Green Epoxy Resin System Based on Lignin and Tung Oil and Its Application in Epoxy Asphalt

Ran Li & Junna Xin & Jinwen Zhang

School of Mechanical and Materials Engineering
Composite Materials and Engineering Center
Washington State University

Aug 10 2017
Outlines

❖ Background

❖ Partially depolymerization of lignin

❖ Preparation and characterization of lignin based epoxy monomer

❖ Preparation and characterization of epoxy asphalt

❖ Conclusions
Background

Rutting

Crack

BPA DETECTED IN 93% OF PEOPLE TESTED

Epoxy resin

Lignin

Epoxy asphalt

Vegetable oil

Bio-based epoxy resins
Conversion of Lignin

Woody biomass

Pretreatment & prefractionation

Lignin

Pyrolysis, thermolysis, hydrogenolysis, gasification, hydrolysis, oxidation

Direct-modification

Methylation, butylation, glycidylation, amination, acetylation

Materials (blends, epoxy resins, PUs, absorbent, etc)

Low compatibility and melt processibility

Depolymerization

Chemicals (phenols, vanillin, syringaldehyde, aliphatics, etc)

Low yield, complicated monomer mixture; severe conditions, high energy cost

Fuel (Gas, C8 or C9 alkanes, etc)
Modification of lignin

Lignin → Mild depolymerization → Partially depolymerized lignin (PDL)

- Partially depolymerize C-O-C rather than C-C

Engineering polymer materials (blends, epoxy resins, PUs)

- Improved compatibility and melt processibility

Major linkages found in lignin: (A) β-O-4, (B) 5-5, (C)α-O-4, (D)β-5, (E) β-β, (F)4-O-5, and (G) β-1
Effect of reaction parameters on yield

Effects of temperature (a) and catalyst content (b) on yield of hydrogenation of enzymolysis lignin. Reaction conditions: lignin/solvent = 15 mg/mL, H\textsubscript{2} pressure = 2.0 MPa, t = 3.5 h, Raney Ni Conc. = 13.3\% (a), T = 160 °C (b).

Solubility of lignin before and after hydrogenolysis

Concentration: 300mg/10mL
NaOH Sol. = NaOH 3% in dioxane/water (1/1, v/v)
**$^{31}$P NMR characterization**

<table>
<thead>
<tr>
<th>Structure</th>
<th>$^{31}$P NMR (ppm)</th>
<th>Hydroxyl value (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic</td>
<td>145.5-150.0</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>Aromatic</td>
<td>136.6-144.7</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.22</td>
</tr>
<tr>
<td>Carboxylic</td>
<td>133.6-136.6</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td>Total</td>
<td>3.58</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.38</td>
</tr>
</tbody>
</table>

Before hydrogenation

Diagram showing NMR characterization with peaks labeled as Aliphatic OH, Aromatic OH, Carboxylic Acid OH, and TMDP hydrolysis product. Diagram also includes a reaction scheme involving oxidative phosphorylation with internal standard.
**Molecular weight of PDL**

<table>
<thead>
<tr>
<th>Hydrogenolysis Temp.</th>
<th>Mw (g/mol)</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 °C</td>
<td>991</td>
<td>714</td>
<td>1.39</td>
</tr>
<tr>
<td>160 °C</td>
<td>1359</td>
<td>804</td>
<td>1.69</td>
</tr>
<tr>
<td>180 °C</td>
<td>1147</td>
<td>764</td>
<td>1.50</td>
</tr>
<tr>
<td>200 °C</td>
<td>959</td>
<td>719</td>
<td>1.33</td>
</tr>
</tbody>
</table>
Preparation of Lignin (PDL)-derived epoxy monomer

**Equation:**

\[
\text{Partially depolymerized lignin (PDL)} + \text{Cat. NaOH, 4 h} \rightarrow \text{PDL-epoxy}
\]

**Chemical Reaction:**

- Partially depolymerized lignin (PDL) + Cat. NaOH, 4 h purification
- Mixing with asphalt

**References:**

$^{31}$P NMR characterization of PDL-epoxy monomers

<table>
<thead>
<tr>
<th></th>
<th>Hydroxyl value (mmol/g)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic</td>
<td>Aromatic</td>
</tr>
<tr>
<td>PDL-epoxy-117 °C</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>PDL-epoxy-70 °C</td>
<td>2.4</td>
<td>1.7</td>
</tr>
<tr>
<td>PDL</td>
<td>0.7</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Cyclohexanol (IS)
Preparation of Lignin (PDL)-derived epoxy based epoxy resin

Thermal mechanical properties and thermal stability

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>$T_g$ (°C)</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_{10%}$ (°C)</th>
<th>Char yield at 585 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDL-epoxy/ME-MA</td>
<td>94.3</td>
<td>272.3</td>
<td>311.1</td>
<td>34.7 %</td>
</tr>
<tr>
<td>DER332/ME-MA</td>
<td>36.1</td>
<td>219.8</td>
<td>289.9</td>
<td>6.43 %</td>
</tr>
</tbody>
</table>

$T_{5\%}$ and $T_{10\%}$ - temperature of 5% degradation and 10% degradation.
Application of Lignin (PDL)-derived epoxy for epoxy asphalt

Effects of epoxy resin contents on the rheological properties of modified asphalt blends by PDL-epoxy and DER332.

![Graph showing the relationship between G*/sin(δ) and temperature for different samples.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>7.5%</th>
<th>15%</th>
<th>22.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DER332/ME-MA</td>
<td>84</td>
<td>89</td>
<td>94</td>
</tr>
<tr>
<td>PDL-epoxy/ME-MA</td>
<td>78</td>
<td>84</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

*The temperature at which G*/sin δ is equal to 1 kPa (Strategic Highway Research Program (SHRP) tests)

*High-performance grade (PG, °C)
Effects of epoxy resin contents on the rheological properties of modified asphalt blends by PDL-epoxy and DER332.
Conclusions

- Lignin can be partially depolymerized to yield low MW oligomers by hydrogenolysis under the catalysis of Raney Ni in alkaline solution of mixed dioxane/H₂O solvent or base catalyzed depolymerization in methanol under moderate temperature and pressure.

- The resulting PDL can be effectively turned into epoxy monomer by reacting with epichlorohydrin.

- Addition of epoxy resin has improved the high temperature performance and viscoelasticity of the asphalt binder.

- The properties of epoxy asphalt increased with the increasing of the epoxy resin contents.

- By varying the epoxy resin content, rheological properties of the modified asphalt can be greatly regulated.
Acknowledgements

Contributors

- Junna Xin
- Mei Li
- Pei Zhang
- Jinwen Zhang

Financial support

- Northwest Advanced Renewables Alliance (NARA), was funded by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30416 from the USDA National Institute of Food and Agriculture.
- The Federal Highway Administration (FHWA). Grant no. DTFH61-12-R-00056
Thank You!