DIC’s epoxy resin products for composite
~Comparison data of Epoxy / DDS cure~

June 2018

Color & Comfort

DIC Corporation
Polymer Technical Group 5, Polymer Technical Div.1
Development policy for CFRP matrix resin (Aerospace)

Mechanical relationship between the fiber and the matrix resin

\[
Ec = EfVf + Em (1 - Vf)
\]

- **Ec**: Elastic modulus (Composite)
- **Ef**: Elastic modulus (Fiber)
- **Em**: Elastic modulus (Matrix)
- **Vf**: Volume fraction
  \[Vf + Vm = 1\]

- CFRP technology challenges
  - Improvement of compressive strength (3-point bending test)
- **Low viscosity**: Good fiber wet-out.
- **High modulus**: Effective to improve the composite strength by high modulus of the matrix resin.
- **High Tg**: Necessary to high heat resistance that can be used for various environment.

Fig. 2 Stress–strain diagram for fiber, composite and matrix.
Product line-up for CFRP matrix (Liquid~Semi-solid)

BPF & EPN resin
- Low viscosity × High modulus

BPF & EPN type (liquid~solid)

Control resin -1
- EPICLON® EXA-850CRP
- EPICLON® 840-S
- EPICLON® 850-S
- EPICLON® 860
- EPICLON® 1055
...

Multi-Functional type
- Low viscosity × High Tg

EXA-7250 (semi-solid)

Modified-Novolac type

Naphthalene type
- Low viscosity × High modulus × High Tg

HP-4032SS (liquid/crystal)

TGDDM type
- No DIC product
Product line-up for CFRP matrix (Solid)

Naphthalene type (solid-type)

- **HP-4700/HP-4710**
  - High modulus
  - High Tg

- **EXA-4750**
  - High modulus
  - High Tg

- **HP-4770**
  - High modulus
  - High Tg

Control resin -1

- **BPA type (liquid ~ solid)**
  - EPICLON® EXA-850CRP
  - EPICLON® 840-S
  - EPICLON® 850-S
  - EPICLON® 860
  - EPICLON® 1055
  - ... 

Control resin -2

- **TGDDM type**
  - No DIC product

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Evaluation method

Evaluation procedure (neat resin)

- **Mix**: Epoxy resin and curing agent (4,4’-DDS) was weighted at stoichiometric ratio.
- **Degas**: The mixture was homogenized and degassed in vacuum. If necessary, the mixture was heated around 80 to 100°C.
- **Casting mold**: The degassed mixture was casted in the mold.
- **Cure**: The mixture in the mold was cured by oven. Curing condition was 150°C/1hr + 180°C/3hr.
- **Cutting**: The cured resin was cut to the sample size for several test (DMA, Flexural test, Tensile test, etc).
BPF & EPN type (liquid ~ solid)

Di- or Multi-functional / liquid ~ solid

- TSCA: Listed
- REACH: Listed (except N-730A)
- ENCS (Japan): Listed
- ECL (Korea): Listed
- IECSC: Listed

Typical property

<table>
<thead>
<tr>
<th>EPICLON®</th>
<th>E.E.W.</th>
<th>Viscosity (25°C, mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>830-S</td>
<td>169</td>
<td>3,450</td>
</tr>
<tr>
<td>N-730A (n=2.6)</td>
<td>174</td>
<td>31,700</td>
</tr>
<tr>
<td>N-740 (n=3.7)</td>
<td>181</td>
<td>Semi-solid</td>
</tr>
<tr>
<td>N-770 (n=6.0)</td>
<td>187</td>
<td>Solid</td>
</tr>
</tbody>
</table>

Diagram:
- Epoxy groups
- Molecular structure
- Temperature vs. Viscosity graph
- Grades: N-770, N-740, N-730A, TGDDM
**BPF & EPN type (liquid~solid)**

*Low viscosity* × *High modulus* ×

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**Flexural test**

- **BPF & EPN** type have the advantage in the point of high modulus, high strength.
- **BPF & EPN** type indicate almost same elongation level, compared with BPA epoxies.

- **Hardener**: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- **Cured condition**: 150°C×1hr + 180°C×3hr
**Modified-novolac type / multi-functional / semi-solid**

- **TSCA**: Listed (non-5(e) SNUR)
- **REACH**: Listed (10~100ton/year)
- **ENCS(Japan)**: Listed
- **ECL(Korea)**: Listed
- **IECSC**: Listed

**Typical Property**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Brown Semi-solid</td>
</tr>
<tr>
<td>E.E.W.</td>
<td>g/eq</td>
</tr>
<tr>
<td>Viscosity 150°C</td>
<td>mPa·s</td>
</tr>
</tbody>
</table>

**Graph**

- **N-740 (EPN)**
- **EXA-7250**
- **TGDDM**
High Tg

EXA-7250 (Td5=386°C)

TG-DTA

EXA-7250

TGDDM (Td5=324°C)

BPADGE

Heat rate: 10°C/min

Test condition: N2

Cured condition: 150°C×1hr + 180°C×3hr

Hardener: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio

Wet Tg(E') = 333°C

Hot-Wet properties

Wet Tg(E') = 200°C

Low viscosity

High Tg

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<Flexural test>

- EXA-7250 was designed for multi-functional, and it has the advantage in the point of high Tg (over than TGDDM).
- EXA-7250 has good Hot-Wet properties compared with TGDDM, due to it’s chemical structure.

- Hardener: DDS (4,4’-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition: 150°C×1hr + 180°C×3hr
Naphthalene / Di-functional / Liquid

Typical Property

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Brownish Liquid (Crystalline)</td>
</tr>
<tr>
<td>E.E.W.</td>
<td>g/eq</td>
</tr>
<tr>
<td>Viscosity 50°C</td>
<td>mPa·s</td>
</tr>
</tbody>
</table>

- TSCA: Listed (5(e) SNUR)
- REACH: Listed (1-10 ton/Y)
- ENCS(Japan): Listed
- ECL(Korea): Listed
- IECSC: Listed

N-740 (EPN)
850-S
HP-4032SS
TGDDM

High modulus
High Tg
Low viscosity

Diagram showing temperature vs. viscosity

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**Water absorption (70°C dip)**

**Good balance of “Heat resistance”, “Mechanical strength” and “Water resistance”**

<table>
<thead>
<tr>
<th>Water Absorption (%)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0%</td>
<td>160</td>
</tr>
<tr>
<td>3.5%</td>
<td>150</td>
</tr>
<tr>
<td>3.0%</td>
<td>140</td>
</tr>
<tr>
<td>2.5%</td>
<td>120</td>
</tr>
<tr>
<td>2.0%</td>
<td>110</td>
</tr>
<tr>
<td>1.5%</td>
<td>100</td>
</tr>
<tr>
<td>1.0%</td>
<td>90</td>
</tr>
</tbody>
</table>

- **Hardener**: DDS (4,4’-Diamino-diphenylsulfone), Stoichiometric ratio
- **Cured condition**: 150°C×1hr + 180°C×3hr
- **Test condition**: 70°C x 2 weeks

**Materials**:
- **HP-4032SS**
- **TGDDM**
- **TGAP**
- **BPFDGE**
- **BPADGE**
### Hot-Wet properties

<table>
<thead>
<tr>
<th></th>
<th>HP-4032SS</th>
<th>TGDDM</th>
<th>BPADGE</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td><img src="image" alt="Chemical Structure" /></td>
<td><img src="image" alt="Chemical Structure" /></td>
<td></td>
</tr>
<tr>
<td><strong>Tg , DMA(E’)</strong> [°C]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>209</td>
<td>261</td>
<td>200</td>
</tr>
<tr>
<td>Wet</td>
<td>156</td>
<td>200</td>
<td>146</td>
</tr>
<tr>
<td><strong>Flexural Modulus [MPa]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>3,630</td>
<td>3,590</td>
<td>2,990</td>
</tr>
<tr>
<td>Wet</td>
<td>3,530</td>
<td>3,230</td>
<td>2,780</td>
</tr>
<tr>
<td><strong>Flexural Strength [MPa]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>163</td>
<td>129</td>
<td>126</td>
</tr>
<tr>
<td>Wet</td>
<td>131</td>
<td>89</td>
<td>110</td>
</tr>
<tr>
<td><strong>Flexural Strain [%]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>7.0</td>
<td>4.6</td>
<td>9.7</td>
</tr>
<tr>
<td>Wet</td>
<td>5.0</td>
<td>3.1</td>
<td>6.4</td>
</tr>
</tbody>
</table>

- Hardener : DDS (4,4’-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition : 150°C×1hr + 180°C×3hr
- Test condition : 70°C x 2weeks

- Low viscosity
- High modulus
- High Tg
High modulus × High Tg × Low viscosity

**HP-4032 series**

**Flexural test & Hot-wet test**

- **Tg vs Modulus**
  - TGDDM
  - BPA
  - HP-4032SS

- **Tg vs Strain**
  - Before Hot-Wet test
  - After Hot-Wet test

- **Tg vs Strength**
  - HP-4032SS
  - BPA
  - TGDDM

**<Flexural test>**

- **HP-4032SS** has the advantage in the point of high modulus, high strength.
- We expected **HP-4032SS** has good Hot-Wet properties compared with TGDDM, due to its chemical structure.

- Hardener: DDS (4,4'-Diamo-diphenylsulfone), Stoichiometric ratio
- Cured condition: 150°C×1hr + 180°C×3hr
Naphthalene / Di-functional / Solid

- TSCA: not Listed (Under Preparation)
- REACH: not Listed
- ENCS(Japan): Listed
- ECL(Korea): Listed
- IECSC: Listed

Typical Property

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Brown Solid</td>
</tr>
<tr>
<td>E.E.W.</td>
<td>g/eq 204</td>
</tr>
<tr>
<td>Softening Point</td>
<td>°C 72</td>
</tr>
<tr>
<td>Viscosity 150°C</td>
<td>mPa·s 90</td>
</tr>
</tbody>
</table>

*150°C ICI
**Naphthalene / Tri-functional / Solid**

- **TSCA**: not Listed
- **REACH**: not Listed
- **ENCS (Japan)**: Listed
- **ECL (Korea)**: Listed
- **IECSC**: Listed

**Typical Property**

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td></td>
<td>Brown Solid</td>
</tr>
<tr>
<td>E.E.W.</td>
<td>g/eq</td>
<td>185</td>
</tr>
<tr>
<td>Softening Point</td>
<td>°C</td>
<td>80</td>
</tr>
<tr>
<td>Viscosity 150°C</td>
<td>mPa·s</td>
<td>140</td>
</tr>
</tbody>
</table>

* 150°C ICI

---

**Graph**

- **EXA-4750**
- **N-740 (EPN)**
- **TGDDM**

**Viscosity vs. Temperature**

- Viscosity (mPa·s) vs. Temperature (°C)

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**Diagram**

- Naphthalene unit

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**Naphthalene / Tetra-functional / Solid**

- **TSCA**: Listed (non-S(e) SNUR)
- **REACH**: not Listed (necessary to register monomer A)
- **ENCS(Japan)**: Listed
- **ECL(Korea)**: Listed
- **IECSC**: Listed

**Typical Property**

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Brown Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.E.W.</td>
<td>g/eq</td>
</tr>
<tr>
<td>Softening Point</td>
<td>°C</td>
</tr>
<tr>
<td>Viscosity 150°C</td>
<td>mPa·s</td>
</tr>
</tbody>
</table>

* 150°C ICI

---

Viscosity (mPa·s) vs. Temperature (°C)

- **HP-4700**
- **N-740 (EPN)**
- **TGDDM**
Naphthalene / Tetra-functional / Solid

- TSCA: Listed (non-S(e) SNUR)
- REACH: not Listed (necessary to register monomer A)
- ENCS(Japan): Listed
- ECL(Korea): Listed
- IECSC: Listed

Typical Property

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Brown Solid</td>
</tr>
<tr>
<td>E.E.W.</td>
<td>g/eq 170</td>
</tr>
<tr>
<td>Softening Point</td>
<td>°C 95</td>
</tr>
<tr>
<td>Viscosity 150°C</td>
<td>mPa·s 900</td>
</tr>
</tbody>
</table>

* 150°C ICI
**Flexural test**

- **HP-4770 & HP-4750** provide high modulus to their cured resin, **HP-4700 & HP-4710** provide excellent high Tg, but their strength and elongation are not so good. We’re trying to improve them by combination.

- **Hardener**: DDS (4,4’-Diamino-diphenylsulfone), Stoichiometric ratio
- **Cured condition**: 150°C×1hr + 180°C×3hr
Mechanical properties

High modulus between wide range

Flexural test

- HP-4770
- TGDDM
- BPADGE

Tensile test

- HP-4770
- TGDDM
- BPADGE

- Hardener: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition: 150°C×1hr + 180°C×3hr
Hot-Wet properties

Dry Tg (E') = 346°C
Wet Tg(E') = 334°C

$\Delta Tg = -12^\circ C$

Dry Tg (E') = 261°C
Wet Tg(E') = 200°C

$\Delta Tg = -61^\circ C$

HP-4700

TGDDM

Hardener : DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
Cured condition : 150°C×1hr + 180°C×3hr
Test condition : 70°C x 2weeks
HP-4770 provides high modulus to its cured resin after Hot-Wet test.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexural Modulus (MPa)</th>
<th>before</th>
<th>after</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-4770 (1.8%)</td>
<td>3,660</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPADGE (2.6%)</td>
<td>2,780</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPFDGE (2.3%)</td>
<td>3,010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TGDDM (3.6%)</td>
<td>3,230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-TGAP (4.1%)</td>
<td>3,180</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hardener: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
Cured condition: 150°C×1hr + 180°C×3hr
Test condition: 70°C x 2weeks
()内: Water Absorption
<table>
<thead>
<tr>
<th>Product name</th>
<th>Production Scale</th>
<th>TSCA</th>
<th>REACH</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXA-850CRP / -830LVP</td>
<td>Liquid</td>
<td>Commercial</td>
<td>Listed</td>
<td>Low viscosity / High purity (Low chlorine content)</td>
</tr>
<tr>
<td>HP-4032D</td>
<td>Liquid</td>
<td>Commercial</td>
<td>SNUR</td>
<td>Listed ~10t/year</td>
</tr>
<tr>
<td>HP-4700 / HP-4710</td>
<td>Solid</td>
<td>Commercial</td>
<td>Non-5(e) SNUR</td>
<td>High curability / High Tg / Low CTE</td>
</tr>
<tr>
<td>HP-4770</td>
<td>Solid</td>
<td>Commercial</td>
<td>Consent order</td>
<td>High modulus / High Tg / High flame retardancy</td>
</tr>
<tr>
<td>HP-9500</td>
<td>Solid</td>
<td>Commercial</td>
<td>Listed</td>
<td>High flame retardancy / High Tg</td>
</tr>
<tr>
<td>HP-6000 / EXA-7311-G4</td>
<td>Solid</td>
<td>Commercial / Pilot</td>
<td>Listed(except N-730A)</td>
<td>High flame retardancy Low CTE</td>
</tr>
<tr>
<td>N-700 series</td>
<td>Liquid-Solid</td>
<td>Commercial</td>
<td>Listed</td>
<td>High modulus / High flexural strength / High Tg</td>
</tr>
<tr>
<td>N-570 / N-570H</td>
<td>Solid</td>
<td>Commercial</td>
<td>Listed</td>
<td>Listed</td>
</tr>
<tr>
<td>HP-7200 series</td>
<td>Solid</td>
<td>Commercial</td>
<td>Listed</td>
<td>Listed(depend on grade)</td>
</tr>
<tr>
<td>HP-5000 / HP-9900-75M</td>
<td>Solid</td>
<td>Commercial</td>
<td>-</td>
<td>Low moisture absorption / Low-Dk, Low-Df</td>
</tr>
<tr>
<td>EXA-1514</td>
<td>Solid</td>
<td>Pilot</td>
<td>LVE</td>
<td>High curability / High Tg / Low CTE</td>
</tr>
<tr>
<td>HP-820</td>
<td>Liquid</td>
<td>Commercial</td>
<td>LVE</td>
<td>Low viscosity / Unique solubility</td>
</tr>
<tr>
<td>EXA-7250</td>
<td>Semi-Solid</td>
<td>Pilot</td>
<td>Non-5(e) SNUR</td>
<td>Listed ~100t/y</td>
</tr>
<tr>
<td>TSR-400</td>
<td>Solid</td>
<td>Commercial</td>
<td>Listed</td>
<td>Listed</td>
</tr>
<tr>
<td>EXA-4850 series</td>
<td>Liquid</td>
<td>Pilot</td>
<td>LVE</td>
<td>Listed</td>
</tr>
<tr>
<td>EXA-4816</td>
<td>Liquid</td>
<td>Pilot</td>
<td>LVE</td>
<td>Listed</td>
</tr>
<tr>
<td>EXB-X</td>
<td>Solid</td>
<td>Pilot</td>
<td>-</td>
<td>High flame retardancy / High mechanical properties</td>
</tr>
<tr>
<td>ATN series</td>
<td>Solution type</td>
<td>Commercial</td>
<td>Listed</td>
<td>Listed</td>
</tr>
<tr>
<td>HPC-8000-65T</td>
<td>Solution type</td>
<td>Commercial</td>
<td>-</td>
<td>Low-Dk, Low-Df / Low moisture absorption</td>
</tr>
</tbody>
</table>