Some Important Thermosets

- Formaldehyde resins (accounted for 70%)
- Epoxy resins
- Polyurethane
Some Applications of Epoxy Resin

Top Coating for laboratory table

Floor coating

An epoxy encapsulated hybrid circuit on a printed circuit board.
Monomers and chemical commonly used for preparing epoxy prepolymer

1. Bisphenol
   - Bisphenol A
   - Bisphenol F (higher crystallinity, better heat resistance, but also more expensive)

2. Epichlorohydrin

3. Catalyst (such as NaOH)
Polymerization mechanism
BPA anion react with epichlorohydrin
The reaction is continued
Formation of epoxy prepolymer
Epoxy monomer in relation to food contact applications

• BPA is currently used as monomers for making
  – PC baby bottle
  – Epoxy coated food & fruit canned
• BPA is known to be an endocrine disruptor (at high dose).
• Migrations of BPA from cans and baby bottles were examined and reported, the migrated levels strongly depend on food type and conditions (temperature, no. of uses).
• Safe limits set by FDA and EU are 0.05 & 0.01 mg/kg/d, respectively.
• Recently, low dose effect of BPA was claimed, but has yet to be proved.

Coating layer inside the food & fruit cannes
# Level of BPA migrated from food cans (epoxy coating) and PC bottles

<table>
<thead>
<tr>
<th>Food and food simulating liquid</th>
<th>Epoxy</th>
<th>Polycarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test condition</td>
<td>BPA level (ppb)</td>
</tr>
<tr>
<td>water</td>
<td>60°C/30 min</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>95°C/30 min</td>
<td>ND to 6</td>
</tr>
<tr>
<td></td>
<td>100°C/9 min</td>
<td>2</td>
</tr>
<tr>
<td>10% Ethanol</td>
<td>100°C/30 min→0°C/3 min</td>
<td>86</td>
</tr>
<tr>
<td>20% Ethanol</td>
<td>60°C/30 min</td>
<td>ND</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>25°C/30 min</td>
<td>ND</td>
</tr>
<tr>
<td>1-10% NaCl</td>
<td>121°C/30 min</td>
<td>7-13</td>
</tr>
<tr>
<td>Vegetable oils</td>
<td>121°C/30 min</td>
<td>16-18</td>
</tr>
<tr>
<td>Coffee</td>
<td>121°C/30 min</td>
<td>33-134</td>
</tr>
<tr>
<td>3% acetic acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4% acetic acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Miglyol</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Safety limits, and the migration levels of BPA

<table>
<thead>
<tr>
<th>Toxicity</th>
<th>Daily intake level</th>
<th>EU migration limit</th>
<th>Non Observe Adverse Effect Level</th>
<th>FDA safety limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Dose Region</td>
<td></td>
<td>0.6 mg/kg</td>
<td>50 mg/kg/day</td>
<td>0.05 mg/kg/day</td>
</tr>
<tr>
<td>Low dose hypothesis?</td>
<td>1,000 times</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PC baby bottle</td>
<td>120 times</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other canned food</td>
<td>60 times</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coconut cream</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tuna</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Measured level of BPA in human urine

Concentration

~0.02 – 20 μg/kg
Cured epoxy resin
Curing of epoxy resin

2. Crosslinked at the hydroxy group by reacting with anhydride
Curing of epoxy pre-polymer with anhydride

“anhydrides require more severe curing conditions than amine based curing agents. It has a longer pot life so suitable for making large molding. It has been used for electrical insulating materials”.
Curing of epoxy resin

• Epoxy pre-polymer can be cured by 2 important mechanisms;
  1. Crosslinked at the epoxy group by reacting with poly(functional) amines
     • Diethylene triamine (DETA, f = 5),
     • Triethylene tetra-amine (TETA, f = 6),
Curing of epoxy resin
Part A and Part B of epoxy coating used for flooring applications
Structure of epoxy coating in flooring application

- 3 layers
  1. Primer layer (adhesion to the substrate and the mortar layer are very important)
  2. Mortar (this part contribute to the strength of the coating)
  3. Top coat (chemicals resistance are very important)
Typical formulation for epoxy coating and flooring

- **Part A (hardener)**
  - DETA or TETA
  - Aminoethyl piperazine
    (Optional, used for enhancing impact strength at the expense of HDT)
  - Silica four or BaSO₄ (extender)
  - Additives

- **Part B (resin)**
  - Diglycidyl ether of bisphenol A
  - Alkyl (C12-C14) glycidyl ether (monoepoxide) [reactive diluent]
  - Aromatic hydrocarbon e.g. xylene
  - Some plasticizer (e.g. pine oil, phthalate)

- **Additional part (sand or silica)**
How to obtain stoichiometric balance between epoxy resin and amine hardener?

- To calculate the desired stoichiometric quantity of amine in weight parts per 100 gram epoxy resin the following formula can be used:

\[
\text{Equivalent weight of amine} \times 100
\]

Equivalent weight of epoxy resin
Calculations

• Equivalent weight of epoxy is the amount of resin (grams) that contains one molecule of an epoxy group.
• The **epoxy equivalent weight** can be calculated as follows:

\[
\text{Molecular weight epoxy resin} \quad \frac{\text{Number of epoxy groups}}{} 
\]
Calculations

**Equivalent weight of amine** =

\[
\frac{\text{Molecular weight of the amine hardener}}{\text{Number of active hydrogen of the amine}}
\]
Calculations

• Alternatively, epoxy number and amine number are defined as follows:
  Epoxy number $= \frac{100}{\text{epoxy eq.weight}}$
  Amine number $= \frac{100}{\text{amine eq.weight}}$
General epoxy flooring formulation

- Epoxy resin: 32-40%
- Reactive diluent: 5-10%
- Extender: 40-65%
- Pigment: 2-5%
- Additives: 2-4%
Some additives for epoxy coating applications

1. **De-foamer and air release** (สารทำลายฟองที่เกิดจากปฏิกิริยาและความดัน โดยมากเป็นสารประเภทซิลิโคน และสารลดฟองใต้ผิว โดยการเร่งการแพร่ของฟองขึ้นมา เช่น พอลิไซลอกเซนผสมพอลิเมอร์ที่เป็นความลับทางการค้า)

2. **Leveling additive** (สารลดความหนืดและช่วยปรับผิวเรียบ) เช่น สารละลาย phosphoric acid polyester in Methoxpropylacetate / alkylbenzene

3. **Anti setting** หรือ **anti-sacking** (สารลดการไหลย้อยของสี) (สำหรับงานที่ไม่เติมผงสี และ filler เยอะ อาจจะไม่จำเป็น) เช่น สารละลายของ modified Urea ใน N-methylpyrrolidone

4. **Wetting % dispersing agent** (สารช่วยในการกระจายตัวของผงสี) (ใช้เฉพาะในกรณีที่เติมผงสี เช่นในชั้น top coat) เช่น สารละลายเกลือ phosphoric ester salt ของโพลิเมอร์ (ความลับ) ที่มีหน่วยฟังก์ชันที่ชอบจับกับ pigment


**Without Additive**  
**With Additive**
Exercises

1. สูตรผสมอีพอกซี ประกอบด้วย
   - Part A ซึ่งประกอบด้วย 85 wt% ของ epoxy resin (Eq.wt. = 187 g/eq) ผสมกับ 10 wt% ของ mono-epoxide reactive diluent (eq.wt. = 280 g/eq)
   - Part B ซึ่งประกอบด้วย 80 wt% ของ DETA ในตัวทำละลาย nonylphenol

จงคำนวณว่า ในการใช้ 100 g ของสารผสม epoxy และ reactive diluent จะต้องใช้ DETA ปริมาณกี่กรัม จึงจะทำปฏิกิริยาถูกต้อง
Exercises

2.  สูตรผสมอีพอกซี่ ประกอบด้วย
   – Part A ซึ่งประกอบด้วย 85 wt% ของ epoxy resin (Eq.wt. = 187 g/eq) ผสมกับ 10 wt% ของ mono-epoxide reactive diluent (eq.wt. = 280 g/eq)
   – Part B ซึ่งประกอบด้วย 80 wt% ของ TETA ในตัวทำละลาย nonylphenol

จงคำนวณว่า ในการใช้ 100 g ของสารผสม epoxy และ reactive diluent จะต้องใช้ TETA ปริมาณกี่กรัม จึงจะทำปฏิกิริยาถูกต้อง
Exercises

3. สูตรผสมอีพอกซีประกอบด้วย

- Part A ซึ่งประกอบด้วย 85 wt% ของ epoxy resin (Eq.wt. = 187 g/eq) ผสมกับ 10 wt% ของ mono-epoxide reactive diluent (eq.wt. = 280 g/eq)
- Part B ซึ่งประกอบด้วย 60 wt% ของ DETA และ 20 wt% aminoethyl piperazine (FW = 129) ในตัวทำละลาย nonylphenol

จงคำนวณว่า ในการใช้ 100 g ของสารผสม epoxy และ reactive diluent จะต้องใช้ PART B รวมกัน ปริมาณกี่กรัม จึงจะทำปฏิกิริยาเกิดผลตี
Exercises

4. สูตรผสมอีพอกซี ประกอบด้วย
   - Part A ซึ่งประกอบด้วย 85 wt% ของ epoxy resin (Eq.wt. = 187 g/eq) ผสมกับ 10 wt% ของ mono-epoxide reactive diluent (eq.wt. = 280 g/eq)
   - Part B ซึ่งประกอบด้วย 60 wt% ของ TETA และ 20 wt% aminoethyl piperazine (FW = 129) ในตัวทำละลาย nonylphenol

จงคำนวณว่า ในการใช้ 100 g ของสารผสม epoxy และ reactive diluent จะต้องใช้ PART B รวมกัน ปริมาณกี่กรัม จึงจะทำปฏิกิริยากันพอดี
Some applications of PU (synthetic running track)
• New urethane bond formed.
• No small by product
• Amine based catalysts are normally used
What are the different isocyanates?

The two most commercially important isocyanates are:
- toluene diisocyanate (TDI); and
- diphenylmethane diisocyanate (MDI).

TDI evaporates most easily and is therefore the most harmful of these isocyanates.

However, all isocyanates can pose a health risk during the spraying of paint or foam, when droplets containing unreacted isocyanates can be inhaled.

Some of the health effects of isocyanate exposure include:
- eye irritation, watering and discomfort;
- irritation of the respiratory tract;
- dryness of the throat;
- tightness of the chest;
- difficulty in breathing;
- headaches;
- asthma attacks;
- reddening, swelling and blistering of exposed skin if not washed off; and
- dermatitis.
Polymerization mechanism
Polymerization mechanism
Pre-polymer
Synthesis of PU fiber

• 6,4-polyurethane [Perlon U®] produced during WW-II.
• Reacting hexamethylene disiocyanate with butane diol.
• 6,4 PU absorb only 1/6 the moisture of Nylon 6,6 (i.e., better dimension stability and good insulation properties).
• However, PU fiber is more expensive.
Synthesis of PU rubber

- Vulkollan®
- Reacting glycol (EG, PG) with adipic acid
- Glycol is excess so that polyester polyol has hydroxyl end groups.
- Polyol is react with excess MDI.
- The prepolymer is further react with chain extenders
- Urea and urethane formed in the chain extension reaction also provide the sites for crosslinking with free isocyanate.
Polyol

- There are two types of polyol;
  - Polyester polyol
  - Polyether polyol

Poly(propylene oxide) glycol

Poly(ethylene adipate)

Polycaprolactone

Polycarbonate
Chain extension reactions

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{+} \quad \text{OCN-R-NCO} \\
\text{Polyol (Mol. wt. 2000)} & \quad \text{MDI} \\
\text{H}_2\text{NNH}_2 & \quad \text{(Chain extender)} \\
\text{OCN-R-NH-C=O} & \quad \text{OCN-R-NH-R-NCO} \\
\text{Prepolymer} & 
\end{align*}
\]
Results from the chain extension reactions

With glycols $\sim \sim \text{NCO} + \text{HO-R-OH} + \text{OCN} \sim \sim \rightarrow \sim \sim \text{NH-C-O-R-O-C-NH} \sim \sim$

Urethane link

With amines $\sim \sim \text{NCO} + \text{H}_2\text{N-R-NH}_2 + \text{OCN} \sim \sim \rightarrow \sim \sim \text{NH-C-NH-R-NH-C-NH} \sim \sim$

Double urea link
Cross-linking of PU pre-polymer
Thermoplastic polyurethane [TPU]

\[
\begin{align*}
\text{stiff, rigid block} & \quad \text{soft, rubbery block} \\
\text{Polyol} & \quad \text{Urethane-terminated polyurea} \\
\text{Polyol soft} & \quad \text{hard segment}
\end{align*}
\]
## PU foam

The basic formulation of PU foam involves the reaction of isocyanate (-NCO) with water (H₂O) and isocyanurate (OCN) to form urea (NH₂-C-NH) and carbon dioxide (CO₂). The diagram illustrates the prepolymerization process.

### Basic formulation of PU foam

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Part by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td>71</td>
</tr>
<tr>
<td>TDI</td>
<td>26</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>1.85</td>
</tr>
<tr>
<td>Water</td>
<td>1.85</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>12</td>
</tr>
<tr>
<td>Others (e.g. surfactant)</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Phenolic resins

- Phenol formaldehyde
  - Resole
  - Novolac
- Urea formaldehyde
- Melamine formaldehyde
Melamine formaldehyde

Melamine + HCOH (excess)

Crosslinked melamine
Melamine formaldehyde

Advantages
• *No staining*
• *Easily coloured (unlike Phenolics).*
• Taste and odour free.
• Good resistance to solvents
• Electrical properties relatively unaffected by high humidity (unlike Phenolic).
• Self-extinguishing.

Disadvantages
• Inferior to Phenolic in dimensional stability in hot dry conditions.
• More expensive than Urea or Phenolic.
• Limited resistance to concentrated acids and alkalies.
Urea formaldehyde resin
(formation of methyol urea)

\[(\text{HOCH}_2\text{)}_2\text{N} - \text{CO} - \text{NH}_2\]

\[(\text{HOCH}_2\text{)}_2\text{N} - \text{CO} - \text{NH} - \text{CH}_2\text{OH}\]

\[(\text{HOCH}_2\text{)}_2\text{N} - \text{CO} - \text{N}(\text{CH}_2\text{OH})_2\]

\[\text{HOCH}_2 - \text{NH} - \text{CO} - \text{NH}_2\]

\[\text{HOCH}_2 - \text{NH} - \text{CO} - \text{NH} - \text{CH}_2\text{OH}\]
Hardening of the urea formaldehyde resin

\[ \text{H}_2\text{NCONHCH}_2\text{OH} \rightleftharpoons \text{H}_2\text{NCON} = \text{CH}_2 + \text{H}_3\text{O}^+ \]

\[ 3\text{H}_2\text{NCON} = \text{CH}_2 \rightarrow \text{Crosslinked urea formaldehyde} \]

Under acidic condition

Crosslinked urea formaldehyde
Phenol-formaldehyde resins

- Two forms of pre-polymer for phenol-formaldehyde resins are RESOLS and NOVOLAC.
- RESOLES are produced by reacting phenol with a molar excess of formaldehyde (~1 : 2), using NH$_3$ or NaOH as a catalyst.
- NOVOLAC is prepared by reacting a molar excess of phenol with formaldehyde (~1.25 : 1) under acidic conditions (e.g. HCl).
Resole

Phenol anion + \text{HCHO} \rightarrow \text{Methylol anion}
Resole (further reactions to form methylene bridge and ether bridge)
Methylol phenols = *Pre-polymer*

Side reaction (staining)
Cross-linked resole
Phenol formaldehyde [Novolac]

\[
\begin{align*}
  \text{HCHO} + \text{H}^+ & \rightarrow \text{HOC}^+ \\
  \text{excess} & \rightarrow \begin{array}{c}
  \text{HO} \\
  \text{CH}_2
  \end{array}
\end{align*}
\]

Application of Novolac includes photoresist:
Novolac Prepolymer
## Typical formulations of phenolic resins (general grade)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novolac resin</td>
<td>100</td>
</tr>
<tr>
<td>Hexamethylene tetraamine</td>
<td>12.5</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>3</td>
</tr>
<tr>
<td>Magnesium stearate</td>
<td>2</td>
</tr>
<tr>
<td>Dye</td>
<td>4</td>
</tr>
<tr>
<td>Wood flour</td>
<td>100</td>
</tr>
</tbody>
</table>
Exercises

1. Write chemical reaction illustrating the synthesis of
   – PU fiber
   – Crosslinked PU elastomer
   – TPU (thermoplastic polyurethane)

2. Read the paper and describe the causes for the explosion of phenol formaldehyde reactor.

3. Read another paper and answer the following points;
   – Differences between anhydride and amine curing systems
   – Differences between aliphatic and aromatic amine curing agents
HOW TO PREVENT RUNAWAY REACTIONS

CASE STUDY:
PHENOL-FORMALDEHYDE REACTION HAZARDS

EPA is issuing this Case Study as part of its ongoing effort to protect human health and the environment by preventing chemical accidents. Under CERCLA, section 104(e) and the Clean Air Act (CAA), EPA has authority to conduct chemical accident investigations. EPA is striving to learn the causes and contributing factors associated with chemical accidents to prevent their recurrence. Major chemical accidents cannot be prevented solely through command and control regulatory requirements, but by understanding the fundamental root causes, widely disseminating the lessons learned, and integrating them into safe operations. EPA will publish Case Studies and Alerts to increase awareness of possible hazards. It is important that facilities, State Emergency Response commissions (SERCs), Local Emergency Planning Committees (LEPCs), emergency responders and others review this information and take appropriate steps to minimize risk.

PROBLEM: Many industrial chemical processes involve exothermic (heat generating) reactions. Uncontrolled, or runaway, reactions can occur as a result of various situations, such as mischarged raw materials, failure of a reactor's cooling system or the presence of contaminants. If the heat generation exceeds the reactor's ability to remove it, the reaction can accelerate - or run away - and cause the temperature and pressure to increase. A sudden energy release from such an uncontrolled reaction has the potential to harm workers, the public, and the environment. The following Case Study aims to increase awareness of possible hazards connected to exothermic reactions.

Columbus, Ohio
Sept. 10, 1997

explosion also resulted in the release of a large quantity of liquid resin and smaller quantities of other chemicals within the facility. There was another
Additional slides
Toxicity of BPA

- Change in reproductive organ weight
- Change in sperm production rate and efficiency
- Change in the anogenital distance (AD) (the distance between anus and penis)
- Change in pubertal characteristics (e.g. vaginal opening date).
- Carcinogenic effect (???)

Human Exposure to BPA

• Trace level of residual BPA in the PC products is typically < 50 ppm. (Due to the advanced polymerization technology)

• Typical migration level of BPA from PC bottles and epoxy coated food cans are less than 90 ppb and 140 ppb, respectively.

• Human exposure to BPA was investigated. The measured value is in the range of 20-30 ng/kg/day. (Arakawa et al., Environ Health & Preventive Medicine, 2004, (2) Tsukioka et al., J. Environ Chemistry, 2004, and more....)

• Children’s exposure to BPA is ~ 43 ng/kg/day. (Wilson, et al., J. Exposure. Anal. Environ Epidemiology, 2003)

• These levels are ~ 400-2000 times lower than the safe limits. [0.05 mg/kg/d (FDA) & 0.01 mg/kg/d (EU)]. And also below the “low dose” level (1000 ng/kg/d). Exposure to BPA poses no known risk to human health.