FIRE RESISTANT POLYMERS BASED ON BISPHENOL-C

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Fire Research Program
Fire Safety Section AAR-422
FEDERAL AVIATION ADMINISTRATION
W.J. Hughes Technical Center
Atlantic City International Airport, NJ 08405
OUTLINE OF TALK

FIRE RESISTANT BISPHENOL-C POLYMERS

- FAA Fire Resistant Materials Program
- Background of Bisphenol-C Polymers
- New Bisphenol-C Polymers
- Fire & Flammability Results
- Conclusions
FAA PROGRAM OBJECTIVE:

Eliminate burning cabin materials as a cause of death in aircraft accidents by 2010.
## A Wide Range of Deliverables

<table>
<thead>
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<th>PRODUCTS</th>
<th>APPLICATIONS</th>
</tr>
</thead>
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<tr>
<td><strong>Supporting Research</strong></td>
<td><strong>New synthetic chemistries</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Predict flammability from polymer chemical structure</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Lab-scale method for measuring polymer fire hazard</strong></td>
</tr>
<tr>
<td><strong>Thermoset Resins</strong></td>
<td><strong>Interior decorative panels</strong></td>
</tr>
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<td></td>
<td><strong>Secondary composites</strong></td>
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<tr>
<td></td>
<td><strong>Adhesives</strong></td>
</tr>
<tr>
<td><strong>Thermoplastics</strong></td>
<td><strong>Decorative facings</strong></td>
</tr>
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<td></td>
<td><strong>Molded seat parts</strong></td>
</tr>
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<td></td>
<td><strong>Electrical wiring</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Thermoacoustic insulation films</strong></td>
</tr>
<tr>
<td><strong>Textile Fibers</strong></td>
<td><strong>Upholstery</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Murals</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Thermoacoustic insulation blankets</strong></td>
</tr>
<tr>
<td><strong>Elastomers (rubber)</strong></td>
<td><strong>Seat cushions</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Pillows</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Sealants/gaskets</strong></td>
</tr>
</tbody>
</table>
A VERSATILE BUILDING BLOCK IS NEEDED

Thermoplastics

Polycarbonate

Polyester

Polyarylether

Thermosets

Phosgene

Epichlorohydrin

Epoxy-Cyanate Ester Blends

Cyanate Ester
GAPS IN MATERIALS FIRE SAFETY TECHNOLOGY

A. Affordable routes to ultra fire resistant polymers

B. Ultra fire resistant polymers with:
   • low/moderate processing temperature
   • good strength & toughness
   • colorability and colorfastness

C. Relationship between material properties and fire performance.

D. Relationship between chemical composition and fire performance.

E. Scaling Relationships: micro-, bench-, quarter-, full-scale

F. Fundamental understanding of fire resistance mechanisms

(Attributes of Bisphenol-C Based Polymers)
BACKGROUND: Bisphenol-C Polymers

1874: Chloral-phenol condensation reaction product (I) first reported.

\[ 2 \text{HO-Phenol} + \text{O-Cl-Chloral} \xrightarrow{\text{H}^+} \text{HO-I} \rightarrow \text{H}_2\text{O} \]

1874: Dehydrochlorination to 1,1-dichloro, 2,2-bis(4-hydroxyphenyl) ethylene (bisphenol-C, BPC) first reported.

\[ \text{I} \rightarrow \text{Bisphenol C (BPC)} \]
BACKGROUND: Bisphenol-C Polymers

1964: Polycarbonate from BPC first reported.

\[
\text{Bisphenol-C (BPC)} + \text{Phosgene} \rightarrow \text{Bisphenol-C Polycarbonate}
\]

1965: “Self-Extinguishing Epoxies” from BPC first reported in Poland.

\[
\text{Bisphenol C (BPC)} + 2 \text{HCl} \rightarrow \text{Diglycidylether of Bisphenol C (DGEBC) III}
\]
1970’s: GE begins research to obtain non-burning (XB) plastics. Investigates bisphenol-C, etherimide, and acetylenic polymers.

- Acetylenic groups increase char yield in flame.
- Too many acetylenes increase flammability (decrease LOI)
BACKGROUND: Bisphenol-C Polymers

1970’s:

GE develops and patents industrial process chemistry to make BPC-polycarbonate (XB-1) and polyetherimide (XB-2).

GE downselects to XB-2 (ULTEM™) because of fire (UL) and high temperature (TEM) capability.
BACKGROUND: Bisphenol-C Polymers

1980’s – 1990’s: Research in chloral condensation polymers continues in Poland and Russia but not in U.S.A.

• Fire testing limited to flame tests (flammability).
• High LOI (50-60) and “self-extinguishing” behavior attributed to chlorine content.
• No commercial activity.

1994: Comprehensive review:

Condensation Polymers Based on Chloral And Its Derivatives,

**BACKGROUND: Flaming Heat Release Rate Measured**

**1997:** FAA measures flaming heat release rate of BPC polycarbonate in OSU fire calorimeter.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Char Yield (%)</th>
<th>L.O.I. [%O₂]</th>
<th>UL 94</th>
<th>FAR Peak/Total* (kW/m²)</th>
<th>(kW-min/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>25</td>
<td>26</td>
<td>V-2</td>
<td>153 / 58</td>
<td></td>
</tr>
<tr>
<td>BPC</td>
<td>54</td>
<td>56</td>
<td>V-0</td>
<td>55 / 33</td>
<td></td>
</tr>
</tbody>
</table>

*1/16-inch (0.063 in) sample thickness*
BACKGROUND: New Flammability Screening Test

1998: FAA develops milligram-scale heat release rate test to accelerate search for new polymers
TEST METHOD REPRODUCES FLAMING COMBUSTION

Flame

Pyrolysis Zone

Polymer Solid

Flaming Combustion

Pyrolysis-Combustion Flow Calorimetry

Combustor

Pyrolyzer

Sample

Gas Scrubbers

Flow-meter

O₂ Analyzer

O₂

N₂

DAQ

Exhaust

Computer
MOLECULAR FIRE PARAMETER IDENTIFIED

Dividing the peak kinetic heat release rate by $\beta$ gives a material property, the Heat Release Capacity

$$\eta_c \equiv \frac{\dot{Q}_C^{\text{max}}}{\beta} = h_c^0 \frac{(1-\mu)E_a}{eRT_p^2} \quad (\text{J/g-K})$$

$h_c^0$ = Heat of Combustion of Fuel Gases
$E_a$ = Global Activation Energy for Pyrolysis
$\mu$ = Char Fraction
$T_p$ = Temperature at Peak Mass Loss Rate
$e$ = The natural number $2.7183\ldots$
$R$ = Gas Constant
HEAT RELEASE CAPACITY PREDICTS FIRE RESPONSE

Provides new capability for rapid screening of research polymers for fire resistance.
BACKGROUND: Flammability Screening Yields Results

1998: FAA collaborates with Ciba Specialty Chemicals Performance Polymers Division, Brewster, NY to develop ultra fire resistant cyanate ester thermoset resins for aircraft interiors

- BPC cyanate ester identified as having lowest heat release capacity of any thermoset tested to date
- BPC cyanate ester patents filed by Ciba
- BPC cyanate ester scaled-up and prepregged for bench scale fire calorimetry testing

1999-present:

University (UMASS, Rice) research continues on BPC copolymers and blends.
BACKGROUND: Thermal Degradation Mechanism Identified


Delta (exothermic) - 80 kJ/mole

350-450°C - 2 HCl (↑)

- Δ (exothermic)

- R (↑)

- R (↑)

- Cl

- phenyl migration

- CCl

- electron transfer

- Cl– +

- - HCl (↑)

- char
Polycarbonate
Polyetherketone
Polyarylates
# Poly Carbonate: BPA vs BPC

<table>
<thead>
<tr>
<th>Property</th>
<th>LEXAN™ Polycarbonate</th>
<th>Chloral Polycarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Morphology</strong></td>
<td>Amorphous</td>
<td>Amorphous</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt; (°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>Heat Release Capacity (J/g-K)</td>
<td>390</td>
<td>29</td>
</tr>
<tr>
<td>FAR 25.853(a-1) Heat Release Peak/Total* (kW/m²) / (kW-min/m²)</td>
<td>153 / 58 *0.063 in</td>
<td>55 / 33 *0.063 in</td>
</tr>
</tbody>
</table>
## POLYETHERKERETONE: Carboxyl vs. DCE

<table>
<thead>
<tr>
<th>Property</th>
<th>ULTRAPEK™</th>
<th>Chloral Polarylether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morphology</td>
<td>Semicrystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>161</td>
<td>166</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>381</td>
<td>N/A</td>
</tr>
<tr>
<td>Flex Modulus (ksi)</td>
<td>530</td>
<td>426</td>
</tr>
<tr>
<td>Flex Strength (psi)</td>
<td>18,900</td>
<td>18,000</td>
</tr>
<tr>
<td>Tensile Yield Strain (%)</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>NBS Smoke ($D_m$)</td>
<td>N/A</td>
<td>17</td>
</tr>
<tr>
<td>Oxygen Index (%)</td>
<td>34</td>
<td>52</td>
</tr>
<tr>
<td>Heat Release Capacity (J/g-K)</td>
<td>124</td>
<td>20</td>
</tr>
</tbody>
</table>
### Polyarylates: BPA vs. BPC

<table>
<thead>
<tr>
<th>Property</th>
<th>BPA (Amorphous)</th>
<th>BPC (Amorphous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDT (°C)</td>
<td>160-174</td>
<td>160</td>
</tr>
<tr>
<td>Flex Modulus (ksi)</td>
<td>325</td>
<td>391</td>
</tr>
<tr>
<td>Flex Strength (psi)</td>
<td>11,000</td>
<td>11,700</td>
</tr>
<tr>
<td>Tensile Failure Strain (%)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>NBS Smoke (Dm)</td>
<td>109</td>
<td>N/A</td>
</tr>
<tr>
<td>Oxygen Index (%)</td>
<td>36</td>
<td>47</td>
</tr>
<tr>
<td>Heat Release Capacity (J/g-K)</td>
<td>460</td>
<td>18</td>
</tr>
</tbody>
</table>
Flammability does not follow simple rules of mixtures.

Polyarylate: BPA-BPC Copolymers & Blends

R = \begin{align*} &\text{Cl} \quad \text{Cl} \\ &\text{C} \quad \text{C} \\ &\text{Cl} \quad \text{CH}_3 \\ &\text{BPC} \quad \text{BPA} \end{align*}

Mole Percent BPC

Mole Percent BPA

Heat Release Capacity, J/g-K

Rules of Mixtures

Upper Bound

Lower Bound

J.R. Stewart, 2000
BPC THERMOSET POLYMERS

Epoxy

Cyanate Ester

Epoxy-Cyanate Ester Blends
EPOXIES: Synthesis as per DGEBA

2 \( \text{HO-} \) Phenol + 2 \( \text{Cl-} \) Chloral → 2 \( \text{Cl-} \) Epichlorhydrin Bisphenol C (BPC) (II)

\( \text{HO-} \) \( \text{CH}_2-\text{CH-CH}_2-\text{OH} \) Bisphenol C (BPC) (II)

\( \text{CH}_2-\text{CH-CH}_2-\text{O-CH}_2-\text{CH-CH}_2-\text{O-} \) Diglycidylether of Bisphenol C (DGEBC) (III)
EPOXY FORMULATIONS: Hardeners Examined

EMI-24
(2 phr)

TETA
(14 phr)

MDA
(58 phr)

BPC
(78 phr DGEBC)

BPA
(66 phr DGEBA)

Cyanate ester of BPC
(53 phr DBEBC)
FIRE RESISTANCE OF BPC EPOXY LIMITED BY HIGH FUEL VALUE OF GLYCIDIYL ETHER

*Dichloroethylidene (DCE) group has zero fuel value, but...*

a) DGEBC-BPC

b) DGEBC-EMI

“R” group for epoxy has relatively high fuel value.

“R” Heat of combustion, 
\[ h_c = \frac{7 \text{ kJ/g-polymer}}{} \text{ (theoretical)} \]

= 11 kJ/g-polymer (measured)
EPOXY HEAT RELEASE CAPACITIES

Heat Release Capacity, J/g-K

Hardener

UL 94 V-0 (typically)
EPOXY FIRE CALORIMETRY: Peak HRR

DGEBA  DGEBC

Glass fabric lamina
FAR 25.853 (a-1)

Peak Rate of Heat Release, kW/m²

<table>
<thead>
<tr>
<th>Hardener</th>
<th>Peak Rate of Heat Release, kW/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI-24</td>
<td></td>
</tr>
<tr>
<td>TETA</td>
<td></td>
</tr>
<tr>
<td>MDA</td>
<td></td>
</tr>
<tr>
<td>BPA</td>
<td></td>
</tr>
<tr>
<td>BPC</td>
<td></td>
</tr>
<tr>
<td>CEBPC</td>
<td></td>
</tr>
</tbody>
</table>

FAA Maximum

Maximum
EPOXY FIRE CALORIMETRY: Total Heat Release

Glass fabric lamina
FAR 25.853 (a-1)

EMI-24 TETA MDA
BPA BPC CEBPC

Hardener

Total Heat Release, kW-min/m²

FAA Maximum

(2-min, flaming)
MECHANICALS: BPA ( ) vs. BPC ( ) Epoxy

**STIFFNESS**
- Young's Modulus, GPa

**STRENGTH**
- Yield Stress, MPa

**HEAT OF POLYMERIZATION**
- \( ^\circ \text{H}_{\text{polym}}, \text{kJ/mole} \)

**GLASS TRANSITION TEMPERATURE**
- Glass Transition Temperature, °C
FLAMMABILITY: BPA ( ) vs. BPC ( ) Epoxy

**Oxygen Index**

<table>
<thead>
<tr>
<th>Hardener</th>
<th>EMI-24</th>
<th>TETA</th>
<th>MDA</th>
<th>BPA</th>
<th>BPC</th>
<th>CEBPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limiting Oxygen Index, %O₂ (v/v)</td>
<td><img src="image1.png" alt="Graph" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**UL 94**

<table>
<thead>
<tr>
<th>Hardener</th>
<th>EMI-24</th>
<th>TETA</th>
<th>MDA</th>
<th>BPA</th>
<th>BPC</th>
<th>CEBPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL 94 Ranking</td>
<td><img src="image2.png" alt="Graph" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
COMBUSTABILITY: BPA (■) vs. BPC (△) Epoxy

Decomposition Temperature

Heat of Combustion

Char Yield
CYANATE ESTER: Polymerization Reaction

BPC cyanate ester monomer

200°C

BPC triazine thermoset polymer
EFFECT OF BISPHENOL ON HEAT RELEASE RATE OF CYANATE ESTERS

ASTM 1354, cone calorimeter at 50 kW/m² heat flux, neat resin, 1/4-inch thick
BPC CYANATE ESTER: FAA Heat Release Rate Test

- Heat Release Rate, kW/m²
- Time, sec
- current AC phenolic panel
- BPC cyanate ester panel
- glass fabric lamina
- 1/8-in NOMEX honeycomb
- glass fabric lamina
STRUCTURAL COMPOSITES FOR NAVY SUBMARINES

Only 3 resins pass fire performance requirements as glass composites:

<table>
<thead>
<tr>
<th>Fire Test/Characteristic</th>
<th>Requirement (MIL-STD-2031)</th>
<th>Composite Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to ignition (s) at irradiance:</td>
<td></td>
<td>BPC-CE</td>
</tr>
<tr>
<td>25 kW/m²</td>
<td>&gt; 300</td>
<td>pass</td>
</tr>
<tr>
<td>50 kW/m²</td>
<td>&gt; 150</td>
<td>pass</td>
</tr>
<tr>
<td>75 kW/m²</td>
<td>&gt; 90</td>
<td>pass</td>
</tr>
<tr>
<td>100 kW/m²</td>
<td>&gt; 60</td>
<td>pass</td>
</tr>
<tr>
<td>Peak/Average Heat Release Rate (kW/m²) at irradiance:</td>
<td></td>
<td>Phthalocyanine</td>
</tr>
<tr>
<td>25 kW/m²</td>
<td>&lt; 50/50</td>
<td>pass</td>
</tr>
<tr>
<td>50 kW/m²</td>
<td>&lt; 65/50</td>
<td>pass</td>
</tr>
<tr>
<td>75 kW/m²</td>
<td>&lt; 100/100</td>
<td>pass</td>
</tr>
<tr>
<td>100 kW/m²</td>
<td>&lt; 150/120</td>
<td>pass</td>
</tr>
<tr>
<td>Smoke Obscuration, ( D_{\text{max}}/D_s ) (avg):</td>
<td>&lt; 200/100</td>
<td>pass</td>
</tr>
<tr>
<td>Combustion Gas Toxicity (CO/CO₂/HCN/HCl):</td>
<td>pass</td>
<td>N/A</td>
</tr>
<tr>
<td>Mechanical Properties</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Cure Temperature</td>
<td>&lt; 200°C</td>
<td>&gt; 375°C</td>
</tr>
</tbody>
</table>

J. Koo, et. al., SAMPE 2001
CYANATE ESTER-EPOXY REACTIVE BLENDS

**BPC Cyanate Ester (Ciba RD 98-228)**

\[
\begin{align*}
\text{C}_{16}\text{H}_{8}\text{O}_{2}\text{Cl}_{2} \\
\text{MW: } 331.16 \text{ g/mol} \\
\text{EW: } 165.58 \text{ g/eq} \\
\text{MP: } 75 \pm 2 \degree \text{C} \\
\text{Cl: } 21.41 \text{ wt\%}
\end{align*}
\]

**BPC Epoxy (Pacific Epoxy XPR-1015)**

\[
\begin{align*}
\text{C}_{20}\text{H}_{18}\text{O}_{4}\text{Cl}_{2} \\
\text{MW: } 393.27 \text{ g/mol} \\
\text{EW: } 209.39 \text{ g/eq} \\
\text{MP: } 91 \pm 4 \degree \text{C} \\
\text{Cl: } 16.93 \text{ wt\%}
\end{align*}
\]

**BPC Blends**

Blend ratios prepared from the reported equivalent weights

<table>
<thead>
<tr>
<th>Cyanate:Epoxy</th>
<th>% Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>21.4</td>
</tr>
<tr>
<td>8:2</td>
<td>20.5</td>
</tr>
<tr>
<td>6:4</td>
<td>19.6</td>
</tr>
<tr>
<td>4:6</td>
<td>18.7</td>
</tr>
<tr>
<td>2:8</td>
<td>17.8</td>
</tr>
<tr>
<td>0:1</td>
<td>16.9</td>
</tr>
</tbody>
</table>
Cyclotrimerization reaction of the cyanate ester (A) and the subsequent reaction with the glycidylether (B) to form the oxazoline.

Rearrangement of the triazine (C) to form isocyanurate and the subsequent reaction with the glycidylether (D) to form the oxazolidone.
FTIR MONITORING OF CE-EP CURE CHEMISTRY

The graph shows the relationship between temperature (°C) and normalized peak height. The temperature range is from 100°C to 300°C. The peaks are labeled for Cyanate Ester, Epoxy, Triazine, and Oxazoline. The graph indicates how these substances react at different temperatures.
FIRE PERFORMANCE OF BPC CYANATE ESTER-EPOXY BLENDS

Heat Release Capacity of Blend, J/g-K

OSU Peak HRR, kW/m² (Baseline Corrected)

Mole Fraction BPC-Epoxy in Blend

0 0.2 0.4 0.6 0.8 1

0 50 100 150 200 250 300 350 400

0 5 10 15 20 25 30 35 40
## CONCLUSIONS: Comparing Properties

**Average Change (5-7 polymers)**

<table>
<thead>
<tr>
<th>Property</th>
<th>BPC / BPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fire Hazard Potential ($\eta_c$):</td>
<td>– 90 %</td>
</tr>
<tr>
<td>Fire Hazard (HRR):</td>
<td>– 60 %</td>
</tr>
<tr>
<td>Glass Transition Temperature, K:</td>
<td>+ 3 %</td>
</tr>
<tr>
<td>Modulus:</td>
<td>+ 10 %</td>
</tr>
<tr>
<td>Yield Strength:</td>
<td>+ 10 %</td>
</tr>
<tr>
<td>Yield Strain:</td>
<td>+ 10 %</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

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Gary Green, Pacific Epoxy