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Washington, DC 20591

# **Fire-Smart DDE Polymers**

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Final Report

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U.S. Department of Transportation  
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16. Abstract  The chemistry and properties of polymers containing the fire-smart moiety 1,1-dichloro-2,2-diphenylethene (DDE) are described. These polymers are typically derived from the bisphenol of chloral and are low-cost, easily processed, and have good mechanical properties and toughness under normal conditions. Under fire conditions, the DDE group undergoes an intramolecular rearrangement to diphenylethynyl with the elimination of hydrogen chloride (a noncombustible gas) and intermolecular cross-linking to form an aromatic char residue in high yield. The flammability and mechanical properties of DDE-containing polymers are described.					
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## LIST OF ACRONYMS

CFR	Code of Federal Regulations
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
FAA	Federal Aviation Administration
FTIR	Fourier Transform Infrared Spectroscopy
HOC	Heat of combustion
HR	Heat release
HRC	Heat release capacity
HRR	Heat release rate
LOI	Limiting oxygen index
PCFA	Pyrolysis combustion flow calorimeter
SEA	Smoke extinction area
TGA	Thermogravimetric analyzer
TP	Thermoplastic
TS	Thermoset

## EXECUTIVE SUMMARY

Polymers based on 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethene (BPC) and/or containing the dichlorodiphenylethene (DDE) group:

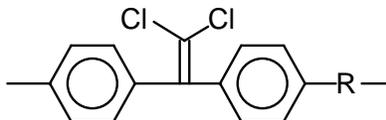


exhibit a unique combination of mechanical properties, processability, and extreme fire resistance when R is a low-fuel-value linking group, such as carbonate (CO<sub>3</sub>), cyanurate (C<sub>3</sub>N<sub>3</sub>O<sub>3</sub>), ester (OCO<sub>2</sub>), ketone (CO<sub>2</sub>), sulfone (SO<sub>2</sub>), or ether (O).

Polymers derived from BPC, and fire tested for this research, included the engineering thermoplastics polycarbonate, polyarylate, polysulfone, and thermoset resins based on diglycidylether (epoxy), and cyanate ester. Also evaluated were BPC-epoxy/BPC-cyanate ester blends and their composites. Polymers based on BPC have mechanical, thermal, and processing characteristics equivalent to or better than bisphenol-A analogs, but they are more ignition resistant and have extremely low heat release rate in forced flaming combustion, typically passing the Federal Aviation Administration heat release requirement for aircraft interior materials Title 14 Code of Federal Regulations 25.853(a-1). Mineral fillers added to BPC polymers are effective at further reducing the peak heat release rate and total heat released, and some of these fillers have the potential of removing HCl from the combustion gases if they can be tolerated by the polymer.

## 1. BACKGROUND.

Organic polymers exhibit a wide range of fire performance. Flame resistance is a low level of fire performance characterized by the tendency of a thin (2-3-mm) bar of material to self extinguish within a specified period of time after a brief exposure to a small flame. Halogen-containing polymers are usually flame resistant and hydrocarbon polymers can be made so by incorporating fire-retardant chemicals. The presence of halogens (chlorine, fluorine, and bromine) in the volatile decomposition products inhibits the combustion reactions in the flame, reducing the efficiency of combustion and lowering the amount of heat that is produced during burning. Flame-retardant chemicals can also act in the condensed phase to promote char formation, which limits the amount of volatile fuel that can be produced by thermal degradation and insulates the underlying polymer from the heat of the flame. Flame-resistant materials will self extinguish after exposure to electrical sparks, cigarettes, or small flames when tested under ambient conditions [1 and 2] but they tend to burn readily in a heated (fire) environment [1 and 3].

Fire resistance is a higher level of fire performance in which the polymer not only resists ignition by a small flame but burns slowly, or not at all, in a high-heat flux (fire) environment. A high level of fire resistance has been achieved to date only by polymers with high thermal stability and heat resistance (e.g., fluoropolymers, polyimides, polyetherimides, polyamideimides, polybenzoxazoles, polybenzimidazoles, etc.) [1-3]. Heat-resistant polymers are fire resistant because they can withstand the heat of a fire without thermally degrading to combustible fuel gases. High-heat resistance and thermal stability is associated with strong primary chemical bonds and a low mole fraction of hydrogen atoms in the polymer backbone [4] so that molecular recombination and cross-linking (char forming) reactions are favored over chain-terminating (fuel-generating) hydrogen-transfer reactions [2]. Conjugated cyclic or heterocyclic structures in the polymer backbone will impart the requisite thermal stability for fire resistance [4] but often result in a high-glass transition (softening) temperature that necessitates elevated temperature processing for adequate flow (thermoplastic) or cure (thermoset). Moreover, the rigidity of the conjugated aromatic backbone often results in a dark and brittle mechanical behavior. Heat-resistant polymers are generally expensive because they are made from specialty (as opposed to commodity) chemicals in a multistep chemical synthesis. Their relatively high-cost, dark color, and high-temperature processing requirements have limited the use of heat-resistant polymers to the most demanding fire applications such as aircraft interiors [3 and 5].

In the 1960s and 70s, highly flame-resistant thermoplastic polymers and thermoset resins based on 1,1,-dichloro-2,2-bis(4-hydroxyphenyl)ethene (bisphenol-C/BPC) were reported by Russian and Polish researchers [6 and 7]. Figure 1 shows the synthesis of BPC, and figure 2 shows some of the BPC thermoplastic and thermoset polymers included in this report, these being a small fraction of the polymers reported to have been synthesized from BPC [6]. It was originally thought that the extremely low flammability of BPC polymers derived solely from the presence of chlorine in the polymer backbone and its action as a flame inhibitor during burning, but the chlorine content alone could not account for the high-limiting oxygen index (LOI) of 56 for BPC polycarbonate (BPC-PC) [8 and 9]. Moreover, BPC polymers were not unusually heat resistant, having similar thermal decomposition temperatures to their bisphenol-A (BPA) analogs [6-20]. Encouraged by the published results on BPC polymers, the General Electric Company developed and patented the industrial process chemistry for a commercially viable BPC-PC in the 1970s [8]

and published an extensive evaluation of the mechanical properties of the material and its combustion behavior [9]. It was found that the BPC-PC polycarbonate had virtually identical mechanical properties to conventional bisphenol-A polycarbonate (BPA-PC), but the flame resistance was significantly higher. Moreover, the toxicity of BPC-PC combustion products was approximately half that of BPA on a mass basis. At the time, modern fire science was just emerging and the methodology for measuring heat release rate (HRR) in flaming combustion was not available, nor was it recognized that HRR is the primary indicator of the fire hazard of a material [21].

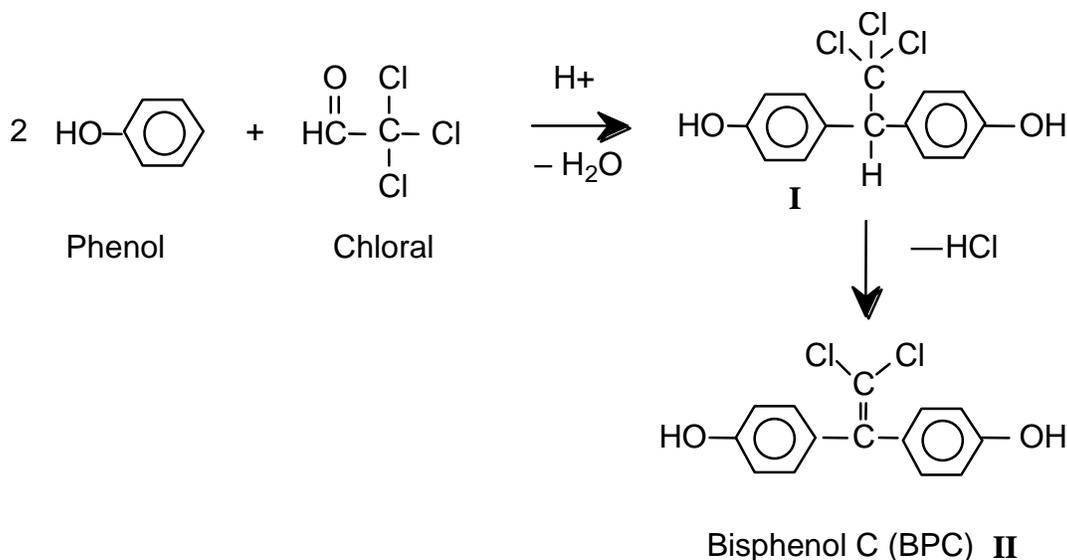


FIGURE 1. SYNTHESIS OF BPC

In 1995, the Federal Aviation Administration (FAA) initiated funding of a long-range research program to develop a fireproof passenger aircraft cabin with the goal of eliminating burning cabin materials as a cause of death in aircraft accidents [5]. The technical objective of the program is an order-of-magnitude reduction in flaming HRR compared to current cabin materials when tested in accordance with Title 14 Code of Federal Regulations (CFR) 25.853(a-1). Because of the variety of polymer types (thermoplastics, thermosets, elastomers, and fibers) used in aircraft cabin components, a novel, versatile, cost-effective polymer chemistry was required to satisfy both the technical and economic constraints on a fireproof cabin. In 1997, the FAA measured the HRR of BPC-PC [22] in a microscale combustion calorimeter [23] and found it to be 13 times lower than bisphenol-A polycarbonate and 4 times lower than the polyetherimide currently used in thermoformed aircraft cabin parts. Because of the potentially low cost of the BPC monomer (figure 1) and the versatility of BPC as a building block for a family of polymers (figure 2), an effort was established at the FAA to synthesize and evaluate the fire behavior of polymers based on BPC [10-20, 24-26] or containing fire-smart moiety 1,1-dichloro-2,2-diphenylethane (DDE) [17, 19, and 20] and identify the molecular mechanism responsible for the high level of fire resistance of these materials [6-20].

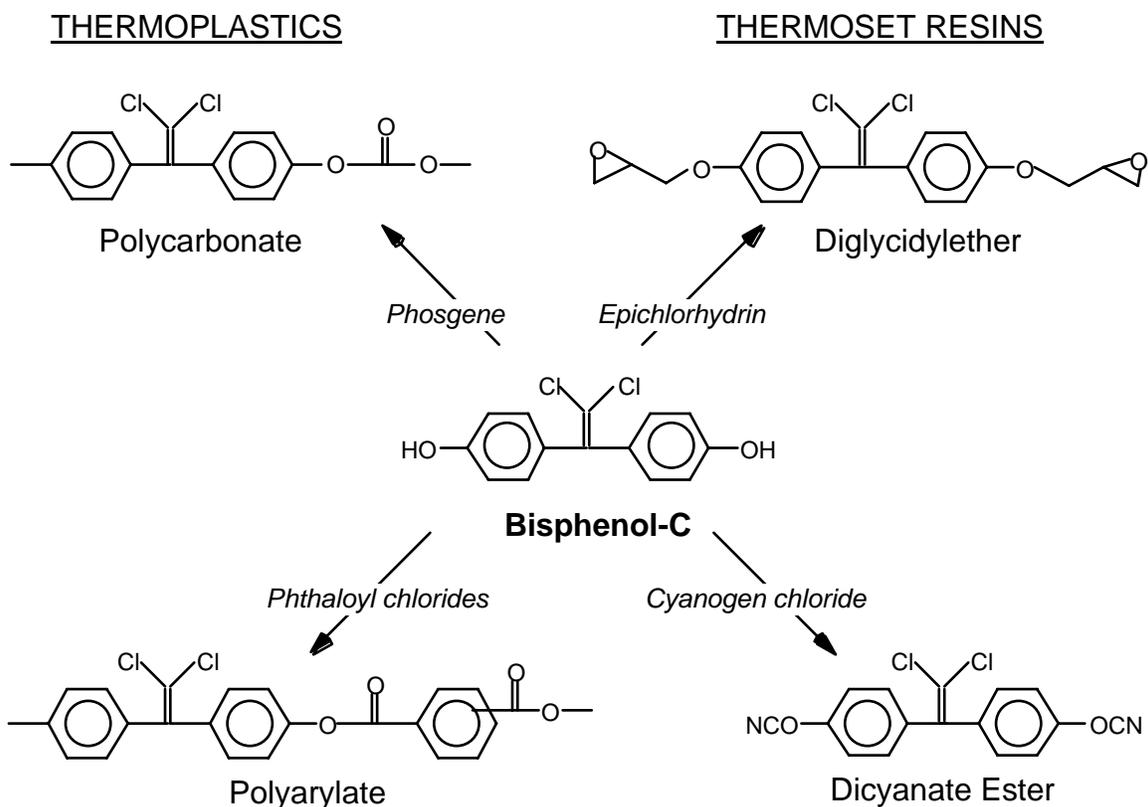


FIGURE 2. SYNTHESIS ROUTES TO BPC POLYMERS

## 2. MATERIALS.

### 2.1 POLYMERS.

Bisphenol C (**II**) was synthesized by Eikos Corporation, Franklin, MA (BPC, Lot# CS05-182, 5 kilograms), in a two-step, environmentally friendly process [8, 14, 27, and 28] yielding only hydrogen chloride (HCl) and water as byproducts, as shown in figure 1. The first step involved reacting 2 moles of phenol with 1 mole of chloral under strongly acidic conditions to give 1,1,1-trichloro-2,2-bis(4-hydroxyphenyl)ethane (compound **I**) followed by recrystallization and subsequent dehydrochlorination in strong base to give 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethene (compound **II**, CAS Reg. No. 14868-03-2), also known as the bisphenol from chloral, bisphenol-C, or BPC. Bisphenol-C is a white crystalline solid with a melting point of  $217 \pm 2^\circ\text{C}$ .

Selected BPC polymers were prepared in sufficient quantity for fire and mechanical testing. Thermoplastic polymers were synthesized from the as-received BPC using synthetic procedures that are similar or identical to those used for the BPA analogs, as shown schematically on the left-hand side of figure 2. Four kilograms of BPC-PC having a weight-average molecular weight of 28,000 g/mole was synthesized by Dow Chemical using phosgene in the commercial emulsion process [25]. Polyarylates were obtained from Southwest Texas University [26] from phthaloyl chlorides in a solvent process. The diglycidyl ether of bisphenol-C (BPC-EP) was prepared by Pacific Epoxy Polymers, Inc., Richmond, MO, using epichlorhydrin, and the BPC cyanate ester

(BPC-CE) thermoset resin was synthesized in pilot scale from cyanogen chloride by VANTICO, Brewster, NY. Gram quantities of polymers derived from BPC polymers or containing the DDE moiety were prepared for flammability screening [14, 17, and 19].

## 2.2 FILLERS AND REINFORCEMENTS.

Inorganic or mineral fillers were added to BPC-PC and BPC-CE in an attempt to modify combustion behavior. Fillers were commercial products including magnesium hydroxide  $Mg(OH)_2$  (680-S, technical grade, Whittaker Chemical), aluminum trihydrate  $Al(OH)_3$ , (Alumina Hydral 710, Whittaker Chemical), basic aluminum oxalate  $Al_2(C_2O_4)_2 \cdot 4H_2O$ , (P-3363, 1 micron, Alcoa), hydrated zinc borates  $4ZnO \cdot B_2O_3 \cdot H_2O$  (Firebrake ZB 415, Borax) and  $2ZnO \cdot 3B_2O_3 \cdot 5H_2O$  (Firebrake ZB fine, Borax), anhydrous zinc borate  $2ZnO \cdot 3B_2O_3$  (Firebrake ZB 500, Borax), and magnesium silicate hydroxide  $Mg_3Si_4O_{10}(OH)_2$  (Talc, R.T. Vanderbilt). The continuous fiber reinforcement for single- (lamina) and multiple-ply (laminated) polymer composites was an 8HS weave, S-glass cloth having an areal weight  $303 \text{ g/m}^2$  (Style 6781, BGF Industries, Inc.).

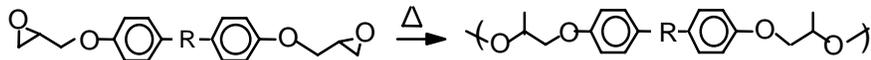
## 3. METHODS.

### 3.1 SAMPLE PREPARATION.

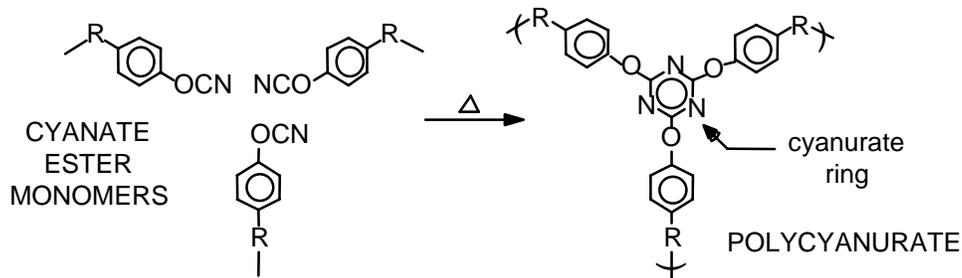
#### 3.1.1 Polymers, Copolymers, and Blends.

Thermoplastic BPC polymers were tested as received in the form of compression molded 1.6-mm thick plaques. Samples of BPC polycarbonate (XUR-YM-2003-150563, Dow Chemical) [25] were prepared by drying the BPC-PC flake in a vacuum oven at  $100^\circ\text{C}$  for a minimum of 3 hours and then compression molding the dried flake at  $248^\circ\text{C}$  in a heated press (Tetrahedron, MTP-14). BPA-PC samples were cut from a commercial extruded sheet (BPA samples) for flammability testing.

Thermoset polymers were cast as neat resins or hand impregnated into fiberglass cloth for fire and mechanical testing. Homopolymerization of the diglycidyl ether of BPA (DER 332, Dow Chemical) and the diglycidyl ether of bisphenol-C (PEP XPR1015, Pacific Epoxy Polymers, Inc.) was accomplished using 2 weight percent of 2-ethyl-4-methylimidazole (EMI 24, Air Products and Chemicals), as shown schematically in figure 3(a), where  $R = C(CH_3)_2$  for BPA. The diglycidylethers of BPC and BPA were also cured with stoichiometric amounts of the parent phenol (BPA or BPC), the cyanate ester of the parent phenol (BPA-CE or BPC-CE), and amine hardeners triethylenetetramine/TETA (DEH-24, Dow Chemical) and 4,4'-methylenedianiline/MDA (Curithane 103, Acros Chemical). The dicyanate ester monomers of BPC (RD 98-228, VANTICO) or BPA (B10, VANTICO) were homopolymerized without catalyst via the cyclotrimerization reaction that yields the highly cross-linked polycyanurate shown schematically in figure 3(b). Neat resin castings of the BPA and BPC and thermoset polymers for fire and mechanical testing were prepared by melting the epoxy and cyanate ester resins at  $60^\circ\text{C}$  and pouring the liquid resins into appropriate size molds followed by curing to completion in a forced-air convection oven as recommended by the manufacturers.



(a) Homopolymerization of the Diglycidylether.



(b) Homopolymerization of Dicyanate Ester to Polycyanurate.

FIGURE 3. HOMOPOLYMERIZATION REACTIONS OF DIGLYCIDYL ETHER AND DICYANATE ESTER RESINS

### 3.1.2 Composites.

Particulate composites of BPC-PC were tested as received in the form of compression molded 1.6-mm-thick plaques that were prepared by melt-blending mineral fillers with the BPC-PC (XUR-YM-2003-150563, Dow Chemical) for 2 minutes at 200°C in a Haake Rheomix 600. The pelletized compound was dried in a vacuum oven at 100°C for a minimum of 3 hours and then compression molded at 248°C in a heated press (Tetrahedron, MTP-14).

Particulate dispersions of commercial mineral fillers in BPC-CE were prepared by melting the BPC-CE (RD98-228, VANTICO) resin at 60°C, adding a measured mass of particulate mineral filler, stirring the mixture with a spatula, and homogenizing the mixture with a mortar and pestle. The addition of the metal hydrates to the heated BPC-CE resin resulted in an accelerated curing reaction and reduced pot life.

Single-ply polymer composites (lamina) were prepared for fire calorimetry tests by hand impregnating the liquid thermoset resin, resin blend, or resin-filler mixture into fiberglass cloth followed by curing in a heated press (Carver Model M) under contact pressure at 200°C for 4 hours and postcuring without pressure at 250°C for 2 hours. Multiple-ply composites (laminates) for fire and mechanical testing were made by hand layup or by resin transfer molding and oven curing in a vacuum bag [24]. Composite panels so prepared contained approximately 40% resin by mass.

## 3.2 THERMAL ANALYSES.

### 3.2.1 Thermogravimetry-Differential Thermal Analysis-Differential Scanning Calorimetry.

The mass loss versus temperature profile of 5-mg samples was measured at a constant heating rate of 10° or 20°C/min in nitrogen flowing at 100 cm<sup>3</sup>/min in a thermogravimetric analyzer

(TGA) between 100° and 900°C with (Mettler Toledo TGA-SDTA 851) or without (Perkin Elmer TGA-7) simultaneous differential thermal analysis (DTA) capability. The thermicity of the decomposition reactions was also studied by differential scanning calorimetry (DSC) (Perkin Elmer DSC-7) at a heating rate of 2-5°C/min between ambient temperature and 600°C. The heat absorbed, or evolved, during the decomposition process was obtained by time integration of the heat flow measured by DSC during the test.

### 3.2.2 Glass Transition Temperature.

Dynamic torsion testing (Rheometrics RDA II) was used to measure the glass transition temperature ( $T_g$ ) and shear storage modulus ( $G'$ ) of rectangular bars measuring 20 x 13 mm with a thickness of 1-6 mm. Samples were heated at a constant rate of 5°C/min between 25° and 250°C at a frequency of 1 Hz. The  $T_g$  was assigned to the temperature at which the tangent to the phase angle ( $\tan \Delta$ ) was at a maximum.

### 3.2.3 Evolved Gas Analysis.

Acid gases HCl and hydrogen cyanide (HCN) produced during anaerobic thermal decomposition of BPC polymers were determined by ion chromatographic analysis of the gases evolved by heating a 10 to 20-mg sample of the BPC polymer to 900°C in quartz tubing at 10°C/min using a pyrolysis probe (Pyroprobe 2000, CDS Analytical Instruments). Pyrolysis gases were purged from the sample tube by nitrogen gas flowing at approximately 0.6 L/min, which then passed through two Teflon™ collection tubes filled with 4-mm-diameter glass beads coated with 1M NaOH to adsorb the acid gases from the gas stream. After cooling to room temperature, the quartz pyrolysis tube was eluted with 30 ml of 0.025M NaOH, as were the two collection tubes. The eluent from all three tubes was combined and diluted 10 fold with additional 0.025M NaOH, filtered, and placed into sample containers for analysis by ion chromatography (DX 500 Ion Chromatographic Analyzer, Dionex) with a high-resolution ion exchange column (Ionpac AS10 analytical column, Dionex). An ED-40 electrochemical detector was used with a conductivity cell for the analysis of chloride. An Ag/AgCl amperometric cell was used in a separate analysis for the determination of cyanide. The ion chromatographic method for the determination of chloride and cyanide ion concentration was a gradient elution program starting from an initial mobile phase of 10% v/v 200mM NaOH and 90% v/v distilled and deionized water [15].

## 3.3 FLAMMABILITY.

### 3.3.1 Flame Resistance.

The propensity for upward vertical burning in the absence of external radiant heat was measured according to the Underwriters Laboratory Test for Flammability of Plastics UL-94 V [29] on rectangular bars measuring 3 x 13 x 76 mm or obtained from handbooks [1,2, 30-33]. The minimum oxygen concentration (volume percent) needed to support candle-like burning (LOI) was measured on rectangular bars 125 mm x 6.5 mm x 3 mm, in dimension according to a standard test method [34] or the data was obtained from the literature where available [1, 2, and 30-33].

### 3.3.2 Combustibility.

The combustibility was measured in a pyrolysis-combustion flow calorimeter (PCFC) [35] that separately reproduces the condensed-phase (fuel generation) and gas-phase (fuel oxidation) processes of flaming combustion. In the test, a 1 to 5-milligram sample that was dried overnight at 70°C and held in a desiccator until testing is heated to 900°C in an inert gas stream (nitrogen) at a constant heating rate of 1 K/s, typically. The fuel gases are swept from the pyrolyzer by the nitrogen purge gas, mixed with excess oxygen, and thermally oxidized at 900°C. The products of complete combustion, water, carbon dioxide, and possibly acid gases are scrubbed from the gas stream, and the mass flow rate and oxygen concentration are measured and used to calculate the HRR. Normalizing the HRR history by the initial sample mass gives the specific HRR  $Q(t)$  (W/g), at each time  $t$  during the test. Time integration of  $Q(t)$  over the entire test gives the heat released by combustion of the volatile pyrolysis products per unit initial sample mass, heat release (HR) (J/g). The pyrolysis residue or char fraction  $\mu$  is obtained by weighing the sample before and after the test. A derived quantity, the heat release capacity (HRC) (J/g-K), is obtained by dividing the maximum value of the specific HRR measured during the test by the heating rate (K/s). The HRC [36] is a measure of the combustion potential of a material and is a good predictor of fire and flame test performance [1 and 2]. Each reported value of HRC, HR, and  $\mu$  is an average of at least three tests having a coefficient of variation (one standard deviation/mean) of  $\pm 5\%$ .

### 3.3.3 Fire Behavior.

The Ohio State University Rate of Heat Release Apparatus modified to conform with Federal Aviation Regulations [37] was used to measure the HRR and HR in forced flaming combustion. Duplicate 150-mm-square samples were tested for HRR and HR in flaming combustion at an external radiant heat flux of 35 kW/m<sup>2</sup> according to 14 CFR 25.853 (a-1) [38]. Thermoplastics and thermoplastic composites were tested as received in 1.6-mm-thick sheets. Thermoset resins were tested as glass fabric-reinforced composites having approximately 40% w/w cured resin. All values reported are averages of at least two tests having a coefficient of variation of  $\pm 15\%$  between tests.

Fire behavior was also measured in a cone calorimeter (Atlas Electric Devices or Fire Testing Technology) according to standard methods [39]. All values reported are averages of at least two tests. Repeatability is  $\pm 15\%$  and reproducibility is  $\pm 20\%$ . Combustion gases were extracted from the exhaust duct through a heated transfer line and analyzed for 14 gases, including HCl and HCN, using Fourier Transform Infrared Spectroscopy (FTIR) [40].

## 3.4 MECHANICAL PROPERTIES.

Mechanical properties were measured on a universal testing machine (INSTRON 4400-R Model 1125), according to standard methods [41 and 42], or were obtained from the literature as typical/generic values where available. Three samples were tested for each experimental value reported. Repeatability is about  $\pm 10\%$ .

## 4. RESULTS.

### 4.1 POLYMERS, COPOLYMERS, AND BLENDS.

#### 4.1.1 Thermal Analyses of Pure Polymers.

Table 1 contains TGA and DSC results at a heating rate of 10°C/min for the onset degradation temperature,  $T_{\text{onset}}$ , the temperature at peak mass loss rate,  $T_{\text{max}}$ , the char fraction at 800°C, the heat of pyrolysis  $\Delta H_{\text{pyr}}$  per gram of original material, and per mole of dichlorodiphenylethene (DDE) repeat unit for the BPC polymers. Also included in table 1 are the mass fraction of acid gases HCl and HCN liberated during pyrolysis at 800°C expressed as a percentage of theoretical yield [15].

TABLE 1. THERMAL DECOMPOSITION TEMPERATURES, CHAR FRACTION, HEAT OF DECOMPOSITION, AND ACID GAS YIELDS FOR POLYMERS MADE FROM BPA AND BPC

Polymer		$T_{\text{onset}}$ (°C)	$T_{\text{max}}$ (°C)	Char Fraction (%)	$\Delta H_{\text{py}}$ (kJ/g)	$\Delta H_{\text{py}}$ (kJ/mol)	HCl Yield (%)	HCN Yield (%)
Polycarbonate	BPA	454	566	19	136	42	0	0
	BPC	420	521	53	-246	-76	91	0
Polyarylate	BPA	469	497	26	(endo)	—	0	0
	BPC	455	476	53	-191	-78	90	0
Epoxy	BPA	437	462	8	(endo)	—	—	—
	BPC	370	373	46	—	—	—	—
Polycyanurate	BPA	460	477	40	(endo)	—	0	—
	BPC	437	462	63	-227	-75	86	3

The data in table 1 show that BPC polymers decompose exothermically as indicated by the negative sign of  $\Delta H_{\text{py}}$ , and they liberate HCl in essentially quantitative yield (90% of theoretical). Moreover, BPC polymers decompose at lower temperatures than their BPA analogs and have significantly higher char yield and lower mass loss rates. Figures 4(a) and 4(b) show simultaneous thermogravimetric and differential thermal analysis (TGA-DTA) data, respectively, for the BPA-PC and the BPC-PC at a heating rate of 20 K/min. Figure 4 shows that BPA-PC thermally decomposes with in a single, endothermic step at a higher temperature but with greater mass loss rate than that of BPC-PC. In contrast, BPC-PC decomposes with a low mass loss rate over a broad temperature range and the thermicity changes sign at 600°C during the course of thermal degradation (figure 4(b)). The integrated heat flow for the exothermic decomposition step obtained by DSC is listed in table 1 for a few BPC polymers. The average value  $\Delta H_{\text{py}} = -76$  kJ per mole of DDE [14 and 15] is shown in table 1 for the BPC polymers.

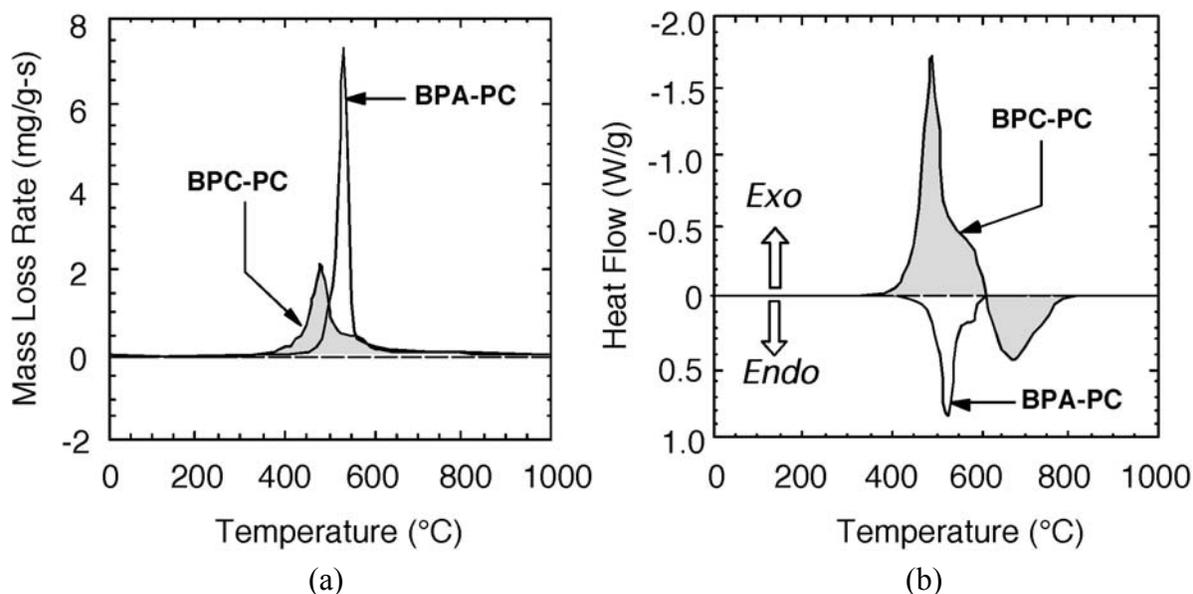


FIGURE 4. THERMAL ANALYSIS DATA FOR BPA AND BPC POLYCARBONATE FROM (a) TGA AND (b) DTA

The data in table 1 and figure 4 are consistent with the proposed thermal degradation mechanism of BPC polymers [14, 15, and 20] shown in figure 5. Thermal degradation of DDE polymers is thought to proceed via an intramolecular rearrangement of the dichlorodiphenylethene moiety to a dichlorodiphenylstilbene at about 350°C followed by dehydrochlorination above 400°C to yield the diphenylethynyl intermediate. With the elimination of HCl, the newly formed backbone diphenylethynyl is thermally unstable and spontaneously undergoes intermolecular reactions to form a highly cross-linked, conjugated aromatic structure. The thermicity of the DDE reaction,  $\Delta H_{py} = -76$  kJ/mole, as per table 1, is comparable to the cross-linking reaction of the diphenylethynyl moiety of phenylethynyl-terminated imide oligomers,  $\Delta H = -77$  to  $-82$  kJ/mole [43], suggesting the same or similar mechanism for both polymers.

Continued heating of DDE polymers above 600°C liberates hydrogen and residual linking groups (e.g., R = carbonate, glycidylether, triazine, etc.) from the cross-linked aromatic structure, leaving a thermally stable carbonaceous char in near-quantitative yield based on the theoretical mole fraction of diphenylethynyl in the polymer.

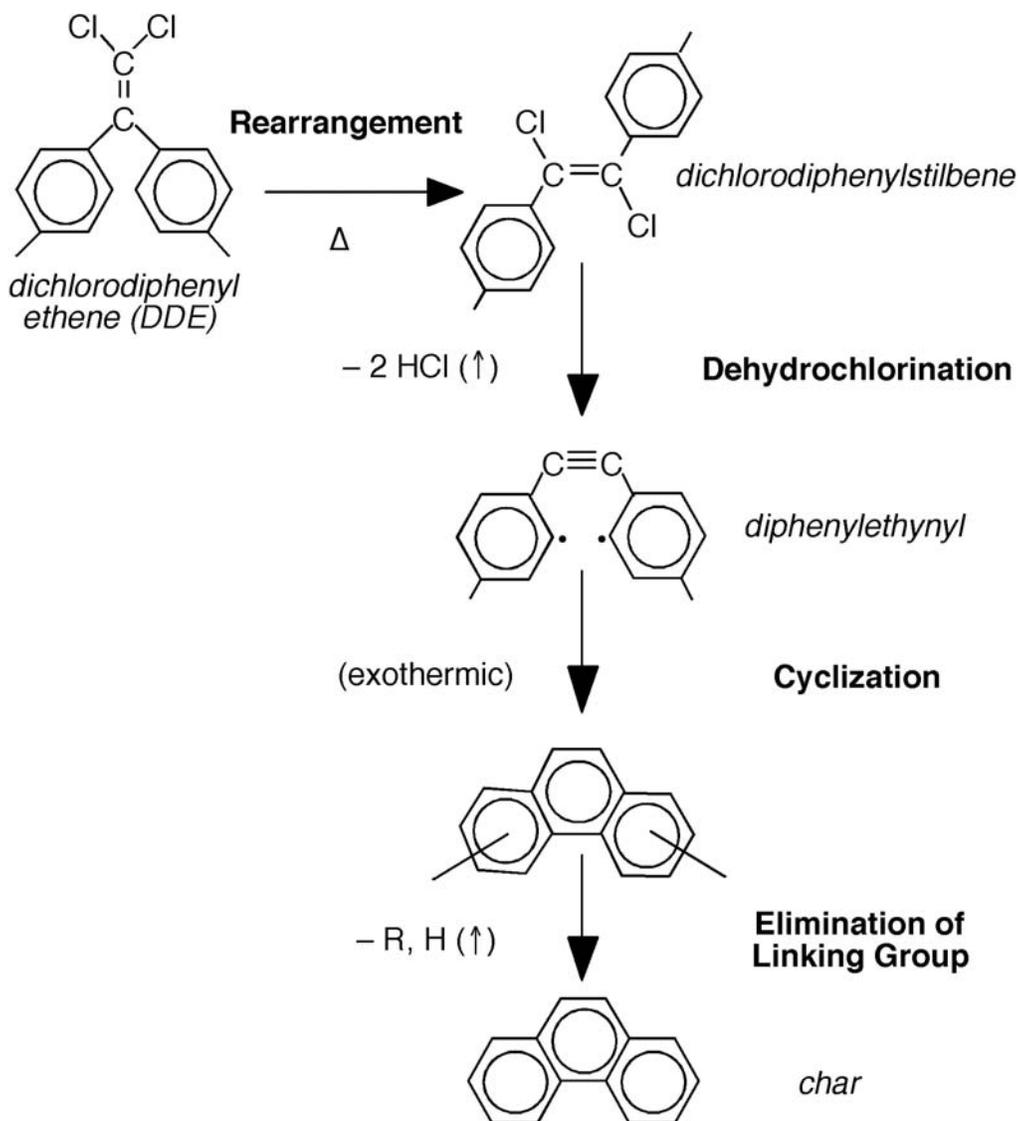


FIGURE 5. THERMAL DEGRADATION MECHANISM OF BPC/DDE POLYMERS

#### 4.1.2 Flammability of Pure Polymers, Copolymers, and Blends.

Table 2 compares flammability results for engineering thermoplastics (TP) (polycarbonate, polyarylate, polysulfone, and phenoxy) and thermoset (TS) resins (epoxy, cyanate ester, and vinyl ester) derived from BPA and BPC. With the exception of the BPC epoxy and vinyl ester, which do not pass any of the UL vertical designations (no rating (NR)), all of the BPC TP and TS resins have low flammability, as indicated by LOI > 27 and UL 94 self-extinguishing ratings of V-0 or 5V and HRC < 200 J/g-K. In contrast, the BPA engineering plastics and TS resins range from V-0 to NR in the Underwriters Laboratory vertical ignition test. Microscale combustibility data indicate a several-fold reduction in HRC and HR for polymers containing a high-mass fraction of DDE in the polymer backbone (polycarbonate, polyarylate, polysulfone, polycyanurate) compared to the isopropylidene (bisphenol-A) backbone analogs.

TABLE 2. FLAME RESISTANCE AND COMBUSTIBILITY OF BPC AND BPA TP AND TS POLYMERS

Polymer	Bisphenol	LOI (% O <sub>2</sub> )	UL 94 V Rating	HRC (J/g-K)	HR (kJ/g)	CHAR (% w/w)
Polycarbonate TP	BPA	26	0/1/2	390	21	24
	BPC	56	0/5V	23	5	50
Polyarylate TP	BPA	34-38	0	460	19	26
	BPC	–	0/5V	20	7	46
Polysulfone TP	BPA	32	0/1/2	336	17	30
	BPC	–	–	24	6	49
Phenoxy TP	BPA	–	–	657	26	4
	BPC	–	–	153	11	44
Epoxy TS	BPA	19-20	NR	833	25	5
	BPC	27-28	NR	487	10	36
Polycyanurate TS	BPA	24	NR	283	18	36
	BPC	53	0/5V	24	4	53
Vinyl Ester TS	BPA	–	–	805	30	0
	BPC	–	–	323	18	24

Microscale combustion calorimetry data is listed in table 3 for 30 pure polymers derived from BPC or containing DDE that were synthesized and tested in the FAA program [23]. The polymers in table 3 are ranked in order of decreasing HRC and flammability. Polymers with HRCs less than HRC = 120 J/g-K typically pass the HR requirements for large area aircraft interiors [38]. Table 3 shows that HRC and flammability decreases with the fuel value (HR) of the chemical group(s) linking the DDE moieties and increases with the thermal stability and aromatic character (char forming tendency) [44] of these same linking groups, which is consistent with the derived relationship [1, 2, 35, and 36]

$$\text{HRC} = \frac{(1-\mu) h_c^0}{eRT_p^2/E_a} \approx \frac{\text{HR}}{\Delta T_p} \quad (1)$$

where  $\mu$  is the char (or inert) fraction,  $h_c^0$  is the specific heat of complete combustion of the volatile fuel, and  $\Delta T_p$  is the temperature interval over which the majority of the pyrolysis reactions take place. Figure 4 shows that the pyrolysis temperature interval for BPC-PC is much broader than for BPA-PC, and this, combined with the higher char fraction  $\mu$  and low heat of combustion of volatiles  $h_c^0$  for DDE polymers, accounts for the factor of 10 difference in HRC between the best BPA and BPC polymers listed in table 3.

TABLE 3. COMBUSTIBILITY OF 30 BPC AND DDE-CONTAINING POLYMERS

	Repeat Unit Chemical Structure	Common Name [Reference]	HRC (J/g-K)	HR (kJ/g)	Char Yield (%)
1		Polyurethane [17]	498	19	8
2		Epoxy (catalytic cure) [12 and 13]	496	10	40
3		Polyester [14]	251	19	47
4		Polyacrylate [17]	224	10	11
5		Polyether [17]	205	13	37
6		Polyurethane [17]	188	18	12
7		Polyacrylate [17]	185	12	17
8		Phenoxy [12]	153	11	44
9		Polyether [17]	146	18	20

TABLE 3. COMBUSTIBILITY OF 30 BPC AND DDE-CONTAINING POLYMERS  
(Continued)

	Repeat Unit Chemical Structure	Common Name [Reference]	HRC (J/g-K)	HR (kJ/g)	Char Yield (%)
10		Polyurethane [17]	135	11	22
11		Polyester [14]	101	9	35
12		Polyarylphosphine Oxide [17]	95	10	60
13		Polyaryl- phosphonate [17]	43	8	51
14		Polyether [17]	37	8	58
15		Polyarylether Ketone [19]	30	6	59
16		Polyarylether [17]	26	7	55
17		Polyarylate [14]	26	4	54

TABLE 3. COMBUSTIBILITY OF 30 BPC AND DDE-CONTAINING POLYMERS  
(Continued)

	Repeat Unit Chemical Structure	Common Name [Reference]	HRC (J/g-K)	HR (kJ/g)	Char Yield (%)
18		Polybromarylate [14]	26	4	35
19		Polycyanurate (cyanate ester) [10, 13, and 16]	24	4	53
20		Polysulfone [26]	24	6	49
21		Polycarbonate [11, 14, 15, 20, 22, and 25]	23	5	50
22		Polyarylate [14]	20	4	50
23		Polyarylate [14 and 26]	19	6	48
24		Polyarylate [14]	18	6	50
25		Polyphenyl acetylene [17]	17	5	50
26		Polyarylether [17]	16	5	57

TABLE 3. COMBUSTIBILITY OF 30 BPC AND DDE-CONTAINING POLYMERS  
(Continued)

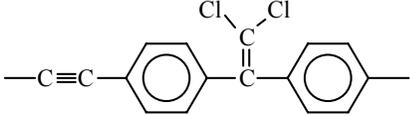
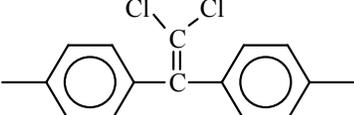
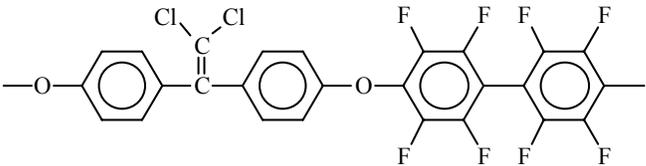
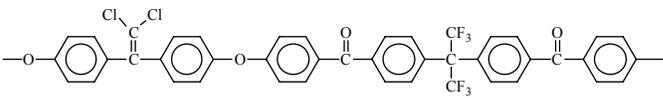
	Repeat Unit Chemical Structure	Common Name [Reference]	HRC (J/g-K)	HR (kJ/g)	Char Yield (%)
27		Polyacetylene [17 and 19]	13	5	67
28		Polyphenylene [17]	12	5	57
29		Polyfluoro Phenyleneether [26]	11	2	46
30		Polyfluoro Etherketone [26]	11	4	53

Table 4 compares fire and thermal parameters of BPC-CE and BPA-CE [16 and 45]. Thermal properties are the  $T_g$  or softening temperature, ignition temperature, heat of gasification, and thermal inertia, which is the effective product of the thermal conductivity  $\kappa$ , density  $\rho$ , and heat capacity  $c$  of the polymer deduced from time-to-ignition data over a range of heat fluxes. Combustion parameters in table 4 were obtained from fire calorimetry data and are average values  $\pm 1$  standard deviation for 6-mm-thick neat resin samples tested at 35, 50, 75, and 100 kW/m<sup>2</sup> external radiant heat flux according to ASTM 1354 [39] with edge frame holder. The HRR histories for these experiments are shown in figure 6. Yields of HCl and HCN in well-ventilated flaming combustion were obtained by FTIR analysis of the combustion gases. Combustion efficiency was calculated by dividing the effective heat of combustion (HOC) by the heat of complete combustion of the fuel gases obtained by high-temperature thermal oxidation of the volatile pyrolysis products in the PCFC. Char yield was determined by weighing the sample before the test and immediately after flaming combustion had ceased to preclude any mass loss due to char oxidation.

Table 4 shows that the thermal properties  $T_g$ ,  $T_{ign}$ ,  $\kappa\rho c$ , and  $L_g$  of the BPC and BPA polycyanurate resins are comparable to each other and to many other thermally stable engineering resins and plastics [1]. The fire response of BPC and BPA polycyanurates is quite different however, with HOC reduced by a factor of 10 at comparable mass loss rate and CO yield. The HCl yield for BPC-CE is essentially quantitative, i.e., the stoichiometric amount of HCl in the polymer (22% w/w). The HCN yield is only about 1/3 of the stoichiometric amount (9% w/w) of this compound in BPC-CE, which is consistent with data showing that 2/3 of the carbon and nitrogen are incorporated into solid char based on elemental analyses [45]. The combustion efficiency  $\chi$ , smoke extinction area (SEA), soot yield, and CO<sub>2</sub> yield of BPA-CE are

typical of char-forming, nitrogenous, hydrocarbon resins in well-ventilated flaming combustion, wherein the majority of fuel gases are converted to CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> [30]. In contrast,  $\chi$ , SEA, soot yield, and CO<sub>2</sub> yield are relatively low for BPC-CE, while the CO yield is comparable to BPA-CE. These data suggest that HCl inhibits BPC-CE combustion in such a way that unburnt hydrocarbons (not measured in these tests) are produced rather than soot or carbon monoxide.

TABLE 4. FIRE PROPERTIES OF BPC AND BPA POLYCYANURATES

Fire Property	Units	BPC-CE	BPA-CE
Softening Temperature ( $T_g$ )	°K	548	530
Ignition Temperature ( $T_{ign}$ )	°K	734	741
Thermal Inertia ( $\kappa\rho c$ )	$\text{kJ}^2/\text{m}^4\text{-s-K}^4$	2.6	1.8
Heat of Gasification ( $L_g$ )	MJ/kg	5.3	4.0
Effective Heat of Combustion (HOC)	MJ/kg	$3.7 \pm 0.5$	$25.9 \pm 1.2$
Smoke Extinction Area (SEA)	$\text{m}^2/\text{kg}$	$128 \pm 66$	$622 \pm 146$
CO Yield	kg/kg	$0.03 \pm 0.01$	$0.04 \pm 0.04$
CO <sub>2</sub> Yield	kg/kg	$0.34 \pm 0.05$	$1.95 \pm 0.18$
HCl Yield (Flaming)	kg/kg	$0.24 \pm 0.01$	0
HCN Yield (Flaming)	kg/kg	$0.007 \pm 0.002$	0.002
Soot Yield	kg/kg	$0.030 \pm 0.004$	$0.09 \pm 0.02$
Combustion Efficiency ( $\chi$ )	dimensionless	$0.41 \pm 0.05$	$0.94 \pm 0.05$
Char Yield (Flaming)	kg/kg	$0.53 \pm 0.07$	$0.29 \pm 0.13$

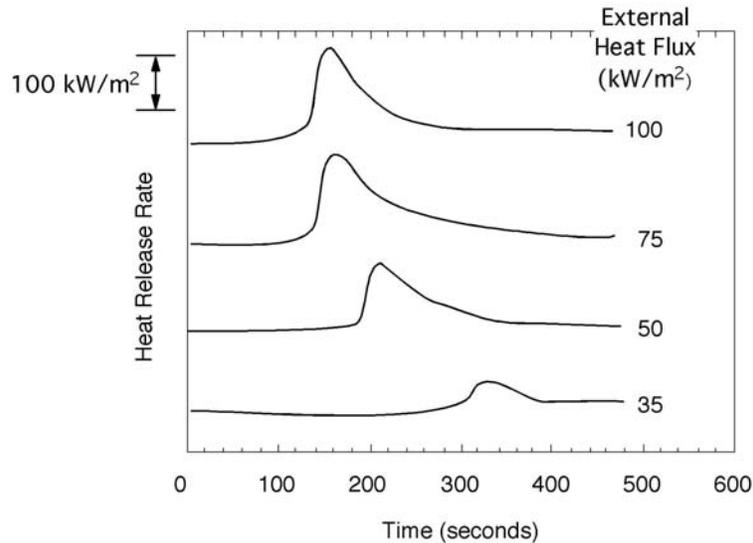


FIGURE 6. HEAT RELEASE RATE HISTORIES FOR BPC-CE TESTED AT 6-mm THICKNESS ACCORDING TO ASTM 1354 AT 35, 50, 75, AND 100  $\text{kW}/\text{m}^2$  EXTERNAL HEAT FLUX (Data is vertically shifted for clarity.)

Table 5 lists data for combustibility of blends of BPC polyarylester (polyarylate), compound 24 in table 3, with the BPA polyarylate analog synthesized using a 1:1 mole ratio of isophthaloyl and terephthaloyl chlorides [14] so as to give a soluble, fusible, amorphous polymer similar to commercial BPA polyarylate. Table 5 also shows copolymers containing various mole ratios of BPC and BPA in combination with 3:1 mole ratio of isophthaloyl and terephthaloyl chlorides [14]. The results in table 5 are plotted in figures 7-9.

TABLE 5. COMBUSTIBILITY OF BPC/BPA POLYARYLATE BLENDS AND COPOLYMERS [14]

Sample	HRC (J/g-K)	HR (kJ/g)	Char Yield (%)
Mole Percent BPC Polyarylate* in BPC/BPA Blends			
100	18	5.7	50
95	19	5.4	52
75	34	7.0	51
50	87	9.7	44
25	184	14.0	37
5	413	18.1	28
0	460	19.4	25
Mole Percent BPC in BPC/BPA Polyarylate** Copolymers			
100	29	5.5	43
75	31	8.3	50
50	103	11.9	41
25	175	14.6	36
0	430	22.4	25

\*1:1 iso/terephthaloyl chloride; \*\*3:1 iso/terephthaloyl chloride

It has been shown that the combustibility parameters are the sum of additive molar contributions of the individual chemical groups comprising the polymer backbone [46 and 47]. Applying the molar group additivity principle to the present case for generalized BPA- and BPC-arylate moieties having mole fraction and molar heat of combustion  $n_i$  and  $H_i$ , where subscripts c and a refer to the BPC- and BPA-arylate, respectively

$$HR = \sum \frac{n_i H_i}{n_i M_i} = HR(0) \left\{ \frac{1 - n_c (1 - H_c / H_a)}{1 - n_c (1 - M_c / M_a)} \right\} \quad (2)$$

where  $HR(0) = HR(n_c = 0) = H_a / M_a = 20.9$  MJ/kg is the average HR of the BPA polyarylates. Equation 2 was solved for  $H_c / H_a$  and  $M_c / M_a$  using the data in table 5. The dashed line through the HR versus  $n_c$  data in figure 7 was calculated using equation 2 for the average values  $H_c / H_a = 1/2$  and  $M_c / M_a = 2$  and shows good agreement with the experimental data.

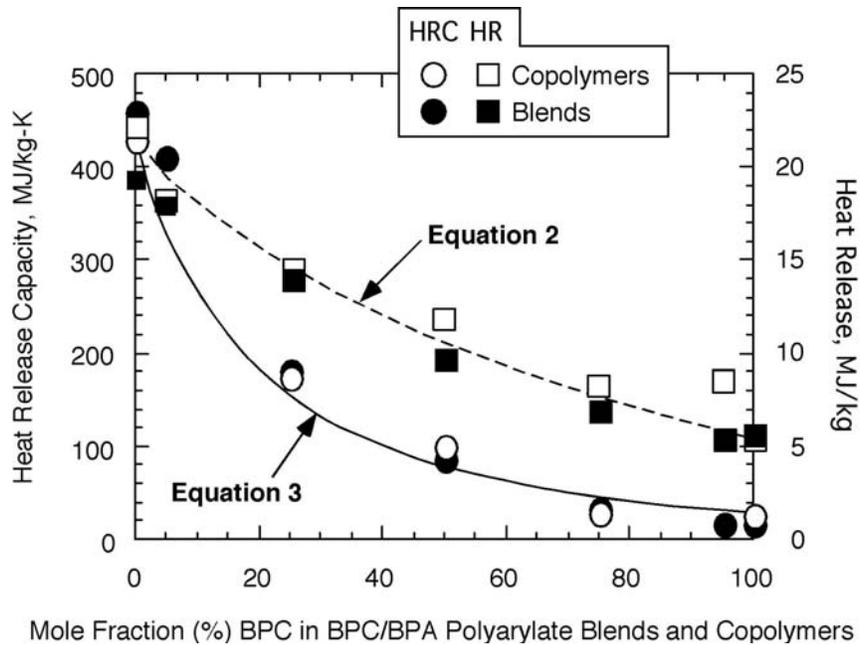


FIGURE 7. HEAT RELEASE CAPACITY AND HR OF BPC/BPA POLYARYLATE BLENDS AND COPOLYMERS [14]  
(Solid line calculated from equation 3. Dashed line calculated from equation 2.)

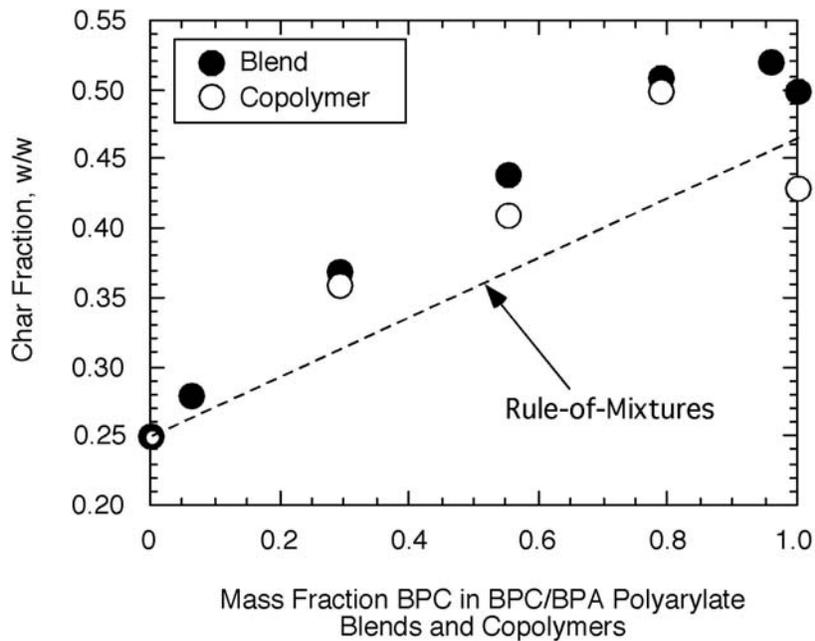


FIGURE 8. CHAR FRACTION OF BPC/BPA POLYARYLATE BLENDS AND COPOLYMERS VERSUS MASS FRACTION BPC  
(Dashed line is upper bound rule of mixtures. Data from reference 14.)

Similar reasoning leads to an expression for HRC. Using equations 1 and 2 with  $\Delta T_p \propto \sum n_i Y_i / \sum n_i M_i$  and the  $Y_i$  are molar thermal decomposition functions for the BPA ( $Y_a$ ) and BPC ( $Y_c$ ) compositions [48]

$$\text{HRC} = \frac{\text{HR}}{\Delta T_p} = \left\{ \frac{\sum n_i H_i / \sum n_i M_i}{\sum n_i Y_i / \sum n_i M_i} \right\} = \frac{\sum n_i H_i}{\sum n_i Y_i} = \text{HRC}(0) \left\{ \frac{1 - n_c (1 - H_c / H_a)}{1 - n_c (1 - Y_c / Y_a)} \right\} \quad (3)$$

where  $\text{HRC}(0) = \text{HRC}(n_c = 0) = H_a / Y_a = 445 \text{ MJ/kg-K}$  is the average HRC of the BPA polyarylates. Equation 3 was solved for  $Y_c / Y_a$  using the data in table 5 with  $H_c / H_a = 1/2$  as per the HR data. The solid line through the HRC versus  $n_c$  data plotted in figure 7 was calculated from equation 3 for  $H_c / H_a = 1/2$  and the average value  $Y_c / Y_a = 7$ . Good agreement between equation 3 and the full range of experimental data is observed for these parameters. These molar ratios give the relative contribution of BPC and BPA to the heats of combustion, molar mass, and thermal stability to the polymers derived from them. On a mass basis, BPC is even more efficient at reducing the combustibility of polymers derived from bisphenol-A. In particular, the ratio of specific HR computed from the composition-average molar ratio  $H_c / H_a = 1/2$ , is

$$\frac{\text{HR}_c}{\text{HR}_a} = \frac{H_c / M_c}{H_a / M_a} = \frac{H_c}{H_a} \frac{M_a}{M_c} = \left( \frac{1}{2} \right) \left( \frac{1}{2} \right) = \frac{1}{4}$$

This value agrees with the average ratio of the pure polymer data table 5,  $\text{HR}_c / \text{HR}_a = (5.6 \text{ kJ/g}) / (21 \text{ kJ/g}) \approx 1/4$ .

The ratio of BPA and BPC HRCs computed from the composition-average molar ratios is

$$\frac{\text{HRC}_c}{\text{HRC}_a} = \frac{H_c / Y_c}{H_a / Y_a} = \frac{H_c}{H_a} \frac{Y_a}{Y_c} = \left( \frac{1}{2} \right) \left( \frac{1}{7} \right) = \frac{1}{14}$$

This value is in fair agreement with the pure polymer and copolymer data in table 5,  $\text{HRC}_c / \text{HRC}_a = (24 \text{ J/g-K}) / (445 \text{ J-g-K}) \approx 1/19$ .

Figure 8 is a plot of the average char fraction of the polyarylates in table 5 versus the mass fraction of BPC in the blend or copolymer. The dashed line in figure 8 is the simple (upper bound) rule of mixtures prediction for noninteracting components,  $\mu$  (mixture) =  $w_1 \mu_1 + w_2 \mu_2 + \dots = \sum w_i \mu_i$ , where  $w_i$  and  $\mu_i$  are the weight fraction and char mass fraction of component  $i$ . The char fraction of the polyarylate blends and copolymers in figure 8 exceeds the upper bound rule of mixtures (dashed line), suggesting that the char fractions are not simply additive (intramolecular). Instead, the DDE charring reaction in BPC polymers is intermolecular and incorporates mass from contiguous aromatic groups in the BPA arylate moiety.

Figure 9 shows a plot of the average specific combustion heat of the pyrolysis gases,  $h_c$  (J/kg-gas) =  $\text{HR} / (1 - \mu)$ , for the polyarylate blends and copolymers in table 5. The specific combustion heat of the pyrolysis gases is the amount of heat given off by complete combustion of unit mass of volatiles produced by pyrolysis. Figure 9 shows that  $h_c$  decreases linearly with the mass

fraction of BPC as HCl and solid char replace the volatile hydrocarbons of the BPA pyrolysis products. The data in table 5 plotted in figures 7-9 show that the DDE moiety effects combustibility with the same efficiency regardless of whether it is in the same (copolymer) or a different (blended) molecule.

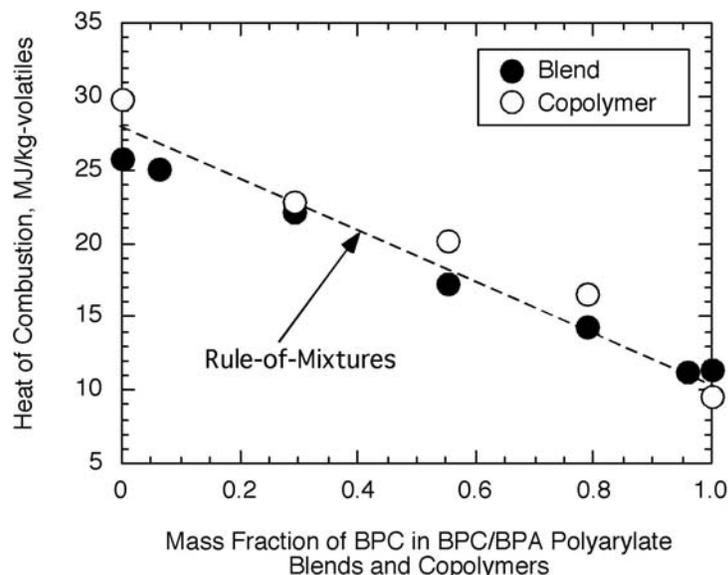


FIGURE 9. HEAT OF COMBUSTION OF PYROLYSIS GASES OF BPC/BPA POLYARYLATE BLENDS AND COPOLYMERS VERSUS MASS FRACTION OF BPC (Dashed line is upper bound rule of mixtures. Data from reference 14.)

Figure 10 is a plot of LOI data [9] for blends and copolymers of BPC and BPA polycarbonate (for BPC polycarbonate see compound 21 in table 3). Unlike HRC and HR, the LOI is not a property of a material. Rather, it is the response of a material to a specific set of test parameters that include sample thickness, orientation, and temperature, as well as gas flow rate. Consequently, LOI data cannot be related to molar or specific (mass based) quantities as described in the HRC and HR data in table 5. Equations 1-3 and figure 9 compare the LOI versus BPC mass fraction data to empirical predictions of an upper bound and lower bound rules of mixtures, where the lower bound is:  $1/\text{LOI}(\text{mixture}) = w_1/\text{LOI}_1 + w_2/\text{LOI}_2 + \dots = \sum w_i/\text{LOI}_i$ . It is clear from figure 10 that the relationship between LOI and mass fraction of BPC is best described by lower bound behavior that emphasizes the effect of the worst performing component of the mixture, in this case, the BPA-carbonate moiety.

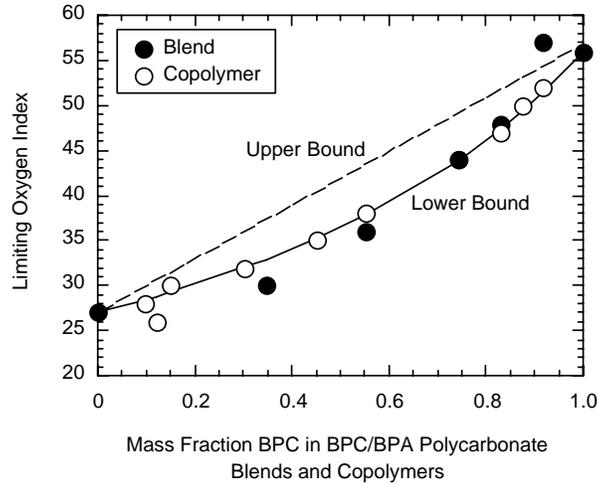


FIGURE 10. LIMITING OXYGEN INDEX OF BPC/BPA POLYCARBONATE BLENDS AND COPOLYMERS

(Dashed line is simple (upper bound) rule of mixtures. Solid line is lower bound rule of mixtures. Data points from reference 9.)

Figure 11 is a plot of the HRR histories of blends of BPC-PC with BPA-PC (LEXAN) tested in flaming combustion, according to ASTM 1354, at an external heat flux of  $50 \text{ kW/m}^2$ , where it is seen that as much as 20% of the BPA-PC can be added to BPC-PC without significantly affecting the HRR. Moreover, the 50/50 blend of BPA- and BPC-PC ignites and burns at roughly the same time as the BPA-PC, but the peak HRR ( $75 \text{ kW/m}^2$ ) is only 1/4 of LEXAN ( $300 \text{ kW/m}^2$ ), probably because of enhanced charring (see figure 8).

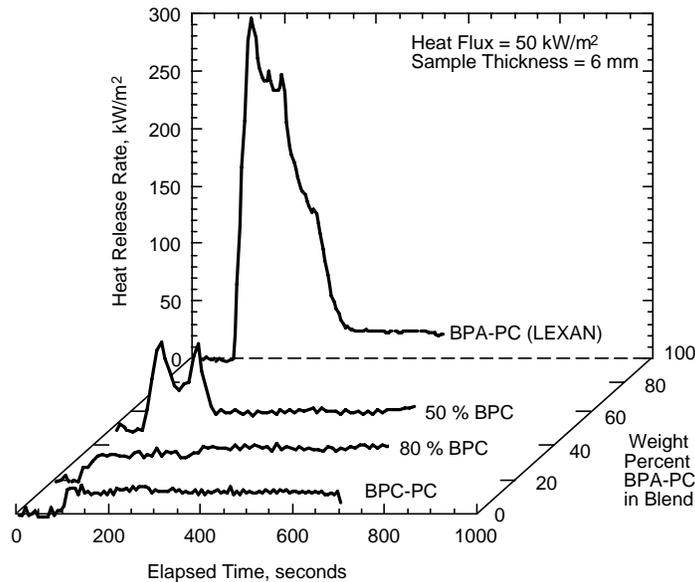


FIGURE 11. HEAT RELEASE RATE HISTORY VERSUS COMPOSITION OF BPA-PC/BPC-PC BLENDS IN FLAMING COMBUSTION AT  $50 \text{ kW/m}^2$  EXTERNAL HEAT FLUX ACCORDING TO ASTM 1354

### 4.1.3 Mechanical Properties of Pure Polymers, Copolymers, and Blends.

Table 6 summarizes mechanical property data for the engineering plastics and cured thermoset resins. Included in table 6 are published data [7] for the polycarbonate of BPA and BPC, the polyarylate of BPA [27] and BPC [6], the epoxy homopolymer of BPA [12 and 32] and BPC [12], and the polycyanurate of BPA [33] and BPC [10]. Glass transition temperatures, Young's moduli, and tensile yield strengths are slightly higher, and ultimate elongations lower, for BPC polymers compared to BPA polymers.

TABLE 6. MECHANICAL PROPERTIES OF BPA AND BPC THERMOPLASTIC AND THERMOSET POLYMERS

Polymer		T <sub>g</sub> (°C)	Strength		Tensile Yield Strain (%)	Tensile Rupture Strain (%)	Young's Modulus (GPa)
			Tensile Yield (MPa)	Flexure (MPa)			
Polycarbonate	BPA	152	58	102	10	110	2.3
	BPC	168	77	117	11	38	2.6
Polyarylate	BPA	205	69	76	4	50	2.3
	BPC	215	80	–	3	15	2.5
Epoxy	BPA	113	39	120	–	2-3	3.1
	BPC	122	–	123	–	2-3	3.0
Polycyanurate	BPA	289	83*	174	–	2-3	3.1
	BPC	275	60*	122	–	2-3	3.5

\*Brittle failure.

## 4.2 POLYMER COMPOSITES.

### 4.2.1 Flammability of BPC Composites.

Figure 12 shows fire calorimetry data according to 14 CFR 25.853(a-1) [37] for a current production aircraft interior panel (phenolic resin-glass fabric face sheets on 6.4-mm NOMEX honeycomb core, one ply each side, no decorative film) compared to a panel of the same construction made with BPC polycyanurate resin in place of phenolic. The maximum allowable HRR in the 5-minute test is 65 kW/m<sup>2</sup> [38]. The BPC polycyanurate panel has a maximum HRR that is 1/3 the HRR of a state-of-the-art phenolic resin panel.

Table 7 lists the fire calorimetry results obtained by standard methods [39] for 18-ply (6-mm-thick) glass fabric laminates prepared by vacuum-assisted resin transfer molding [24, 49, and 50] of bisphenol-A epoxy (BPA-EP), BPA-CE, BPC-EP, and BPC-CE. As expected from the single-ply test results in table 7, the BPC epoxy laminates have lower HR and SEA than the BPA epoxy laminates at 50 kW/m<sup>2</sup> heat flux. However, the HRR reduction is not as significant as that for the BPC and BPA polycyanurates, where a ten-fold reduction in peak HRR and total HR at 50 kW/m<sup>2</sup> external heat flux is observed.

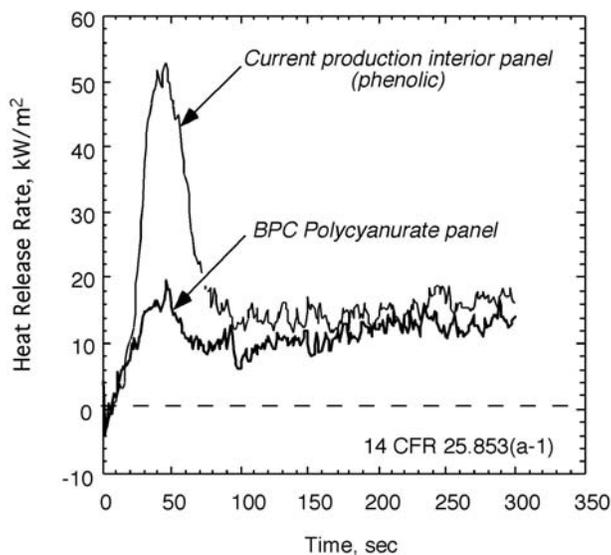
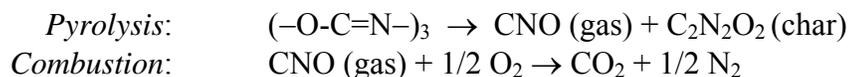


FIGURE 12. HEAT RELEASE RATE HISTORIES (14 CFR 25.853) FOR INTERIOR PANELS MADE WITH CURRENT PHENOLIC RESIN AND BPC POLYCYANURATE RESIN FACE SHEETS

TABLE 7. FIRE BEHAVIOR (ASTM 1354) OF FIBERGLASS LAMINATES MADE FROM BPA-EP, BPC-EP, BPA-CE, AND BPC-CE

Resin	Heat Flux (kW/m <sup>2</sup> )	Time to Ignition (sec)	Peak HRR (kW/m <sup>2</sup> )	Average HRR (kW/m <sup>2</sup> )	Total HR (MJ/m <sup>2</sup> )	SEA (m <sup>2</sup> /kg)
BPA-EP	50	102	155	78	36	1315
BPC-EP	50	74	77	51	27	508
BPA-CE	50	129	118	24	13	413
BPC-CE	25	NI	0	0	0	0
BPC-CE	50	NI	3 ±3	0	0	26 ±26
BPC-CE	75	282 ±72	22 ±9	16 ±14	5 ±1	127 ±65
BPC-CE	100	143 ±7	45 ±6	29 ±12	7 ±1	76 ±43

The reason for the large difference in flammability and fire behavior between epoxies and cyanurates derived from BPC is the heat of combustion and char forming tendency of the DDE linking groups. It can be shown that the glycidylether linking group is volatilized completely during pyrolysis or burning [44], while 2/3 of the mass of the cyanurate ring remains behind as char during pyrolysis or burning [45]. The stoichiometry of the pyrolysis and combustion reactions of the cyanurate ring (formula weight 126 g/mole) as they occur in a fire are, therefore,



The molar heat of combustion of the cyanurate ring in a fire, assuming complete combustion of the volatile CNO component, is  $h_c^0 = (0.5 \text{ mole-O}_2/\text{mole-cyanurate})(419 \text{ kJ/mole-O}_2) = 210 \text{ kJ/mole-cyanurate}$ . This is only about 4% of the molar heat of combustion of the noncharring glycidylether group,  $h_c^0 = 5400 \text{ kJ/mole-epoxide}$ , by the same reasoning. The large difference in the molar heat of combustion of linking (or pendant) groups between DDE moieties is a consequence of their atomic composition and char forming tendency, and it accounts for the difference in flammability of these and all of the polymers in table 3. The exceptional fire performance, ignition resistance, and extremely low HRRs of BPC polycyanurates even at high heat fluxes has prompted studies [24, 49, and 50] that have shown that BPC polycyanurate resin structural composites meet all of the ignitability and HR requirements of MIL-STD-2031 [51] for use on Navy submarines. These data indicate that BPC polycyanurate is unique among low-temperature curing organic resin systems in the ability to pass the full-scale ISO 9705 room corner fire test as a fiber reinforced composite without the need for a fire protection barrier [49].

Table 8 shows flammability results for neat resin samples of the diglycidylether of BPC (see figure 3) cured with a stoichiometric amount of 2-ethyl-4-methyl imidazole (EMI 24), triethylenetetramine (TETA), 4,4'-methylenedianiline (MDA), 1,1-dichloro-2,2-bis(4-hydroxy phenyl)ethylene (BPC), 1,1-dichloro-2,2-bis(4-cyanatophenyl)ethylene (BPC-CE). Also listed in table 8 are the fire calorimetry tests results obtained as per 14 CFR 25.853 on hand impregnated single ply fiberglass cloth lamina containing about 5 grams of cured resin. It is seen that the BPC epoxy formulated with aromatic hardeners (MDA, BPC, BPC-CE) that are capable of participating in intermolecular charring reactions with DDE (see figure 8) exhibit low HRR in flaming combustion and self-extinguishing behavior as neat resins.

TABLE 8. FLAMMABILITY OF BPC EPOXY CURED WITH VARIOUS HARDENERS

Hardener (phr)	Fire Behavior (Single Ply)		Resin Flammability		
	Peak HRR (kW/m <sup>2</sup> )	Total HR (kW-min/m <sup>2</sup> )	HRC (J/g-K)	LOI (% O <sub>2</sub> )	UL 94
EMI-24 (2)	50	26	487	27-28	B
TETA (14)	70	32	577	—	—
MDA (56)	44	32	261	—	V-0
BPC (66)	30	19	153	35-36	V-0
BPC-CE (53)	34	18	291	—	—

Fire behavior is for glass lamina tested according to 14 CFR Part 25. Flammability results are for neat resins.

Fire calorimetry results for cocured mixtures of BPC dicyanate/BPC diglycidylether tested as glass fabric lamina according to 14 CFR 25.853(a-1) [37 and 38] are listed in table 9 and plotted graphically in figure 13 for the full range of BPC cyanate ester/BPC epoxy compositions. Figure 13 shows that both HRR and HR follow simple (upper bound) rule-of-mixtures behavior. Moreover, all of the BPC cyanurate or epoxy compositions pass the FAA requirement for large transport aircraft of 65 kW/m<sup>2</sup> peak HRR and 65 kW-min/m<sup>2</sup> total HR.

TABLE 9. FLAMMABILITY OF BPC-CE/BPC-EP THERMOSET COPOLYMERS

Sample	Fire Behavior		Flammability		
	Peak HR (kW/m <sup>2</sup> )	2-min HR (kW-min/m <sup>2</sup> )	HR Capacity (J/g-K)	Total HR (kJ/g)	Char Yield (%)
BPC-CE	14	13	13	4	59
8:2	18	18	13	5	53
6:4	30	15	149	6	52
4:6	34	18	291	8	42
2:8	32	22	393	9	33
BPC-EP	49	27	506	10	36

Fire behavior is for glass fabric lamina tested according to 14 CFR Part 25. Flammability is for cured neat resin.

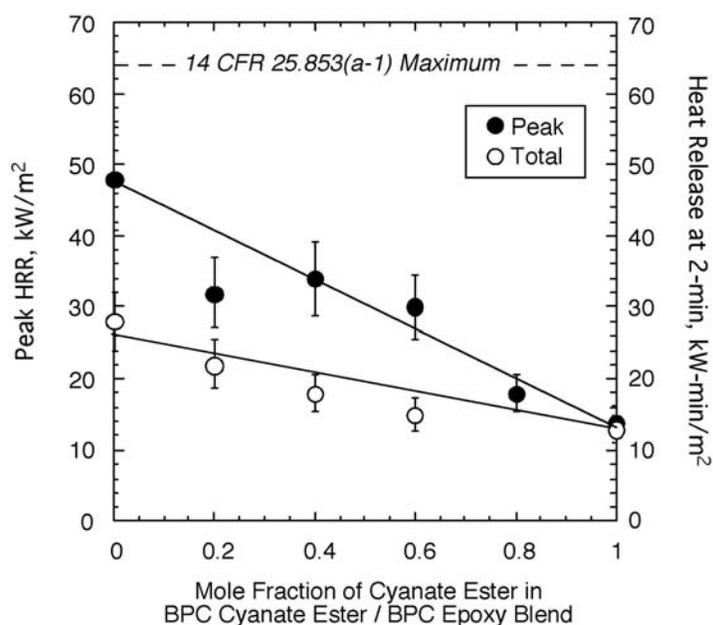


FIGURE 13. FLAMING HRR AND TOTAL HR (14 CFR PART 25) OF FIBERGLASS LAMINA CONTAINING BPC-CE/BPC-EP COPOLYMER

Table 4 showed that the BPC polycyanurate yields 0.24 kg of HCl per kg resin in well-ventilated flaming combustion, which is essentially the stoichiometric yield. Experiments were conducted to determine if the addition of mineral fillers (e.g., metal hydroxides, M(OH)) would be effective at scavenging HCl from the combustion gases through a solid state reaction of the type:



Table 10 shows data for HCl scavenging efficiency of metal hydrates and oxides deduced from gas analysis and expressed as the mole percent of chlorine converted to metal chloride salt during anaerobic pyrolysis. In addition to the results for mineral filled BPC-CE, table 10 also

contains fire calorimetry results for BPA-CE, BPA-EP, and the current aircraft cabin phenol-formaldehyde (phenolic) resin also tested as a single-ply fiberglass cloth lamina for comparison. The results in table 10 show that between 0.5 and 2 moles of Cl react with each mole of metal in the compound, depending on the mineral. However, metal compounds including minerals catalyze polymerization of the dicyanate monomers and destabilize the polycyanurate, particularly at the loading levels, needed to achieve significant reductions of HCl in the pyrolysis or combustion products during burning. The HRR and 2-minute HR in flaming combustion of the pure BPC-CE resin was reduced by all of the minerals in rough proportion to the inert loading level. Negative 2-minute HR values are an artifact of the test method, although no flames were observed on the zinc borate (ZB) sample surfaces.

TABLE 10. FIRE BEHAVIOR (14 CFR PART 25) OF NEAT RESINS AND BPC-CE BLENDED WITH MAGNESIUM HYDROXIDE, ALUMINUM HYDROXIDE, BASIC ALUMINUM OXALATE, AND ZB TESTED AS GLASS FABRIC LAMINA

Resin/ Mineral	Mineral Loading (Weight %)	[Cl]/[M] in Compound (Mole/Mole)	Moles Cl Scavenged/ Mole Metal (Mole Fraction)	$\epsilon$ (mole %)	Peak HRR (kW/m <sup>2</sup> )	2-min Heat Release (kW-min/m <sup>2</sup> )
BPA-EP	0	0	0	N/A	111	44
BPA-CE	0	0	0	N/A	72	28
Current AC Phenolic	0		0	N/A	23	21
BPC-CE	0	N/A	N/A	0	14	13
BPC-CE/MgOH	5%	6.7	0.13	2	12	-2
	10%	3.2	0.47	15	13	-1
	20%	1.4	0.48	34	33	8
BPC-CE/AlOH	10%	4.2	0.59	14	11	0
	20%	1.9	0.26	14	10	1
BPC-CE/BAO	5%	17	1.39	8	11	-1
	10%	8.2	1.23	15	10	-1
BPC-CE/ZB	30%	2.6	1.55	59	0	-18

Hydrogen chloride scavenging efficiency  $\epsilon$  is mole percent HCl remaining in resin after burning.

N/A = Not applicable

MgPH = Magnesium hydroxide

AlOH = Aluminum hydroxide

BAO = Basic aluminum oxalate

Fire calorimetry data obtained according to 14 CFR Part 25 for 1.6-mm-thick samples of natural- and mineral-filled thermoplastics are presented in table 11. The Bisphenol-A polycarbonate (BPA-PC) does not pass the FAA requirement of 65 kW/m<sup>2</sup> maximum allowable HRR for the test, forcing aircraft manufacturers to use heat-resistant polyetherimide (PEI) or polyphenylsulfone (PPSU) plastics for thermoformed parts in large area cabin interior applications. These data show that flaming HR and HRR are reduced 2 to 6 fold for natural and filled BPC-PC resins, respectively, compared to BPA-PC. The maximum allowable HRR for

large area cabin materials, when tested according to 14 CFR 25.853(a-1), is 65 kW/m<sup>2</sup>. The BPC polycarbonate passes the FAA HRR test for large area cabin materials as a natural (unmodified) resin in the same thickness.

TABLE 11. FIRE BEHAVIOR AND FLAMMABILITY OF THERMOPLASTICS

Sample	14 CFR 25.853(a-1)		Flammability		
	Peak HRR (kW/m <sup>2</sup> )	2-min HR (kW-min/m <sup>2</sup> )	HRC (J/g-K)	HR (kJ/g)	Char Yield (%)
AC Grade PEI	52 ±6	22 ±6	121	12	49
AC Grade PPSU	61	20			
BPA PC (clear)	153 ±10	58 ±3	390	21	24
PPSU (clear)	66 ±6	16 ±5	203	12	42
BPC PC (clear)	50 ±8	38 ±6	23	5	50
BPC Polyether	86	56	26	4	54
BPC Polyarylate	27	19	18	6	50
BPC-PC containing					
1% TiO <sub>2</sub>	66	48	15	3	51
10% BAO	31	26	22	5	43
20% Talc	25	19	9	3	58

Results are for 1.6-mm-thick samples of BPA polycarbonate, aircraft-grade PEI, aircraft-grade polyphenylsulfone, clear polysulfone, and BPC polycarbonate (natural/clear) containing titanium dioxide (TiO<sub>2</sub>), basic aluminum oxalate (BAO), and talc at the indicated loading level (wt %).

#### 4.2.2 Mechanical Properties.

Table 12 includes flexural strength, strain, and stiffness data for 18-ply glass fabric laminates of the epoxy homopolymer (compound 2 in table 3) and polycyanurate (compound 13 in table 3) resins. The BPC resin laminates appear to have slightly lower strength and stiffness than the BPA resin laminates, although the epoxy data is the result of only a single test.

TABLE 12. FLEXURAL PROPERTIES OF 18-PLY GLASS FABRIC-REINFORCED STRUCTURAL LAMINATES

Thermoset Resin		Yield Stress (MPa)	Yield Strain (%)	Flexural Modulus (GPa)
Epoxy	BPA	620	2.3	29
	BPC*	490	2.1	25
Polycyanurate	BPA	570	1.8	32
	BPC	520	2.2	26

\*Single test result.

## 5. DISCUSSION.

Polymers based on 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethene (BPC) or containing dichlorodiphenylethane (DDE) groups

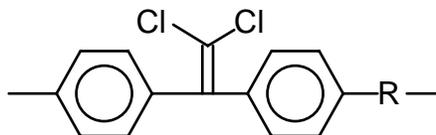


exhibit a unique combination of mechanical properties, processability, and extreme fire resistance when R is a low-fuel-value linking group such as carbonate (CO<sub>3</sub>), cyanurate (C<sub>3</sub>N<sub>3</sub>O<sub>3</sub>), ester (OCO<sub>2</sub>), ketone (CO<sub>2</sub>), sulfone (SO<sub>2</sub>), or ether (O).

Polymers derived from BPC and fire tested for this report include the engineering thermoplastics polycarbonate polyarylate, polysulfone, and thermoset resins based on diglycidylether (epoxy), cyanate ester. Also evaluated were BPC-epoxy and BPC-cyanate ester blends and their composites. Polymers based on BPC have mechanical, thermal, and processing characteristics equivalent to or better than bisphenol-A analogs, but they are more ignition resistant and have extremely low HRR in forced flaming combustion, typically passing the FAA HR for aircraft interiors 14 CFR 25.853(a-1). Mineral fillers added to BPC polymers are effective at further reducing the peak HRR and total heat released, and some of these fillers have the potential of removing HCl from the combustion gases if they can be tolerated by the polymer.

## 6. REFERENCES.

1. R.E. Lyon, "Plastics and Rubber," Chapter 3 in *Handbook of Materials for Fire Protection*, C.A. Harper, ed., McGraw-Hill, New York, 2004.
2. R.E. Lyon, "Solid State Thermochemistry of Flaming Combustion," in *Fire Retardancy of Polymeric Materials*, A.F. Grand and C.A. Wilkie, (eds.), Marcel Dekker, Inc., NY, 2000, pp. 391-447
3. R.E. Lyon, S. Gandhi, and R.N. Walters, "Flammability Study of Advanced Engineering Thermoplastics," *Society for the Advancement of Materials and Process Engineering (SAMPE) 44th International Symposium and Exhibition*, Long Beach, CA, May 23-27, 1999.
4. *High Temperature Polymers*, C.L. Segal, ed., Edward Arnold Publ., London, UK 1967.
5. R.E. Lyon, "Federal Aviation Research in Fire Safe Materials for Aircraft Interiors," *SAMPE Journal*, **32**(3), 1996, pp. 29-33.
6. A.L. Rusanov, "Condensation Polymers Based on Chloral and Its Derivatives," *Progress in Polymer Science*, 19, 1994, pp. 589-662.

7. J. Kielkiewicz and S. Porejko, "Characteristics of Self-Extinguishing Polyarylesters of an Aromatic Dicarboxylic Acid and 2,2-bis(4-hydroxyphenyl)-1,1-dichloroethylene," *Die Angewandte Chemie*, 78 (1062), 1979, pp. 75-87.
8. A. Factor, M.R. MacLaury, and J.L. Webb, US Patent 4,097,538 (1978).
9. A. Factor and C.M. Orlando, "Polycarbonates From 1,1-dichloro-2,2-bis(4-hydroxyphenyl) Ethylene and Bisphenol A: A Highly Flame-Resistant Family of Engineering Thermoplastics," *J. Polym. Sci., Polym. Chem. Ed.*, 1980, Vol. 18, pp. 579-592.
10. B. Lin, "Cyanate Esters With Improved Fire Resistance," *44<sup>th</sup> International SAMPE Symposium*, Long Beach, CA, May 23-27, 1999.
11. R.E. Lyon, "Fire Resistant Bisphenol-C Polymers," *Aircraft Fire & Cabin Safety Research Conference*, Atlantic City, NJ, October 22-25, 2001.
12. R.E. Lyon, L.M. Castelli, and R.N. Walters, "A Fire Resistant Epoxy," FAA report DOT/FAA/AR-01/53, August 2001.
13. R.N. Walters and R.E. Lyon, "Fire Resistant Cyanate Ester-Epoxy Blends," *Fire and Materials*, 27(4), 2003, pp. 183-194.
14. J.R. Stewart, "Synthesis and Characterization of Chlorinated Bisphenol-Based Polymers and Polycarbodiimides as Inherently Fire Safe Polymers," FAA report DOT/FAA/AR-00/39, August 2000.
15. M. Ramirez, "Thermal Degradation Mechanism of 2,2-bis-(4-hydroxyphenyl)-1,1-Dichloroethylene-Based Polymers," FAA report DOT/FAA/AR-00/42, February 2001.
16. R.E. Lyon, R.N. Walters, and S. Gandhi, "Combustibility of Cyanate Ester Resins," FAA report DOT/FAA/AR-02/44, June 2002.
17. J. L. Jurs, "Novel Flame Retardant Additives and Polymers: Synthesis and Testing," Ph.D. Thesis, William Marsh Rice University, August 2003.
18. H. Zhang, "Fire Safe Polymers and Polymer Composites," FAA report DOT/FAA/AR-04/11, September 2004.
19. K. Elzey, "Fire Resistant Polymers Containing 1,1-Dichloro-2,2-Diphenylethene and Deoxybenzoin Derivative," Ph.D. Thesis, Polymer Science & Engineering Department, University of Massachusetts, June 2004.
20. S.I. Stoliarov and P.R. Westmoreland, "Mechanism of the Thermal Decomposition of Bisphenol C Polycarbonate: Nature of Its Fire Resistance," *Polymer* 44, pp. 5469, 2003.

21. V. Babrauskas and R.D. Peacock, "Heat Release Rate: The Single Most Important Variable in Fire Hazard," *Fire Safety Journal*, 18, 1992, pp. 255-272.
22. Private Communication, Polymer Samples, Dr. Arnold Factor, General Electric Corporation, Schenectady, NY.
23. R.E. Lyon, "Fire Resistant Materials: Research Overview," FAA report DOT/FAA/AR-97/99, December 1997.
24. R.N. Walters, "Fire-Safe Polymer Composites, 46<sup>th</sup> International SAMPE Symposium, Long Beach, CA, June 2002.
25. J. Osby, M. Robertson, J.L. Aguilar, and A. Wang, "Synthesis, Compounding, and Flammability Testing of Polycarbonate Based on 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene," Contract DTFA0301P10098, Final Report, The Dow Chemical Company, Freeport, TX, January 17, 2002.
26. A.V. Bray, S. Venumbaka, and J.B. Oba, "Synthesis of Bisphenol-C (BPC) Ultra Fire Resistant Plastics," DTRS57-02-C-10011, SBIR Phase I Final Report, Systems and Materials Research Consultancy, Spicewood, TX, September 2002.
27. M. H. Hubacher, "Bis(p-hydroxyphenyl)acetic Acid," *J. Org. Chem.*, December 1959, pp. 1949-1951.
28. M.R. MacLaury, A.D. Chan, A.M. Colley, A. Saracino, and A.M. Toothaker, "Synthesis of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)-ethylene via Ammonia or Methylamine Dehydrochlorination. A Bisphenol for the Preparation of Highly Flame-Resistant Polycarbonates," *J. Polym. Sci.: Polym. Chem. Ed.*, 18, 1980, pp. 2501-2511.
29. *Flammability of Plastic Materials*, Northbrook, IL: Underwriters Laboratories Inc., 1991, UL 94 Section 2 (Horizontal: HB) and Section 3 (Vertical: V-0/1/2).
30. A.H. Landrock, "*Handbook of Plastics Flammability and Combustion Toxicology*," Noyes Publications, Park Ridge, NJ, 1983.
31. "Flammability Data," in *Plastics Digest: Thermoplastics and Thermosets*, 17(1), D.A.T.A. Business Publishing, Englewood, CO, 1996, pp. 773-889.
32. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw Hill, New York, Chapter 10, 1967, pp. 17-18.
33. Hamerton, "Properties of Unreinforced Cyanate Ester Matrix Resins," in *Chemistry and Technology of Cyanate Ester Resins*, I. Hamerton, ed., Blackie Academic & Professional, London, 1994, pp. 210-2193-227.

34. "Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)," ASTM 2863, American Society for Testing of Materials, Philadelphia, PA, 1990.
35. R.E. Lyon and R.N. Walters, "Pyrolysis Combustion Flow Calorimetry," *Journal of Analytical and Applied Pyrolysis*, 71(1), 2004, pp. 27-46.
36. R.E. Lyon, "Heat Release Kinetics," *Fire and Materials*, 24, pp. 179-186, 2000.
37. "Aircraft Material Fire Test Handbook," Section 5, Heat Release Rate Test for Cabin Materials, April Horner, ed., FAA report DOT/FAA/AR-00/12, April 2000.
38. "Improved Flammability Standards for Materials Used in the Interiors of Transport Category Airplane Cabins," Federal Register, August 25, 1988, Vol. 53, No. 165, p. 32,564.
39. "Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter," ASTM E 1354, American Society for Testing of Materials, Philadelphia, PA, 1997.
40. L.C. Speitel, "Fourier Transform Infrared Analysis of Combustion Gases," FAA report DOT/FAA/AR-01/88, October 2001.
41. "Standard Test Method for Compressive Properties of Rigid Cellular Plastics," ASTM D1621, American Society for Testing of Materials, Philadelphia, PA, 1994.
42. "Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials," ASTM D 790-95a, American Society for Testing of Materials, Philadelphia, PA, 1995.
43. J.A. Hinckley, "DSC Study of the Cure of a Phenylethynyl terminated Imide Oligomers," *J. Advanced Materials*, April 1996, pp. 55-59.
44. D.W. Van Krevelen, "Some Basic Aspects of Flame Resistance of Polymeric Materials," *Polymer*, 16, 1975, pp. 615-620.
45. M.L. Ramirez, R.N. Walters, R.E. Lyon, and E.P. Savitski, "Thermal Decomposition of Cyanate Ester Resins," *Polymer Degradation and Stability*, 78, 2002, pp. 73-82.
46. R.N. Walters, "Molar Group Contributions to the Heat of Combustion," *Fire and Materials*, 26, 2002, pp. 131-145.
47. R.N. Walters and R.E. Lyon, "Molar Group Contributions to Polymer Flammability," *Journal of Applied Polymer Science*, 87, 2003, pp. 548-563.
48. D.W. Van Krevelen, *Properties of Polymers, 3<sup>rd</sup> Edition*, Elsevier, Amsterdam, 1990.

49. U. Sorathia and I. Perez, "Improving the Fire Performance Characteristics of Composite Materials for Naval Applications," *Proc. of the Fire & Materials 2005 Conference*, Interscience Communications, London, UK, 2005, pp. 415-424.
50. J.H. Koo, B. Muskopf, G. McCord, P. Van Dine, B. Spencer, U. Sorathia, and S. Venumbaka, "Characterization of Fire Safe Polymer Matrix Composites for Naval Applications," *Proc. of the 46<sup>th</sup> International SAMPE Symposium*, 46(2), Society for the Advancement of Materials and Process Engineering, Covina, CA, 2001, pp. 2170-2180.
51. MIL-STD-2031, "Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used in Hull, Machinery, and Structural Applications Inside Naval Submarines," *Military Standard 2031*, February 1991.