Sustainable Epoxy Materials From Vegetable Oils

Matthew Ravalli
Ph.D. Graduate Student
Department of Chemistry
Rensselaer Polytechnic Institute, Troy, NY, USA

Drs. James V. Crivello & Chang Y. Ryu

Theodore Yang

NSF – DMR – 1308617 (Polymer Program)
Overview

Develop new, reactive monomers and polymers from sustainable, bio-renewable sources and understand their structure-property relationships, considering:

- Substrates should be readily available in substantial quantities
- Minimum chemical modification should be needed
- Avoid use of any solvents
- Minimize reaction byproducts
- Use energy efficient polymerization schemes

Dream

- e.g. 1,3-propandiol
- By DuPont
- e.g. Polylactic acid
- NatureWorks
- e.g. “epoxy tree?”
Approach

Vegetable oils
: Ester-based Monomer Source
with Unsaturated Bonds
(Triglycerides with unsaturated fat)

*Linseed oil*

www.foodservicedirect.com

“Green” Epoxy Coating & Composite Matrix
Epoxy Resins for thermoset composite matrix

Conventional “Two part” Epoxy

Epoxy monomers
+ Amine curing agent
(“hardware store” epoxy)

Slow curing

Our “one part” approach

Epoxy monomers & photo-cationic catalyst

POTENTIALLY Fast curing (“INK”)

Epoxidized Soybean Oil

Cross-linked Network Polymers (Thermoset)

Z. J. Thompson and F. S. Bates et al.
Macromolecules (2009) 42, 2333-2335
Structures of Vegetable Oils

Soybean oil Price: $0.54/lb (2012)
Phase Transfer Epoxidation of Vegetable Oils

\[ \begin{align*}
CH_2O\overset{\text{O}}{\text{C}}-(CH_2)_7\cdot CH=CH-CH₂-CH=CH-(CH₂)₄\cdot CH₃ \\
CH-O\overset{\text{O}}{\text{C}}-(CH₂)₄\cdot CH=CH-CH₂\cdot CH=CH-(CH₂)₄\cdot CH₃ \\
CH₂O\overset{\text{O}}{\text{C}}-(CH₂)₇\cdot CH=CH-(CH₂)₇\cdot CH₃
\end{align*} \]

\[ [(C₈H₁₇)₃N(CH₃)]_₃^[PO₄[W(O)(O₂)]₄]^3^- \]

30% H₂O₂

\[ \text{Easy separation} \]

\[ \text{High yield (90%)} \]

\[ \text{By-product} = \text{water} \]

Epoxidized Soybean Oil


Photo-Cationic Initiators “ONIUM Catalyst”

Abs Quantum Yield
For Photo-acid generation
~ 20%

Photo Polymerization of Epoxidized Oils

Epoxidized Soybean Oil (ESO)

\[
\text{hv} \rightarrow \text{SbF}_6^+ \rightarrow \text{OC}_{10}H_{21}
\]

Crosslinked Network Polymer
Drawbacks to Epoxidized Vegetable Oils as Monomers

• Low glass transition (Tg < RT) temperatures limit use to non-structural applications

• Relatively slow photo-polymerization kinetics

ELO (Epoxidized Linseed Oil)
ESO (Epoxidized Soybean Oil)
Copolymerization with Terpene Oxides

Photo-polymerization of $\alpha$-Pinene Oxide and Limonene Oxide are much more reactive than EVOs.

Co-polymerizations take increase the polymerization rate for EVOs.

ELO (Epoxidized Linseed Oil)

ESO (Epoxidized Soybean Oil)
Rheology of ELO

ELO (Epoxidized Linseed Oil)

Thermally-Cured ELO:

2% wt. IOC-8
0.75% wt. 8%, Cu Napthenate
(Thermal Catalyst)

\[ G' \sim \omega^0 \]
### Elastic Moduli of Crosslinked EVOs

<table>
<thead>
<tr>
<th>Oil</th>
<th># Epoxy Groups / Monomer</th>
<th>G', Pa $(\omega = 10 \text{ rad/s})$</th>
<th>$M_x$</th>
<th>$M_x$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELO</td>
<td>7</td>
<td>$2.78 \times 10^8$</td>
<td>10.4 g/mol</td>
<td></td>
</tr>
<tr>
<td>ESO</td>
<td>6</td>
<td>$8.27 \times 10^6$</td>
<td>310 g/mol</td>
<td></td>
</tr>
<tr>
<td>VGO</td>
<td>3</td>
<td>$5.63 \times 10^5$</td>
<td>4500 g/mol</td>
<td></td>
</tr>
</tbody>
</table>

*Diagram showing the relationship between angular frequency ($\omega$, rad/s) and elastic modulus ($G'$, Pa) for Thermally-Cured EVOs.*

**Equation:**

$$G_N = \frac{\rho RT}{M_x}$$

*Note: $\rho$ is density, $R$ is the gas constant, and $T$ is temperature.*
Rheology of ELO

\[ G_N = \frac{\rho RT}{M_x} \]

\( M_x \sim 10 \text{ g/mol (?)} \)

\( M_x \sim 2000 \text{ g/mol} \)

Thermally-Cured ELO

\( M_x \sim 10 \text{ g/mol (?)} \)

Photo-Cured ELO

\( M_x \sim 2000 \text{ g/mol} \)

Crosslinked Network Polymer

\[ G', \text{ Pa} \]

\[ \omega, \text{ rad/s} \]

\[ 25^\circ C \]

\[ \gamma, 1\% \]
Conclusions

• Epoxidized vegetable oils (EVOs) can be photo-crosslinked into a thermoset materials used for “green” composite matrix and coating.

• The elastic shear moduli ($G'$) of EVOs ranges from 100 MPa ~ 1 MPa with $G' (G_N) \sim \omega^0$

• $G_N$ (thermally cured) > $G_N$ (photo-cured)

$M_x \sim 10$ g/mol (?)

$M_x \sim 2000$ g/mol
Future Work

• **Mechanical and thermal properties** of the crosslinked epoxidized vegetable oils that provide different levels of crosslinking densities.
  • Synthesis of ELO of varied degrees of epoxidation
  • $M_x$ of networked EVOs from $G_N$
  • $T_g$ at different levels of network density (i.e. $M_x$)

• **Photo-curing Process**: Interplay between **Photopolymer kinetics** and the **arrest of network formation** during crosslinking (due to the formation of “network gels”)

• **Search for co-monomers** to improve reaction kinetics and mechanical properties.
Acknowledgements

Scalable Green Chemistry

Crivello/Ryu Research Group