Core-shell Rubber (CSR) Toughening System for Thermoset Resins

Kane Ace® MX Toughening Agent for Thermoset Systems
Content:
1. What is Core-Shell Rubber?
2. The MX Difference
3. Why Pre-dispersed Core-Shell Rubber?
4. How does CSR Toughen?
5. Properties of Kane Ace® MX.
6. Comparing Kane Ace® MX to Other Toughening Agents.
7. Summary
1. What is Core-Shell Rubber (CSR)?

**CORE:**
- Various rubbers and (co)polymers can be used.
- 100 nm ~ 300 nm primary particle size

**SHELL**
- Make core compatible with various matrix resins by its adjusting chemistry.

CSR is a Major Toughening Agent for Thermoplastic Resins
1. What is Core-Shell Rubber (CSR)?

Over the last fifty years CSR have been successfully used to toughen items ranging from plastic packaging to automobile parts to building products. Employed primarily in thermoplastic resins (PVC, styrenics, engineering plastics) global production of CSR today is estimated in excess of 1 billion pounds.
2. The MX Difference

**Conventional CSR**

- **Powder form** comprised of agglomerated primary CSR particles
- Widely used as a toughener suitable for **thermoplastics**
- Difficult to disperse powder CSR into **thermosets** like epoxy resin

**Thermoplastics**

- Mixing at high temperature/shear
- Dispersed to primary particles

**Thermosets**

- High shear during mixing is difficult to effectively apply to thermosets
- Difficult to disperse
2. The MX Difference

**Toughening Systems with CSR**

- **Kane Ace® MX**
  - Suitable toughening system for epoxy resins
  - Uniformly pre-dispersed CSR (25 ~ 40wt%) in epoxy resin

- **Advantage of Kane Ace® MX**
  - Consistent morphology
  - Outstanding toughening effect
  - Minimum effect on Temperature Performance
  - Wide cure window

*Data and descriptions are for informational purposes only, provided without warranty and are not to be interpreted as specifications.*
2. The MX Difference

The use of Kane Ace® MX allows for efficient and uniform distribution of CSR particles into thermoset resins, while reducing processing time, processing cost, and excess energy.
3. Why Pre-Dispersed Core-Shell Rubber?

**Advantage of Using Kane Ace® MX**

- **Particle morphology**
  - Optimized particle size distribution

- **Two-phase separation**
  - Minimum disruption of matrix properties

- **Compatibility to matrix resins**
  - Better particle stability

- **Finely tuned particle chemistry and structure**
  - Applicable to various resin systems

**Suitable for Toughening Fragile Matrix Resins**

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3. Why Pre-Dispersed Core-Shell Rubber?

Cured epoxy thermosets comparing efficiency of dispersion of powder vs master batch CSR

TEM analysis shows complete dispersion of CSR particles via MX while conventional Powder CSR suffers from agglomeration issues.

DISPERSION is the key to improvement of mechanical properties!
3. Why Pre-Dispersed Core-Shell Rubber?

Kane Ace® MX under Various Cure Conditions

- **Amine cure at 60°C**
  BisA epoxy/CSR 15wt%
- **Amine cure at 200°C**
  BisA epoxy/CSR 5wt%
- **Phenolic cure at 190°C**
  BisA epoxy/CSR 3wt%

**Consistent CSR Compatibility in a Broad Range of Applications**

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4. Toughening Mechanism of Kane Ace® MX?

**Toughening Mechanism**
- Energy absorption by **plastic deformation** of the epoxy matrix is the key to enhance fracture toughness.
- Cavitation of **finely dispersed CSR** can induce shear yield of epoxy resin, followed by initiation of continuous shear band and plastic deformation.

**Diagram**
- Tri-axial tensile stress at crack tip
- Stress concentration around CSR
- Cavitation of CSR
- Tri-axial tensile stress converts to uniaxial tensile stress state
- Shear yield
- Initiation of shear band
- Plastic deformation

**Figure**
- TEM photo of crack termination in epoxy thermoset

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5. Properties of Kane Ace® MX

Kane Ace® MX for Toughening Epoxy Resins

Key Development in Epoxy Adhesives

- Maintain good shear strength
- Enhance peel strength and impact strength
5. Properties of Kane Ace® MX

K_{1c}/G_{1c} Plane-Strain Fracture Toughness

Three-Point Bending

- Specimen: 6cm x 1.2cm x 0.5cm
- Pre-crack: 0.6cm depth by blade-tapping
- Head speed: 1mm/min.

Strength
Stress
Energy
Strain

ASTM 5045 Casting
ASTM 5528 Reinforced

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5. Properties of Kane Ace® MX

Adhesive Strength Evaluation

T-Peel

Lap Shear

Impact Peel
JIS K 6865/ISO 11343

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5. Properties of Kane Ace® MX

T-Peel Strength Evaluation

ASTM D1876

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5. Properties of Kane Ace® MX

T-Peel Strength of DGEBA Epoxy/MX System

T-Peel Strength increases with active CSR loading

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5. Properties of Kane Ace® MX

Lap-Shear Strength of Kane Ace® MX

ASTM D1002

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5. Properties of Kane Ace® MX

Lap-shear Strength of DGEBA Epoxy/MX

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### 5. Properties of Kane Ace® MX

**Improved thermal shock resistance**

Test results for unfilled epoxy systems

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>MX system</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bisphenol-A Epoxy 1) (phr)</td>
<td>90</td>
<td>74</td>
</tr>
<tr>
<td>Cycloaliphatic Epoxy 2) (phr)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Kane Ace MX (CSR 37%)</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td><strong>Part B</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylhexahydrophthalic anhydride (phr)</td>
<td>83</td>
<td>83</td>
</tr>
<tr>
<td>2-Ethyl-4-methylimidazole (phr)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>CSR wt% in the formulation</strong></td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td><strong>Thermal shock (1cycle: 120°C/20min-&gt; -70°C/10min) x 10</strong></td>
<td>Failed at 1 cycle</td>
<td>Passed</td>
</tr>
</tbody>
</table>

Cure condition: 100°C/2hrs+150°C/3hrs
1) Momentive Epikote 828
2) Daicel Celoxide2021P,
# 5. Properties of Kane Ace® MX

## Kane Ace® MX toughened silica filled epoxy system

<table>
<thead>
<tr>
<th>Part A (phr)</th>
<th>Control</th>
<th>MX system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol-A Epoxy 1)</td>
<td>17.5</td>
<td>14.1</td>
</tr>
<tr>
<td>Cycloaliphatic Epoxy 2)</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Crystalline silica (D50 21μm) 3)</td>
<td>65</td>
<td>63</td>
</tr>
<tr>
<td>Kane Ace MX 257 (CSR 37%)</td>
<td>-</td>
<td>5.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part B (phr)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified phthalic anhydride 4)</td>
<td>15.6</td>
<td>15.6</td>
</tr>
<tr>
<td>Imidazole 5)</td>
<td>0.19</td>
<td>0.19</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle fraction</th>
<th>Control</th>
<th>MX system</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSR wt% in the total formulation</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>(Silica+CSR) vol% in total formulation 6)</td>
<td>43</td>
<td>44</td>
</tr>
</tbody>
</table>

Cure condition: 100°C/2hrs+150°C/3hrs

1) Mitsubishi Chemical jER828EL, 2) Daicel Celoxide2021P, 3) Tatsumori Crystalite KA-C, 4) New Japan Chemical RikacidMH700, 5) Shikoku Chemical Curezol 2E4MZ, 6) Based on assumed density: epoxy (1), silica (2.5), CSR (1), partB (1)

*MX system replaced 2phr of silica with 2phr of CSR. 5.4 phr of MX contains 2 phr of CSR and 3.4 phr of Bisphenol-A Epoxy.

⇒ Both systems have 17.5 phr of Bisphenol A Epoxy

### Test items
- Viscosity
- Heat resistance (Tg)
- Adhesion (lap shear)
- Charpy impact
- Flexural properties
- Heat cycle with spring washer

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5. Properties of Kane Ace® MX

Kane Ace® MX toughened silica filled epoxy system

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control</th>
<th>MX system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>Part A+ Part B., Pa.s @25°C (Shear rate = 1/sec)</td>
<td>56</td>
</tr>
<tr>
<td>Tg (DSC inflection point) °C 7)</td>
<td>164</td>
<td>164</td>
</tr>
<tr>
<td>Adhesion (Lap shear) @23°C, MPa (n=2, STD) 8)</td>
<td>9.34 (0.57)</td>
<td>11.28 (0.60)</td>
</tr>
<tr>
<td>Charpy, unnotch @23C, kJ/m2 (n=5; STD)</td>
<td>4.453 (0.764)</td>
<td>6.059 (0.800)</td>
</tr>
<tr>
<td>Flexural properties (n=3, STD)</td>
<td>Str. Strength MPa</td>
<td>95 (2)</td>
</tr>
<tr>
<td></td>
<td>Modulus GPa</td>
<td>9.31 (0.32)</td>
</tr>
<tr>
<td></td>
<td>Strain to failure %</td>
<td>1.08 (0.05)</td>
</tr>
<tr>
<td>Heat cycle test (150C/1.5h-&gt; -50C/1.5h) x 200 (n=2)</td>
<td>Failed</td>
<td>Passed</td>
</tr>
</tbody>
</table>

Cure condition: 100oC/2hrs+150C/3hrs
7) heating rate 20°C/min, 8) Substrate is cold rolled steel

- Viscosity: MX system showed 25% lower viscosity than control system.
- Tg: MX system maintained high Tg of control system.
- Adhesion to steel: MX system had a higher adhesion strength than control system.
- Impact strength: MX system showed improved impact resistance.
- Flexural properties: MX improved flexural behavior (see next slide).

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6. Comparing Kane Ace® MX to Other Toughened Systems.

Kane Ace® MX toughened silica filled epoxy system

Flexural test (S-S curve)

- Addition of MX extended the strain curve and enlarged the area of S-S curve, indicating the toughening effect of CSR.
6. Comparing Kane Ace® MX to Other Toughened Systems.

**Liquid Rubber such as Rubber Modified Epoxy**

- Conventional toughening agent typically used for epoxy resins
- Dissolved liquid rubber in epoxy resin phase forms rubber domain during cure
  - Enlarged rubber domain particle size
    - inferior toughening effect
  - Domain size and dispersion depend on processing condition
    - unstable reproducibility in morphology and quality
  - Rubber component remains in epoxy phase
    - sacrifice epoxy resin’s heat resistance

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**Epoxy/CSR master-batch**

Dispersion of pre-designed particles

**Epoxy/Liquid rubber**

Phase separation of dissolved rubber during cure

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**Rubber Domain Morphology in Cured Epoxy**
### 6. Comparing Kane Ace® MX to Other Toughened Systems.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>MX CSR</th>
<th>CTBN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Epoxy Resin</strong></td>
<td>BPA (828)</td>
<td>100</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>MX-PBd (40wt% CSR)</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>CTBN adduct (40wt% CTBN)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Reactive diluent</strong></td>
<td>Cardura E10P</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>Dicyandiamide</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td><strong>Co-catalyst</strong></td>
<td>1,1-Dimethyl-3-phenylurea</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Fumed silica</strong></td>
<td>TS720</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Carbon Black</strong></td>
<td>MONARCH 280</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>CaCO₃</strong></td>
<td>Whiton SB</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td><strong>CaO</strong></td>
<td>CML-31</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>141.3</td>
<td>171.3</td>
</tr>
<tr>
<td><strong>Toughner Content (wt%)</strong></td>
<td></td>
<td>0</td>
<td>17.5</td>
</tr>
<tr>
<td><strong>Viscosity &lt;23°C&gt;</strong></td>
<td>2 rpm</td>
<td>210</td>
<td>258</td>
</tr>
<tr>
<td><strong>BH-Type</strong></td>
<td>10 rpm</td>
<td>70</td>
<td>152</td>
</tr>
<tr>
<td><strong>Viscosity Ratio &lt;2rpm/10rpm&gt;</strong></td>
<td></td>
<td>3.0</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>T-Peel &lt;23°C&gt;</strong></td>
<td>(N/25mm)</td>
<td>&lt;failure mode&gt;</td>
<td>65</td>
</tr>
<tr>
<td><strong>Lap Shear &lt;23°C&gt;</strong></td>
<td>(MPa)</td>
<td>&lt;failure mode&gt;</td>
<td>24.4</td>
</tr>
<tr>
<td><strong>Lap Shear &lt;23°C&gt; after 90°C/95%RH x 7d</strong></td>
<td>(MPa)</td>
<td>&lt;failure mode&gt;</td>
<td>16.8</td>
</tr>
<tr>
<td><strong>Wedge Impact &lt;23°C&gt;</strong></td>
<td>(kN/m)</td>
<td>&lt;failure mode&gt;</td>
<td>0</td>
</tr>
<tr>
<td><strong>Wedge Impact &lt;-40°C&gt;</strong></td>
<td>(kN/m)</td>
<td>&lt;failure mode&gt;</td>
<td>0</td>
</tr>
</tbody>
</table>

**MX (CSR) Improves T-Peel and Wedge Impact efficiently**

* **MX-154**: 828/CSR = 60wt%/40wt%, CTBN adduct (1300 x 13): 828/CTBN = 60wt%/40wt%  
  * Cure schedule: 170°C/1h  
  * T-Peel: ASTM D 1876  
  * Lap Shear: ASTM D 1002  
  * Wedge Impact: ISO 11343
6. Comparing Kane Ace® MX to Other Toughened Systems.

**Viscosity of CSR Master-batch vs CTBN**

MX (CSR) system has much lower viscosity than CTBN system

* MX: 40% CSR in Epon 828, CTBN adduct: 40% CTBN in Epon 828

* Graphs of varying dilutions of CSR and CTBN in Epon 828 resin for comparison of relative viscosity.

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6. Comparing Kane Ace® MX to Other Toughened Systems.

Toughening and Thermal Performance
- Fracture toughness (G\textsubscript{1C}) and Glass Transition Temperature (T\textsubscript{g}) -

MX (CSR) Improves toughness efficiently without reduction of T\textsubscript{g}

* MX-PBd: 828/CSR = 60wt%/40wt%, CTBN adduct: 828/CTBN = 60wt%/40wt%
  - BPA/DDS (Stoichiometric amount), Cure schedule: 150°C/1h + 180°C/2h
  - G\textsubscript{1c}: ASTM D 5045
## 6. Comparing Kane Ace® MX to Other Toughened Systems.

### Properties of Kane Ace® MX:
Kane Ace® MX and other toughening methods in Epoxy Adhesive

<table>
<thead>
<tr>
<th></th>
<th>No Toughener</th>
<th>KANE ACE MX</th>
<th>Rubber modified epoxy</th>
<th>Blocked Urethane</th>
<th>Urethane modified epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lap shear</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23°C</td>
<td>23.1</td>
<td>27.1</td>
<td>5.1</td>
<td>24.0</td>
<td>23.3</td>
</tr>
<tr>
<td>Failure mode</td>
<td>C40A60</td>
<td>T60A40</td>
<td>T100</td>
<td>C100</td>
<td>C25T75</td>
</tr>
<tr>
<td><strong>T peel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23°C</td>
<td>16</td>
<td>174</td>
<td>78</td>
<td>119</td>
<td>81</td>
</tr>
<tr>
<td>Failure mode</td>
<td>C95T5</td>
<td>C70A30</td>
<td>C40T60</td>
<td>C100</td>
<td>C50T50</td>
</tr>
<tr>
<td><strong>Impact peel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23°C</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Failure mode</td>
<td>C70A30</td>
<td>C100</td>
<td>C20T80</td>
<td>C100</td>
<td>C70A30</td>
</tr>
<tr>
<td><strong>Impact peel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-40°C</td>
<td>0</td>
<td>10</td>
<td>1</td>
<td>&lt; 2</td>
<td>0</td>
</tr>
<tr>
<td>Failure mode</td>
<td>C70A30</td>
<td>C100</td>
<td>C20T80</td>
<td>C100</td>
<td>C70A30</td>
</tr>
</tbody>
</table>

KANEKA experimental adhesive formula, Formulation: jER828EL/Toughener/Cardura E10P/Dicy/Dyhard UR300/Carbon Black/CaCO3/CaO/TS720 = 100/30/10/5/1/0.3/15/1.5/3
Cure Schedule: 170oC x 30min,
Substrate: Steel (SPCC-SD)
jER828EL/Toughener/Cardura E10P/Dicy/Dyhard UR300/Carbon Black/CaCO3/CaO/TS720 = 100/30/10/5/1/0.3/15/1.5/3

Superior T-peel and Impact Peel Strength
Provided by Kane Ace® MX.

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6. Comparing Kane Ace® MX to Other Toughened Systems.

Lap Shear Strength At Elevated Temperatures

Formulation: jER828EL/Toughener/Cardura E10P/Dicy/Dyhard UR300/Carbon Black/CaCO₃/CaO/TS720
  = 100/30/10/5/1/0.3/15/1.5/3
Cure Schedule: 170°C x 30min, Substrate: Steel (SPCC-SD)

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6. Comparing Kane Ace® MX to Other Toughened Systems.

**Mechanical/Thermal Property**

### Fracture Toughness

- Control
- Epoxy/CSR master-batch
- Rubber modified epoxy

### Heat Resistance

- Control
- Epoxy/CSR master-batch
- Rubber modified epoxy

BisA epoxy / **KANE ACE MX** or Rubber modified epoxy / DDS, toughener content 10wt%
Cure condition: 150°C1hr/180°C2hrs
ASTM D 5045

**Improvement of Fracture Toughness Without Loss of Tg**

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7. Summary

CSR Options For Epoxy/CSR Master-batch

Four basic CSR species have been incorporated into the Kane Ace MX product line.
Shell composition and functionality (type) can be tailored to optimize performance and compatibility with the matrix.

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Epoxy/CSR Master-batch is the effective toughening system for epoxy resins and can enhance the performance of epoxy adhesives.

- Improves fracture toughness and fatigue resistance
- Increase T-peel and impact peel strength
- Maintain Thermal Performance

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