Synthesis & Properties of multifunctional epoxy resins containing naphthalene units

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Contents

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  Applications of epoxy resin
  Need for high thermal resistance, high modulus and excellent Hot-Wet properties.

- Our recent work
  Design of naphthalene type epoxy resin

- This work
  Synthesis and properties of new multi-functional epoxy resins containing naphthalene unit
In the Weeds of Chemistry to Materials & Applications
Abstract

We synthesized the new multi-functional epoxy resins containing Naphthalene unit.

Cured resins exhibited high Tg, high modulus and excellent hot-wet properties suitable for composite and electronic applications.
Uses for Epoxy Resin

Applications

- Coatings
- Adhesives
- Molding Compounds
- Composite Materials
- Aerospace
Industry Challenges

High Temperature Resistance (hot/wet)
Moisture Resistance
Time/Cure
Higher Quality Requirements
Mechanical Property Requirements
Conventional molecular design of high thermal resistance resin

Di-functional type (Standard)

Poly-functional type (oligomer)

Tetra-functional type (oligomer)

E-BPA

EPN

TGDDM
Molecular design of epoxy resin with Naphthalene unit

Naphthalene type (recent work)

- **E-DHN**
  - High modulus
  - High flexural strength
  - Liquid state (but may cause crystallization)

- **E-DHNN**
  - High modulus
  - Solid state
  - High melt viscosity

- **E-2HND**
  - High modulus
  - Crystalline state (melting point is more than 200°C)

This chemical structure is expected excellent properties, but there are a lot of difficulties due to highly crystalline structure.
Reaction scheme of our recent work

**E-DHNN**

\[
\begin{align*}
E \text{-DHNN} & \quad + \quad \text{HCHO} \\
\text{1,6-DHN} & \quad \text{cat. NaOH} \quad \rightarrow \quad \text{- H}_2\text{O} \\
\end{align*}
\]

Difficult handling, strong crystallinity (melting point is more than 200°C, beyond the curing temperature)

**E-2HND**

\[
\begin{align*}
E \text{-2HND} & \quad + \quad \text{HCHO} \\
2 \text{-HN} & \quad \text{cat. NaOH} \quad \rightarrow \quad \text{- H}_2\text{O} \\
\end{align*}
\]

Difficult handling, solid state (high melt viscosity)
This work

To suppress the crystallinity by combination of naphthalene unit monomer.

2-HN + 2,7-DHN + HCHO $\xrightarrow{\text{cat. NaOH}}$ R$_1$: H or OH
R$_2$: H or OH

<table>
<thead>
<tr>
<th></th>
<th>D-2F</th>
<th>D-3F</th>
<th>D-4F</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_1$</td>
<td>-H</td>
<td>-OH</td>
<td>-OH</td>
</tr>
<tr>
<td>R$_2$</td>
<td>-H</td>
<td>-H</td>
<td>-OH</td>
</tr>
</tbody>
</table>

Chemical structure:

- D-2F
- D-3F
- D-4F
Epoxidation of the dimeric naphthols

Dimeric naphthols

Epoxidation

Epoxy resins

D-2F

E-2F

D-3F

E-3F

D-4F

E-4F
Synthesis results of this work

$$\text{2-HN} + \text{2,7-DHN} + \text{HCHO} \xrightarrow{\text{cat. NaOH}} - \text{H}_2\text{O}$$

<table>
<thead>
<tr>
<th>Run</th>
<th>Starting materials (mol ratio (%))</th>
<th>Reaction products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-HN</td>
<td>2,7-DHN</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

$R_1$: H or OH
$R_2$: H or OH
## Epoxy resin properties

<table>
<thead>
<tr>
<th>Run</th>
<th>Dimeric Naphthols</th>
<th>Epoxy resins</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Product code</td>
<td>Product code</td>
<td>E.E.W (g/eq)</td>
<td>Softening point (°C)</td>
<td>Melt viscosity (150°C, mPa.s)</td>
</tr>
<tr>
<td>4</td>
<td>DN-a</td>
<td>E-a</td>
<td>165</td>
<td>91</td>
<td>450</td>
</tr>
<tr>
<td>5</td>
<td>DN-b</td>
<td>E-b</td>
<td>189</td>
<td>79</td>
<td>250</td>
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<tr>
<td>6</td>
<td>DN-c</td>
<td>E-c</td>
<td>205</td>
<td>72</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>E-BPA</td>
<td>188</td>
<td>liquid</td>
<td>15</td>
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<tr>
<td></td>
<td></td>
<td>E-PN</td>
<td>181</td>
<td>semi-solid</td>
<td>34</td>
</tr>
</tbody>
</table>
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℃.

Casting mold

The degassed mixture was casted in the mold.

Cure

The mixture in the mold was cured by oven.
Curing condition was 150℃/1hr + 180℃/3hr.

Cutting

The cured resin was cut to the sample size for several test (DMA,
Flexural test, Tensile test, etc).
Glass Transition Temperature of Cured Resins

- **EPN** - Epoxy Phenol Novolac TGDDM
- **TGDDM** - Tetraglycidyl 4,4 Diaminodiphenyl Methane

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

- **Cured condition** : 150°C×1hr + 180°C×3hr
Modulus of Cured Resins

Modulus (Flexural, Tensile)

- **E-BPA**: 3,030 MPa
- **EPN**: 3,370 MPa
- **TGDDM**: 3,730 MPa
- **E-a (f=4.0)**: 3,200 MPa
- **E-b (f=3.0)**: 3,710 MPa
- **E-c (f=2.6)**: 4,510 MPa

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

**Cured condition**: 150°C x 1hr + 180°C x 3hr
Ea provide excellent high Tg, and Eb & Ec provide high modulus to their cured resin.

- Hardener: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition: 150°C×1hr + 180°C×3hr
Moisture Absorption of Cured Resins

- **Hardener**: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- **Cured condition**: 150°C × 1hr + 180°C × 3hr
- **Test condition**: Dipping cured samples in Hot water (70°C)

\[ Ec \] provide the cured resin with low moisture absorption, about 2/3 that of E-BPA, about 1/3 that of TGDDM.
Hot-Wet properties (Flexural Modulus changes after wet condition)

- **Hardener**: DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- **Cured condition**: 150°C × 1hr + 180°C × 3hr
- **Test condition**: Dipping cured samples in Hot water (70°C)

Ec provide excellent Hot-Wet properties to its cured resin.
Processes & Applications
CFRP’s (carbon fiber reinforced plastic) compressive strength

CFRP’s compressive strength greatly depends on the shear rigidity of the resin, and it is theoretically and experimentally confirmed that the high modulus resin is effective.

Why it matters?

To the Freezer

B Stage
Prepreg
Filament Winding
Preparation and pre-forming of wrought materials → Laying-up SMC and prepreg → Moulding and curing under heat and pressure → Demoulding of the cured part
Film Adhesive

Heat Sink for PCB (printed circuit board)
Film & Direct Impregnation
Vacuum Bagging-Autoclave Cure
The chassis of the BMW 7-series combines steel, aluminum, and carbon-fiber-reinforced plastic. In the image above, the black parts around the door frames and across the roof are carbon fiber.
B-2 Bomber Aerostructure

Hot/Wet; High Modulus; Low Moisture
Fracking Plug
PAC-3
Conclusion

We synthesized the new multi-functional epoxy resins containing Naphthalene unit.

Cured resins exhibited high Tg, high modulus and excellent hot-wet properties suitable for composite and electronic applications.
Thank You!

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- Bio: 30+ years in the materials & processing arena for aerospace, defense, electronics and transportation industries.