Advantages of Azelate-Based Polyester Polyols and Their Performance Benefits in Model Polyurethane Coatings

Eric Geiger, Technical Director
Overview

➢ Background
  ▪ Azelate (C₉ Diacid) and Dimerate (C₃₆ Diacid) Polyols
  ▪ Odd-Even Effect and Influence on Properties
  ▪ Production Process and Performance Benefits

➢ Polyols for CASE Applications
  ▪ Product Overview – Commercial and Experimental
  ▪ Structure-Property Relationships
  ▪ Model Formulation Comparisons
  ▪ Performance Properties Achieved For Model Formulations

➢ Conclusions
Background

- Aliphatic polyester polyol for PU most commonly based on adipic acid (C₆ diacid)
  - Petrochemical based, known to form lactone, high NOx emissions
  - No significant manufacturer using renewable feedstock
- Limited options for commercial aliphatic diacids
  - Succinic (C₄), Sebacic (C₁₀)
  - Azelaic (C₉)
- Capitalizing on the “odd-even” effect in polyol structure-property

Odd-Even Effect: Melting Point of Linear Diols and Diacids vs. Carbon Chain Length
Azelaic Acid Production via Ozonolysis
Dimer Diacid Production via Addition

Oleic acid (C\textsubscript{18:1} monoacid from triglyceride)

$\text{O}_3, \text{O}_2$

Pelargonic acid (nonanoic acid)
Azelaic acid (nonanedioic acid)

Representative structure:
Dimer diacid (C\textsubscript{36} dibasic acid)
Esterification of Azelaic and Dimer Diacids

Glycols Used in Stepwise Polymerization

- Ethylene Glycol (EG)
- Diethylene Glycol (DEG)
- Propylene Glycol (PG)
- 1,3-Propanediol (PDO)
- 1,4-Propanediol (PDO)
- 1,4-Butanediol (BDO)
- 1,6-Hexanediol (HDO)
- Neopentyl Glycol (NPG)
- 2,4-Diethyl Pentanediol (PD-9)
- Cyclohexane Dimethanol (CHDM)
- 2-Butyl-2-Ethyl Propanediol (BEPD)
## Polyols for CASE Applications

### Typical Polyol Properties

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (Daltons)</td>
<td>320</td>
<td>1000</td>
<td>2200</td>
<td>2200</td>
<td>410</td>
<td>1000</td>
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<tr>
<td>Diacid Used</td>
<td>Azelaic (C₉)</td>
<td>Azelaic (C₉)</td>
<td>Azelaic (C₉)</td>
<td>Azelaic (C₉)</td>
<td>Azelaic (C₉)</td>
<td>Dimer (C₃₆)</td>
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<tr>
<td>Glycol Used</td>
<td>EG</td>
<td>EG</td>
<td>EG</td>
<td>EG</td>
<td>Glycerol</td>
<td>EG</td>
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<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.7</td>
<td>2.2</td>
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<tr>
<td>Hydroxyl Value (mg KOH/g)</td>
<td>350</td>
<td>105</td>
<td>50</td>
<td>50</td>
<td>370</td>
<td>105</td>
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<tr>
<td>Acid Value (mg KOH/g)</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Brookfield Viscosity @ 25C (cP)</td>
<td>310</td>
<td>1320</td>
<td>5125</td>
<td>n/a*</td>
<td>1715</td>
<td>2600</td>
</tr>
<tr>
<td>Glass Transition Temperature (°C)</td>
<td>-67</td>
<td>-58</td>
<td>-51</td>
<td>-54</td>
<td>-57</td>
<td>-59</td>
</tr>
<tr>
<td>Bio-content (wt%)</td>
<td>69</td>
<td>78</td>
<td>82</td>
<td>82</td>
<td>99</td>
<td>90</td>
</tr>
</tbody>
</table>

*Waxy solid at 25°C, 500 cP @ 75°C
### Experimental Azelate Polyols

Typical Polyol Properties for 1000 MW diols

<table>
<thead>
<tr>
<th>Glycol Used</th>
<th>EG</th>
<th>DEG</th>
<th>PG</th>
<th>PDO</th>
<th>BDO</th>
<th>HDO</th>
<th>NPG</th>
<th>CHDM</th>
<th>PD-9</th>
<th>BEPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>State @ 25°C</td>
<td>Solid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Brookfield Viscosity @ 25°C (cP)</td>
<td>n/a</td>
<td>1400</td>
<td>1500</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>4300</td>
<td>7100</td>
<td>2300</td>
<td>1900</td>
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<tr>
<td>Glass Transition Temperature (°C)*</td>
<td>n/a</td>
<td>n/a</td>
<td>-55</td>
<td>-30</td>
<td>-45</td>
<td>-26</td>
<td>-61</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Bio-content, calculated (wt%)</td>
<td>67</td>
<td>58</td>
<td>65</td>
<td>65</td>
<td>62</td>
<td>55</td>
<td>58</td>
<td>47</td>
<td>45</td>
<td>46</td>
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</tbody>
</table>

* Tg to be determined for some polyols, will be furnished upon request.
Rheology Studies Azelate Polyols
25C, 50C Shear Sweep

Viscosity (Poise) vs. Shear Rate (s⁻¹)

- EG azelate 1K
- PDO azelate 1K
- NPG azelate 1K
- CHDM azelate 1K
- PD-9 azelate 1K
- BEPD azelate 1K

Viscosity (Poise) vs. Shear Rate (s⁻¹)

- DEG azelate 2K
- PG azelate 2K
- NPG azelate 2K
- CHDM azelate 2K
- PD-9 azelate 2K
- BEPD azelate 2K
Rheology Studies Dimerate Polyols
Shear Sweep and Temperature Ramp 1000 MW Polyols

- Viscosity less dependent on glycol used than seen in azelates
- Viscosity trends up as glycol chain length increases
- NPG shows more shear thinning than others
- All dimerates are liquid at ambient
Hansen Solubility Parameters

Commercial Polyols

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Polyol (Dalton)</th>
<th>MW (Dalton)</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG Dimerate</td>
<td>F</td>
<td>1000</td>
<td>16.7</td>
<td>5.8</td>
<td>7.9</td>
<td>8.9</td>
</tr>
<tr>
<td>EG Azelate</td>
<td>E</td>
<td>410</td>
<td>16.6</td>
<td>9.9</td>
<td>11.4</td>
<td>8.0</td>
</tr>
<tr>
<td>EG Azelate</td>
<td>A</td>
<td>320</td>
<td>16.7</td>
<td>9.4</td>
<td>10.8</td>
<td>8.0</td>
</tr>
<tr>
<td>EG Azelate</td>
<td>D</td>
<td>2200</td>
<td>17.0</td>
<td>9.0</td>
<td>7.2</td>
<td>8.0</td>
</tr>
<tr>
<td>EG Azelate</td>
<td>C</td>
<td>2200</td>
<td>17.0</td>
<td>9.0</td>
<td>7.2</td>
<td>8.0</td>
</tr>
<tr>
<td>EG Azelate</td>
<td>B</td>
<td>1000</td>
<td>17.0</td>
<td>9.0</td>
<td>7.2</td>
<td>8.0</td>
</tr>
<tr>
<td>GLY Azelate</td>
<td>E</td>
<td>410</td>
<td>16.6</td>
<td>9.9</td>
<td>11.4</td>
<td>8.0</td>
</tr>
<tr>
<td>EG Dimerate</td>
<td>F</td>
<td>1000</td>
<td>16.7</td>
<td>5.8</td>
<td>7.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

A and E Polyols
- Show more polar and hydrogen-bonding character
- Only hydrocarbons failed to dissolve

B, C, and D Polyols
- Common polar aprotic solvents were successful
- Protic solvents and aliphatic hydrocarbons were unsuccessful

F Polyol
- Lower polarity due to dimer structure
- Slightly higher hydrogen-bonding due to higher functionality

14535 polyol
- 14637 polyol showed more complex behavior, and even higher polar and hydrogen-bonding character
## Hansen Solubility Parameters

### Experimental Azelate and Dimerate 1000 MW Polyols

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG Azelate</td>
<td>17.0</td>
<td>9.0</td>
<td>7.2</td>
<td>8.0</td>
</tr>
<tr>
<td>DEG Azelate</td>
<td>16.8</td>
<td>9.2</td>
<td>9.0</td>
<td>7.6</td>
</tr>
<tr>
<td>PG Azelate</td>
<td>16.7</td>
<td>8.7</td>
<td>9.7</td>
<td>11.5</td>
</tr>
<tr>
<td>PDO Azelate</td>
<td>16.6</td>
<td>7.7</td>
<td>6.7</td>
<td>7.7</td>
</tr>
<tr>
<td>BDO Azelate</td>
<td>16.9</td>
<td>8.5</td>
<td>8.2</td>
<td>11.2</td>
</tr>
<tr>
<td>HDO Azelate</td>
<td>16.6</td>
<td>6.9</td>
<td>6.6</td>
<td>9.4</td>
</tr>
<tr>
<td>NPG Azelate</td>
<td>16.7</td>
<td>8.7</td>
<td>9.7</td>
<td>11.5</td>
</tr>
</tbody>
</table>

- **Experimental Azelate Polyols**
  - EG azelate (experimental) results identical to commercial 1K, 2K polyols
  - DEG azelate: alcohols successful
  - PG and NPG azelate: alcohols successful, unsuccessful only in aliphatic hydrocarbon and DEG
  - BDO azelate: larger HSP and $R_0$ values than expected, may be due to odd-even effect
  - HDO azelate: cyclohexane successful

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG Dimerate</td>
<td>16.7</td>
<td>5.8</td>
<td>7.9</td>
<td>8.9</td>
</tr>
<tr>
<td>DEG Dimerate</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>PG Dimerate</td>
<td>16.6</td>
<td>5.1</td>
<td>7.6</td>
<td>9.0</td>
</tr>
<tr>
<td>BDO Dimerate</td>
<td>16.7</td>
<td>4.6</td>
<td>7.6</td>
<td>9.8</td>
</tr>
<tr>
<td>HDO Dimerate</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>NPG Dimerate</td>
<td>16.5</td>
<td>4.7</td>
<td>7.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

- **Experimental Dimerate Polyols**
  - Dimerate results close to one another, less dependent on glycol used
  - EG dimerate successful in DMF, other dimers not
  - BDO dimerate: unsuccessful in acetone
  - NPG dimerate: hexane successful
Formulation of Azelate Polyols
Coatings Based on Model Formulations

- Simple model formulas to demonstrate polyol comparisons
  - 2K PU formulas, unpigmented/unfilled
  - Target similar formulations for each polyol chemistry for ease of comparison
  - Chain extend/crosslink with amine tetrol
  - Cure w/ HDI trimer, 1:1 vol
  - Apply via air spray from 50% MEK, DTM ground CRS, cure 1 d @ 70C

- Basic coating characteristics compared
  - Chemical resistance
  - Weathering resistance (QUV)
  - Hydrolysis resistance (solid elastomer)
  - Water Vapor Transmission (ASTM D1653)
Model Coating Properties
Azelate vs. Alternative

- Azelate-based systems give soft, glossy coatings, transparent films, acceptable adhesion DTM, good compatibility with amine tetrol chain extender
- Azelate-based systems show large variation in gel time depending on glycol used to form azelate, improved compatibility with chain extender compared to adipate
- Finished products using azelate polyols may require less solvent for reactivity moderation (potential benefits include lower VOC or longer pot life)

<table>
<thead>
<tr>
<th>Gel time (hr)</th>
<th>B</th>
<th>DEG adipate</th>
<th>DEG azelate</th>
<th>PG azelate</th>
<th>NPG azelate</th>
<th>CHDM azelate</th>
<th>PD-9 azelate</th>
<th>BEPD azelate</th>
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<tbody>
<tr>
<td></td>
<td>0.75</td>
<td>0.25</td>
<td>4</td>
<td>0.75</td>
<td>5</td>
<td>0.75</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td><strong>Film quality</strong></td>
<td></td>
<td></td>
<td>clear, good quality film</td>
<td>clear, good quality film</td>
<td>clear, good quality film</td>
<td>clear, good quality film</td>
<td>clear, good quality film</td>
<td>clear, good quality film</td>
</tr>
<tr>
<td>B</td>
<td>3B</td>
<td>2B</td>
<td>3B</td>
<td>3B</td>
<td>2B</td>
<td>F</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Gloss 60°</td>
<td>105</td>
<td>99</td>
<td>102</td>
<td>101</td>
<td>100</td>
<td>105</td>
<td>104</td>
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## Azelate Polyol Coating Chemical Resistance
### 24 Hour Spot Test

<table>
<thead>
<tr>
<th>Substance</th>
<th>B</th>
<th>DEG adipate</th>
<th>DEG azelate</th>
<th>PG azelate</th>
<th>NPG azelate</th>
<th>CHDM azelate</th>
<th>PD-9 azelate</th>
<th>BEPD azelate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid, glacial</td>
<td>G</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
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<td>NR</td>
</tr>
<tr>
<td>Chloroform</td>
<td>E</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>DEET (Insect repellent)</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>E</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>E</td>
<td>E</td>
<td>G</td>
</tr>
<tr>
<td>Disinfectant</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Hydrochloric acid 37%</td>
<td>G</td>
<td>E</td>
<td>NR</td>
<td>G</td>
<td>G</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Ketchup</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Methanol</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
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<tr>
<td>Methylene chloride</td>
<td>G</td>
<td>E</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Skydrol LD-4</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Sodium hypochlorite 8% (bleach)</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>E</td>
<td>E</td>
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</tr>
<tr>
<td>Sulfuric acid 30%</td>
<td>G</td>
<td>NR</td>
<td>NR</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Sunscreen lotion</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>Vinegar</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>G</td>
<td>E</td>
</tr>
</tbody>
</table>

- PU based on azelate polyols showed
  - Excellent resistance to aliphatic and aromatic hydrocarbons, glycols, water, polar aprotic solvents, bleach
  - Least differentiation against acids and chlorinated solvents
  - Strongest performance against bases
  - CHDM azelate PU notable for Skydrol

- 32 different individual chemicals or substances used for this testing included:
  - Acids & Bases
  - Polar aprotic solvents
  - Hydrocarbons
  - Polar and non-polar organics
  - Aqueous mixtures
  - Commonly encountered substances

E = Excellent  
G = Good  
NR = Not recommended
Accelerated Weathering (QUV)

DTM Panels, evaluated at 3000 hr exposure, 500 hr intervals

- Azelate polyol samples’ gloss retention was excellent after 3000 hours. No chalking or discoloration were noted for any of the azelate polyol systems.
- Epoxy control discolored, chalked
Solid Elastomer Tensile Properties
Initial Tensile Strength, Elongation, C-Tear

CHDM Azelate sample tested at 2”/min, all others @ 20”/min
Solid Elastomer Hydrolysis Resistance
Water Soak 75C - Water Uptake
Solid Elastomer Hydrolysis Resistance
Water Soak 75C - Tensile Strength Loss
Water Vapor Transmission
ASTM D1653 Procedure B

Water Vapor Transmission (g/m²/24hr)

- DEG adipate
- Caprolactone
- B
- F
- EG azelate
- DEG azelate
- PG azelate
- PDO azelate
- BDO azelate
- HDO azelate
- NPG azelate
- CHDM azelate
- PD-9 azelate
- BEPD azelate

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Conclusions

- Azelate and dimerate polyol structure-property relationships
  - Choice of glycol used and how this affects polyol properties and performance
  - Compare to alternative commercial chemistry where possible

- Azelate and dimerate polyols offer application and performance benefits over alternative commercial chemistry
  - More hydrophobic and hydrolytically stable than alternative polyol
  - Versions with branched diol offer potential for high performance with improved formulation, ease of handling and use
  - Flexibility in the backbone, with very low Tg
  - Unique chemistry available in polyesters with alternative glycols
  - High renewable carbon content

- Model formulations based on azelate and dimerate polyols offer:
  - Excellent combination of moisture, chemical and UV resistance
  - Good to excellent elastomeric properties, depending on the diol
  - Low water pick up, good retention of properties
  - Low water vapor transmission
  - High gloss

Emery Oleochemicals has commercialized azelate and dimerate polyols to meet the market demand for performance-oriented polyols that also offer the benefit of sustainability due to high renewable carbon content. Ongoing development is revealing new approaches for high-performance renewable content polyol products to meet the evolving needs of the polyurethane industry.
Renewable CASE Polyols
Performance Benefits

Unique polyol technology platform based on naturally-derived azelaic acid or dimer diacid. Produced with similar structure/method to petrochemical polyester polyols, providing a high degree of design freedom and ease of use.

- Structural similarity to CASE petrochemical polyols, but with high renewable content
- Engineered to perform (process and properties)
- More hydrophobic
- Based on well-established feedstocks
- Overall value

Renewable CASE Polyols Performance Benefits
THANK YOU

For more information, contact: efp.americas@emeryoleo.com