AESO-b-Styrene)} \\
\text{Hard} & \quad \text{Soft} & \quad \text{Hard} \\
\text{Hard} & \quad \text{Soft} & \quad \text{Hard}
\end{align*}
\]
Our elastomers

SBS elastomers

Figure 9: Graph shows the SAXS of the PS-PAESO-PS#1.

Figure 10: Graph showing storage and loss modulus $G'$ and $G''$ as a function of temperature of bitumen with 1% mass poly(styrene-b-AESO-styrene) triblock and of bitumen with 1% Kraton R⃝.

by EQN. (1), which is derived by making scaling arguments for number of active sites in the shell. The rate of transfer is going to be the same as for free radical modified by a percentage of active sites, which can be estimated by the ratio of the volume of the shell to the volume of the sphere.

$$R_{tr,P} \propto 2.4 k_p N_n \frac{V_{shell}}{V_{sphere}}$$ (1)
Hundreds of value-added market opportunities

Potential Markets for Renewable Thermoplastic Elastomers

- Consumer
  - Footwear & Sporting Goods
  - Appliances & Tools
  - Housewares & Toys

- Industrial
  - Construction Equipment
  - Hose & Tubing
  - Safety Equipment
  - Adhesives & Sealants

- Transportation
  - Coatings & Paints
  - Tires
  - Asphalt Modification

- Packaging
  - Films
  - Bottles
  - Caps & Closures

- Wire & Cable
  - Connectors
  - Jackets
  - Insulators

- Electrical & Electronics
  - Covers, Aesthetics
  - Display Components
  - Shock/Impact Protection

- Healthcare
  - Tubing
  - Devices
  - Films, Gaskets, Seals

- Bio-based Thermoplastics
  - Putting the technology to work...

Bio-based Thermoplastics
Hundreds of value-added market opportunities

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Transportation
- Asphalts
- Modification
- Tires

Industrial
- Safety Equipment
- Construction Equipment
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Putting the technology to work...

Bio-based Thermoplastics
Early promise as asphalt modifier

\[ \frac{G^*}{\sin \delta}, \text{kPa} \]

- Flint Hills 46-34
- 3% Kraton 1101
- 3% Kraton 1118
- 3% Bio-SBS 2012
- 2% Bio-SBS 2013

Temperature, °C

Putting the technology to work...
So is it worth it?
Back-of-the-napkin technoeconomic analysis...

What we’re up against
- SBS for asphalt modification is around $1.35/#
- Cost per ton of asphalt is $100–120
- Fully amortized capital in place, process optimized over 30 years

What we have to offer
- Vegetable oil @ $0.37 per pound
- Epoxidation cost @ $0.35 per pound
- Acrylation cost @ $0.07 per pound
- CTA cost @ $0.03 per pound
- Solvent cost (95% recovery) @ $0.08 per pound
- Operating costs @ $0.25 per pound (at full scale)
- Capital costs @ $150M for 100,000 kt per year

Raw material + OPEX ≈ $1.15 per pound + CAPEX
(Looks close)
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BUT...don’t forget the “bioadvantage”

Enhanced efficacy of PS-PAESO means asphalt modification requires only 50–75% of the polymer.

Economic opportunity.

Raw material + OPEX ≈ $1.15 per pound + CAPEX
(Looks close)
So where how did this partnership evolve?
(and continue to evolve)

A solid portfolio of protected IP

#03949 Thermoplastic Elastomers Via Atom Transfer Radical Polymerization of Plant Oil

#04064 Thermoplastic Elastomers via Reversible Addition-Fragmentation Chain Transfer Polymerization of Triglycerides

#04126 Poly(Acrylated Polyol) and Method For Making and Using Thereof as Asphalt Rubber Modifiers, Fracking Additives or Fracking Fluids.

#04255 Radical Polymerization Macro-Chain Transfer Agents and Initiators from Condensation Polymers
So where how did this partnership evolve?  
(and continue to evolve)

A fortuitous relationship built on mutual trust and respect

- Years of contract and fee-for-service research
- Leader in asphalt supply to the upper-midwest
- A privately held company with a history of forward thinking and strategic investing
- A shared vision → early licensing

Putting the technology to work…

Iowa State University
Institute for Transportation
Bioeconomy Institute

Seneca Petroleum Company

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So where how did this partnership evolve? (and continue to evolve)

Plans that evolve over time.

**TPE End Markets**
- Tires, Asphalt, Sealants, …
- $15.1 billion in 2012
- Up to 1.5 million tons of Petroleum can be replaced

**Plastics Industry**
- DuPont
- Goodyear
- Kraton

**Soybeans**
- Iowa & US Growers

**Cochran & Williams**
- Lab scale & Pilot plant
- Product development
- Structure/property relationships
- Explore product diversification opportunities

**Oil Producers**
- West Central Co-op, IA

**Facility Operation**
- Argo Genesis Chemical (IL)
So where how did this partnership evolve?
(and continue to evolve)

Leverage amplifies the investment and distributes the risk.
THANK YOU!