Bio-based Thermoset Resins and Their Composites


Michigan State University
2100 Engineering Building, East Lansing, MI, 48824
Presentation Out-line

- Introduction and motivation
- Bio-based resins, Bio-fibers and Bio-Composites
  - Biobased Epoxies and Their Composites
  - Biobased Polyurethanes and Their Composites
  - Biobased Unsaturated Polyesters and Their Composites
- Conclusions

Acknowledgements
Motivation

TECHNOLOGY:
To Improve Toughness

ECONOMY:
Economically Viable HOW?
Example: Epoxy Resin Costs 126 cents/lb.
Whereas Epoxidized Oils Costs ~ 60 Cents/lb

BLEND
of Functionalized Oil WITH Thermoset Resins?
(Thermoset Resins: Brittle & Expensive)

ECOLOGICAL BENEFIT:
Incorporation Of Bio-resources To the Maximum Permissible Extent To achieve Required Properties
Natural Fibers

- Flax
- Hemp
- Kenaf
- Jute
- Henequen
- Coir
- Wood
- Corn
- Grass
Natural/Bio-Fiber Composites (Bio-Composites)

Thermoplastic based

Biofiber- Thermoplastic (Polypropylene/PVC/PS)
Green: PLA, Cellulose esters etc.

Thermoset based

Biofiber-Thermosets (Epoxy, Polyesters, Polyurethanes)
Bio-based: Blend with functionalized Vegetable oil

HYBRID BIO-COMPOSITES
(Fiber blending/Matrix blending)
Thermoset vs. thermoplastic composites

- Use of reinforced thermoset composites: ~doubled in the last decade
- Expected to increase 47% during next 5 years through 2004
- ~65% of all composites use glass fiber - polyester composites.
- Natural fiber polyester composites: target is to replace glass-polyester composites

Matrix pattern in Polymer Composites
Bio-based Epoxies and their Composites
Reagents

DGEBA (Diglycidylether of bisphenol A)

\[
\begin{align*}
\text{O} & \quad \text{CH}_2 \text{O} \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 \text{CH}_2 \text{O} & \quad \text{OH} \\
\text{O} & \quad \text{CH}_2 \text{CH}_2 \text{O} \\
\text{C} & \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_3 \\
m = 0, 1, 2
\end{align*}
\]

J-T403 (Jeffamine T403)

\[
\begin{align*}
\text{CH}_2 & \quad \text{[OCH}_2\text{CH(CH}_3\text{)]}_X \text{NH}_2 \\
\text{CH}_3\text{CH}_2 & \quad \text{C} \quad \text{CH}_2 \quad \text{[OCH}_2\text{CH(CH}_3\text{)]}_Y \text{NH}_2 \\
\text{CH}_2 & \quad \text{[OCH}_2\text{CH(CH}_3\text{)]}_Z \text{NH}_2
\end{align*}
\]

MPDA (m-phenylene diamine)

\[
\begin{align*}
\text{NH}_2
\end{align*}
\]
Reagents: Epoxidized Soy (ESO)/Linseed Oils (ELO)

Epoxy equivalent wt. of ESO: 225-230

Epoxy equivalent wt. of ELO: 173-178
Epoxy-Primary Amine Curing Reaction

\[
\begin{align*}
\text{Epoxy:} & \quad \text{OH} \quad \text{CH}_2\text{CH}_2\text{CHCH}_2\text{O} \quad \text{CH}_3 \\
\text{Amine:} & \quad \text{R} \quad \text{NH}_2 \\
\text{Curing Reaction:} & \quad \text{HO} - \text{C} - \text{C} - \text{NHR} \\
\text{Product:} & \quad \text{HO} - \text{C} - \text{N} - \text{C} - \text{C} - \text{OH}
\end{align*}
\]
Dynamic Mechanical Analysis of Bio-based Epoxy Resin with Jeffamine T403 at 30°C

* taken from Tensile Measurements
Impact Strength and Glass Transition Temp. of Bio-based Epoxy Resin with T 403
Modulus of Elasticity & Bending Strength of Epoxy Samples containing ELO and MPDA

![Graph showing Modulus of Elasticity (MOE) and Bending Strength for different ELO concentrations.](image-url)
Impact Strength of Epoxy Samples containing MPDA and ELO

Impact Strength (J/m)

0% ELO | 30% ELO | 40% ELO | 50% ELO

Impact Strength (J/m)
ESEMs of Impact Fractured Epoxy Resin containing MPDA and ELO

Phase separation between epoxy-rich phase and ELO-rich phase
Thermogravimetric Analysis of Surface Modified Henequen (HQ)

*550 W with O₂ for 10 min.
**120 sec. of UV at 60 °C
***Epoxy compatible silane
Modulus of Elasticity (MOE) & Bending Strength of Epoxy Composites containing 30% ELO and 30V% HQ
Conclusion

- The impact strength was directly proportional to the concentration of the epoxidized oils when using J-T403.
- The modulus, bending strength, and Tg were inversely proportional to the concentration of the epoxidized oils when using J-T403.
- The impact strength was directly proportional to the concentration of the ELO when using 30 or 40% ELO and MPDA.
Bio-based Polyurethananes & their Composites
Polyurethanes: Synthesis and Uses

POLYOL + DIISOCYANATE

Fast reaction, no by-product
Wide range of polyols and isocyanates ⇒ numerous uses
## Distinguishing Characteristics of Polyols

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Elastomers, Coatings, Flexible foams</th>
<th>Rigid coatings, Rigid foams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>1,000 to 6,500</td>
<td>150 – 1,000</td>
</tr>
<tr>
<td>Functionality</td>
<td>2.0 to 3.0</td>
<td>3.0 to 8.0</td>
</tr>
<tr>
<td>Hydroxyl number</td>
<td>28 to 160</td>
<td>250 to 1,000</td>
</tr>
</tbody>
</table>

Soy phosphate ester polyol

Mw = 2304 g/mol
Functionality = 20
492 mg KOH/g
## Properties of Biobased Polyurethane's

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polyol OH ratio (JEFFOL / SOPEP)</th>
<th>Tg (℃) (DMA)</th>
<th>G’ (30℃) (MPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 / 0</td>
<td>167</td>
<td>2100</td>
<td>1.072</td>
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<tr>
<td>2</td>
<td>90 / 10</td>
<td>154</td>
<td>1431</td>
<td>0.855</td>
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<tr>
<td>3</td>
<td>75 / 25</td>
<td>142</td>
<td>1427</td>
<td>1.051</td>
</tr>
<tr>
<td>4</td>
<td>50 / 50</td>
<td>111</td>
<td>1200</td>
<td>1.088</td>
</tr>
<tr>
<td>5</td>
<td>25 / 75</td>
<td>71</td>
<td>518</td>
<td>1.069</td>
</tr>
<tr>
<td>6</td>
<td>0 / 100</td>
<td>52</td>
<td>202</td>
<td>1.064</td>
</tr>
</tbody>
</table>

**Isocyanate / OH ratio = 1.1. Jeffol 495 polyol:** polyether polyol (495 mg KOH /g) and **SOPEP** (154 mg KOH /g). Isocyanate: *polymeric diphenylmethane diisocyanate* (MDI).
“Polyol” Hybridization ⇒ Biobased PURs with acceptable properties (thermal, mechanical performances) and effective cost
Glass reinforced Polyurethanes from soy phosphate ester polyol: DMA Study

Effect of glass fiber on G’ of soy phosphate ester PU

- No fiber
- 15 wt %
- 30 wt %
- 50 wt %

Temperature (°C)

G’ (MPa)
Modulus of Elasticity (MOE), Bending Strength and Impact Strength of Glass reinforced Polyurethanes

⇒ Improvement of mechanical properties (dynamic, flexural and impact)
Impact Fractured surfaces of Glass reinforced Polyurethanes
Conclusions

- Preparation of PURs from soy phosphate ester combined with petroleum-based polyol (tuning of properties).

- Commercially available plant-based polyols: low OH content for preparation of RIGID polyurethanes ⇒ Glass reinforced PURs from SOPEP.
Unsaturated Polyester Resins and their Composites

Exterior (Natural Fiber-Polyester): Under-floor panels, engine & transmission covers

Ref.: DaimlerChrysler High Tech Report 1999
Classification

Unsaturated Polyester Resins

- Ortho resins
- Isoresins
- Bisphenol-A fumarates
- Chlorendics
- Vinyl ester resins

General purpose polyester resins (Cheapest resin)
Nonwoven Hemp – Unsaturated Polyester Composites

A: Neat polyester, B: Raw Hemp (30 vol.%)-polyester, C: Surface treated Hemp-polyester
CONCLUSIONS

- Thermoset resins can be effectively blended with functionalized vegetable oil (Stiffness-toughness balance)
- Different Bio-based polyurethanes can be designed and engineered - Reinforcement with bio-fiber/glass fiber result in superior physico-mechanical properties.
- Bio-Composites can Replace/Substitute Glass Fiber Composites
  - Energy benefit
  - Renewability, biodegradability, CO₂ sequestration
  - Independent of dwindling petro-sources
  - Value-Added Opportunity for Agriculture Industry
Acknowledgements

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