FIRE RESISTANT POLYMERS BASED ON BISPHENOL-C

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Fire Safety Section AAR-422
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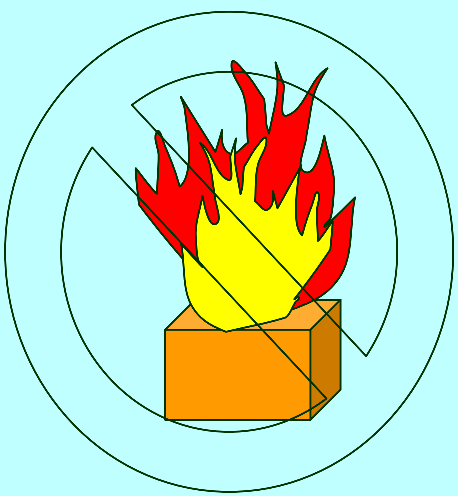
OUTLINE OF TALK

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.

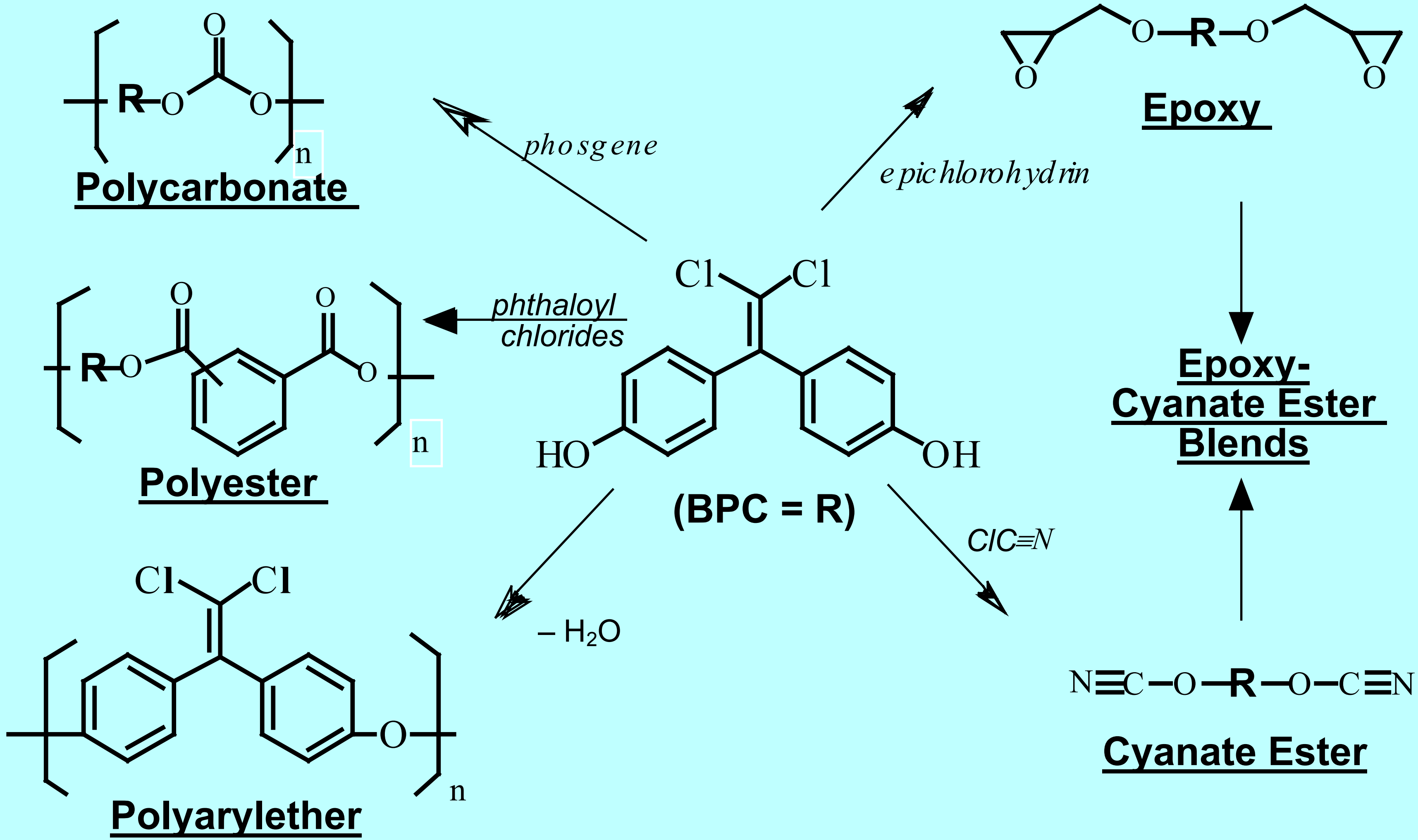
A WIDE RANGE OF DELIVERABLES

PRODUCTS	*APPLICATIONS*
Supporting Research	• New synthetic chemistries • Predict flammability from polymer chemical structure • Lab-scale method for measuring polymer fire hazard
Thermoset Resins	• Interior decorative panels • Secondary composites • Adhesives
Thermoplastics	• Decorative facings • Molded seat parts • Electrical wiring • Thermoacoustic insulation films • Telecommunications equipment • Passenger service units • Transparencies/glazing
Textile Fibers	• Upholstery • Murals • Thermoacoustic insulation blankets • Carpets • Tapestries
Elastomers (rubber)	• Seat cushions • Pillows • Sealants/gaskets

A VERSATILE BUILDING BLOCK IS NEEDED

Thermoplastics

Thermosets



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.

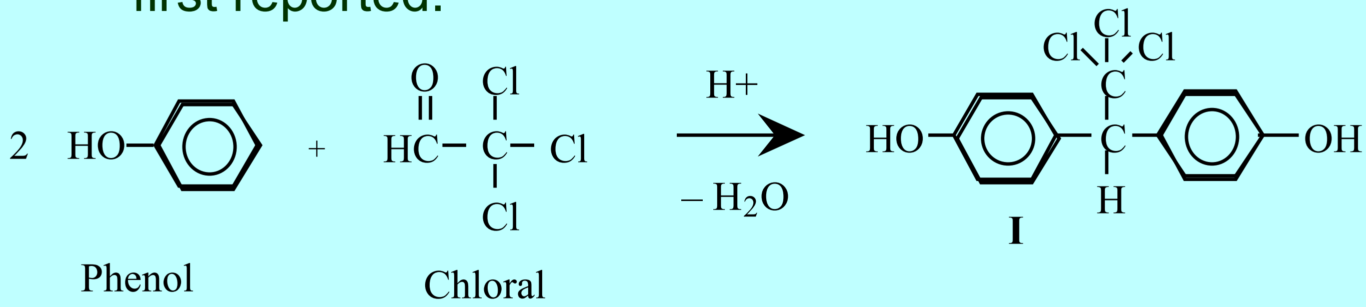
E. Scaling Relationships: micro-, bench-, quarter-, full-scale

F. Fundamental understanding of fire resistance mechanisms

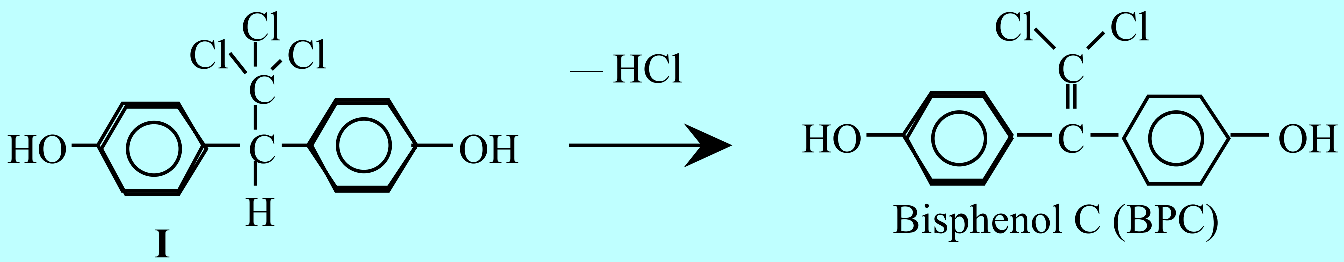
(Attributes of Bisphenol-C Based Polymers)

BACKGROUND: Bisphenol-C Polymers

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

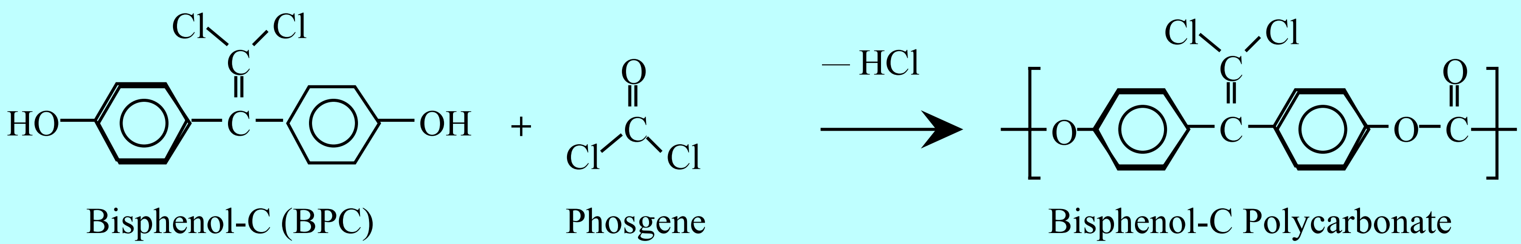


1874: Dehydrochlorination to 1,1-dichloro, 2,2-bis(4-hydroxyphenyl) ethylene (bisphenol-C, BPC) first reported.

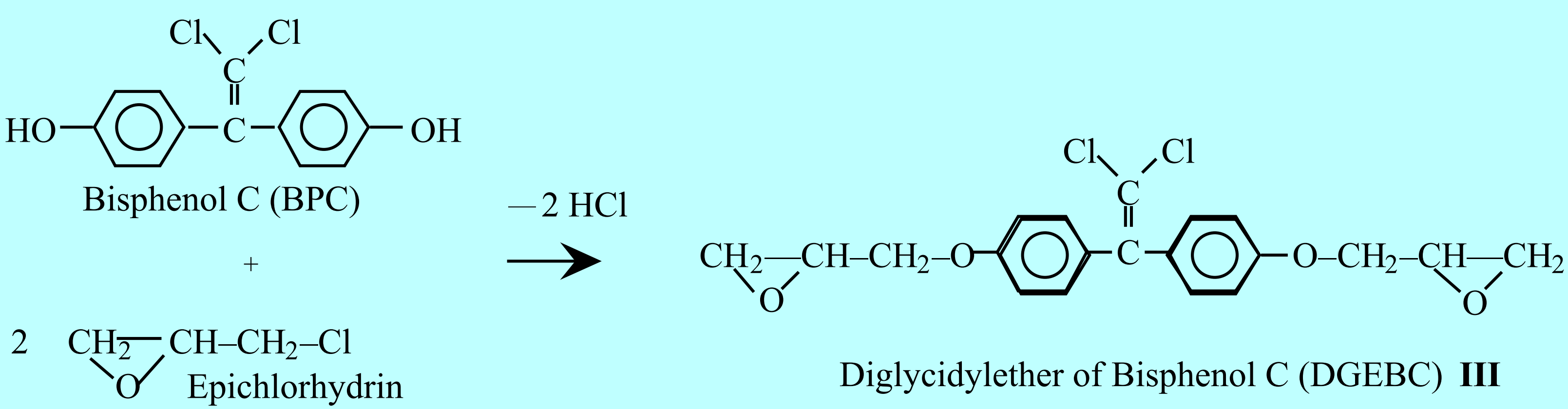


BACKGROUND: Bisphenol-C Polymers

1964: Polycarbonate from BPC first reported.

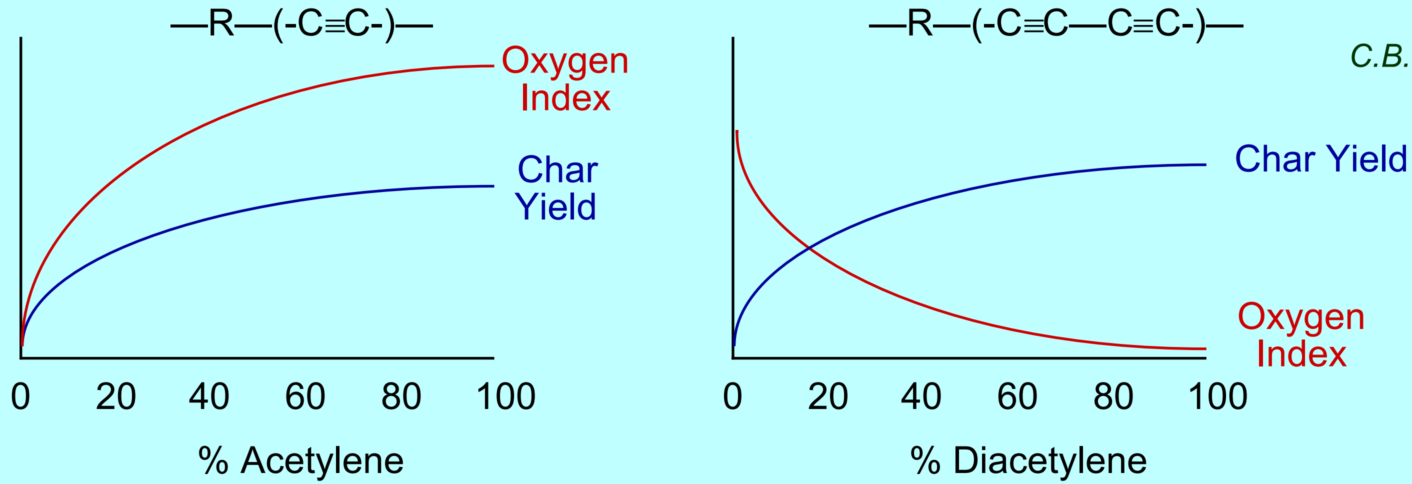


1965: “Self-Extinguishing Epoxies” from BPC first reported in Poland.



BACKGROUND: Bisphenol-C Polymers

1970's: GE begins research to obtain non-burning (XB) plastics. Investigates bisphenol-C, etherimide, and acetylenic polymers.



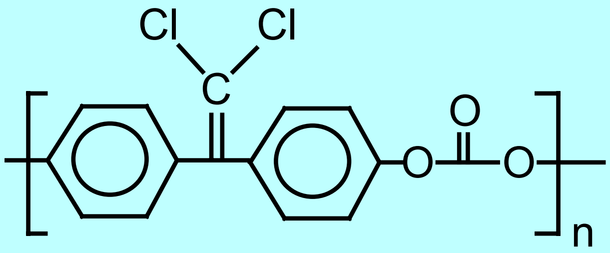
C.B. Quinn, 1967

- Acetylenic groups increase char yield in flame.
- Too many acetylenes *increase* flammability (decrease LOI)

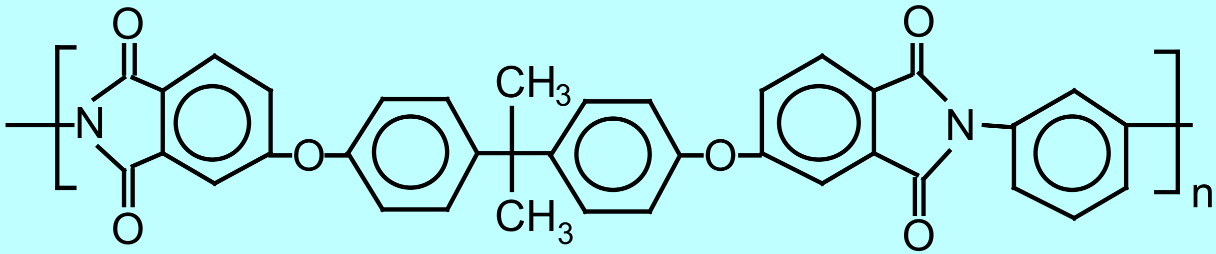
BACKGROUND: Bisphenol-C Polymers

1970's:

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



XB-1



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.

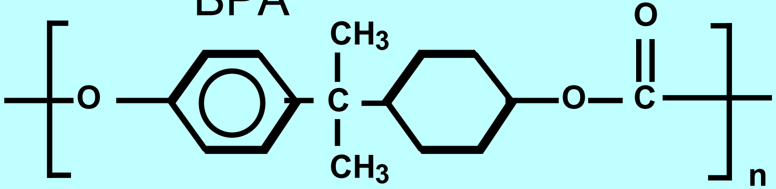
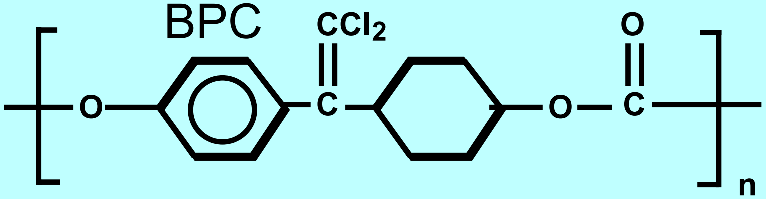
1994: Comprehensive review:

Condensation Polymers Based on Chloral And Its Derivatives,

A.L. Rusanov, Progress In Polymer Science, Vol. 19, pp. 589-662 (1994)

BACKGROUND: Flaming Heat Release Rate Measured

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

Polymer	Char Yield (%)	L.O.I. [$\%O_2$]	UL 94	FAR 25.853(a-1) Peak/Total* (kW/m^2) ($kW\text{-}min/m^2$)
BPA 	25	26	V-2	153 / 58
BPC 	54	56	V-0	55 / 33

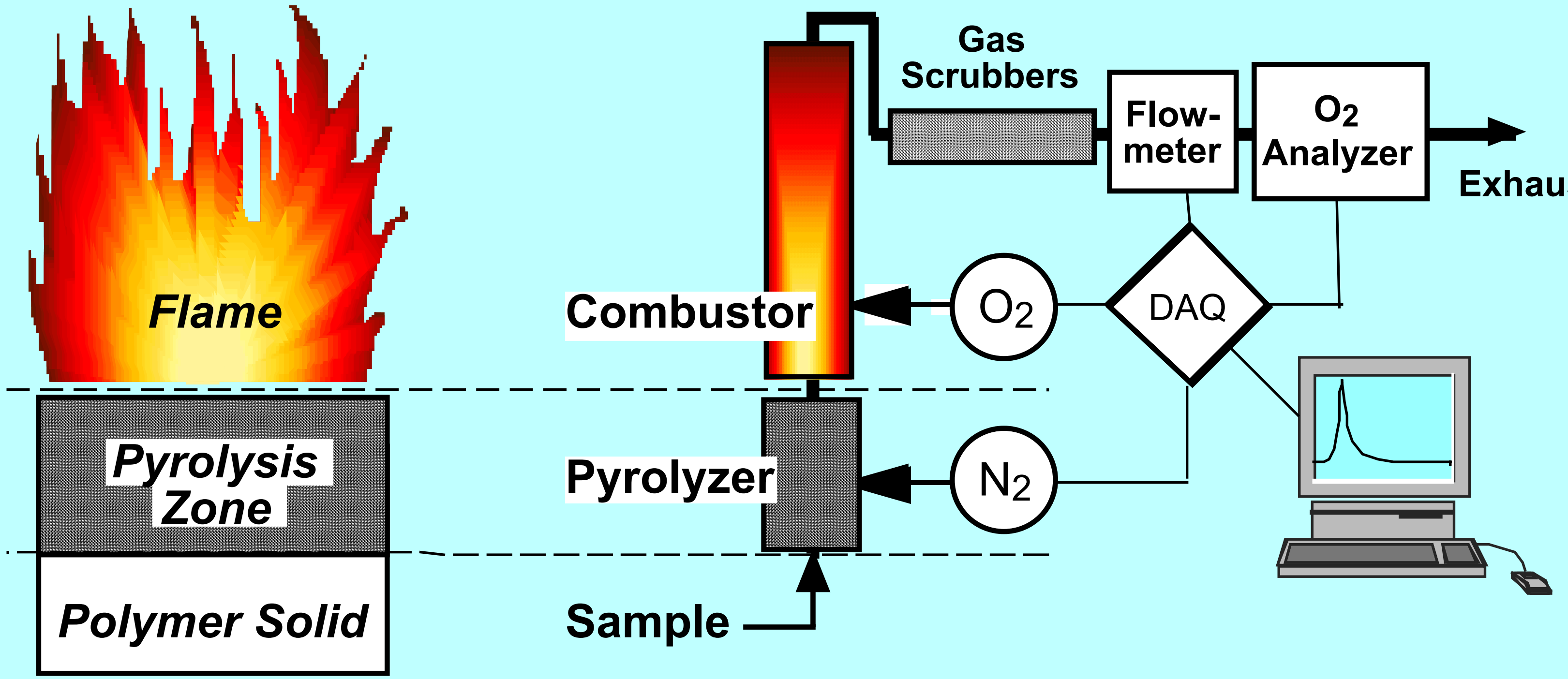
*1/16-inch (0.063 in) sample thickness

BACKGROUND: New Flammability Screening Test

1998: **FAA develops milligram-scale heat release rate test to accelerate search for new polymers**

ing

TEST METHOD REPRODUCES FLAMING COMBUSTION



Flaming Combustion

Pyrolysis-Combustion Flow Calorimetry

MOLECULAR FIRE PARAMETER IDENTIFIED

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

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

h_c^0 = Heat of Combustion of Fuel Gases

E_a = Global Activation Energy for Pyrolysis

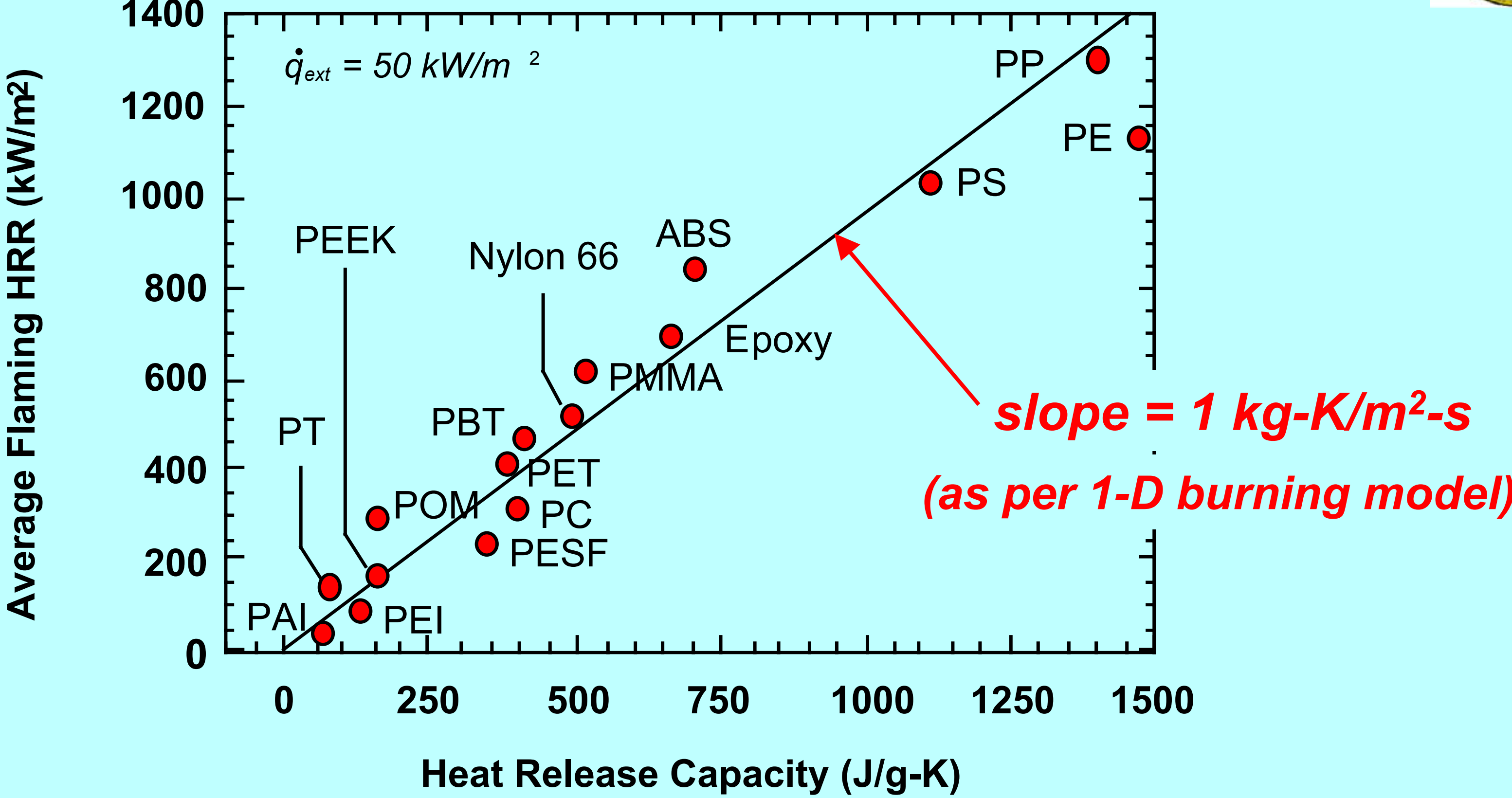
μ = Char Fraction

T_p = Temperature at Peak Mass Loss Rate

e = The natural number 2.7183…

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

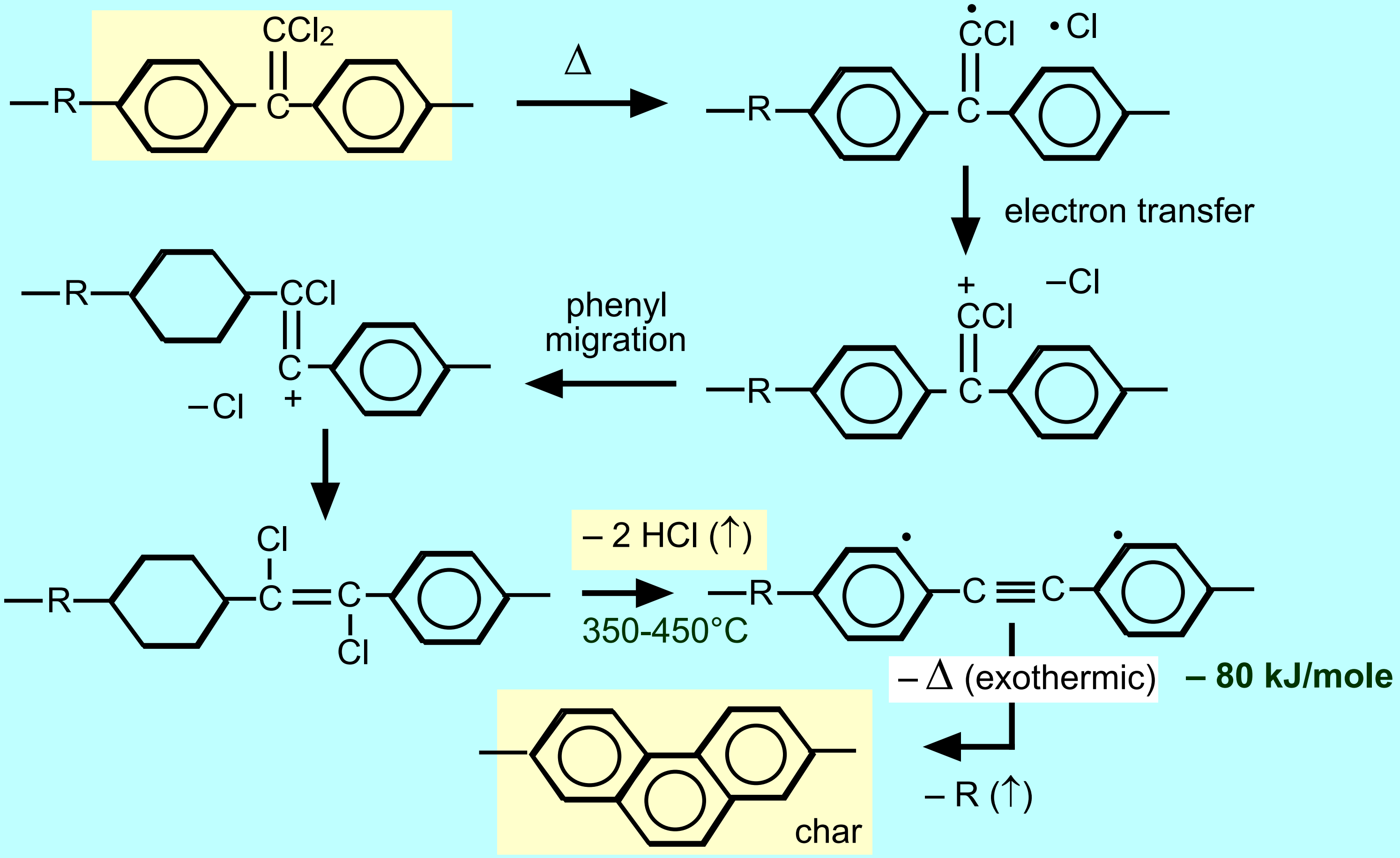
- BPC cyanate ester identified as having lowest heat release capacity of any thermoset tested to date
- BPC cyanate ester patents filed by Ciba
- BPC cyanate ester scaled-up and prepregged for bench scale fire calorimetry testing

1999-present:

University (UMASS, Rice) research continues on BPC copolymers and blends.

BACKGROUND: Thermal Degradation Mechanism Identified

2000: "Thermal Decomposition Mechanism of…", M. Ramirez, DOT/FAA/AR-00/42, and A. Factor, GE Plastics



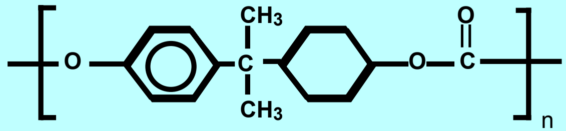
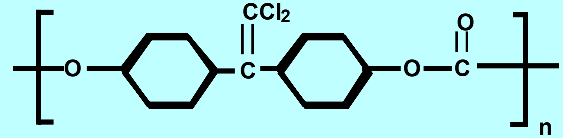
BPC THERMOPLASTICS

Polycarbonate

Polyetherketone

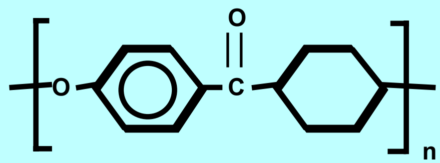
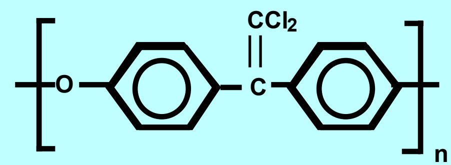
Polyarylates

POLYCARBONATE: BPA vs BPC

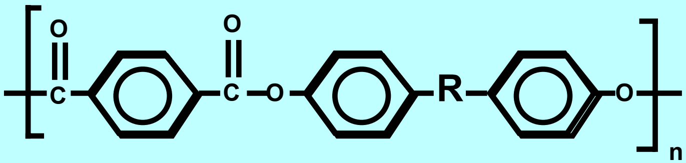
	LEXAN™	Chloral Polycarbonate
		
Morphology	Amorphous	Amorphous
T_g (°C)	152	168
Flex Modulus (ksi)	336	376
Flex Strength (psi)	16,300	16,200
Tensile Yield Strain (%)	10	11
NBS Smoke (D_m)	165	75
Oxygen Index (%)	26	56
Heat Release Capacity (J/g-K)	390	29
FAR 25.853(a-1) Heat Release Peak/Total* (kW/m^2) / ($kW\text{-}min/m^2$)	153 / 58	55 / 33

*0.063 in

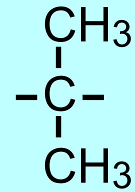
POLYETHERKETONE: Carboxyl vs. DCE

	ULTRAPEK™	Chloral Polarylether
		
Morphology	**Semicrystalline**	**Amorphous**
T_g (°C)	**161**	**166**
T_m (°C)	**381**	**N/A**
Flex Modulus (ksi)	**530**	**426**
Flex Strength (psi)	**18,900**	**18,000**
Tensile Yield Strain (%)	**7**	**10**
NBS Smoke (D_m)	**N/A**	**17**
Oxygen Index (%)	**34**	**52**
Heat Release Capacity (J/g-K)	**124**	**20**

POLYARYLATES: BPA vs. BPC



R =



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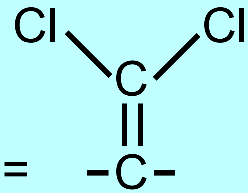
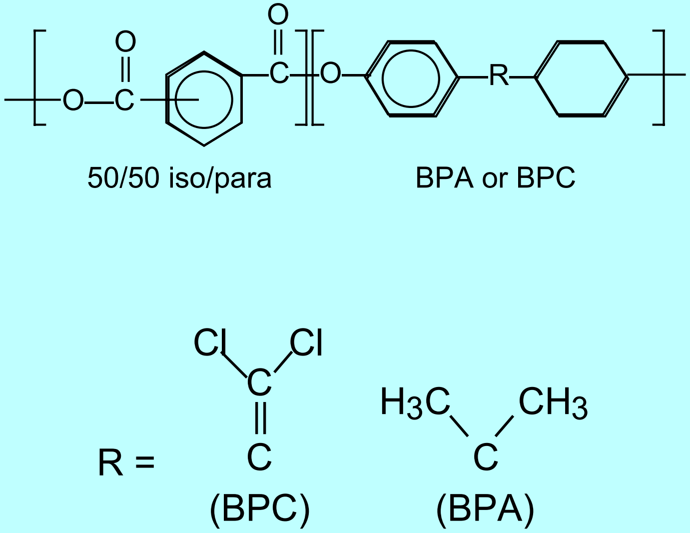
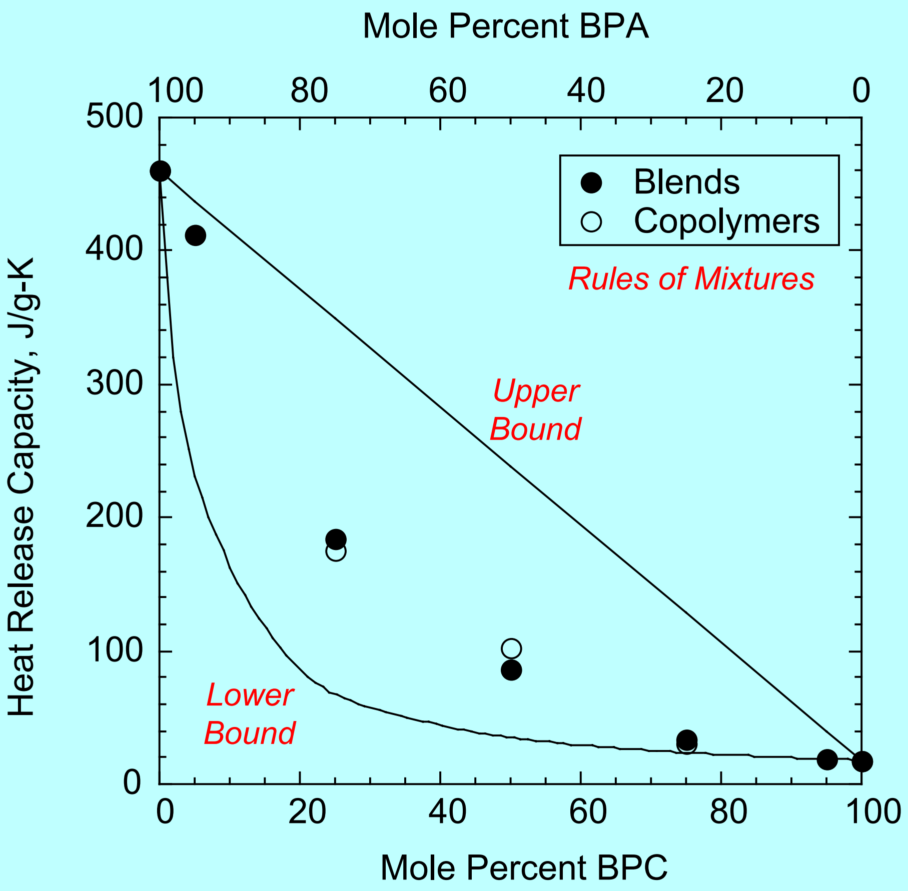


Morphology	**Amorphous**	**Amorphous**
HDT (°C)	**160-174**	**160**
Flex Modulus (ksi)	**325**	**391**
Flex Strength (psi)	**11,000**	**11,700**
Tensile Failure Strain (%)	**50**	**50**
NBS Smoke (D_m)	**109**	**N/A**
Oxygen Index (%)	**36**	**47**
Heat Release Capacity (J/g-K)	**460**	**18**

POLYARYLATE: BPA-BPC Copolymers & Blends

Flammability does not follow simple rules of mixtures.





J.R. Stewart, 2000

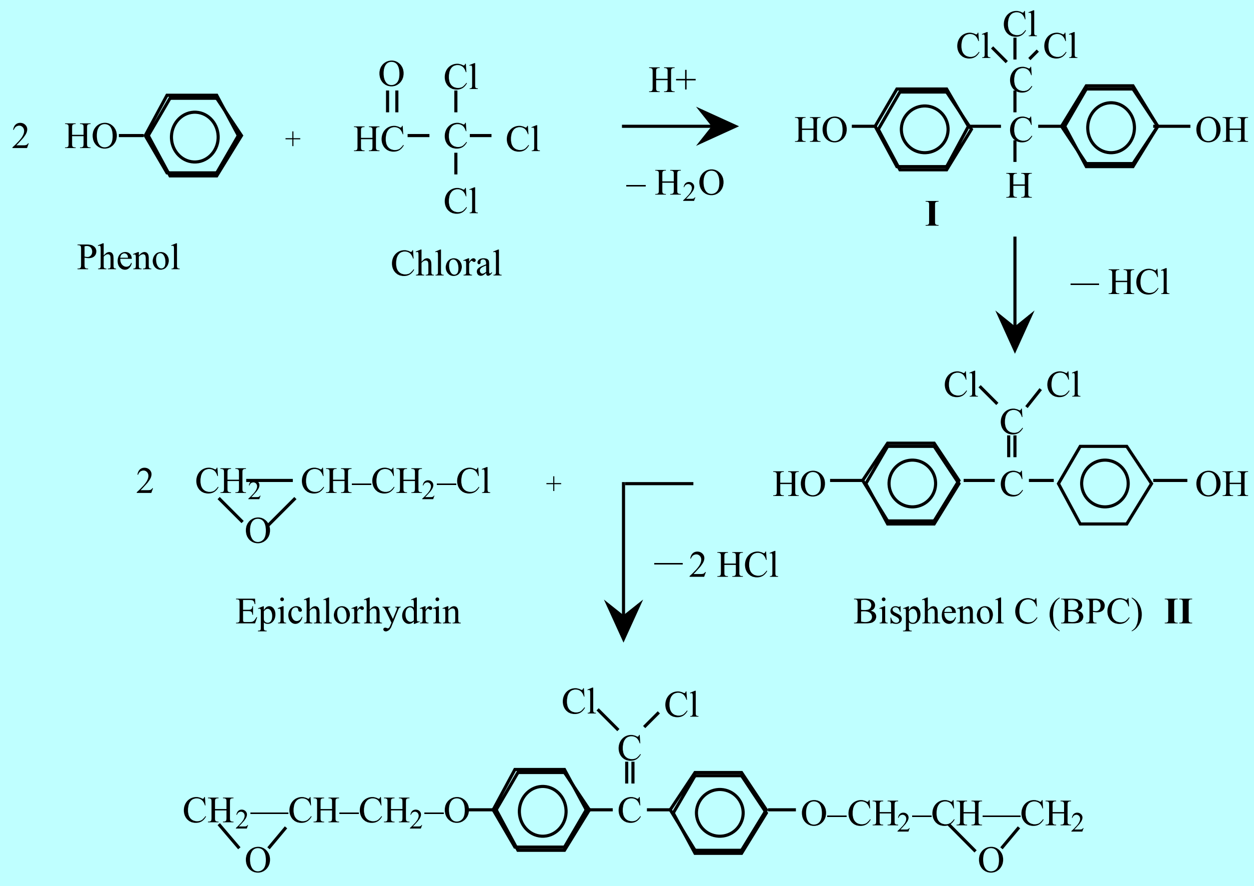
BPC THERMOSET POLYMERS

Epoxy

Cyanate Ester

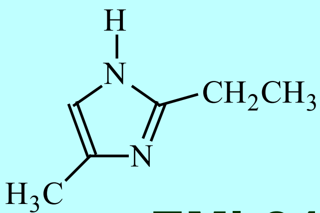
Epoxy-Cyanate Ester Blends

EPOXIES: Synthesis as per DGEBA

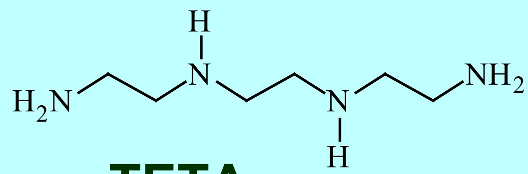


Diglycidylether of Bisphenol C (DGEBC) III

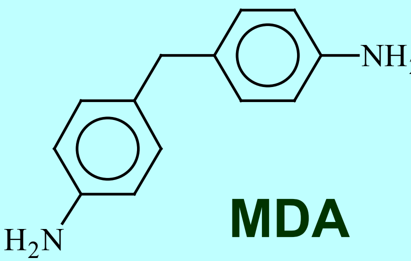
EPOXY FORMULATIONS: Hardeners Examined



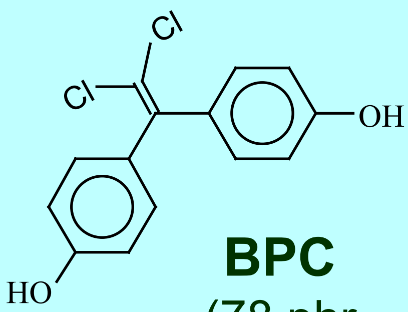
EMI-24
(2 phr)



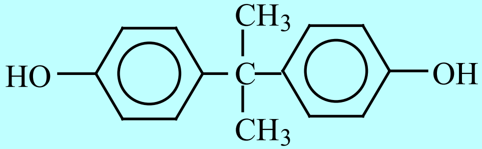
TETA
(14 phr)



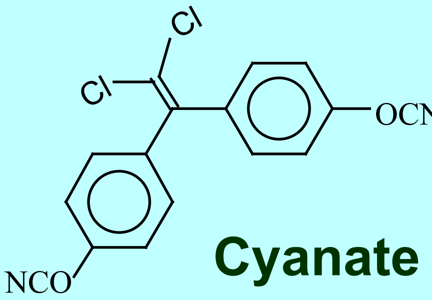
MDA
(58 phr)



BPC
(78 phr DGEBC)



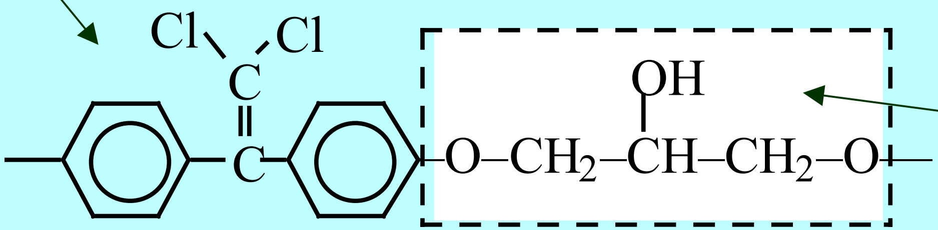
BPA
(66 phr DGEBA)



Cyanate ester of BPC
(53 phr DBEBC)

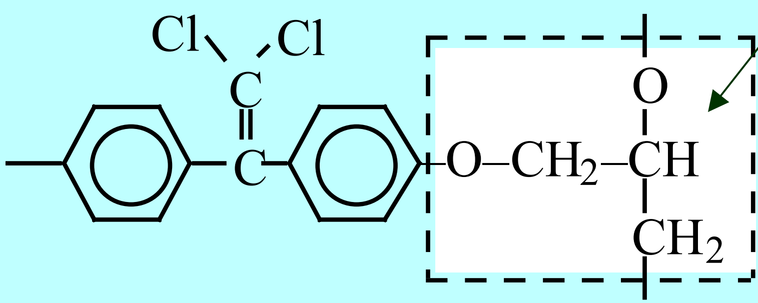
FIRE RESISTANCE OF BPC EPOXY LIMITED BY HIGH FUEL VALUE OF GLYCIDYL ETHER

Dichloroethylidene (DCE) group has zero fuel value, but…



a) DGEBC-BPC

"R" group for epoxy has relatively high fuel value.



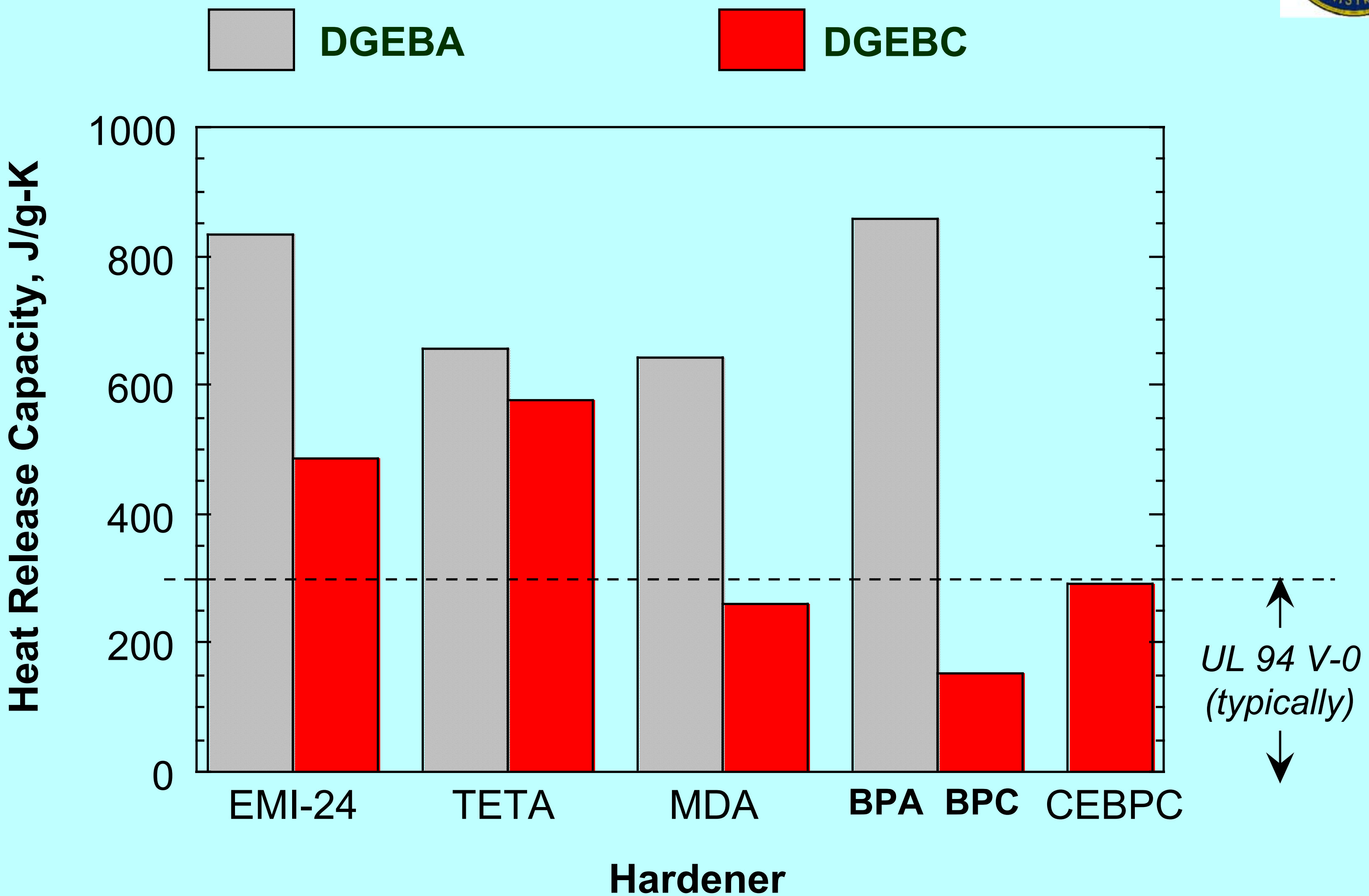
b) DGEBC-EMI

"R" Heat of combustion,

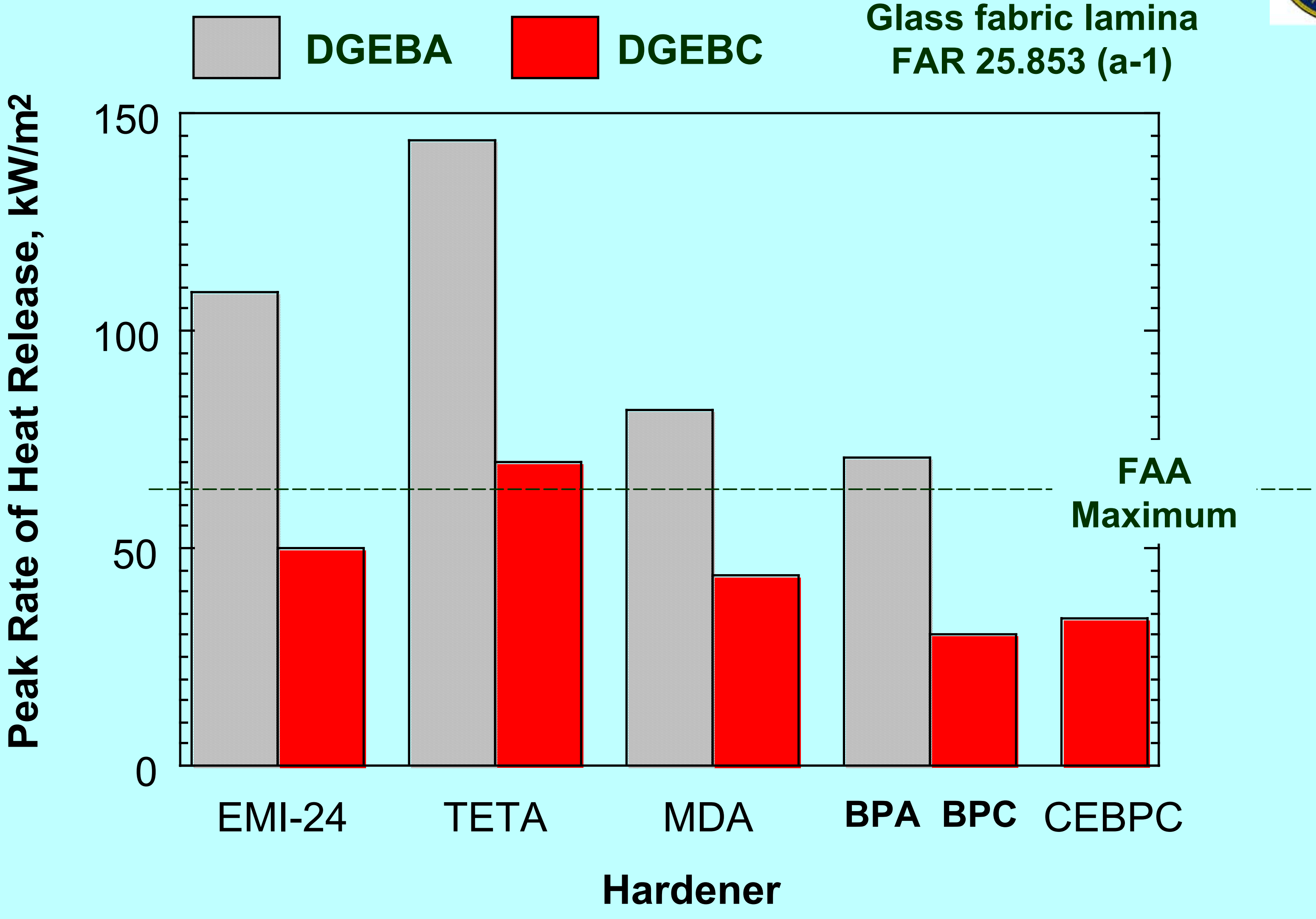
h_c = ***7 kJ/g-polymer (theoretical)***

= 11 kJ/g-polymer (measured)

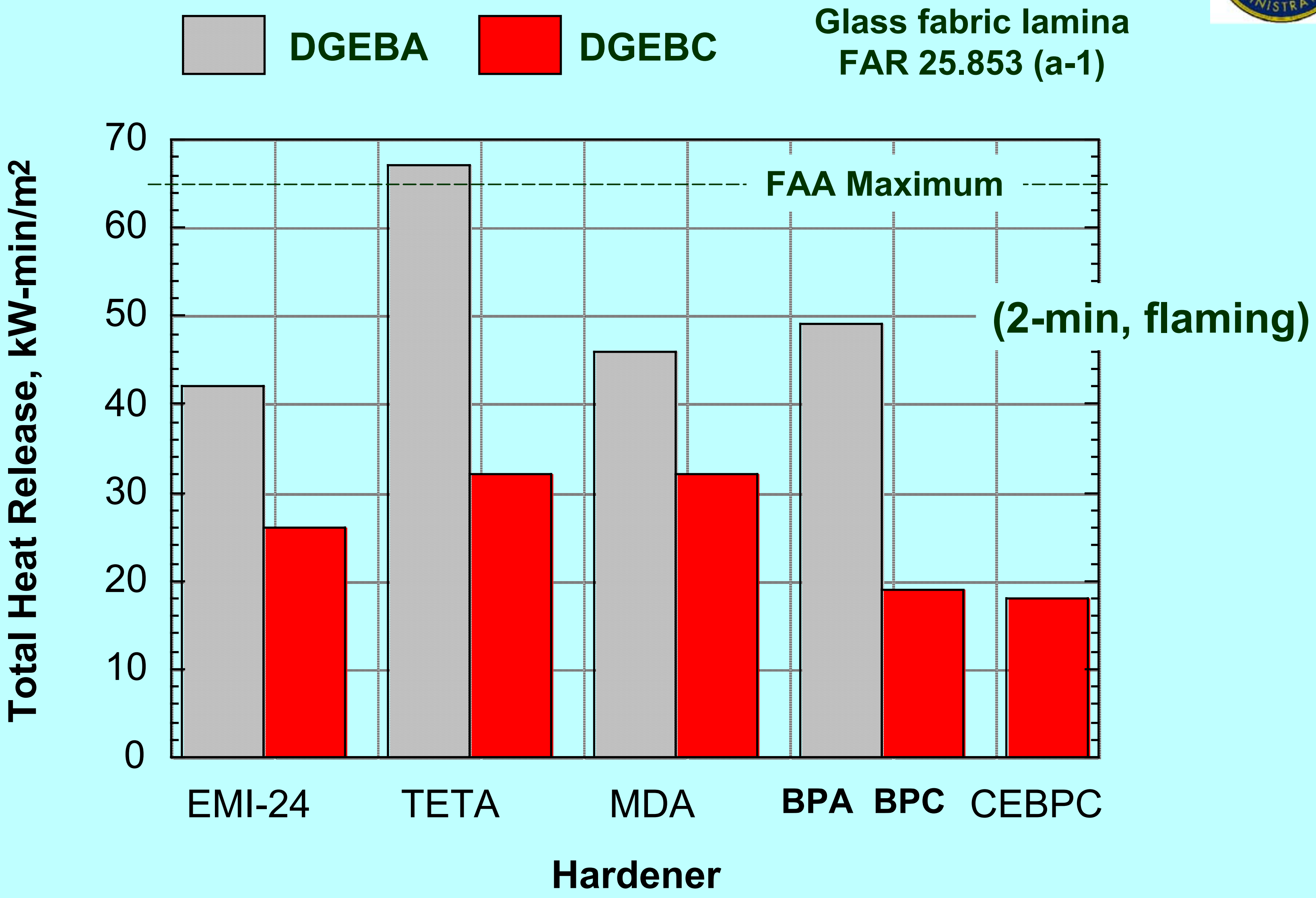
EPOXY HEAT RELEASE CAPACITIES



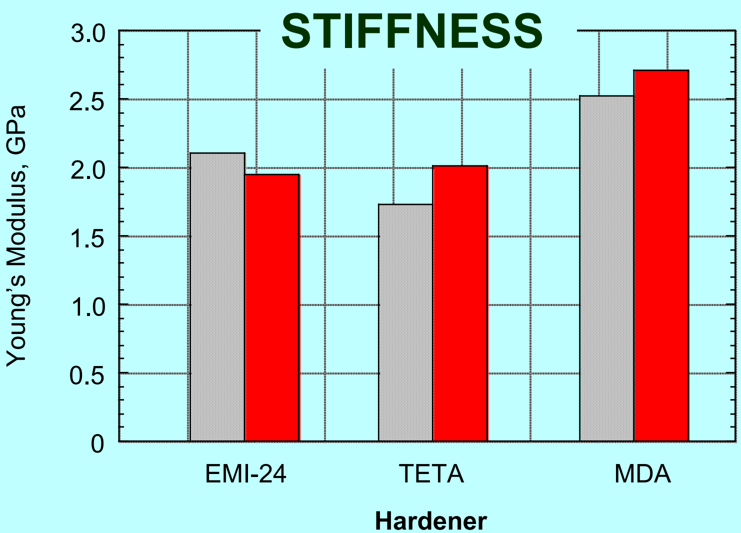
EPOXY FIRE CALORIMETRY: Peak HRR

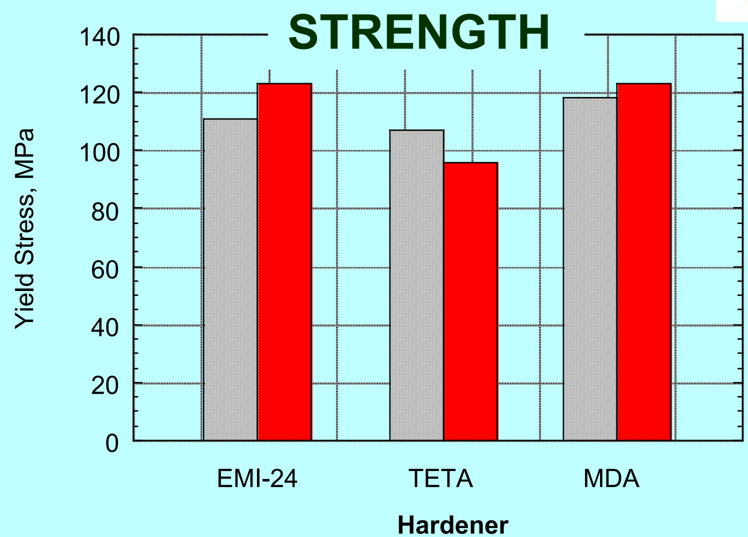


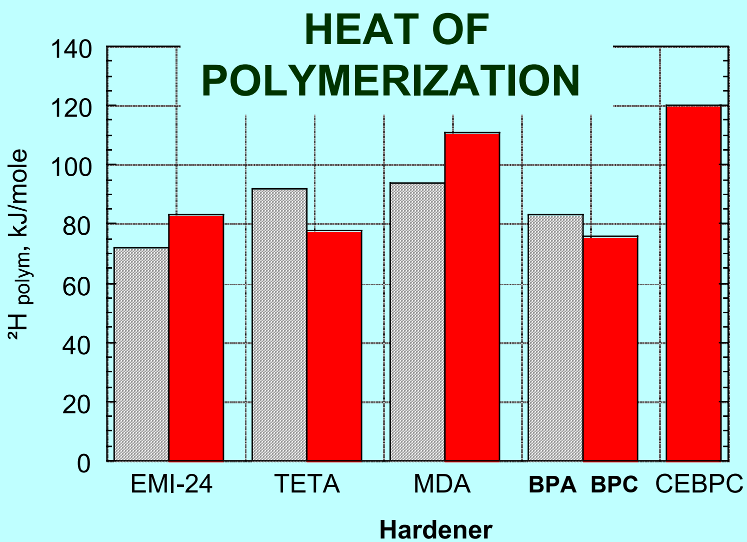
EPOXY FIRE CALORIMETRY: Total Heat Release

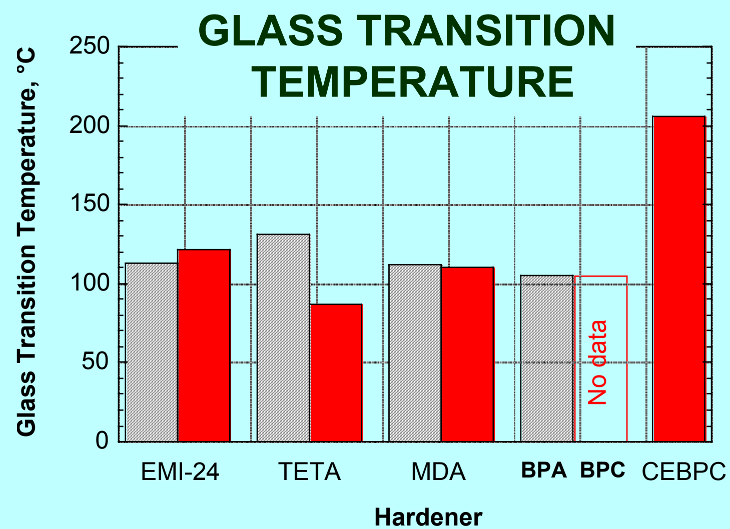


MECHANICALS: BPA ( ) vs. BPC ( ) Epoxy



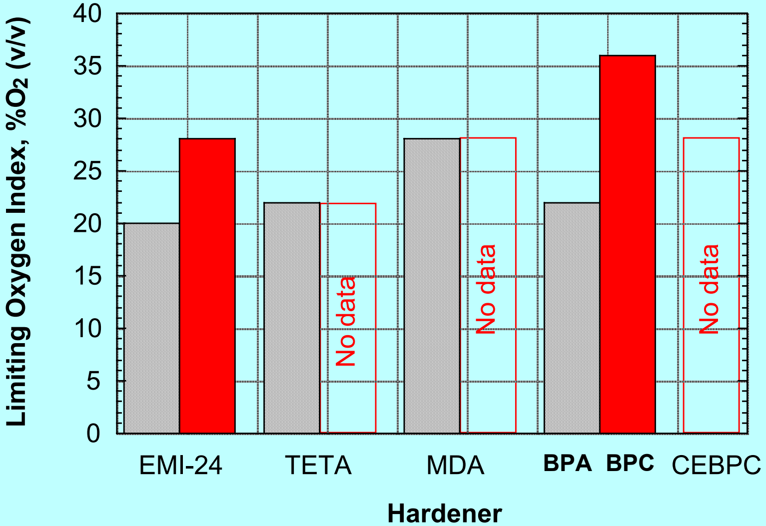




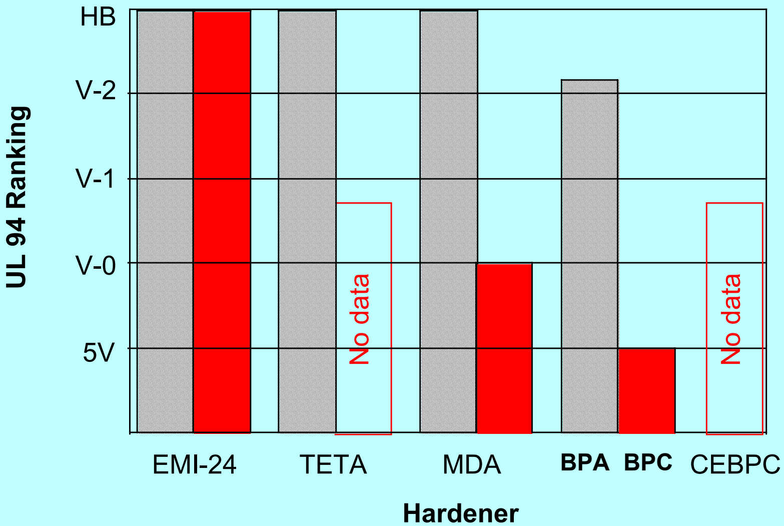


FLAMMABILITY: BPA ( ) vs. BPC ( ) Epoxy

Oxygen Index

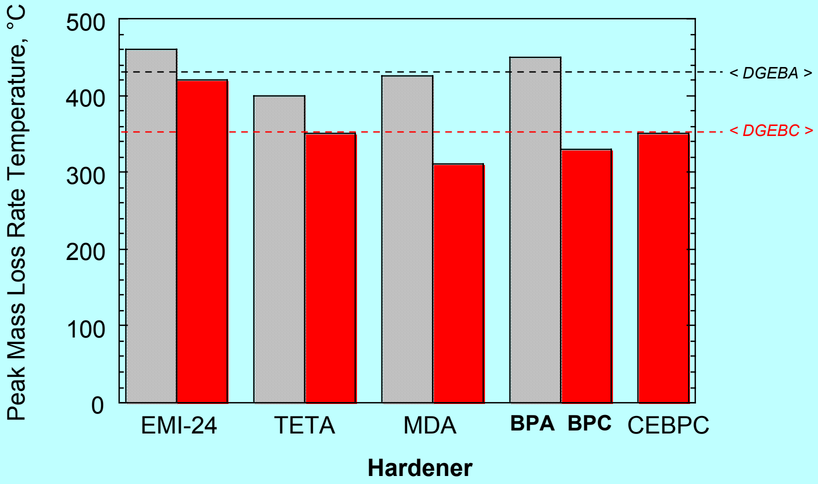


UL 94

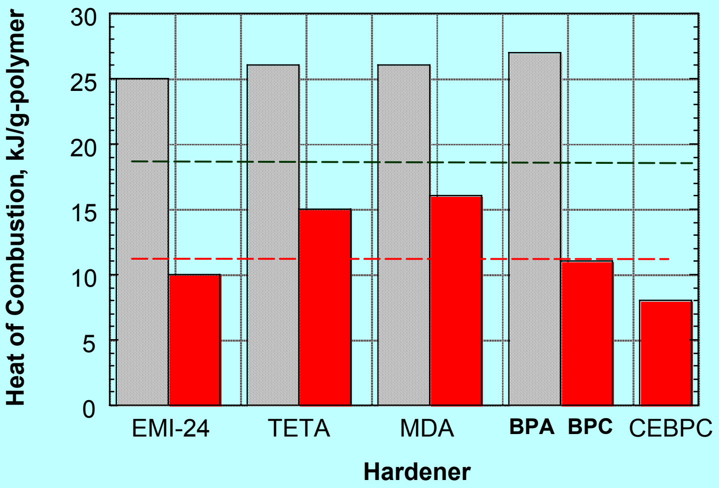


COMBUSTABILITY: BPA ( ) vs. BPC ( ) Epoxy

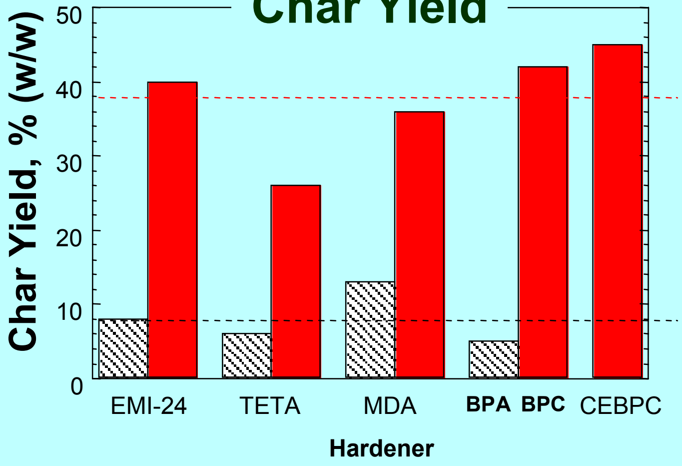
Decomposition Temperature



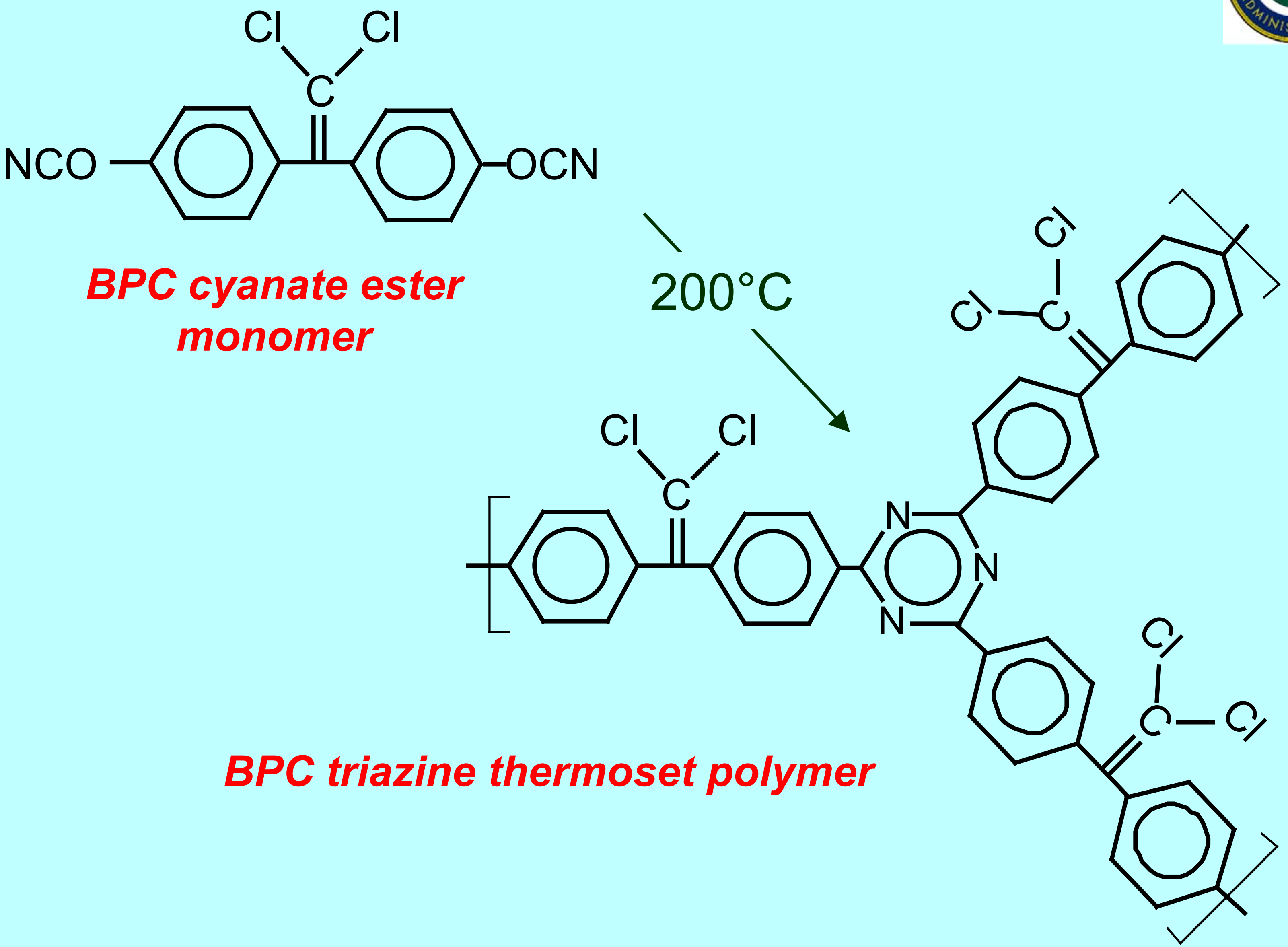
Heat of Combustion



Char Yield



CYANATE ESTER: Polymerization Reaction

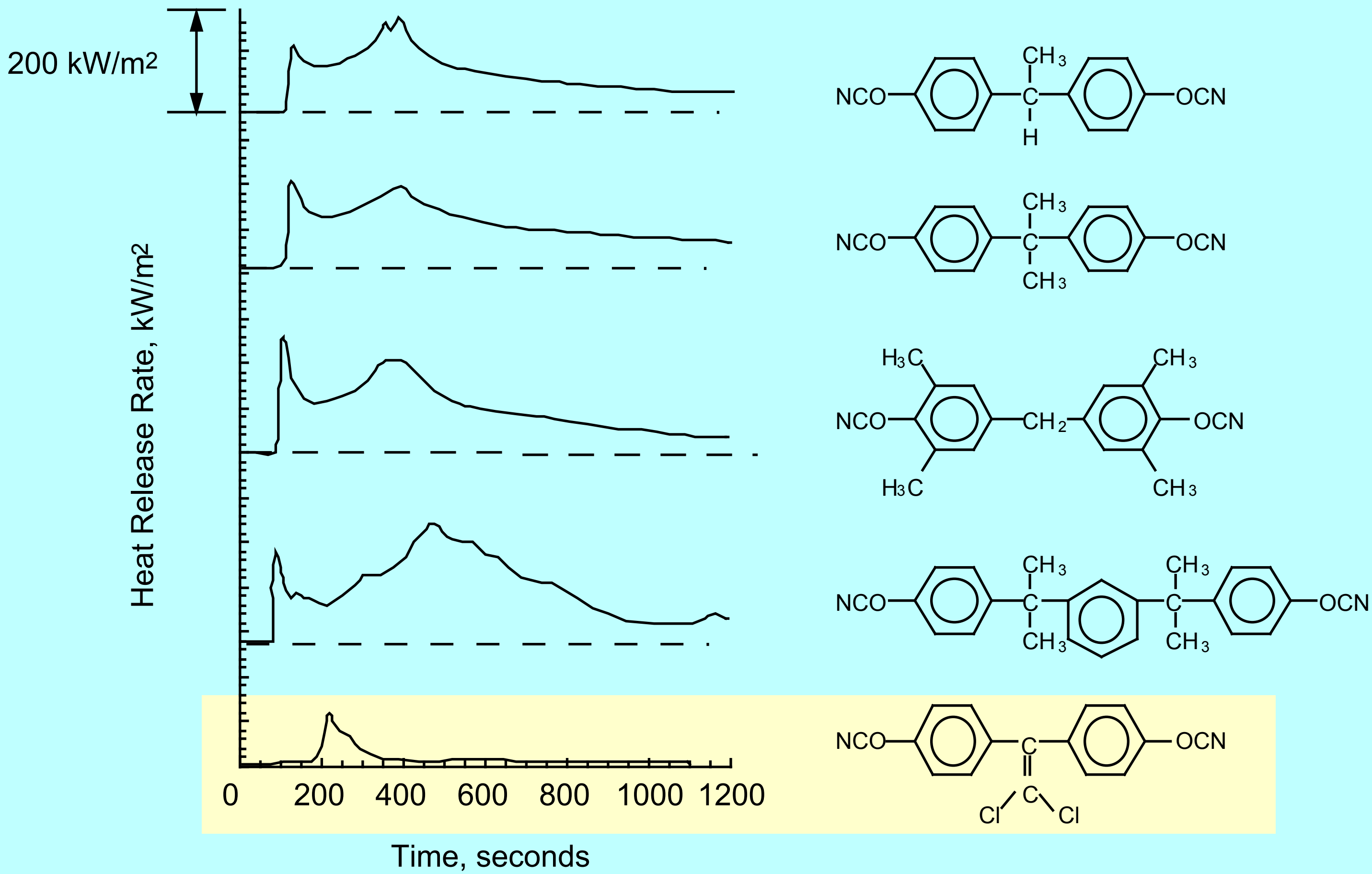


BPC cyanate ester monomer

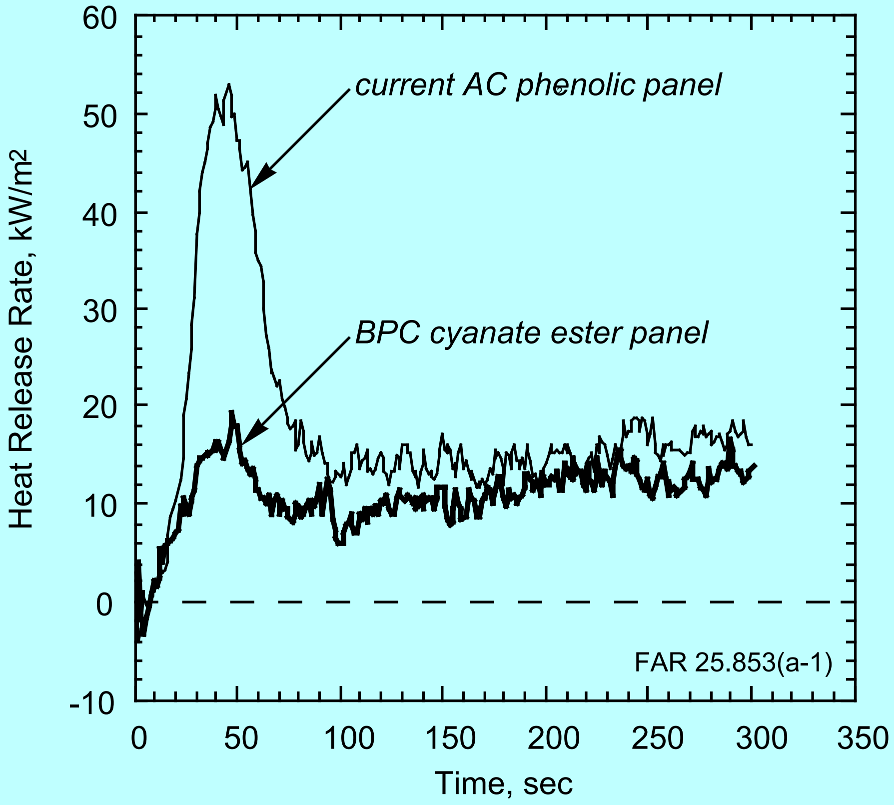
BPC triazine thermoset polymer

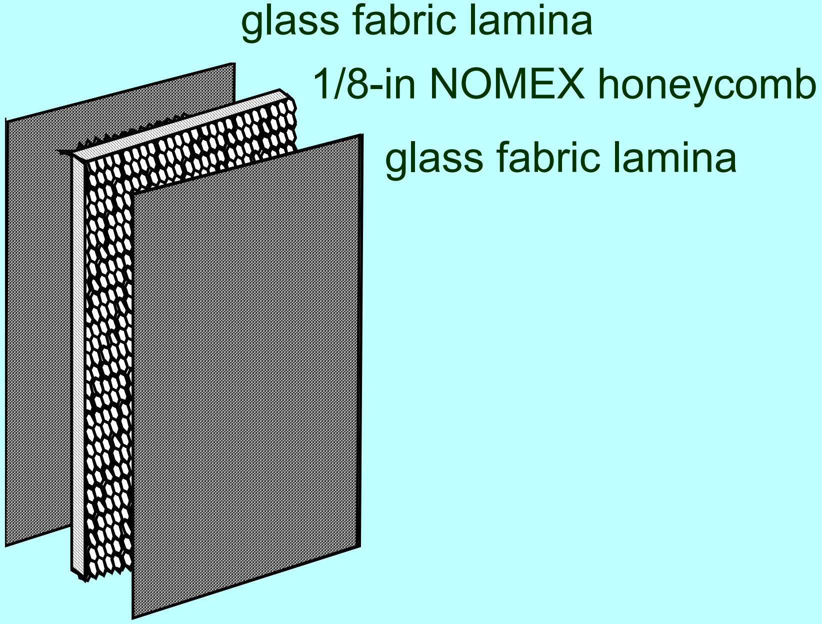
EFFECT OF BISPHENOL ON HEAT RELEASE RATE OF CYANATE ESTERS

ASTM 1354, cone calorimeter at 50 kW/m^2 heat flux, neat resin, 1/4-inch thick



BPC CYANATE ESTER: FAA Heat Release Rate Test





STRUCTURAL COMPOSITES FOR NAVY SUBMARINES

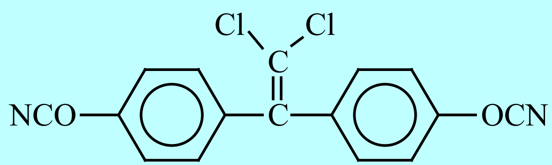
Only 3 resins pass fire performance requirements as glass composites:

Fire Test/Characteristic	Requirement (MIL-STD-2031)	BPC-CE	Phthalo-nitrile	Silicone
Time to ignition (s) at irradiance:				
25 kW/m^2	> 300	pass	pass	pass
50 kW/m^2	> 150	pass	pass	pass
75 kW/m^2	> 90	pass	pass	pass
100 kW/m^2	> 60	pass	pass	pass
Peak/Average Heat Release Rate (kW/m^2) at irradiance:				
25 kW/m^2	< 50/50	pass	pass	pass
50 kW/m^2	< 65/50	pass	pass	pass
75 kW/m^2	< 100/100	pass	pass	pass
100 kW/m^2	< 150/120	pass	pass	pass
Smoke Obscuration, D_{max}/D_s (avg):	< 200/100	pass	N/A	pass
Combustion Gas Toxicity ($CO/CO_2/HCN/HCl$):		pass	N/A	pass
Mechanical Properties		good	good	poor
Cure Temperature		< 200°C	> 375°C	N/A

J. Koo, et. al., SAMPE 2001

CYANATE ESTER-EPOXY REACTIVE BLENDS

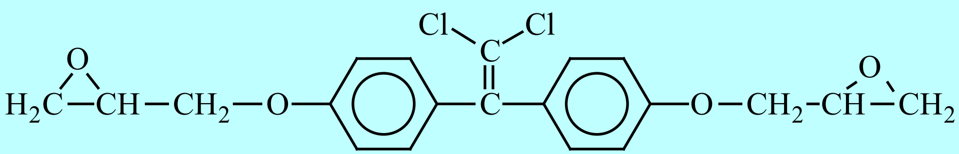
BPC Cyanate Ester (Ciba RD 98-228)



$C_{16}H_8O_2Cl_2$

MW: 331.16 g/mol
EW: 165.58 g/eq
MP: 75 ± 2 °C
Cl: 21.41 wt%

BPC Epoxy (Pacific Epoxy XPR-1015)



$C_{20}H_{18}O_4Cl_2$

MW: 393.27 g/mol
EW: 209.39 g/eq
MP: 91 ± 4 °C
Cl: 16.93 wt%

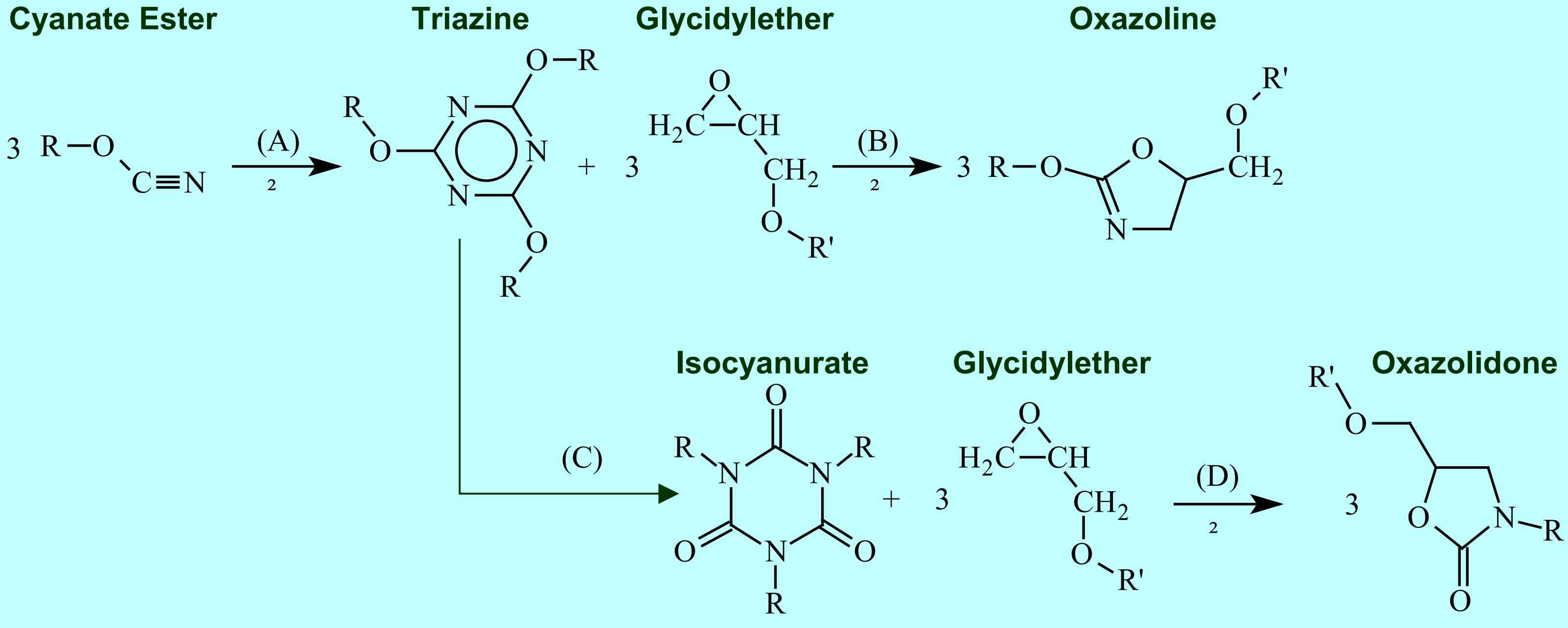
BPC Blends

Blend ratios prepared from the reported equivalent weights

Cyanate:Epoxy	%Cl
1:0	21.4
8:2	20.5
6:4	19.6
4:6	18.7
2:8	17.8
0:1	16.9

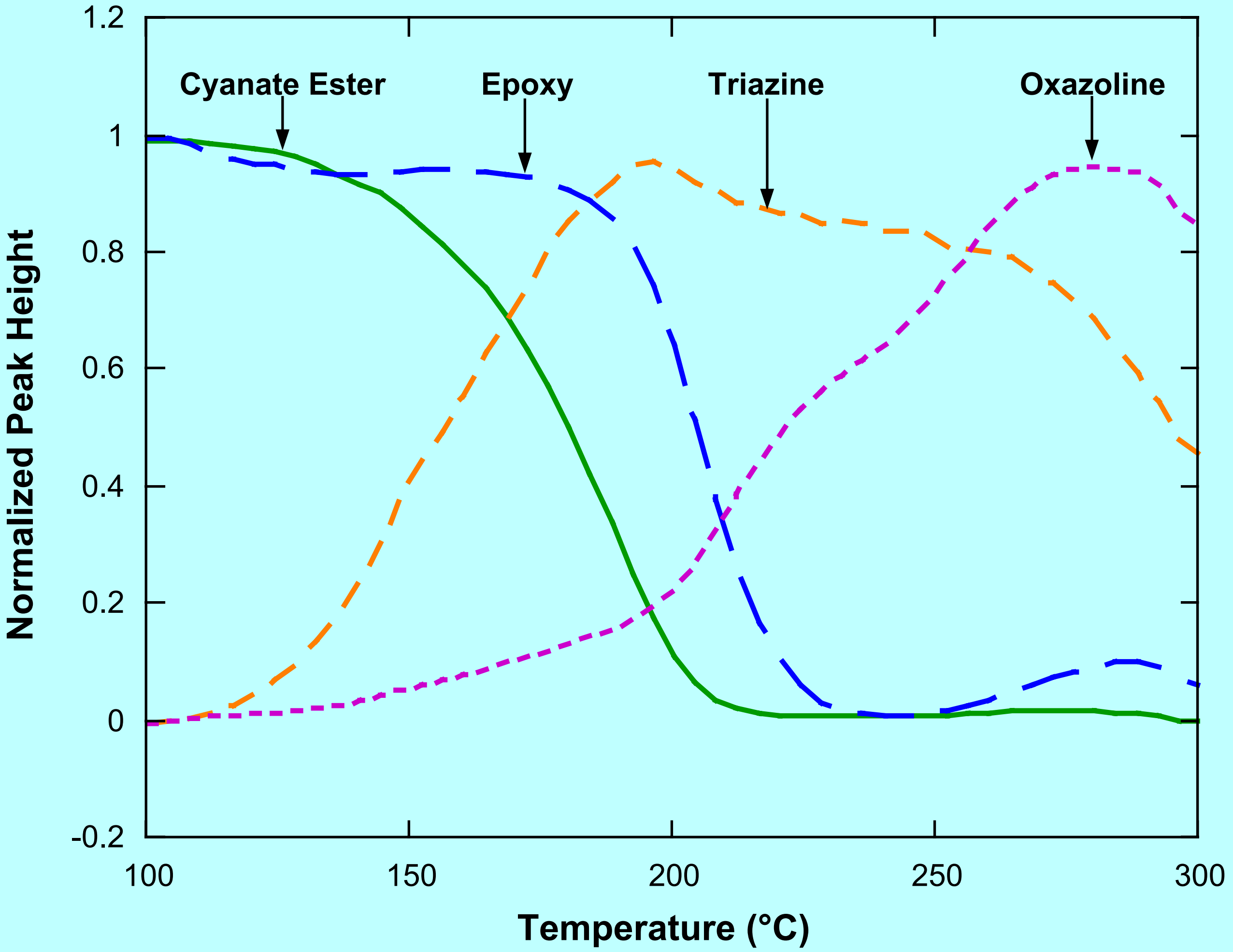
CYANATE ESTER-EPOXY REACTION

Cyclotrimerization reaction of the cyanate ester (A) and the subsequent reaction with the glycidylether (B) to form the oxazoline

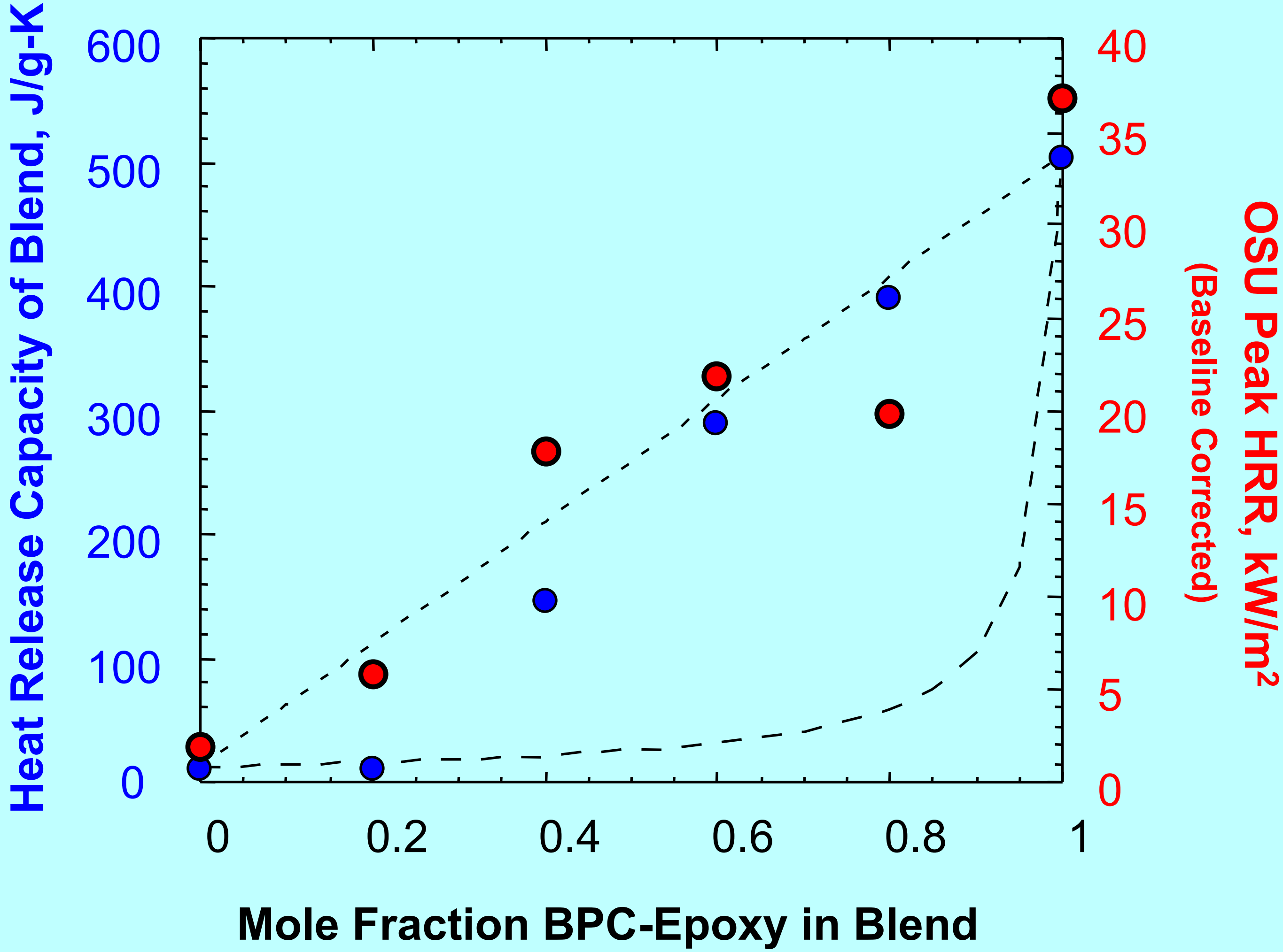


Rearrangement of the triazine (C) to form isocyanurate and the subsequent reaction with the glycidylether (D) to form the oxazolidone

FTIR MONITORING OF CE-EP CURE CHEMISTRY



FIRE PERFORMANCE OF BPC CYANATE ESTER-EPOXY BLENDS



CONCLUSIONS: Comparing Properties

Average Change (5-7 polymers)

	BPC / BPA
Fire Hazard Potential (η_c):	– 90 %
Fire Hazard (HRR):	– 60 %
Glass Transition Temperature, K:	+ 3 %
Modulus:	+ 10 %
Yield Strength:	+ 10 %
Yield Strain:	+ 10 %

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