Alternatives in Epoxy Toughening

TRFA 2008 Annual Meeting
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Chicago, ILL
A Study on Liquid Epoxy Modifiers

Effect on formulation viscosity and cured formulation performance
Two Primary Uses of Modified Epoxies

- Adhesives
- Structural Support
Adhesion

- Modified Epoxies are known for good adhesion
- Modifiers may or may not be compatible in cured formulation
- Modifier backbone has impact on adhesion believed to be tied to polarity
Structural Support

- Modified epoxies are used extensively in structural reinforcement.
- Modifiers provide either ductility or toughening to epoxies.
- Ductility provided by compatible modifier.
- Toughening provided by incompatible modifier.
How Toughening Works

- Modifier phase separates during cure because of modifier incompatibility
- Generates micro size occlusions in the epoxy matrix
- Absorbs fracture energy
Modifier Compatibility
SEM Micrographs
Modifier Compatibility

IA  IB  IC
Project Overview

- What’s this about?
- How does it work?
- What’s the model?
- What materials?
- What’s the chemistry?
- What tests?
- What’s the results?
- What are the conclusions?
Structure/Property Relationship of Liquid Epoxy Modifiers
How Terminal and Backbone Functionalities & Backbone Size Affect Formulation Viscosity, and Tg, Adhesion & Fracture Toughness of Cured Epoxy Formulations
Modifier Types Studied

- **Glycidyl Polypropylene ether**
  - 450 mw, 2000 mw triol, 3000 mw triol, 4000 mw triol and 4000 mw diol

- **Glycidyl Esters**
  - CTB and CTBN based – differing in ACN content
  - 3000 mw Dimer Ester
Modifier Types Studied

- **Bis A Epoxy Adducted Polyesters**
  - Dimer acid based – 1500 & 3000 mw
  - CTB and CTBN based – differing in ACN content

- **Diluent Adducted CTBN**
  - Neopentylglycol diglycidyl ether
  - Cyclohexanenedimethanol diglycidyl ether
Back Bone Structures

Polyether

Polyester

Butadiene/acrylonitrile copolymer
End Group Chemistries

Epichlorohydrin Reaction products
Glycidyl Polyethers

Glycidyl CTBNs & Polyesters
End Group Chemistries

Epoxy Adduction Products from Resin or Diluent

Epoxy Adducted CTBN & Dimer Esters (Contains excess resin)

\[
\begin{align*}
R & \quad O \quad O \quad OH \quad O \quad | \quad O \quad O \\
& \quad C \quad O \quad C
\end{align*}
\]

Diluent Adducted CTBN (contains excess diluent)

\[
\begin{align*}
R & \quad O \quad O \quad OH \quad O \quad R' \quad O \quad \text{O} \\
& \quad C \quad O \quad C
\end{align*}
\]
Investigation setup

- Determine Model & Set Conditions
  - Bisphenol A liquid epoxy resin
  - 15% Modifier based on epoxy resin
  - 6 phr dicyandiamide
  - 3 phr U52m
  - 2 phr fumed silica

- Cure Schedule – 125°C for 2 hours
Test Procedures

- Modifier viscosity at 25°C  
  ASTM D2393
- Formulation viscosity at 25°C  
  ASTM D2393
- Tg  
  ASTM E1356
- Lap shear  
  ASTM D1002
- T Peel  
  ASTM D1876
- Fracture toughness (K1c & G1c)  
  ASTM D5045
### Glycidyl Polyether Glycols

<table>
<thead>
<tr>
<th>Modifier</th>
<th>none</th>
<th>425 mw diol</th>
<th>caster oil triol</th>
<th>2000 mw triol</th>
<th>3000 mw triol</th>
<th>4000 mw triol</th>
<th>4000 mw diol</th>
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</thead>
<tbody>
<tr>
<td>Modifier Viscosity (cps)</td>
<td>0</td>
<td>75</td>
<td>400</td>
<td>275</td>
<td>420</td>
<td>750</td>
<td>912</td>
</tr>
<tr>
<td>Mix Viscosity (cps)</td>
<td>38900</td>
<td>11700</td>
<td>15550</td>
<td>13225</td>
<td>21050</td>
<td>26000</td>
<td>26000</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>134.8</td>
<td>89.72</td>
<td>90.14</td>
<td>106.34</td>
<td>116.78</td>
<td>118.11</td>
<td>120.64</td>
</tr>
<tr>
<td>Lap Shear (PSI)</td>
<td>1242</td>
<td>1844</td>
<td>1812</td>
<td>2143</td>
<td>1690</td>
<td>1302</td>
<td>1131</td>
</tr>
<tr>
<td>T-Peels (PLI)</td>
<td>7.89</td>
<td>8.3</td>
<td>7.9</td>
<td>13.37</td>
<td>11.85</td>
<td>10.74</td>
<td>8.55</td>
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<tr>
<td>K1c (MN/m^1.5)</td>
<td>0.56</td>
<td>2.46</td>
<td>2.61</td>
<td>1.94</td>
<td>1.56</td>
<td>1.26</td>
<td>1.29</td>
</tr>
<tr>
<td>G1c (KJ/m^2)</td>
<td>0.3</td>
<td>1.8</td>
<td>1.9</td>
<td>1.6</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>
What does this tell us about glycidyl polyethers

- Provide low modifier and formulation viscosities
- TG increases & compatibility decreases with Mw and molecular size
- Adhesion decreases with increasing Mw
- Toughness (K1c) decreases with increasing Mw
Bis A Epoxy Adducted Polyesters

<table>
<thead>
<tr>
<th>Modifier</th>
<th>none</th>
<th>1500 mw</th>
<th>3000 mw</th>
<th>3550 mw</th>
<th>3150 mw</th>
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<tbody>
<tr>
<td>Polyester</td>
<td>18% AN</td>
<td>26% AN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adduct</td>
<td>CTBN adduct</td>
<td>CTBN adduct</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modifier Viscosity (cps @ 25°C)</td>
<td>0</td>
<td>131500</td>
<td>106750</td>
<td>200000</td>
<td>450000</td>
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<tr>
<td>Mix Viscosity (cps @ 25°C)</td>
<td>38900</td>
<td>106000</td>
<td>96000</td>
<td>117500</td>
<td>157000</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>134.8</td>
<td>106.1</td>
<td>113.0</td>
<td>117.7</td>
<td>112.6</td>
</tr>
<tr>
<td>Lap Shear (psi)</td>
<td>1242</td>
<td>1507</td>
<td>2317</td>
<td>2211</td>
<td>2421</td>
</tr>
<tr>
<td>T-Peel (pli)</td>
<td>7.9</td>
<td>15.7</td>
<td>17.5</td>
<td>17.3</td>
<td>19.0</td>
</tr>
<tr>
<td>K1c (MN/m^{1.5})</td>
<td>0.56</td>
<td>2.04</td>
<td>1.93</td>
<td>1.33</td>
<td>1.65</td>
</tr>
<tr>
<td>G1c (KJ/m²)</td>
<td>0.3</td>
<td>1.5</td>
<td>1.4</td>
<td>1.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>
What does this tell us about Bis A Epoxy Adducted Polyesters

- Dimer polyester adducts have lower viscosity
- CTBN adducts provide higher Tgs
- Adhesive properties are similar through the set
- Dimer polyester adducts have slightly better Fracture Toughness
**Glycidyl Polyesters**

<table>
<thead>
<tr>
<th>Modifier</th>
<th>none</th>
<th>3000 mw</th>
<th>4200 mw</th>
<th>3800 mw</th>
<th>3550 mw</th>
<th>3150 mw</th>
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</thead>
<tbody>
<tr>
<td>Glycidyl Dimer</td>
<td>CTB</td>
<td>CTBN</td>
<td>CTBN</td>
<td>CTBN</td>
<td>CTBN</td>
<td></td>
</tr>
<tr>
<td>Modifier Viscosity (cps@ 25°C)</td>
<td>0</td>
<td>38500</td>
<td>43900</td>
<td>79200</td>
<td>120900</td>
<td>576000</td>
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<tr>
<td>Mix Viscosity (cps @ 25°C)</td>
<td>38900</td>
<td>47800</td>
<td>40200</td>
<td>50000</td>
<td>60600</td>
<td>68900</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>134.8</td>
<td>116.9</td>
<td>126.2</td>
<td>122.3</td>
<td>124.0</td>
<td>123.6</td>
</tr>
<tr>
<td>Lap Shear (psi)</td>
<td>1242</td>
<td>1914</td>
<td>2100</td>
<td>2381</td>
<td>2477</td>
<td>2468</td>
</tr>
<tr>
<td>T-Peel (pli)</td>
<td>7.9</td>
<td>17.6</td>
<td>13.4</td>
<td>28.4</td>
<td>20.9</td>
<td>21.3</td>
</tr>
<tr>
<td>K1c (MN/m^1.5)</td>
<td>0.56</td>
<td>1.80</td>
<td>1.38</td>
<td>1.35</td>
<td>1.31</td>
<td>1.43</td>
</tr>
<tr>
<td>G1c (KJ/M2)</td>
<td>0.3</td>
<td>1.2</td>
<td>0.7</td>
<td>0.8</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>
What does this tell us about Glycidyl Esters

- Formulation viscosity is < or = modifier viscosity
- Tg are notably higher than past studies
- Lap Shears higher with nitrile content
- Glycidyl CTBNs have higher T’peel
- Glycidyl dimer ester exhibits highest toughness
## Diluent addducted CTBNs

<table>
<thead>
<tr>
<th>Modifier</th>
<th>none</th>
<th>1300X13</th>
<th>1300X8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentyl glycol</td>
<td>Cyclohexane</td>
<td>diglycidyl ether</td>
<td>dimethanol</td>
</tr>
<tr>
<td>diglycidyl ether adduct</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Modifier Viscosity (cps@25°C) | 0 | 6000 | 20000 |
| Mix Viscosity (cps@25°C) | 38900 | 31400 | 50400 |
| Tg (°C) | 134.8 | 102.4 | 106.6 |
| Lap Shear (psi) | 1242 | 2314 | 1958 |
| T-Peels (pli) | 7.9 | 12.0 | 9.5 |
| K1c (MN/m1.5) | 0.56 | 0.79 | 1.17 |
| G1c (KJ/M2) | 0.3 | 0.5 | 0.8 |
What does this tell us about Diluent Adducted CTBNs

- Tg is significantly lowered by the presence of the diluent
- Adhesive and Toughening properties are better than unmodified formulation but not great
# Comparison of the Best

<table>
<thead>
<tr>
<th>Modifier</th>
<th>1550 mw</th>
<th>4000 mw</th>
<th>3000 mw</th>
<th>3150 mw</th>
<th>3000 mw</th>
<th>4200 mw</th>
<th>3150 mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor oil</td>
<td>Glycidyl</td>
<td>Polyester</td>
<td>26% AN</td>
<td>Glycidyl</td>
<td>Glycidyl</td>
<td>Glycidyl</td>
<td></td>
</tr>
<tr>
<td>Glycidyl Ether triol</td>
<td>Ether diol</td>
<td>Adduct</td>
<td>CTBN adduct</td>
<td>Polyester</td>
<td>CTB</td>
<td>CTBN</td>
<td></td>
</tr>
<tr>
<td>Modifier Viscosity</td>
<td>400</td>
<td>912</td>
<td>106750</td>
<td>450000</td>
<td>38500</td>
<td>43900</td>
<td>576000</td>
</tr>
<tr>
<td>Mix Viscosity (cps)</td>
<td>15550</td>
<td>26000</td>
<td>96000</td>
<td>157000</td>
<td>47800</td>
<td>40200</td>
<td>68900</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>90.1</td>
<td>120.6</td>
<td>113.0</td>
<td>112.6</td>
<td>116.9</td>
<td>126.2</td>
<td>123.6</td>
</tr>
<tr>
<td>Lap Shear (psi)</td>
<td>1812</td>
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<td>7.9</td>
<td>8.6</td>
<td>17.5</td>
<td>19.0</td>
<td>17.6</td>
<td>13.4</td>
<td>21.3</td>
</tr>
<tr>
<td>$K_{1c}$ (MN/m$^{1.5}$)</td>
<td>2.6</td>
<td>1.29</td>
<td>1.93</td>
<td>1.65</td>
<td>1.8</td>
<td>1.38</td>
<td>1.43</td>
</tr>
<tr>
<td>$G_{1c}$ (KJ/m$^2$)</td>
<td>1.9</td>
<td>0.8</td>
<td>1.4</td>
<td>1.1</td>
<td>1.2</td>
<td>0.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Overall Comparison

- **Viscosity:**
  Glycidyl Polyethers << Glycidyl Polyesters < Polyester Adducts

- **Tg:**
  Glycidyl Polyesters > High Mw Glycidyl Polyethers > Polyester Adducts > Low Mw Glycidyl Ethers

- **Adhesion:**
  Glycidyl Polyesters > Polyester Adducts > Glycidyl Polyethers

- **Toughness:**
  Low Mw Glycidyl Polyethers > Polyester Adducts > Glycidyl Polyesters > High Mw Glycidyl Polyethers
Overall Conclusions

- Tg increases backbone increases in Mw and size
- Tg affected by end-group functionality, a compatibility issue
- Adhesion affected by modifier backbone
  - CTBN=CTB=DPE>DACTBN>GPEG
Overall Conclusions

- Adhesion increases with backbone polarity
- Fracture toughness (K1c) affected by:
  - Molecular weight/Compatibility
  - End-group functionality
  - Backbone structure

  DimerPE > CTBN=CTB>> DACTBN > GPEG
Best in Study

Glycidyl Polyesters

Glycidated carboxylic acid terminated dimer polyesters, polybutadiene, or butadiene/acrylonitrile copolymers
Acknowledgements

- James Shirk for synthesis efforts
- Scott Boryschuk for applications testing
- Charles Zarnitz for technical advise
- David Egan for applications advise
Thank You