Advanced Materials

Raising performance with accelerators and hardeners
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<td></td>
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<td></td>
</tr>
</tbody>
</table>
**Synopsis**

- Anhydrides are well appreciated curing agents for epoxy resins when formulators look for hardeners providing low viscosity, high latency, low heat release (thick parts) and high thermal performance (Tg) of the cured products. They are mainly used in composite applications (e.g. filament winding process, pultrusion) and also for electrical insulating materials.

- Anhydrides require sever curing conditions and for this reason they are in general used in combination with Accelerators.

**Huntsman proposes a range of accelerators with different latency to help formulators adjusting the polymerisation kinetic of their systems.**
# Accelerators for anhydride hardeners

## Product selection

<table>
<thead>
<tr>
<th>Product</th>
<th>Latency / reactivity</th>
<th>Impact on mechanical properties</th>
<th>Form / processability</th>
<th>EHS status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Methyl Imidazole (MI)</td>
<td>Very fast</td>
<td>High Tg Standard modulus</td>
<td>Liquid (~ 40 mpa.S)</td>
<td></td>
</tr>
<tr>
<td>Aradur® 1167</td>
<td>Very long latency at 80°C</td>
<td>Higher modulus Lower Tg</td>
<td>Solid: easy to incorporate Softening point: 95°C</td>
<td>Not classified</td>
</tr>
<tr>
<td>Aradur® 3123</td>
<td>Medium latency (80°C)</td>
<td>Higher modulus Medium Tg</td>
<td>Solid: to be dispersed Melting temperature: 190°C</td>
<td></td>
</tr>
<tr>
<td>Accelerator DY 061</td>
<td>Faster than reference</td>
<td>Higher modulus Medium Tg</td>
<td>Liquid (~ 1500 mpa.S)</td>
<td></td>
</tr>
<tr>
<td>Accelerator 2950</td>
<td>Almost equivalent to reference</td>
<td>Higher modulus medium Tg</td>
<td>Liquid (~ 4000 mpa.S)</td>
<td></td>
</tr>
<tr>
<td>Accelerator 960-1</td>
<td>Faster than reference</td>
<td>Higher modulus Medium Tg</td>
<td>Liquid (~ 225 mpa.S)</td>
<td></td>
</tr>
</tbody>
</table>
Accelerators for anhydride hardeners

Kinetics

Viscosity build-up, time to reach 1 000 Pa.s

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 90 parts Aradur® 917 (MTHPA) + 3 parts accelerator
Measured with plate / plate rheometer
Accelerators for anhydride hardeners

Thermo-mechanical properties
Modulus and Tg

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 90 parts Aradur® 917 (MTHPA) + 3 parts accelerator
Cure profile: 4h at 120°C - Tg measured via DMA (Tan delta Peak)
Accelerators for anhydride hardeners

Mechanical properties
Elongation at break and flexural strength

100 parts Araldite® GY 250 (Bis-A-diglycidyl ether) + 90 parts Aradur® 917 (MTHPA) + 3 parts accelerator
Cure profile: 4h at 120°C
Synopsis

- Dicyandiamide (DICY) is a latent hardener widely used to prepare one-part systems in composites (prepregs), adhesives (pastes and films) and coatings (powder).
- The reaction of dicyandiamide (DICY) with epoxy groups necessitate high temperature and long curing time if accelerators are not used in association with DICY.

Huntsman proposes a range of accelerators with different latency to help formulators adjusting the polymerisation kinetic of their systems.
## Accelerators for dicyandiamide hardeners

### Product selection 1/2

<table>
<thead>
<tr>
<th>Product</th>
<th>Latency / reactivity</th>
<th>Impact on mechanical properties</th>
<th>Form / processability</th>
<th>EHS status</th>
</tr>
</thead>
</table>
| Reference Methyl Imidazole (MI) | Poor latency  
Very fast in reactivity | High modulus  
Medium Tg | Liquid (~ 40 mpa.S) | Not classified |
| Reference TDI-uron    | Good latency  
Medium reactivity | Standard modulus  
Medium / high Tg | Solid: to be dispersed | Not classified |
| Aradur® 1167          | Outstanding latency at 80°C  
Lower reactivity than TDI-uron at 120°C | Standard modulus  
High Tg | Solid: easy to incorporate  
Softening point: 95°C | Not classified |
| AcCELERATOR 1573      | Good latency  
Lower reactivity than TDI-uron at 120°C | Similar to TDI-uron | Paste (75 000 mpa.S):  
easy to incorporate | Not classified |
| Aradur® 3123          | Slightly lower latency  
Faster reactivity than TDI-uron at 120°C | Standard modulus  
High Tg | Solid: to be dispersed | Not classified |
## Accelerators for dicyandiamide hardeners

### Product selection 2/2

<table>
<thead>
<tr>
<th>Product</th>
<th>Latency / reactivity</th>
<th>Impact on mechanical properties</th>
<th>Form / processability</th>
<th>EHS status</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reference</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Imidazole (MI)</td>
<td>Poor latency</td>
<td>High modulus</td>
<td>Liquid (~ 40 mPa.s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Very fast in reactivity</td>
<td>Medium Tg</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reference</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDI-uron</td>
<td>Good latency</td>
<td>standard modulus medium / high Tg</td>
<td>Solid: to be dispersed</td>
<td>Not classified</td>
</tr>
<tr>
<td></td>
<td>Medium reactivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Accelerator</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DY 061</td>
<td>Similar latency and reactivity</td>
<td>Similar to TDI-uron</td>
<td>Liquid (~ 1500 mPa.s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>than MI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>960-1</td>
<td>Similar latency and reactivity</td>
<td>Similar to TDI-uron</td>
<td>Liquid (~ 225 mPa.s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>than MI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2950</td>
<td>Faster than MI</td>
<td>Similar to TDI-uron</td>
<td>Liquid (~ 4000 mPa.s)</td>
<td></td>
</tr>
</tbody>
</table>

- **Table of content**
  - Accelerators
    - for anhydride
    - for dicyandiamide
    - for amine RT / 60°C
  - < Table of content>
Accelerators for dicyandiamide hardeners

Kinetics
Viscosity build-up, time to reach 1 000 Pa.s

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 25 parts Aradur® 1571 (DICY paste) + 6 parts accelerator
Measured with plate / plate rheometer
**Accelerators for dicyandiamide hardeners**

**Kinetics**

Time to reach 90% conversion at different temperatures

![Graph showing the time to reach 90% conversion at different temperatures](image)

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 25 parts Aradur® 1571 (DICY paste) + 6 parts accelerator
Conversion measured with DSC (isotherm)
Accelerators for dicyandiamide hardeners

Kinetics - DICY / TDI-Uron vs. DICY / Aradur® 1167
Gel time measured at 80°C

Stoichiometric cure with DICY hardener / TDI-Uron or DICY hardener / Aradur® 1167 (100/46 pbw)
Gel time measured with Gelnorm®
Accelerators for dicyandiamide hardeners

Kinetics - DICY / TDI-Uron vs. DICY / Aradur® 1167
Gel time measured at 120°C

Stoichiometric cure with DICY hardener / TDI-Uron or DICY hardener / Aradur® 1167 (100/46 pbw)
Gel time measured with Gelnorm®
Accelerators for dicyandiamide hardeners

Thermo-mechanical properties
Modulus and Tg

<table>
<thead>
<tr>
<th>Accelerators</th>
<th>for anhydride</th>
<th>for dicyandiamide</th>
<th>for amine RT / 60°C</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Flexural modulus (MPa)</th>
<th>3500</th>
<th>3300</th>
<th>3100</th>
<th>2900</th>
<th>2700</th>
<th>2500</th>
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<tbody>
<tr>
<td>A</td>
<td>3500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>3500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td>3500</td>
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<tr>
<td>D</td>
<td></td>
<td></td>
<td></td>
<td>3500</td>
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<td>E</td>
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<td>3500</td>
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<td>F</td>
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<td>3500</td>
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<td>G</td>
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<tr>
<td>H</td>
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</tr>
</tbody>
</table>

Glass transition temperature (°C)

A TDI-uron
B Methyl Imidazole (MI)
C Aradur® 1167
D Accelerator 1573
E Aradur® 3123
F Accelerator DY 061
G Accelerator 960-1
H Accelerator 2950

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 25 parts Aradur® 1571 (DICY paste) + 6 parts accelerator
Cure profile: 2h at 100°C + 2h at 150°C - Tg measured via DMA (Tan delta Peak)
Accelerators for dicyandiamide hardeners

Mechanical properties
Elongation at break and flexural strength

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 25 parts Aradur® 1571 (DICY paste) + 6 parts accelerator
Cure profile: 2h at 100°C + 2h at 150°C
Accelerators for dicyandiamide hardeners

Mechanical properties - DICY / TDI-Uron vs. DICY / Aradur® 1167

Tg and flexural modulus

Stoichiometric cure with DICY hardener / TDI-Uron or DICY hardener / Aradur® 1167 (100/46 pbw)
Cure profile: 2h at 100°C + 2h at 150°C + 2h at 220°C - Tg measured via DMA (G’ Onset)
Accumulators for amine cure from RT to 60°C

Synopsis

- Aliphatic and cycloaliphatic amines are hardeners commonly used for 2-part epoxy systems in composite, adhesives, coating... applications.
- Although they in general react with epoxy resins at room or medium temperature, several need acceleration to ensure acceptable level of conversion (depending on the type of application).

Huntsman proposes a range of accelerators suitable for ambient and medium temperature curing, with different latency to help formulators adjusting the polymerisation kinetic of their systems.
# Accelerators for amine cure from RT to 60°C

## Product selection

<table>
<thead>
<tr>
<th>Product</th>
<th>Reactivity at room temperature</th>
<th>Reactivity at 60°C</th>
<th>Form / processability</th>
<th>EHS status</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reference</strong> Ethylamine-boron trifluoride</td>
<td>Reference</td>
<td>Reference</td>
<td>Solid (softening point: 88°C)</td>
<td>![Alert]</td>
</tr>
<tr>
<td>Accelerator 3130</td>
<td>Very fast</td>
<td>Extremely fast</td>
<td>Liquid (~ 55 mPa.s)</td>
<td>![Alert]</td>
</tr>
<tr>
<td>Aradur® 1167</td>
<td>Equivalent to reference</td>
<td></td>
<td>Solid: easy to incorporate / dissolve in the amine part</td>
<td>Not classified</td>
</tr>
<tr>
<td>Accelerator 2950</td>
<td>1.5 times more stable than reference</td>
<td>Medium acceleration 1.5 times more stable than reference</td>
<td>Liquid (~ 4000 mPa.s)</td>
<td>![Alert]</td>
</tr>
<tr>
<td>Accelerator 960-1</td>
<td>1.8 times more stable than reference</td>
<td></td>
<td>Liquid (~ 225 mPa.s)</td>
<td>![Alert]</td>
</tr>
<tr>
<td>Accelerator DY 061</td>
<td>Almost no acceleration effect at room temperature</td>
<td></td>
<td>Liquid (~ 1500 mPa.s)</td>
<td>![Alert]</td>
</tr>
</tbody>
</table>
Accelerators for amine cure from RT to 60°C

Kinetics
Pot life and time to reach 90% conversion at 60°C

100 parts Araldite® GY 250 (BisA-diglycidyl ether) + 22.5 parts isophorone diamine + 6 parts accelerator
Conversion measured with DSC (isotherm) - Pot life measured with Geltimer (TECAM) on 100 g mix at 25°C
Synopsis

- Aliphatic and cycloaliphatic amines are hardeners commonly used for 2-part epoxy systems in composite, adhesives, coating… applications.
- A wide choice of unmodified amines is available but in general final formulations consist of formulated amines: blends of amines targeting a certain application or chemical modification of the amines to provide additional benefits in processing, performances…

Huntsman proposes a range of formulated amines designed for composites, adhesives or coating applications, helping formulators adjusting the processing capabilities, the curing kinetic or the final performances of their systems.
## Hardeners for RT to 80°C cure

### Product selection 1/2

<table>
<thead>
<tr>
<th>Product</th>
<th>Latency / reactivity</th>
<th>Impact on mechanical properties</th>
<th>Processability: viscosity (mPa.s)</th>
<th>EHS status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aradur® 70</td>
<td>Very slow cure at RT</td>
<td>Very high flexibility Max elongation 400 % at RT and &gt; 250 % at -10°C</td>
<td>16 000 - 27 000</td>
<td>!</td>
</tr>
<tr>
<td>Aradur® 3275</td>
<td>Good compromise between pot life and curing time at RT</td>
<td>High level of flexibility Elongation 110% at RT and up to 50 % down to -10 °C</td>
<td>200 - 300</td>
<td>!</td>
</tr>
<tr>
<td>Aradur® 15-1</td>
<td>Fast cure at RT</td>
<td>Flexible Elongation 50% at RT</td>
<td>100 - 300</td>
<td>!</td>
</tr>
<tr>
<td>Aradur® 90</td>
<td>Extremely fast cure at RT</td>
<td>Good modulus combined with a 8% elongation at RT</td>
<td>10 000 - 16 000</td>
<td>!</td>
</tr>
<tr>
<td>Aradur® 140</td>
<td>Slow cure at RT</td>
<td>Good modulus when cured at RT or 80°C</td>
<td>300 - 600 at 75°C</td>
<td>!</td>
</tr>
</tbody>
</table>
# Hardeners for RT to 80°C cure

## Product selection 2/2

<table>
<thead>
<tr>
<th>Product</th>
<th>Latency / reactivity</th>
<th>Impact on mechanical properties</th>
<th>Processability: viscosity (mPa.s)</th>
<th>EHS status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aradur® 2992</td>
<td>Very fast cure at RT</td>
<td>Good modulus and good Tg when post cured</td>
<td>10 - 20</td>
<td>![EHS status icons]</td>
</tr>
<tr>
<td>Aradur® 20250</td>
<td>Fast cure at RT</td>
<td>Very high modulus</td>
<td>130 - 210</td>
<td>![EHS status icons]</td>
</tr>
<tr>
<td>Aradur® 20315</td>
<td>Slow cure at RT</td>
<td>Very good modulus and Very good Tg</td>
<td>5 500 - 8 000</td>
<td>![EHS status icons]</td>
</tr>
<tr>
<td>Aradur® 42</td>
<td>Slow cure at RT</td>
<td>Very good modulus and Very good Tg</td>
<td>10 - 20</td>
<td>![EHS status icons]</td>
</tr>
</tbody>
</table>
Hardeners for RT to 80°C cure

Kinetics
Pot life and time to reach 90% conversion at 60°C and 80°C

Araldite® GY 250 (BisA-diglycidyl ether) + hardener mixed at stoichiometry
Conversion measured with DSC (isotherm) - Pot life measured with Geltimer (TECAM) on 100 g mix at 25°C
Hardeners for RT to 80°C cure

Thermo-mechanical properties
Modulus and Tg

Araldite® GY 250 (BisA-diglycidyl ether) + hardener mixed at stoichiometry
RT cure profile: 2 weeks at 25°C - HT cure profile: 10h at 80°C - Tg measured via DMA (Tan delta Peak)
Hardeners for RT to 80°C cure

Mechanical properties
Elongation at break

Elongation at break (%)
- HT cure
- RT cure

Araldite® GY 250 (BisA-diglycidyl ether) + hardener mixed at stoichiometry
RT cure profile: 2 weeks at 25°C - HT cure profile: 10h at 80°C

Huntsman
Enriching lives through innovation

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Hardeners for high temperature cure

Synopsis

- High temperature resistance, high chemical resistance, and high mechanical properties are the main attributes of aromatic amine hardeners. Unfortunately, most of them have non favorable toxicological assessment. Except diaminodiphenyl sulfone, widely known as DDS.
- DDS isomers are the hardeners of choice for high end composites (prepregs) or adhesives (films) providing, in addition to the above mentioned attributes, an appreciated latency.

Huntsman proposes well proven Aradur® 4,4’- and 3,3’-DDS isomers in micronized form to ease dispersion into epoxy resins, as well as developmental DDS-based hardeners designed for processability improvement in order to reduce processing costs and/or open new application possibilities (e.g. infusion).
## Product selection

<table>
<thead>
<tr>
<th>Product</th>
<th>Latency / reactivity</th>
<th>Impact on mechanical properties</th>
<th>Form / processability</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-Methylenebis-(2-isopropyl-6-methylaniline)</td>
<td>Reference</td>
<td>Reference</td>
<td>Viscosity ~ 40 mPa.s at 90°C</td>
</tr>
<tr>
<td>Aradur® 9664-1</td>
<td>Very latent at RT Lower reactivity at 120 / 180°C</td>
<td>Very high Tg</td>
<td>4,4’-DDS Solid: fine powder easily dispersible Softening point 176 - 185°C</td>
</tr>
<tr>
<td>Aradur® 9719-1</td>
<td>Latent at RT Similar reactivity at 120 / 180°C</td>
<td>Highest modulus</td>
<td>3,3’-DDS Solid: fine powder easily dispersible Softening point 170 - 180°C</td>
</tr>
<tr>
<td>XB 3473</td>
<td>Faster at 120 / 180°C</td>
<td>Similar Tg and modulus</td>
<td>Liquid Viscosity 80 - 125 mPa.s at 25°C</td>
</tr>
</tbody>
</table>
Hardeners for high temperature cure

Kinetics
Time to reach 90% conversion at 120°C and 180°C

Araldite® GY 250 (BisA-diglycidyl ether) + hardener mixed at stoichiometry
Conversion measured with DSC (isotherm)
Hardeners for high temperature cure

Thermo-mechanical properties
Modulus and Tg

Araldite® GY 250 (BisA-diglycidyl ether) + hardener mixed at stoichiometry
Cure profile: 2h at 150°C + 4h at 180°C + 2h at 200°C - Tg measured via DMA (Tan delta Peak)
Mechanical properties
Elongation at break and tensile strength

Araldite® GY 250 (BisA-diglycidyl ether) + hardener mixed at stoichiometry
Cure profile: 2h at 150°C + 4h at 180°C + 2h at 200°C
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