Advances in Low Flammability Non-halogenated Polymers

The 7th Triennial International Fire and Cabin Safety Research Conference
December 2 – 5, 2013 Philadelphia, PA

Investment in Research to Enhance Safety in a Changing World

Todd Emrick University of Massachusetts Amherst

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Acknowledgements

Emrick research group   UMass Amherst   Summer 2013
I. Polymer flammability: a persistent problem with plastics

II. BHDB-polymers
   A new molecule for anti-flammable polymers
   (and, a potential bisphenol A replacement)

III. Non-flammable adhesive materials:
     BEDB, BPT, and more

Materials design criteria:

1. Inherently non-flammable polymers – design polymers to char instead of burn
2. Practical advantage: no flame retardants needed (major cost benefit)
Synthetic organic polymers
A mainstay of modern society, used in textiles, upholstery, construction materials, vehicles, and electronic devices

Pose a significant threat due to their inherent flammability

Background: burning plastics and polymer foams

Transportation

Sound insulation foam

How advanced plastics saved lives on Asiana Flight 214

Plastics Today  July 2013
Halogenated flame retardants (HFRs)

HFRs have demonstrated effectiveness for suppressing flammability when used as additives in polymer materials.

HFRs face legislative scrutiny due to their health and environmental concerns (bioaccumulation and toxicity).

Dibromodichloropropane (DBD)

Tris(2,3-dibromopropyl) phosphate

Tris(1,3-dichloro-2-propyl) phosphate

Polybrominated diphenyl ether (PBDEs)
Small molecule flame-retardants

Halogenated aromatics

\[ \text{Halogenated aromatics} \]

\[ \text{Inorganic fillers: non-halogenated} \]

- Aluminum trihydrate
- Magnesium hydroxide
- Phosphorus, nitrogen, and silicon-based inorganics

Alternatives: 1) include halogenation directly on the polymer backbone (prevents leaching) or 2) develop polymers that are both non-halogenated and non-flammable
Brominated Flame Retardant Polymers

FR-803P, ICL-IP
SAYTEX® HP-310, Albemarle

FR-1025, ICL-IP

BC-58™, Chemtura

BC-52™, Chemtura

FR-3100, F-3014, F-3020, ICL-IP

Thermoplastic additives
Thermal stability
Bloom-free
Suitable for extrusion and injection molding
Microscale combustion calorimetry (MCC) enables effective analysis of milligram quantities of novel and known materials.


Richard Lyon
Federal Aviation Administration
Presentation Topics

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Bisphenolic monomers

Well-known structures:
- Bis-phenol A (BPA)
- Bis-phenol C (BPC)

New molecules:
- Bis-hydroxydeoxybenzoin (BHDB)
- Bis-phenol triazole (BPT)
### BPA vs. BPC

<table>
<thead>
<tr>
<th>Property</th>
<th>BPA Polycarbonate (Lexan)</th>
<th>BPC Polycarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morphology</td>
<td>Amorphous</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>152</td>
<td>168</td>
</tr>
<tr>
<td>Flex Modulus (ksi)</td>
<td>336</td>
<td>376</td>
</tr>
<tr>
<td>Flex Strength (psi)</td>
<td>16,300</td>
<td>16,200</td>
</tr>
<tr>
<td>Tensile Yield Strain (%)</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>NBS Smoke (Dm)</td>
<td>165</td>
<td>75</td>
</tr>
<tr>
<td>Oxygen Index (%)</td>
<td>26</td>
<td>56</td>
</tr>
<tr>
<td><strong>HR Capacity (J/g.k)</strong></td>
<td><strong>390</strong></td>
<td><strong>29</strong></td>
</tr>
</tbody>
</table>

BPC and BHDB: common pathways towards char formation?

- Presence of chlorine sets up rearrangement chemistry
- Conversion into diphenylacetylene – key step in char formation
- Deoxybenzoin conversion to diphenylacetylene at high temperatures

No prior reports of polymerization chemistry using BHDB

Ramirez, M. L. Thermal Decomposition Mechanism of 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethylene Based Polymers. DOT/FAA/AR-00/42.; Department of Transportation, Federal Aviation Administration, National Technical Information Service: Springfield, VA, 2001; Stoliorav, S.I.; Westmoreland, P.R. Polymer 2003, 44, 5469; van der Waals et al. J. Mol. Cat. A 1998, 134, 179
BHDB preparation from desoxyanisoin, and integration into polyarylates

Desoxyanisoin

\[
\text{BHDB-Polyarylate}
\]

- One step synthesis of monomer in high yields, up to 500 g scale
- **Polyarylate:** HRC = 65 J/g-K; Char yield = 45%
- Low solubility and low molecular weight (\(M_w < 5000\) g/mol)

BHDB polymers:
halogen free, ultra-low heat release, high char yield

Synthesized structures: polyesters, polyphosphonates, polyurethanes, polycarbonates, epoxy polymers, cyanate esters,….

Heat release capacity = 65 J/g-K
Char yield = 45 %

Heat release capacity = 80 J/g-K
Char yield = 52 %

UL-94 results
- Predominant charring
- No flame spread
- No dripping
- V-0 and 5VA ratings
(from microcalorimetry data analysis, sample had a 96% probability of achieving V-0)


4 awarded patents (2008-2013)
Presentation Topics

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Deoxybenzoin-based epoxy resins

Bis-epoxydeoxybenzoin (BEDB), or Deoxybenzoin diglycidyl ether (DB-DGE)

Desoxyanisoin (commercially available)

BEDB: Easily prepared at 100 gram scale
Would be trivial to scale to kilogram levels
Cured BEDB resins: thermal and mechanical properties

**Epoxies**

- **BEDB**
- **EBPA**
- **ETBBA**

**Amines (25 examples)**

- **DDS**
- **PDA**
- **DDM**

Curing conditions:
Mix epoxies with amines at 60-130°C

Cure in DSC instrument, then measure Tₐ

DDM example: Tₐ and decomposition

- **BEDB-DDM** Tₐ: 145°C; dec: 354°C
- **EBPA-DDM** Tₐ: 179°C; dec: 372°C
- **ETBBA-DDM** Tₐ: 192°C; dec: 274°C

- BEDB gives lower Tₐ epoxy resins
- Decomposition not complicated by liberation of HBr, and effect on carbon monoxide, as for brominated epoxy resins
Cured BEDB resins: thermal and mechanical properties

Heat release capacity (HRC) and total heat release (THR) from pyrolysis combustion flow calorimetry

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Thermal property</th>
<th>Flammability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (°C)$^b$</td>
<td>Residue$^c$</td>
</tr>
<tr>
<td>EBPA/4,4'-DDS</td>
<td>198</td>
<td>12</td>
</tr>
<tr>
<td>EBPA/4,4'-DDS$<em>{0.8}$ 4,4'-DDM$</em>{0.2}$</td>
<td>196</td>
<td>14</td>
</tr>
<tr>
<td>EBPA/4,4'-DDS$<em>{0.5}$ 4,4'-DDM$</em>{0.5}$</td>
<td>185</td>
<td>15</td>
</tr>
<tr>
<td>EBPA/4,4'-DDS$<em>{0.2}$ 4,4'-DDM$</em>{0.8}$</td>
<td>178</td>
<td>16</td>
</tr>
<tr>
<td>EBPA/4,4'-DDM</td>
<td>179</td>
<td>16</td>
</tr>
<tr>
<td>BEDB/4,4'-DDS</td>
<td>181</td>
<td>30</td>
</tr>
<tr>
<td>BEDB/4,4'-DDS$<em>{0.8}$ 4,4'-DDM$</em>{0.2}$</td>
<td>180</td>
<td>33</td>
</tr>
<tr>
<td>BEDB/4,4'-DDS$<em>{0.5}$ 4,4'-DDM$</em>{0.5}$</td>
<td>173</td>
<td>34</td>
</tr>
<tr>
<td>BEDB/4,4'-DDS$<em>{0.2}$ 4,4'-DDM$</em>{0.8}$</td>
<td>160</td>
<td>35</td>
</tr>
<tr>
<td>BEDB/4,4'-DDM</td>
<td>145</td>
<td>35</td>
</tr>
</tbody>
</table>

THR: heat of combustion of pyrolysis gas
HRC: maximum heat release rate / heating rate

Lap shear strengths: BEDB/DDS: 15.4 MPa; BEDB/DDM: 12.8 MPa
EBPA/DDS: 11.0 MPa; EBPA/DDM: 9.2 MPa

ASTM D 1002 protocol

BEDB vs. EBPA:
comparable storage modulus; higher plain-strain fracture toughness
Aromatic triazoles: thermal decomposition mechanisms


Diphenyl-1,2,3-triazole

Flash vacuum pyrolysis

-N$_2$(g)

Benzyl benzotriazoles

Isoquinoline product

Objective:
Synthesize BPT-containing monomers and test their polymerization chemistry and thermal properties
BPT-monomer syntheses

Monomers recrystallized from acetic acid/water
Melting points: 275 C (4-BPT); 205 C (3-BPT)

No prior reports of polymerization chemistry using BPTs
**BPT epoxy resins**

**Synthesis of BPT diglycidyl ethers**

3-BPT

- **Epichlorohydrin**
  - 
  - **Isopropanol, NaOH, H₂O**

Diglycidyl ether of 3-BPT (3-DGE-BPT, 82% yield)

4-BPT

- **Epichlorohydrin**
  - 
  - **Isopropanol, NaOH, H₂O**

Diglycidyl ether of 4-BPT (4-DGE-BPT, 62% yield)

**High resolution mass spectroscopy**

**EI mode:**

\[ [M-N₂]^+ \text{ 337.13 m/z observed} \]

**FAB mode**

\[
3\text{-DGE-BPT} [\text{M+H}]^+ : 366.1462 \text{ m/z}
\]

\[
4\text{-DGE-BPT} [\text{M+H}]^+ : 366.1426 \text{ m/z observed}
\]

(calculated : 366.1454 m/z)

**DSC: curing BPT-epoxies**

- 3-DGE-BPT
  - **Temperature (°C)**
  - **Heat flow (mW, Exo...)**

- 4-DGE-BPT
  - **Temperature (°C)**
  - **Heat flow (mW, Exo...)**

**Macromolecules 2011**
BPT epoxy resins are self-curing

DSC thermograms of 3-DGE-BPT/DGE-BPA (−) and 4-DGE-BPT/DGE-BHDB(---)

Heat flow (mW; Exo ⋯→)

Temperature (°C)

1H-NMR spectra of the mixtures
(top: before reaction; bottom: after reaction)

\[ \begin{align*}
5 & \quad 3-\text{DGE-BPT} \\
6 & \quad 4-\text{DGE-BPT} \\
\end{align*} \]

Propagation

Zwitterion
**BPT epoxy resins**

Heat release and char properties of cured resins

<table>
<thead>
<tr>
<th>Entry</th>
<th>Composition (w/w)</th>
<th>HRC (J/(g K))</th>
<th>THR (kJ/g)</th>
<th>Char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DGE-BPA/DDS $^a$</td>
<td>513 ± 10</td>
<td>25.3 ± 0.2</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>DGE-BPA/3-DGE-BPT (1/1)</td>
<td>408 ± 10</td>
<td>16.9 ± 0.2</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>DGE-BHDB/DDS $^a$</td>
<td>420 ± 14</td>
<td>17.2 ± 0.2</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>DGE-BHDB/DDM $^a$</td>
<td>439 ± 7</td>
<td>17.6 ± 0.2</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>DGE-BHDB/4-DGE-BPT (4/1)</td>
<td>265 ± 5</td>
<td>16.6 ± 0.4</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>DGE-BHDB/3-DGE-BPT (1/1)</td>
<td>222 ± 5</td>
<td>12.5 ± 0.2</td>
<td>43</td>
</tr>
<tr>
<td>7</td>
<td>3-DGE-BPT (self-cured)</td>
<td>200 ± 7</td>
<td>10.9 ± 0.3</td>
<td>45</td>
</tr>
</tbody>
</table>

$^a$ Equivalent amount of aromatic diamine was used.

**Adhesion demonstration using 3-DGE-BPT resin (a) before loading additional weight and (b) after loading 700 g weight**

*Macromolecules 2011*
**BPT cyanate ester**

**Synthesis**

BPT cyanate ester was synthesized by reacting 3-BPT with BrCN in the presence of TEA in acetone at 0-5 °C, yielding the dicyanate ester of 3-BPT (3-BPTCE, 90% yield).

**High resolution mass spectroscopy**

- **FAB mode**
  - 3-BPTCE [M+H]+: 304.0822 m/z (cald: 304.0834 m/z)
- **EI mode**
  - [M-N2]+: 275.1 m/z

**Melting point:** 155-160 °C

**Curing by cyclization to triazines**

Gelation times were measured by using a magnetic stir bar (1 cm) in a 100 mg of sample at 170 °C, noting the time required for a mixture stirring initially at 200 rpm to stop completely.

<table>
<thead>
<tr>
<th>Composition (w/w)</th>
<th>Gel. time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BPACE</strong></td>
<td>a</td>
</tr>
<tr>
<td>BPACE/BPTCE (9/1)</td>
<td>230</td>
</tr>
<tr>
<td>BPACE/BPTCE (8/2)</td>
<td>105</td>
</tr>
<tr>
<td>BPACE/BPTCE (7/3)</td>
<td>55</td>
</tr>
<tr>
<td>BPACE/BPTCE (5/5)</td>
<td>25</td>
</tr>
<tr>
<td>BPTCE</td>
<td>5</td>
</tr>
</tbody>
</table>

*a BPACE did not show evidence of curing over 360 min.*
BPT cyanate ester

Heat release and char properties of the BPT/BPA cyanate ester blends

Sample preparation
1. homogeneous mixture (BPACE/BPTCE = 9/1, 2/8, 3/7, and 5/5, w/w) at 170 °C
2. curing at 170 °C for 4 h, and 4 h at 240 °C
3. post-curing at 280 °C for 1 h

<table>
<thead>
<tr>
<th>composition (w/w)</th>
<th>HRC (J/(g K))</th>
<th>THR (kJ/g)</th>
<th>char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPACE</td>
<td>332 ± 10</td>
<td>14.5 ± 0.2</td>
<td>44</td>
</tr>
<tr>
<td>BPACE/BPTCE (9/1)</td>
<td>285 ± 14</td>
<td>13.4 ± 0.3</td>
<td>44</td>
</tr>
<tr>
<td>BPACE/BPTCE (8/2)</td>
<td>280 ± 15</td>
<td>12.5 ± 0.2</td>
<td>46</td>
</tr>
<tr>
<td>BPACE/BPTCE (7/3)</td>
<td>261 ± 12</td>
<td>11.2 ± 0.4</td>
<td>48</td>
</tr>
<tr>
<td>BPACE/BPTCE (5/5)</td>
<td>200 ± 15</td>
<td>9.2 ± 0.2</td>
<td>53</td>
</tr>
<tr>
<td>BPTCE</td>
<td>10 ± 2</td>
<td>2.0 ± 0.2</td>
<td>67</td>
</tr>
</tbody>
</table>

TGA thermograms of cured blends

Lyon, R. E. et al Fire Mater. 2006, 30, 89-106

hexafluorobisphenol A CE

HRC : 62 J/(g K)  
THR : 4.6 kJ/g  
Char : 43%

Bisphenol C CE

HRC : 24 J/(g K)  
THR : 4.2 kJ/g  
Char : 53%
BPT cyanate ester

Small scale flame tests
Specimen (1 × 0.35 × 0.1) cm placed in a propane torch flame at a 45° angle for 3 s, noting time required for the sample to self-extinguish upon removal from the flame.

<table>
<thead>
<tr>
<th>composition (w/w)</th>
<th>flame test</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPACE</td>
<td>&gt; 5 s burn</td>
</tr>
<tr>
<td>BPACE/BPTCE (9/1)</td>
<td>&gt; 5 s burn</td>
</tr>
<tr>
<td>BPACE/BPTCE (8/2)</td>
<td>&gt; 5 s burn</td>
</tr>
<tr>
<td>BPACE/BPTCE (7/3)</td>
<td>&gt; 5 s burn</td>
</tr>
<tr>
<td>BPACE/BPTCE (5/5)</td>
<td>1-2 s burn</td>
</tr>
<tr>
<td>BPTCE</td>
<td>extinguished instantly</td>
</tr>
</tbody>
</table>

Macromolecules 2011
Tetrahydroxydeoxybenzoin (THDB)
A new multifunctional compound for anti-flammable materials

Houben-Hoesch conditions

\[
\text{HO-} \quad + \quad \text{N=C-} \quad \xrightarrow{1. \text{AlCl}_3, \text{HCl in ether 0 }^\circ\text{C}} \quad \xrightarrow{2. \text{H}_2\text{O, } 100^\circ\text{C}} \quad \text{HO-}
\]


86% yield on 10 g scale
Pale yellow powder