TRiiSO™
A Tri-iso TryLine Company

 Delivering Better Chemistry.
Epoxy Materials

WHY?
Epoxy Materials

• Wide range of performance possibilities
  • Dozens of epoxy resin types commercially available from global manufacturers
  • Hundreds of curative and accelerator options
  • Compatible with a wide range of modifying resins, reactive and non-reactive diluents, additives, rheology modifiers, and fillers
  • FR capable
  • Thousands of formulation options

• Wide range of applications
  • Low viscosity liquid systems to solid systems (i.e. powder coatings)
  • “B” stage capable (pre-preg & film)
Epoxy Materials

• High performance capable
  • Addition reaction – low shrinkage
  • Excellent adhesion – OH groups and low shrinkage/stress
  • Suitable for highly aggressive environments
    • Moisture and chemical resistant
    • High temperature capable

• Cost effective
  • A dozen global manufacturers with significant production capacity

• Decades of research and application data in many applications

• Well established processing methods, and new methods in development
Epoxy Resin Applications

Industrial Maintenance Coatings

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Epoxy Resin Applications

Shipping Container and Marine Coatings
Epoxy Resin Applications

Industrial Floor & Terrazzo Coatings
Epoxy Resin Applications

Faux Finishes

Garage Floor Coatings
Epoxy Resin Applications

Aerospace coatings supplied by Pexa

- Cabin interior coatings
- Antislip walkway coatings
- Flexible wing coatings
- Long term interior corrosion resistant coatings
- Durable exterior topcoats and primers
- Rain erosion resistant coatings
- Composite coatings
- Insulative coatings
- High temperature resistant engine coatings
- Fluid and heat resistant wheel coatings
- Conductive antistatic coatings
- Contrast paints
- Abrasion resistant coatings for moving parts

Skydrol resistant landing gear coatings

Integral fuel tank coatings

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Epoxy Resin Applications
Epoxy Resin Applications
Epoxy Resin Applications

- Electronic Coatings
- LED encapsulants

Potting Compounds
Epoxy Resin Applications

Polymer Insulator
From 10kV
To 765kV

High Voltage
Composite
Epoxy Insulators
Epoxy Resin Applications

Composites
Epoxy Resin Chemistry

Diglycidyl Ether of Bisphenol A or Bisphenol A Diglycidyl Ether (BADGE)
Bisphenol A Epoxy Resins (BADGE or DGEBA)

- Largest volume – Over 90% of all epoxy sold is Bis A epoxy
- Commoditized material and very competitive landscape
- Wide range of applications
- Wide range of performance possibilities
  - Hundreds of curative and accelerator options
  - Thousands of formulations options
- Maximum Tg < 350 F – highest with DETDA, DDS, NMA
- Kukdo – Epokukdo YD-128 (standard grade)
Bisphenol A Epoxy Resin Synthesis

Bisphenol A + Epichlorhydrin → Diglycidyl ether of bisphenol A (DGEBA)

\[
\text{OH} + \text{CH}_2\text{CCH}_3 \rightarrow \text{OH} + \text{CH}_2\text{CCH}_3
\]

\[
\text{OH} - \text{H}_2\text{O}
\]

\[
\text{OH} + \text{OH} + \text{HO}\text{C-CCH}_2\text{Cl} \xrightarrow{\text{NaOH}} \text{bisphenol A} + \text{epichlorhydrin}
\]

\[
\text{CH}_3\text{CCH}_3
\]

\[
\text{OH}
\]
Epoxy Resin Chemistry

Bisphenol A Epoxy Advancement – Fusion Process

Diglycidyl ether of bisphenol A (DGEBA) + Bisphenol A

High molecular weight epoxy resin
# Epoxy Resin Chemistry

## Bisphenol A Epoxy Resins

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>n</th>
<th>Molecular Weight</th>
<th>Epoxy Equivalent Weight&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Hydroxyl Equivalent Weight&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Hydroxyl Functionality&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Melting Point (C)</th>
<th>Viscosity cps (25 C)</th>
<th>Usage</th>
<th>Commercial Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard liquid</td>
<td>&lt;1</td>
<td>180</td>
<td>185-192</td>
<td>85</td>
<td>2</td>
<td>8.12</td>
<td>11.14</td>
<td>High solids, ambient-cured two-pack systems</td>
<td></td>
</tr>
<tr>
<td>Type 2 resin</td>
<td>2</td>
<td>900</td>
<td>450-525</td>
<td>130</td>
<td>6</td>
<td>64-76</td>
<td>0.8-1.7&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Conventional solids, ambient-cured two-pack systems</td>
<td></td>
</tr>
<tr>
<td>Type 4 resin</td>
<td>3.7</td>
<td>1,400</td>
<td>905-985</td>
<td>175</td>
<td>7+</td>
<td>95-105</td>
<td>4.3-6.3&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Epoxy ester resin intermediates; powder coatings</td>
<td></td>
</tr>
<tr>
<td>Type 7 resin</td>
<td>8.8</td>
<td>2,900</td>
<td>1,600-1,900</td>
<td>190</td>
<td>13</td>
<td>125-132</td>
<td>17.5-27&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Epoxy/phenolic and epoxy/ amino baking systems</td>
<td></td>
</tr>
<tr>
<td>Type 9 resin</td>
<td>12</td>
<td>3,800+</td>
<td>2,400-4,000</td>
<td>200</td>
<td>17+</td>
<td>140-155</td>
<td>36.2-98.5&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Epoxy/phenolic and epoxy/ amino baking systems</td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup> Grams of resin containing 1 equivalent of epoxy

<sup>2</sup> Grams of resin to esterify 1 mole of monobasic acid

<sup>3</sup> Figure includes hydroxyl functionality from hydroxyl groups formed from oxirane ring opening.

<sup>4</sup> Forty percent solution in diethylene glycol monobutyl ether

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Delivering Better Chemistry.
Feedstocks for Epoxy

Naphtha
- NaCl
  - NaOH
- Propylene
- Cumene
- Acetone
- Phenol
  - Phenol Novolac
  - Cresol Novolac
  - Bisphenol-F
- Epichlorohydrine
  - Bromine
    - TBBA
      - BPA Epoxy
      - Br Epoxy
      - PN Epoxy
      - CN Epoxy
      - BPF Epoxy
Bisphenol F Epoxy Resins

- Similar molecular structure to Bisphenol A epoxy
- Lower viscosity & higher overall performance
- Not as susceptible to crystallization like Bisphenol A epoxy
- Higher cost but still a cost effective resin for many applications
- Can be blended with Bis A and other resins to reduce viscosity & improve crystallization resistance
Bisphenol F Epoxy Resins

- Maximum Tg is about 320 F with DDS, NMA,
- Excellent fit for many applications – very little effort put forth to sell its value
- Kukdo is basic in Bis F production, and are very competitive on these resins (as well as phenol novolac resins, which are also synthesized from Bis F)
- Kukdo – Epokukdo YDF-170 (standard grade)
Epoxy Resin Chemistry

Bisphenol F Epoxy

Bisphenol A Epoxy
Bisphenol F Epoxy Synthesis

\[ \text{OH} + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH} \quad \text{&} \quad \text{CH}_2\text{OH} \]

\[ - \text{H}_2\text{O} \quad \downarrow \quad + \]

\[ \quad \text{OH} \quad \text{OH} \]

\[ \text{OH} \quad \text{CH}_2 \quad \text{OH} \]

\[ \text{OH} \quad \text{CH}_2 \quad \text{OH} \]

\[ \text{OH} \quad \text{CH}_2 \quad \text{OH} \]

PHENOL NOVOLAC

"BIS F" ISOMERS
Epoxy Resin Chemistry

Bisphenol F Epoxy

\[
\begin{align*}
\text{CH}_2\text{-CH-CH}_2\text{-O-} & & \text{C}_6\text{H}_4\text{-CH}_2\text{-O-CH}_2\text{-CH-CH}_2\text{-O-} \\
\text{O} & & \text{O}
\end{align*}
\]

\[\text{p}_4\text{p}'\text{-DGEBF}\]  
\[\alpha_2\text{p}'\text{-DGEBF}\]  
\[\alpha_2\alpha'\text{-DGEBF}\]
Epoxy Resin Chemistry

Phenol Novolac Epoxy Resins

- Liquid and semi-solid resins (higher functionality = higher molecular weight/viscosity and solid at >3 functional)
- Can be used as sole binder or as modifying resins to increase performance of Bis A epoxy systems
- High mechanical strength
- > 3 functionality may need toughening additives to improve fracture toughness
- Excellent high temperature performance
- Maximum Tg about 450 F – highest with DETDA, DDS, NMA
When \( n \geq 0 \), Bis F epoxy resins are termed phenol novolac resins.
Epoxy Resin Chemistry

(2) Bisphenol A diglycidyl ether

(3) Bisphenol F diglycidyl ether

(4) Epoxy novolac
Modified Bisphenol A Epoxy Resins

- Hydrogenated Bisphenol A Epoxy

- Brominated Bisphenol A Epoxy

- Rubber toughened Bisphenol A Epoxy

- Dimer Acid Modified Bisphenol A Epoxy

- DCPD Modified Bisphenol A Epoxy

Tetrabromobisphenol A (TBBA)
High Performance Multifunctional

- Glycidyl amine epoxy resins
  - Huntsman dominates global supply, but Kukdo also provides reliable supply
- Highly cross-linked systems – typically cross-linked with aromatic diamine curatives
- Primary system used for structural components in military and commercial aircraft – DDS curative
- High cost comes with high performance
- Maximum Tg > 500 F with DDS
Epoxy Resin Chemistry

High Performance Multifunctional

TGDDM

TGmAP

TGpAP
Cycloaliphatic Epoxy Resins - Daicel

• Only 4 global manufacturers
  • TRiiSO represents Daicel, the largest and most reliable source of cycloaliphatic epoxy resins.

• Manufactured without epichlorohydrin – excellent for electronic applications – potting compounds, LED, high voltage insulators, etc.

• Resins available at very low viscosity to semi-solid grades

• Water white clarity and UV stable!

• Extremely high temperature performance > 500 F with NMA
Cycloaliphatic Epoxy Resins

- CELLOXIDE 2021 P
  - Standard grade
- CELLOXIDE 2081
  - Flexibility grade
- EPOLEAD GT401
  - Multifunctional grade
- CYCLOMER M100
  - Hybrid grade
- CELLOXIDE 2000
  - Diluted grade
- EHPE3150
  - High Tg grade
- EPOLEAD PB
- EPOFRIEND

Applications of CELLOXIDE & EHPE
- Coatings
- Composite materials
- Adhesives
- Electronics
  - (Potting for semiconductor, LED, Insulating varnish)
- Stabilizer for plastics
- Acid and halogen scavenger

Delivering Better Chemistry.
1. **Waterborne Epoxy Type 1** = Surfactant additive stabilized standard liquid epoxy emulsion = long dry time, not shear stable (some stability issues in can possible, shorter shelf-life than conventional acrylic WB coatings). Typically used with water soluble amine curing agents (poor water resistant system)

2. **Waterborne Epoxy Type 2** = Surfactant additive stabilized solid epoxy dispersion (Ancarez AR555) = shorter dry time, not shear stable (some stability issues in production & storage possible, shorter shelf-life than conventional acrylic WB coatings). Have to use coalescing solvents, so these are higher VOC systems. They do have a bit better water resistance (not much) vs. Waterborne Epoxy Type 1, due to less water soluble amine curing agent required (higher EEW of solid epoxy).

3. **Waterborne Epoxy Type 3** = Surfactant additive stabilized liquid or solid epoxy dispersion, and a carboxyl-functional acrylic curatives. Still some stability issues, not shear stable, long dry time, but more resistant to yellowing and chalking.
4. **Waterborne Epoxy Type 4** = Hydrophobic amine curative emulsions combined with straight liquid epoxy resin (100% solids) or with surfactant additive stabilized epoxy resins. Overall still poor systems with long dry-time, and only slightly better water resistance.

5. **Waterborne Epoxy Type 5** = Internally stabilized (non-ionic surfactant built into the backbone of the epoxy) - SHEAR STABLE, much better water resistance, excellent dry-time. Also has the advantage of noticeable end of pot-life, when combined with internally stabilized hydrophobic amine emulsions (viscosity builds at end of pot-life). Both Kukdo KEM-101-50 (internally stabilized solid epoxy dispersion) and KEM-128-70 (internally stabilized liquid epoxy emulsion) are Type 5 WB epoxy resins. Combined with Kukdo KH-705 (internally stabilized hydrophobic amine curative), the performance is as good or better than conventional 2k epoxy systems.
Reactive Diluents

- Reactive diluents reduce viscosity, without significant damage to performance
  - Cure response
  - Cured resin performance
- Depending on system being modified and choice of RD, targeted properties can be improved
- Wide range of available reactive diluents to meet most application needs
## Mono-Functional Reactive Diluents

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkyl C12-C14 Glycidyl Ether</strong></td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td><strong>Butyl Glycidyl Ether</strong></td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td><strong>2-Ethylhexyl Glycidyl Ether</strong></td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td><strong>Cresyl Glycidyl Ether</strong></td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td><strong>p-tert-Butylphenyl Glycidyl Ether</strong></td>
<td><img src="image5" alt="Structure" /></td>
</tr>
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</table>
### Di & Tri-Functional Reactive Diluents

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethyl Propane Triglycidyl Ether</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>1,4 Butanediol Diglycidyl Ether</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Neopentyl Glycol Diglycidyl Ether</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>Cyclohexane Dimethanol Diglycidyl Ether</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
</tbody>
</table>

*Image placeholders provided for structure images.*

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*Delivering Better Chemistry.*
## Kukdo Reactive Diluents

### Mono-functional

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C–BGE</td>
</tr>
<tr>
<td>n-Butylglycidyl ether</td>
<td>LGE</td>
</tr>
<tr>
<td>Aliphatic glycidyl ether (C12–C14)</td>
<td>2-EHHE</td>
</tr>
<tr>
<td>2–Ethylhexylglycidyl ether</td>
<td>AGE</td>
</tr>
<tr>
<td>Aliphatic glycidyl ether (C8–C10)</td>
<td>2–Ethyhexylglycidyl ether</td>
</tr>
<tr>
<td>Phenyl glycidyl ether</td>
<td>PGE</td>
</tr>
<tr>
<td>Nonylphenyl glycidyl ether</td>
<td>PGE</td>
</tr>
<tr>
<td>3–alkylphenol glycidyl ether</td>
<td>PGE</td>
</tr>
<tr>
<td>3–alkylphenol glycidyl ether</td>
<td>PGE</td>
</tr>
<tr>
<td>Fluorinate d Alcohol Epoxy Resin</td>
<td>FGE</td>
</tr>
<tr>
<td>o–Phenylphenol glycidyl ether</td>
<td>OPPGE</td>
</tr>
<tr>
<td>Benzyl glycidyl ether</td>
<td>DPGE</td>
</tr>
<tr>
<td>Dodecylphenyl glycidyl ether</td>
<td>DPGE</td>
</tr>
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</table>

### Di-functional

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4–Butanediol diglycidyl ether</td>
<td>BDDGE</td>
</tr>
<tr>
<td>1,6–Hexanediol diglycidyl ether</td>
<td>HDDGE</td>
</tr>
<tr>
<td>Neopentyl glycol diglycidyl ether</td>
<td>NPGDGE</td>
</tr>
<tr>
<td>1,4–Cyclohexane dimethanol diglycidyl ether</td>
<td>CHDMDGE</td>
</tr>
<tr>
<td>Polypropylene glycol diglycidyl ether</td>
<td>PPGDGE</td>
</tr>
<tr>
<td>Ethyleneglycol diglycidyl ether</td>
<td>EGDGE</td>
</tr>
<tr>
<td>Polyethylene glycol diglycidyl ether</td>
<td>PEGDGE (200)</td>
</tr>
<tr>
<td>Polyethylene glycol diglycidyl ether</td>
<td>PEGDGE (400)</td>
</tr>
<tr>
<td>Diethylene glycol diglycidyl ether</td>
<td>DGDGE</td>
</tr>
<tr>
<td>Roscercinol diglycidyl ether</td>
<td>RDGE</td>
</tr>
<tr>
<td>Tiodiphenyl diglycidyl ether</td>
<td>TDPGE</td>
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### Multi-functional

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylolpropane triglycidyl ether</td>
<td>TMPTGE</td>
</tr>
<tr>
<td>Glycerol polyglycidyl ether</td>
<td>GPGE</td>
</tr>
<tr>
<td>Diglycerol polyglycidyl ether</td>
<td>DGPGE</td>
</tr>
<tr>
<td>Pentaerythritol polyglycidyl ether</td>
<td>panta</td>
</tr>
<tr>
<td>Sorbitol polyglycidyl ether</td>
<td>CPGE</td>
</tr>
<tr>
<td>Sorbitol polyglycidyl ether</td>
<td>SPGE</td>
</tr>
<tr>
<td>Neodecanolic acid glycidyl ester</td>
<td>E–10</td>
</tr>
<tr>
<td>1,2–cyclohexanedicarboxylate</td>
<td>HHPA</td>
</tr>
<tr>
<td>N,N–Diglycidyl aniline</td>
<td>GAN</td>
</tr>
<tr>
<td>N,N–Diglycidyl–o–toluidine</td>
<td>GOT</td>
</tr>
<tr>
<td>Triglycidyl–p–Aminophenol</td>
<td>TGPAP</td>
</tr>
<tr>
<td>Tetraglycidyl–diamino–diphenyl methane</td>
<td>TGMDA</td>
</tr>
<tr>
<td>Cyclic/alphatic epoxy resin</td>
<td>–</td>
</tr>
</tbody>
</table>

### KF EPIOL

<table>
<thead>
<tr>
<th>Chemical name</th>
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<tbody>
<tr>
<td>ME 100</td>
<td>ME 101</td>
</tr>
<tr>
<td>ME 102</td>
<td>ME 103</td>
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<tr>
<td>ME 104</td>
<td>ME 105</td>
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<td>ME 700</td>
<td>ME 701</td>
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<tr>
<td>ME 702</td>
<td>ME 703</td>
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<tr>
<td>ME 704</td>
<td>ME 705</td>
</tr>
<tr>
<td>ME 706</td>
<td>ME 707</td>
</tr>
<tr>
<td>ME 708</td>
<td>ME 709</td>
</tr>
</tbody>
</table>

## Delivering Better Chemistry.

TRiiSO™
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Epoxy Curatives

- Aliphatic Amines
  - Polyalkylene amine
  - Poly oxyalkylene amines
  - Cycloaliphatic amines
- Fatty Acid Modified Amines
  - Polyamides
  - Amido-amines
  - Mannich Bases
- Aliphatic Amine Adducts
- Aromatic Amines
- Anhydrides

Delivering Better Chemistry.
Epoxy Curatives

- Dicyandiamine
- Lewis Acids – Boron Tri-fluoride monoethylamine (BF3-MEA)
- Dihydrazides
- Acrylic & Methacrylic Resins
- Phenolic Novolacs
- Cyanate Esters
- Isocyanates
Curing Epoxy Resins

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{N} & \text{R} \text{N} \text{CH}_2\text{CH}_2\text{CH}_2\text{N} \\
\text{H} & \text{H} \\
\text{OH} & \text{OH}
\end{align*}
\]

Delivering Better Chemistry.
Curing Epoxy Resins
Curing Epoxy Resins

1. \[ R-\text{NH}_2 + \text{CH}_2-\text{CH} \xrightarrow{\text{H}} R-\text{N}-\text{CH}_2-\text{CH} \]
   - Primary Amine + Epoxide → Secondary Amine + Hydroxyl

2. \[ R'-\text{N}-\text{CH}_2-\text{CH} \xrightarrow{\text{CH}_2-\text{CH}} R'-\text{N}-(\text{CH}_2-\text{CH}) \]
   - Secondary Amine + Epoxide → Tertiary Amine + Hydroxyl

3. \[ R''-\text{N}-(\text{CH}_2-\text{CH}) \xrightarrow{\text{CH}_2-\text{CH}} R''-\text{N}-(\text{CH}_2-\text{C-O})n \]
   - Tertiary Amine + Epoxide → Quaternary Ammonium polyether

4. \[ \text{CH} \xrightarrow{\text{O}} \text{CH}-\text{CH}_2-\text{CH} \xrightarrow{\text{OH}} \text{CH} \]
   - Secondary Hydroxyl + Epoxide → Ether + Hydroxyl
Curing Epoxy Resins

Secondary alcohols from the epoxy backbone or other alcohols (aliphatic) react with the anhydride forming a monoester.

\[
\text{HOC}O \; \text{CO} + \text{HO-CH} \rightarrow \text{HOC}O \; \text{CO} + \text{HO-CH}
\]

The corresponding carboxylic acid can then react with an epoxy group forming a diester.

\[
\text{HOC}O \; \text{CO} + \text{HO-CH} \rightarrow \text{HOC}O \; \text{CO} + \text{HO-CH}
\]

A competing reaction is epoxy groups reacting with a secondary alcohol forming an (β-hydroxy) ether linkage.

\[
\text{CH}_2-\text{CH-CH}_2-\text{R} + \text{HO-CH} \rightarrow \text{CH}_2-\text{CH-CH}_2-\text{R} + \text{HO-CH}
\]
Curing Epoxy Resins

\[
\begin{align*}
\text{F-B-N-H} & \quad + \quad \text{HC-O-CH}_2 \\
\text{F-B-N-H} & \quad \rightarrow \quad \text{[F-B-N-H]^-} \\
\text{[F-B-N-H]^-} & \quad + \quad \text{HC-O-CH}_2 \\
\text{[F-B-N-H]^-} & \quad \rightarrow \quad \text{CH-CH}_2 \\
n \text{HC-O-CH}_2 & \quad \rightarrow \quad \text{[F-B-N-H]^-} \\
\end{align*}
\]
Complimentary Additives

- Fillers – ATH, Talc, Blanc Fixe, etc.
- Pigments
- FR Additives – TBBA, APP, MC, Zinc Borate, DOPO, other phosphate and bromine based materials – ICL, Shandong Tianyi
- Phase Separation Toughening Additives – Kukdo, Kaneka
- Silanes – AB Specialty Silicones
- Polyols
Composite Industry is looking for new materials & process technology (new chemistry) to improve performance, process and cure profiles outside of older established offerings.

NEW SYSTEMS
FASTER CURE
BETTER PROCESSING
LOWER HSE
HIGH TOUGHNESS
BETTER SHELF-LIFE
NON-HALOGEN FR

Figure 1 – Limited view of available thermoset resin systems for aerospace. Table published by Hexion.