Nonhalogen Fire-Resistant Plastics for Aircraft Interiors

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January 2008

DOT/FAA/AR-TN08/5

U.S. Department of Transportation
Federal Aviation Administration

NOTICE

Technical Report Documentation Page

1. Report No. DOT/FAA/AR-TN08/5	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle NONHALOGEN FIRE-RESISTANT PLASTICS FOR AIRCRAFT INTERIORS		5. Report Date January 2008
		6. Performing Organization Code
7. Author(s) Richard E. Lyon		8. Performing Organization Report No.
9. Performing Organization Name and Address Airport and Aircraft Safety R&D Division Federal Aviation Administration Atlantic City International Airport, NJ 08405		10. Work Unit No. (TRAIS)
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Air Traffic Organization Operations Planning Office of Aviation Research and Development Washington, DC 20591		13. Type of Report and Period Covered Technical Note
		14. Sponsoring Agency Code ANM 115

15. Supplementary Notes

16. Abstract

Strategies for developing fireproof aircraft cabin materials are reviewed in light of environmental legislation that restricts the use of halogens in plastics. The important physical and chemical processes of flaming combustion in terms of their effect on the heat release rate of a burning material are flame inhibition, fuel replacement, heat resistance, and intumescence. These fire resistance mechanisms, acting simultaneously or synergistically, are particularly effective at reducing heat release rate of a new generation of transparent plastics suitable for aircraft cabin interiors.

17. Key Words Fire, Flammability, Halogen, Heat release rate, Plastics, Microscale combustion calorimeter		18. Distribution Statement This document is available to the U.S. public through the National Technical Information Service (NTIS), Springfield, Virginia 22161.	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 33	22. Price

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

ACKNOWLEDGEMENTS

The author would like to thank Sean Crowley for Title 14 Code of Federal Regulations Part 25 heat and smoke testing, Richard Walters for microscale combustion calorimeter testing, Solvay Advanced Polymers for providing the clear polyphenylsulfone, GE Plastics for providing the polyestercarbonate, and the Polymer Science & Engineering Department at the University of Massachusetts, Amherst, for helpful discussions and bishydroxydeoxybenzoin polymer data. Certain commercial equipment, instruments, materials, and companies are identified in this report to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by the Federal Aviation Administration.

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LIST OF ACRONYMS

BHDB	Bishydroxydeoxybenzoin
BPA	Bisphenol-A
BPC	Bisphenol-C
BR	Burning rate
CFR	Code of Federal Regulations
EEE	Electrical and electronic equipment
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FS	Flame spread
HRR	Heat release rate
IR	Ignition resistance
MCC	Microscale combustion calorimeter
NRC	National Research Council
OSU	Ohio State University Fire Calorimeter
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenylether
PBT	Persistent bioaccumulative toxic
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
PPDC	Phenylphosphonic dichloride
PPSU	Polyphenylsulfone
PVC	Polyvinylchloride
SM	Smoke density
WEEE	Waste of Electrical and Electronic Equipment Directive

EXECUTIVE SUMMARY

Strategies for developing fireproof aircraft cabin materials are reviewed in light of environmental legislation that restricts the use of halogens in plastics. The important physical and chemical processes of flaming combustion in terms of their effect on the heat release rate of a burning material are flame inhibition, fuel replacement, heat resistance, and intumescence. These fire resistance mechanisms, acting simultaneously or synergistically, are particularly effective at reducing heat release rate of a new generation of transparent plastics suitable for aircraft cabin interiors.

INTRODUCTION

The Fire Research Program is a long-range effort that was initiated in 1993 [1 and 2] by the 1988 Aviation Safety Research Act [3] with the goal of developing a fireproof aircraft cabin. The fireproof cabin is consistent with the Federal Aviation Administration's (FAA) National Aviation Research Plan milestone to reduce the number of aviation fatalities and injuries by the year 2015 by 2/3 [4], because 40% of fatalities in impact-survivable aircraft accidents are due to the fire and smoke. At the inception of the Fire Research Program, the National Research Council (NRC) [5] recommended performance goals of eliminating in-flight fires, preventing fuselage burnthrough, and delaying cabin flashover in a postcrash fire for over 10 minutes. To meet these performance goals, a fireproof cabin would need to be constructed of ultra-fire-resistant materials having 10 times lower heat release rate (HRR) than current materials [6]. To achieve this reduction in HRR with low smoke within the timeframe of the program, it was necessary to pursue parallel, cross-cutting, application-specific materials technologies [7]. In particular, research focused on thermoplastic polymers for thermoformed parts, thermosetting polymers for liners and composite panels, rubber for seat cushions, and fiber-forming polymers for textiles [8]. Most performance milestones for these material types were met with a novel family of halogen-containing "fire-smart" polymers based on 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethane, having the common name bisphenol-C or BPC [9]. These fire-smart polymers were low-cost, high-performance thermoplastics and thermosetting resins that exhibited the order of magnitude reduction in HRR and the low smoke toxicity required for a fireproof cabin. Unfortunately, BPC polymers contain chlorine (a halogen), which have not been commercialized because recent European regulations targeting halogen-containing plastics and flame-retardants in consumer items [10] limited the application of BPC polymers to durable applications such as aircraft, which reduced the market incentive for private investment.

The 1995 NRC study identified the drivers and barriers for FAA research to develop a fireproof cabin. Drivers included the 1988 Aviation Safety Research Act [3], the reduction in aircraft fire fatalities, and the fact that government investment was necessary because aircraft interiors are a small (niche) market that does not justify the large investment by private industry needed to meet performance goals. Among the barriers cited by the NRC to the development of a fireproof aircraft cabin were the small, cyclical aviation market; regulatory and industry inertia; potentially higher cost; and the difficulty of sustaining a long-term fire research program within the U.S. government. Absent from the 1995 NRC study was the barrier that new European environmental regulations targeting halogen-containing polymers and flame-retardants would pose to the development of ultra-fire-resistant materials. At the time, fire-retardant chemicals containing the halogens (fluorine, chlorine, and bromine) accounted for nearly half of the flame-retardants added to plastics and were a viable and efficient route to ultra-fire-resistant materials.

The European movement to ban all halogen-containing polymers and flame-retardants originated in the 1960s with the discovery that some chlorinated organic compounds, including certain polychlorinated biphenyls (PCB) and polychlorinated dibenzodioxins (PCDD/dioxins), were highly toxic and/or persistent in the environment. PCBs were manufactured as cooling and insulating fluids for industrial transformers and capacitors, and also as plasticizers in flexible polyvinylchloride (PVC) coatings of electrical wiring and flame-retardants for electronic components. Production of PCB was banned in the 1970s due to the high toxicity of most PCB congeners and mixtures, which are classified as persistent organic pollutants [11]. Polybrominated biphenyls (PBB) were also widely used as flame-retardants, but production of these compounds ended voluntarily in 1976. PCDDs are not produced or used commercially but are contaminants of PCB and herbicides. Dioxins are produced in small concentrations when organic material is burned in the presence of chlorine, whether the chlorine is present as chloride ions or as organic chlorine, so they are widely produced in many contexts. According to the most recent U.S. Environmental Protection Agency (EPA) data, the majority of dioxins enter the environment from coal fired utilities, metal smelting, diesel trucks, land application of sewage sludge, burning treated wood, and trash burn barrels. These man-made sources account for 80% of dioxins, while incineration of municipal, industrial, and hazardous waste accounts for only 3%, and forest fires account for the remainder. Polybrominated diphenylethers (PBDE) are also widely used flame-retardants, but pentabromo-BDE and octabromo-BDE were discovered to be harmful to mice in laboratory tests in recent years. The sole U.S. producer of penta-BDE and octa-BDE has voluntarily agreed to stop producing and selling them by the end of 2004 and 2005, respectively. The continued use of decabromo-BDE, meanwhile, may depend on the results of current or future studies. All of these organic halogen compounds are thermally and chemically stable so they are persistent in the environment. They are soluble in fatty tissue, so they have been accumulating in fish, animals, and humans over the past few decades, to the point that levels of many of these compounds in humans are becoming significant [10 and 11].

The European Union Risk Assessment program, which has been in place for over 10 years to evaluate the human and environmental health characteristics of a variety of high-production volume chemicals, recently banned the use of two bromine flame-retardants with demonstrated toxicity, penta- and octa-brominated diphenlyether, which commonly used in polyurethane foams, electrical/electronic equipment, and automobiles [10]. Other bromine flame-retardants, found primarily in computer printed wiring boards, are also under scrutiny. The European Chemical Agency has implemented a Registration, Evaluation, and Authorization of Chemicals program beginning in 2008 that requires industry to register all new and existing substances. Substances of very high concern are those that are persistent in the environment and/or accumulate in biological tissue and/or are toxic (PBT). These PBT substances include halogenated flame-retardants and will require authorization to sell and use. Beginning July 1, 2006, the European Parliament and Council imposed a Restriction on the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (EEE). Under this legislation, the heavy metals lead, mercury, cadmium, and chromium VI, as well as PBDE flame-retardants, are restricted to less than 0.1% by weight of the product. The European directive on the Waste of Electrical and Electronic Equipment (WEEE) directive, which became effective in February 2003, addresses the recycling of EEE and requires end-users to separate and remove plastic components that contain brominated flame-retardants so they do not enter the groundwater when landfilled or the atmosphere (as dioxins) when incinerated. The WEEE legislation is costly and is under review [10]. These European directives are driven mainly by the precautionary principle (i.e., in the absence of scientific data, it is better to be safe than sorry) in setting directives, but they have had a negative impact on fire safety in Europe [10].

In addition to the European environmental directives, there is a plethora of voluntary ecological labels (eco-labels) that equate environmental friendliness to the absence of halogens in products. Using computers as an example, the German Blue Angel eco-label designation cannot be given to computers encased in plastics having more than 0.1% by weight of organic chlorine or bromine compounds, i.e., flame-retardants. The European Union Flower eco-label specifies that plastic parts weighing more than 25 grams shall not contain flame-retardant substances or preparations that are undergoing risk assessment or chlorinated paraffin flame-retardants with chain lengths of 10-17 carbon atoms and chlorine content greater than 50% by weight. The Nordic Swan eco-label goes further in banning all chlorinated plastics including PVC and any plastic part that contains more than 0.1% of a halogenated flame-retardant.

In the United States, risks (fire deaths) associated with banning flame-retardants are considered as well as their environmental and toxicological impact in formulating regulatory policy [11]. A proposed Significant New Use Rule by the EPA requires review and approval of flame-retardants prior to their manufacture or import. Meanwhile, the Consumer Product Safety Commission has recommended that 14 flame-retardants be tested for various toxicology endpoints, although the National Toxicology Program has asked for a public comment on this recommendation. The only legislation that has been enacted in the U.S. to ban flame-retardant chemicals occurs at the state level (CA, HI, IL, MD, ME, MI, NY, and OR) and concerns the penta- and octa-brominated diphenylethers identified by the European Risk Assessment as having toxicity issues.

The impact of European environmental directives and eco-labels that specifically target halogenated polymers and flame-retardants on the development of a fireproof cabin is that manufacturers of consumer products that could eventually become solid waste are forced to seek nonhalogen alternatives to fire safety as a long-term solution [12]. Although aircraft cabin materials are durable (as opposed to disposable) products, the market is relatively small, so the products will need to be halogen-free to justify the large investment in manufacturing and marketing required for commercial production.

MATERIALS USED IN COMMERCIAL AIRCRAFT

The various Title 14 Code of Federal Regulations (CFR) refer mostly to 14 CFR Part 25 for flammability requirements. For simplicity, this discussion will, therefore, refer only to 14 CFR Part 25. The weight of combustible cabin materials covered by 14 CFR Part 25 ranges from about 3000 kilograms for a narrow-body aircraft to over 7000 kilograms for a wide-body aircraft, as shown in table 1 [13]. The distribution of weight by major classes of materials for a wide-body aircraft is shown in figure 1. The fire load represented by the mass of materials in table 1 is of the order (7100 kg)(20 MJ/kg) = 142,000 MJ, which approximates the heat of combustion of 500 gallons of jet fuel. Materials used in aircraft are roughly the same regardless of the type of aircraft involved (normal and transport category airplanes and/or rotorcraft), and they are listed in table 2 by application and fire test requirement.

Table 1. Combustible Materials in Wide-Body Transport Category Aircraft [13]

Component	Weight, kg	Component	Weight, kg
Seats	1500	Linings	500
Acoustic insulation	400	Electrical insulation	200
Decorative panels	1600	Windows	500
Textiles	900	Small parts and rubber	500
Air ducts	500	Safety equipment	1000

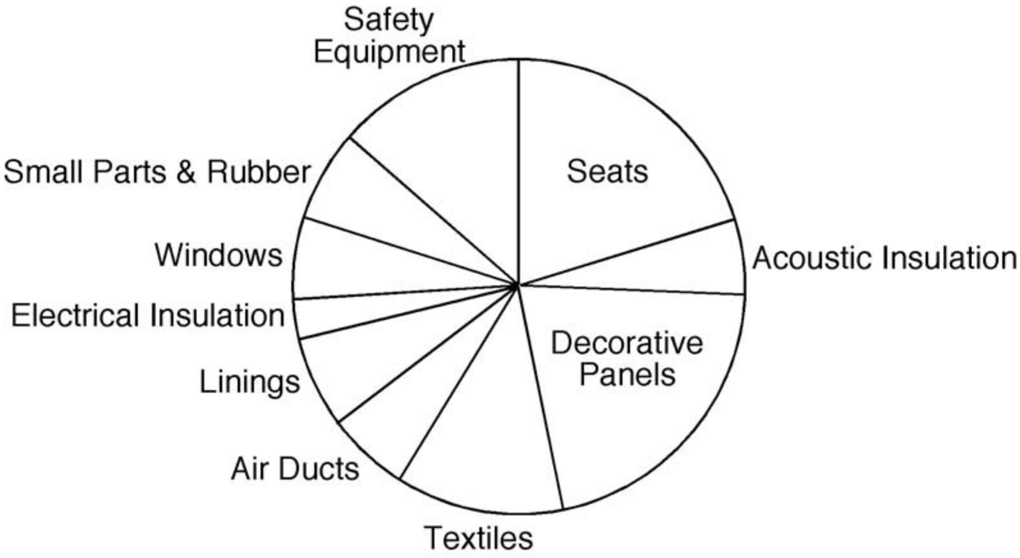


Figure 1. Distribution of Combustible Materials in Wide-Body Transport Category Aircraft

FIRE TESTS FOR AIRCRAFT MATERIALS

Transport category aircraft that carry more than 19 passengers are required to comply with the fire testing regulation of 14 CFR Part 25, which includes the following tests [14]:

- Heat release (HR) and heat release rate (HRR)
- Smoke density (SM)
- Ignition resistance (IR) when subjected to a Bunsen burner flame for an amount of time and at an angle of inclination that depends on the application
- Fire resistance (FR) ability to resist penetration by an oil burner flame
- Burning rate (BR) as measured by mass loss after exposure to an oil burner for a specified period of time
- Flame spread (FS) under radiant heating

Table 2. Typical Materials and Fire Tests by Aircraft Application [5]

Application	Material
Floor and floor covering (IR)	• Glass/carbon-reinforced epoxy/phenol-formaldehyde thermosetting (phenolic) resin over aramide fiber (Nomex®) honeycomb with flexible urethane seat track covers and urethane foam edge band • Mylar film over galley and entry floor panels • Wool or nylon carpet attached to floor by double-backed tape with optional Nomex felt underlay • PVC galley mats
Lower sidewall panel (HR, HRR, SM, IR)	Glass/carbon-reinforced phenolic with decorative thermoplastic laminated film having PVF outer layer
Upper sidewall panel (HR, HRR, SM, IR)	Glass/carbon-reinforced phenolic with decorative thermoplastic laminated film having PVF outer layer
Light covers (IR)	Polycarbonate
Overhead storage bins (HR, HRR, SM, IR)	Glass/carbon fiber-reinforced phenolic surfaced with decorative thermoplastic laminated film having polyvinylfluoride outer layer, urethane foam edge
Gap Fillers (IR)	Silicone or urethane
Passenger seats (BR)	• Wool, wool/nylon, or leather upholstery • Urethane foam cushions • Polybenzimidazole or aramide fiber fire-blocking layer • Polyurethane flotation foam • Thermoplastic seat trays and telecommunication equipment
Cabin attendant seats (BR)	• Wool, wool/nylon, or leather upholstery • Urethane foam cushions • Polybenzimidazole or Nomex/Kevlar® fire-blocking layer • Polyethylene flotation foam
Partitions (HR, HRR, SM, IR)	Glass/carbon fiber-reinforced phenol-formaldehyde (phenolic) surfaced with decorative thermoplastic laminated film having PVF outer layer or wool/Nomex textile or leather
Stowage bins (HR, HRR, SM, IR)	Glass/carbon fiber-reinforced phenol-formaldehyde (phenolic) surfaced with decorative thermoplastic laminated film having PVF outer layer, wool textile interior liner (infrequent)
Placards (N/A)	PVC or polyurethane
Insulation (FS, FR)	Fiberglass batt with phenolic binder and PVF or polyimide (Kapton®) cover, or PVC, nitrile rubber, polyethylene, or polyimide foam.
Windows (IR)	• Outer pane stretched acrylic (polymethylmethacrylate) • Inner pane cast acrylic • Dust cover polycarbonate or acrylic
Passenger service units (HR, HRR, SM, IR)	Molded heat-resistant thermoplastics- polyetherimide, polyphenylsulfone, or polyetherketoneketone or aluminum or glass/carbon reinforced phenolic
Hoses (IR)	Silicone, nylon, or urethane
Air ducting (IR)	• Glass fiber-reinforced phenolic, epoxy or polyester resin over polyisocyanurate foam (large ducts) • Fire-retarded nylon, glass-reinforced silicone, Nomex felt over polyimide foam

N/A = Not applicable
PVF = Polyvinylfluoride

FIRE RESISTANCE MECHANISMS

A general description of fire resistance mechanisms of plastics follows.

FLAME INHIBITION (χ).

Halogens, some phosphorus compounds, and water inhibit combustion in the gas phase (flame) by kinetic and thermodynamic mechanisms that can lead to quenching [15 and 16]. Flame inhibition results in incomplete combustion, as evidenced by increased smoke density and carbon monoxide yield [15]. The combustion efficiency in the flame can be represented parametrically as the ratio of the effective heat of combustion H_c to the heat of complete (100%) combustion, $\chi = H_c / H_c^o$.

FUEL REPLACEMENT (ϕ).

The energy required to liberate unit mass of volatile fuel from a polymer in a fire, $L_g = h_g/(1-\phi)$, is the ratio of the heat of gasification per unit original mass of solid, h_g, and the fuel fraction $(1-\phi)$, where ϕ is the fraction of the original mass remaining after burning (combustion residue). The combustion residue may be generated in situ during the burning process as a result of chemical reactions in the polymer that produce a carbonaceous solid char fraction μ at the expense of volatile fuel, or the combustion residue can be inert (typically mineral) fillers that are added to the polymer during processing. Flame retardancy by fuel replacement is proportional to the mass fraction of char or filler, so a high combustion residue ϕ is needed to achieve significant reductions of flammability, which usually compromises toughness and strength.

HEAT RESISTANCE (T_p).

Heat resistance is associated with strong, thermally stable primary chemical bonds in the polymer backbone that do not rupture and liberate fuel gases until very high temperature [17 and 18]. Polymers with a high thermal decomposition temperature T_p are able to store more heat and radiate a larger fraction of the incident heat back to the environment, reducing the net heat flux available to vaporize the surface. The net heat flux at a steadily burning surface is

$$q''_{ext} + q''_{flame} - \sigma T_p^4$$

where

q''_{ext} is the effective external heat flux from a radiant heater or fire

q''_{flame} is the effective heat flux from the flame

σT_p^4 is the heat lost to the surroundings by reradiation

σ is the Boltzmann constant

Heat resistance increases the amount of energy required to liberate unit mass of volatile fuel and is usually associated with a relatively high char fraction (combustion residue) because conjugated, thermally stable chemical bonds in the polymer backbone decompose to a polycyclic aromatic solid (char) in a fire. Recently, it has been shown that the heat of gasification of the solid is related to the thermal decomposition temperature, $h_g \approx c_0 T_p^2/T_0$, where c_0 is the heat capacity of the polymer at the ambient temperature T_0 [19].

INTUMESCENCE (θ).

Intumescence is the process by which a substance swells and chars as a result of heat exposure, thus increasing the volume and decreasing the density and thermal conductivity of the surface layer. Intumescence acts to insulate the underlying material from the heat of the fire and thus delays ignition or reduces burning rate. Plastics can be made to intumesce by the addition of chemical compounds [15] or by molecular design of the polymer molecule itself [20]. The fraction of the incident heat flux transmitted through the intumescent barrier can be parameterized as a heat transfer efficiency, $\theta = (q''_{ext} + q''_{flame})/(q''^{0}_{ext} + q''^{0}_{flame})$, where the numerator and denominator represent the heat flux at the underlying polymer and the incident heat flux at the exposed surface, respectively.

HEAT RELEASE RATE OF BURNING MATERIALS

The mechanisms of fire resistance can be described parametrically in terms of their effect on the HRR in flaming combustion. For steady burning, the HRR can be written

$$HRR = \frac{H_c}{L_g}\left(q''_{ext} + q''_{flame} - q''_{rerad}\right) \tag{1}$$

Substituting the parameters that account for flame inhibition (χ), fuel replacement (ϕ), heat resistance (T_p), and intumescence (θ) into equation 1,

$$HRR = \chi\theta(1-\phi)\left(\frac{a}{T_p^2} - \frac{b}{\theta}T_p^2\right) = \chi\theta(1-\phi)R_T \tag{2}$$

where

$$a = \frac{T_0 H_c^0 (q''^{0}_{ext} + q''^{0}_{flame})}{c_0} \qquad , \qquad b = \frac{T_0 H_c^0 \sigma}{c_0}.$$

and,

$$R_T = \left(\frac{a}{T_p^2} - \frac{b}{\theta}T_p^2\right)$$

is the heat resistance expressed as a thermal compliance. Equation 2 is explicit in the effects of flame inhibition, fuel replacement, heat resistance (as thermal compliance), and intumescence on HRR. To pass 14 CFR Part 25, a maximum sensible rate of heat release, HRR ≤ 65 kW/m^2, is required. Defining a critical HRR for 14 CFR Part 25 compliance, HRR* ≈ 50 kW/m^2 [19], the parameterized HRR must satisfy

$$\chi\theta(1-\phi)R_T \leq HRR^* = 50\ kW/m^2 \qquad (3)$$

Evaluating the thermal compliance, R_T, for the conditions of the 14 CFR Part 25 HRR test, q''^{0}_{ext} = 35 kW/m^2 and $q''^{0}_{flame} \approx$ 15 kW/m^2, using typical nonhalogen polymer properties [21], H_c^0 = 30 ±10 MJ/kg and c_0 = 1.5 ±0.5 kJ/kg at T_0 = 298K (25°C), with T_p = 723 ±100K (450 ±100°C),

$$R_T = \frac{3x10^{8}\,kW - K^2/m^2}{(723K)^2} - \frac{3x10^{-4}\,kW/m^2 - K^2}{\theta = 1}(723K)^2 = 400 \pm 200\ \text{kW/m}^2$$

For a halogen-free (χ = 1), nonintumescing (θ = 1) plastic with typical thermal compliance (R_T = 400 kW/m^2), the HRR criterion for 14 CFR Part 25 materials according to equation 3 is

$$(1-\phi) \leq \frac{50\,kW/m^2}{R_T} \approx \frac{50\,kW/m^2}{400\,kW/m^2} = 0.13$$

Thus, the fuel fraction 1- ϕ must be less than 13% of the initial mass so that the combustion residue ϕ is on the order of 87 weight percent for a halogen-free, nonintumescing plastic of typical thermal stability to satisfy the heat release requirements of 14 CFR Part 25 for aircraft cabin interiors. This mass fraction corresponds to a volume fraction of 77% for mineral fillers, which is beyond the range where mechanical properties are viable. Consequently, mineral fillers alone are unable meet the requirement for heat release of aircraft cabin materials.

Equation 3 provides a conceptual framework for designing 14 CFR Part 25 compliant aircraft cabin materials using multiple mechanisms of fire resistance. Flame-retardants usually target a single mechanism, e.g., halogens reduce χ and mineral fillers reduce (1-ϕ), but the effects of combining flame-retardants are multiplicative according to equation 3. Molecular engineering of the polymer backbone is required to reduce R_T, and an order of magnitude reduction in HRR can be obtained without halogens ($\chi \approx 1$) if each of θ, 1-ϕ, and R_T in equation 3 are reduced by about 50%. Recent examples of nonhalogen, fire-resistant polymers obtained by molecular design that are optically clear and potentially useful for aircraft cabin applications, such as windows, transparencies, and partitions, are the subject of this report.

METHODS

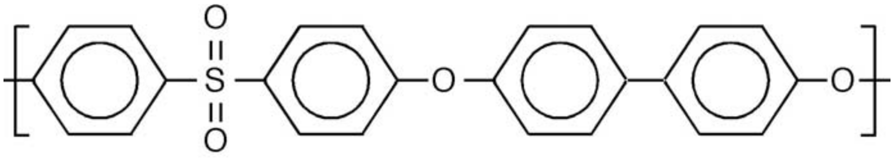
Fire testing was performed according to 14 CFR Part 25 for heat release and smoke density using retaining wires on the sample holder in an attempt to prevent melt dripping. At least two samples were tested and averaged to obtain reported values. All samples for fire testing were commercial or precommercial materials obtained as extruded thermoplastic sheet from the manufacturer. The flammability of research samples that were available only in gram quantities was estimated by microscale combustion calorimetry performed according to a standard method [22] using 3-5 mg samples and a heating rate of 1 K/s.

MATERIALS

The wide variety of combustible aircraft cabin products, the significant fire load they represent (tables 1 and 2), and the recent requirement for a halogen-free solution for economic viability make the development of a fireproof aircraft cabin a formidable task. To achieve the technical objectives of an order of magnitude reduction in HRR and low smoke with nonhalogen chemistry and within the timeframe of the program, it will be necessary to understand and pursue parallel, mechanistic routes to ultra-fire-resistant materials. Mechanisms of fire resistance include flame inhibition, fuel replacement, heat resistance, and intumescence. Of these mechanisms, flame inhibition by halogen compounds and fuel replacement by inert fillers account for the overwhelming majority of flame-retardants added to plastics. Intumescence is becoming an important additive strategy as halogens are being phased out, while heat resistance is an intrinsic mechanism achieved by molecular engineering. Recently, molecular engineering has been used to design fire-smart polymers that are tough and serviceable under normal conditions, but react to the heat of a fire by one or more of the fire resistance mechanisms.

POLYPHENYLSULFONE.

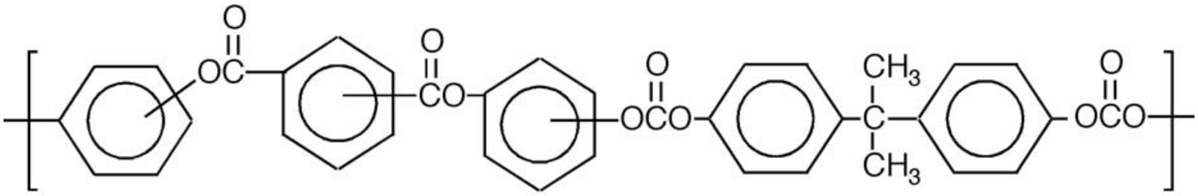
Heat resistant polymers typically have short-term use temperatures above 500°C and thermally decompose (ignite) above 600°C. The most common heat resistant polymers are the halogen (fluorine) containing plastics including Teflon®. Commercial nonhalogen, heat resistant polymers that pass the heat and smoke requirements of 14 CFR Part 25 include aromatic backbone and heterocyclic polymers such as polyimide, polyetherketones, polyetherimide, and polyphenylsulfone (PPSU). The PPSU, whose repeat unit chemical structure is shown below, has recently been developed into a transparent plastic for large area aircraft cabin materials applications [23].



Transparent PPSU samples of RADEL R-7000 TR, Solvay Advanced Polymers, Alpharetta, GA, were obtained as EUROPLEX PPSU Clear extruded sheet from Rohm Performance Plastics/Degussa, Darmstadt, Germany, having thickness, 1, 2, 3, 4, 5, and 6 mm.

POLYESTERCARBONATE.

Aromatic polyester (polyarylate) carbonates having the generalized chemical structure [24] below have been developed recently in clear/transparent and pigmented versions that pass all aircraft manufacturers' service requirements as well as the heat and smoke requirements of 14 CFR Part 25 [25].



The commercial development of a transparent glazing material that passes all of the flammability requirements for large area materials enables the design of larger windows and dust covers, transparent/translucent partitions, on modern (e.g., Boeing 787, Airbus 380) aircraft. Commercial samples of polyestercarbonate were obtained as 1.5-, 2.5-, and 3.2-mm extruded thermoplastic sheet from General Electric Plastics, Pittsfield, MA, in clear (IN326-88-1), grey (EXRL0379-GY4D211), and white (EXRL0379-WH9D211).

BISHYDROXYDEOXYBENZOIN POLYMERS.

Polymers that incorporate one or more mechanisms of fire resistance directly into the polymer backbone as a latent effect are called fire smart [20] and have the advantage of facile processing and good mechanical properties under normal (pre-fire) conditions. But the synthesis of halogen-free, low heat release, fire-smart materials presents a major challenge to polymer chemists. One approach to this problem involves the use of polymers that char upon decomposition, reducing the evolution of flammable gases and acting as an insulating layer. Polymers derived from the bisphenol of chloral, or BPC, show exceptionally good fire resistance [9]. Investigations into decomposition pathways of BPC-containing polymers suggest that char formation may proceed through diphenylacetylene derivatives at elevated temperatures. Thus, while chlorine in BPC sets up the rearrangement chemistry, the role of diphenylacetylene as pre-char intermediate structures must be of considerable importance. In another study, the catalyzed conversion of deoxybenzoin to diphenylacetylene was reported by flash vacuum pyrolysis at 300°-500°C. The temperature range over which deoxybenzoin converts to diphenylacetylene suggests its utility as a char precursor during burning. Deoxybenzoin was, therefore, explored as part of the effort to develop nonhalogen char precursor alternatives to BPC.

THE BISHYDROXYDEOXYBENZOIN POLYARYLATES [26]. Bisphenolic forms of deoxybenzoin have considerable promise for integration into condensation polymers, given the rich polymerization chemistry of bisphenols, such as bisphenol-A (BPA), and the range of polymer materials into which it could potentially be incorporated. The monomer 4,4'-bishydroxydeoxybenzoin (BHDB) was prepared by the demethylation reaction of desoxyanison using pyridine hydrochloride. The synthesis of novel polyarylates was carried out by interfacial polycondensation of BHDB and isophthaloyl chloride (figure 2). These BHDB-containing polyarylates were found to have char yield values of ~45% (by thermogravimetric analysis), and heat release capacity values of ~65 J/g-K (by pyrolysis combustion flow calorimetry). The exceptional thermal properties of these novel polymers provided impetus to overcome the low molecular weights and low solubility inherent to BHDB polyarylates. Thus, a variety of polyarylate copolymers were prepared, containing a mixture of BHDB and BPA as the bisphenol monomers and isophthaloyl chloride as the aromatic diacid chloride (figure 3). These copolymers with greater extents of BHDB relative to BPA exhibit desirable fire-resistant properties with appreciable polymer solubility and processability.

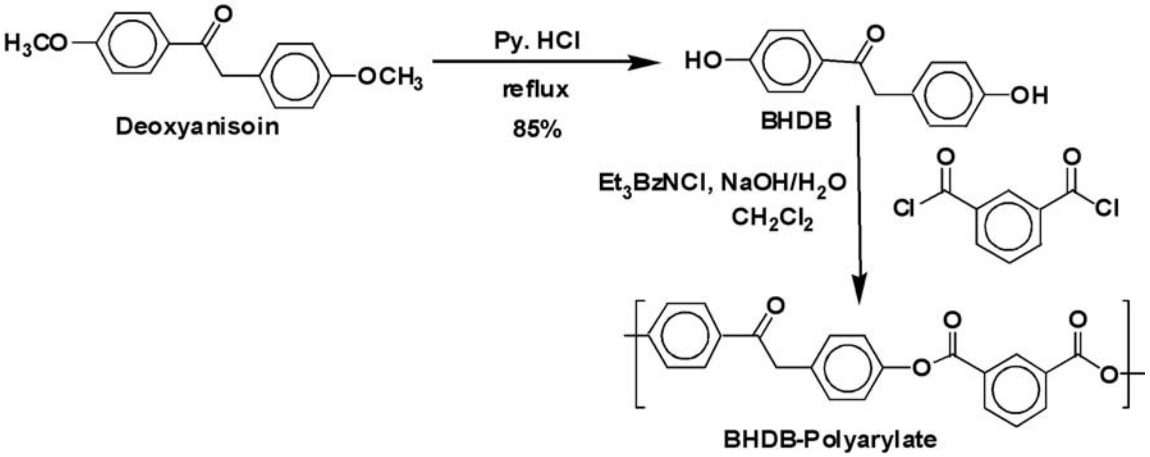


Figure 2. Synthetic Scheme for BHDB Polyarylate

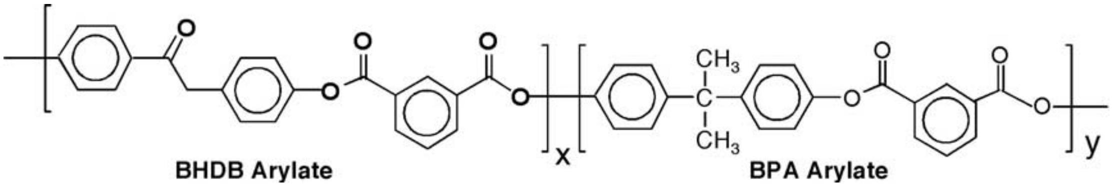


Figure 3. Structure of BHDB-BPA Copolyarylates

<ins>THE BHDB POLYPHOSPHONATES</ins> [27]. It was expected that the solubility of BHDB polyarylates could be improved by integration of phosphonate into the polymer backbone using phosphonic dichloride as a replacement monomer for isophthaloyl chloride of figure 2. This method is particularly appealing as phosphonates are known to have low flammability and promote char formation in hydroxy-functional polymers or polymer-degradation products. Solution polymerization of BHDB with phenylphosphonic dichloride (PPDC) was performed under anhydrous conditions to give BHDB-polyphosphonate, as shown in figure 4. This aromatic polyphosphonate was seen to have very low heat release capacity (HRC ~80 J/g-K), high char yield (~52%), and high solubility in most common organic solvents. In addition, the use of solution polymerization enabled the preparation of high molecular weight polymers, as high as M_w = 150,000 g/mole.

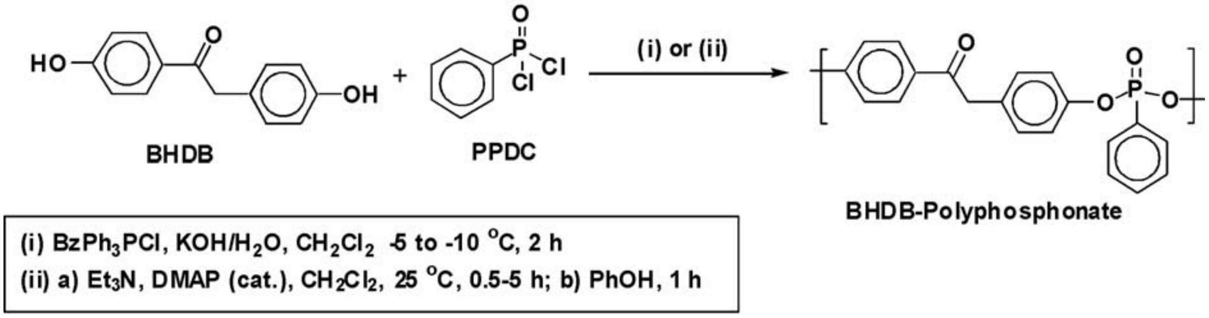


Figure 4. Synthetic Scheme for BHDB Polyphosphonates

THE BHDB POLY(ARYLATE-PHOSPHONATE) COPOLYMERS [28]. The high reactivity of aromatic acid chlorides and PPDC allows them to be used together to make copolymers. This is appealing in the case of BHDB because the phophonate moiety should increase solubility in common solvents, while the arylate moiety should raise the melting and glass transition temperatures. Thus, a wide range of physical and mechanical properties can be achieved by copolymerizing arylate and phophonate units into the BHDB backbone, all of which should exhibit low heat release capacity. These novel poly(arylate-phosphonate) copolymers are prepared by solution polycondensation of BHDB with different isophthaloyl chloride:PPDC ratios, as depicted in figure 5. The presence of phosphonate units in the polymer backbone serves to improve solubility over arylate homopolymers, and also promote char formation and low heat release capacity. Moreover, a synergetic effect was seen, arising from the phosphonate and isophthalate moieties when coupled with deoxybenzoin units. Such copolymers were found to possess exceptionally low HRC values (as low as 35 J/g-K) and high char yields (up to nearly 60%).

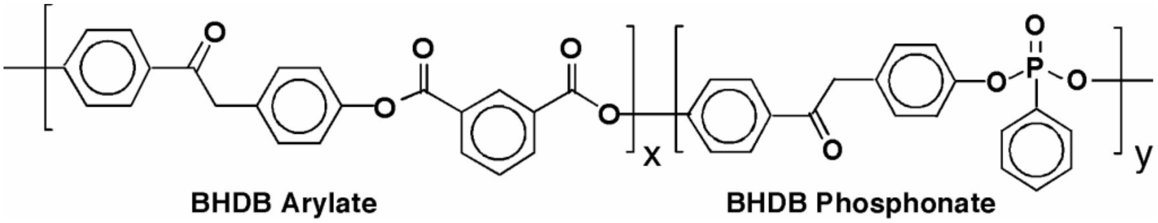


Figure 5. Structure of BHDB Arylate-Phosphonate Copolymers

RESULTS

Table 3 summarizes the HRC, HR, ignition temperature (T_{max}), and char fraction (μ) of the polymers in this report.

Table 3. Flammability Screening Results From Microscale Combustion Calorimeter for Nonhalogen Plastics

Material	HRC (J/g-K)	HR (kJ/g)	T_{max} (°C)	Char Fraction μ (%)
PPSU (Clear)	228	13.5	622	42
Polyestercarbonate (White)	213	10.9	496	36
Polyestercarbonate (Grey)	192	10.4	495	35
Polyestercarbonate (Clear)	168	10.3	531	38
BHDB Polyphosphonate	80	9.5	470	50
BHDB Polyarylate	65	6.0	520	43
BHDB Poly(arylate-co-phosphonate) (1:1)	35	5.1	490	57

POLYPHENYLSULFONE.

Table 3 shows that PPSU has low HRC and HR, as well as a high char yield and very high decomposition temperature. These factors are expected to contribute to HRR as per equation 2, with $\mu = 0.42$, the char fraction; $H_c^0 = HR/(1-\mu) = (13.5\text{ kJ/g-solid})((1-0.42)^{-1}\text{ g-fuel/g-solid}) = 23.3\text{ kJ/g-fuel}$, the heat of combustion per unit mass of the PPSU pyrolysis gases; and $T_{max} = 895\text{K}$, the thermal decomposition temperature. The thermal compliance of PPSU, assuming no intumescence, is $R_T = 80\text{ kW/m}^2$ and the $HRR = \chi\theta(1-\phi)R_T = (1)(1)(1-0.42)(80\text{ kW/m}^2) = 46\text{ kW/m}^2 \approx HRR^*$. Thus, PPSU is expected to pass 14 CFR Part 25 heat release primarily as a result of its heat resistance (low thermal compliance) and to a lesser extent fuel replacement (charring). The PPSU data in table 3 is consistent with this analysis.

Table 4 contains the results of HRR testing in the Ohio State University Fire Calorimeter (OSU) for clear PPSU at 1-, 2-, 3-, 4-, 5-, and 6-mm thickness. The average values of peak HRR and 2-minute HR for each thickness are plotted in figure 6. Error bars are one standard deviation. Samples above and below 2-mm thickness passed both HRR during the 5-minute test and total heat release at 2 minutes, although there was a lot of molten material still burning in the catch tray at the end of the 5-minute test. Smoke density measured on 2-mm thickness was $^4D_s < 1$ at 4 minutes, which is well below the $^4D_s = 200$ maximum allowable value.

Table 4. Heat and Smoke Results for PPSU Clear as per 14 CFR Part 25

Thickness (mm)	Peak HRR (kW/m^2)	Total HR (2-min.) (kW-min/m^2)	Smoke Density ^4D_s
1	67	16	–
1	64	20	–
1	58	3	–
2	59	6	< 1
2	59	3	< 5
2	50	0	< 1
2	37	0	< 1
2	38	-1	–
3	38	-4	–
3	40	-3	–
4	67	16	–
4	64	20	–
5	58	3	–
5	59	6	–
6	59	3	–
6	50	0	–
Global Average	54 ±11	6 ±8	2 ±2
14 CFR Part 25 Maximum	65	65	200

– = Not measured

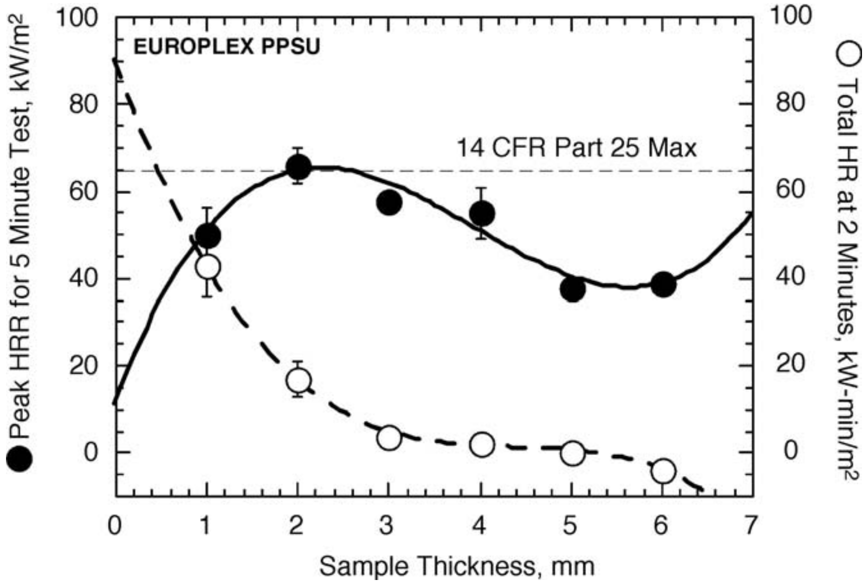


Figure 6. Peak HRR and Total HR in 14 CFR Part 25 HR Test for Clear PPSU at Various Thicknesses
(Lines through data are third-order polynomial fits.)

POLYESTERCARBONATE.

As a group, the polyestercarbonates in table 3 have average $H_c^0 = 16.5$ kJ/g and $R_T \approx 160$ kW/m^2. Consequently, the HRR requirement for 14 CFR Part 25 with no flame inhibition ($\chi = 1$) is $HRR^* = \chi\theta(1-\phi)R_T = (1)(\theta)(1-0.36)(160\ \text{kW/m}^2) = 100\theta\ \text{kW/m}^2$, which is satisfied for $\theta = 0.5$. For the polyestercarbonate, all available fire resistance parameters θ, $(1-\phi)$, and R_T are about 1/2 of their nominal or unit values at HRR*; so polyestercarbonate has the characteristics of a fire-smart nonhalogen polymer obtained by molecular design. Figure 7 is a photograph of the white polyestercarbonate (2.5-mm thickness) before and after burning in the OSU Fire Calorimeter according to the 14 CFR Part 25 test. The large amount of swelling and charring of the sample (intumescence) is consistent with the mechanistic analysis. However, the sample melts during the test, and 25% of the sample mass drips out of the sample holder and catchtray and accumulates as a fibrous melt on the second-stage air distribution plate of the OSU apparatus, as shown in the foreground of the left-hand side of figure 7. This molten mass does not contribute to the flaming HRR measured in the 14 CFR Part 25 test. Table 5 contains the 14 CFR Part 25 results for HR and smoke for the polyestercarbonates. No particular color or thickness effect is observed for peak HRR or smoke density, but the total HR at 2 minutes decreases somewhat with increasing sample thickness due to the increased thickness of the intumescent layer or thermal inertia, or both.

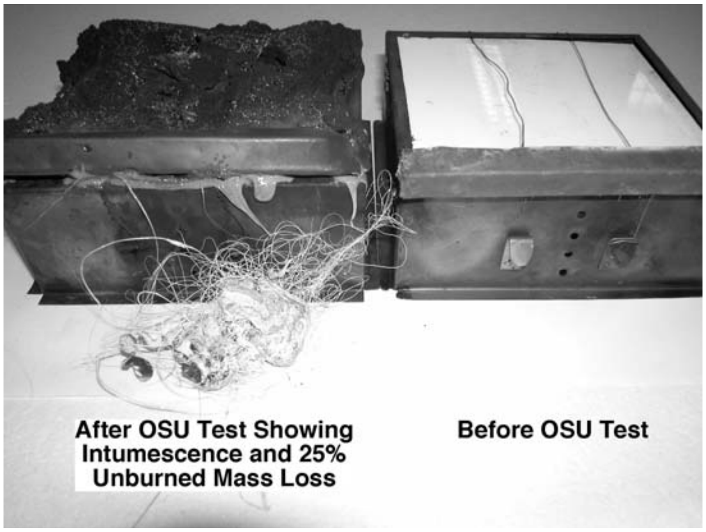


Figure 7. White Polyestercarbonate Before and After 14 CFR Part 25 Testing for HR in the OSU

Table 5. Heat and Smoke Results for Polyestercarbonate as per 14 CFR Part 25

Thickness (mm)	Peak HRR (kW/m^2)	2-min. HR, ($kW\text{-}min./m^2$)	Smoke Density (^4D_m)
Clear/Transparent			
1.5	37	25	6
1.5	39	29	6
2.5	64	17	10
2.5	58	18	3
3.2	47	7	10
3.2	54	10	Not measured
Grey			
1.5	57	41	12
1.5	42	26	8
2.5	55	21	8
2.5	35	14	11
3.2	59	16	15
3.2	44	7	7
White			
1.5	42	30	15
1.5	54	29	4
2.5	58	27	5
2.5	60	18	9
3.2	51	12	5
3.2	42	12	6
Global average	50±9	20±9	8±4
14 CFR Part 25 Maximum	65	65	200

THE BHDB POLYMERS.

The BHDB polyarylate, polyphosphonate, and poly(arylate-co-phosphonate), as a group, have $R_T \approx 100$ kW/m^2, so the nonburning requirement, $HRR^* = \chi\theta(1-\phi)R_T$ for $\phi = \mu \approx 0.5$ in table 3, is satisfied for $\chi = 1$ by $\theta = HRR^*/R_T(1-\mu) = 50\ kW/m^2/(100kW/m^2)(1-0.5) \approx 1$. Consequently, the BHDB polyarylate, polyphosphonate, and poly(arylate-co-phosphonate) do not require intumescence to satisfy 14 CFR Part 25. Instead, these nonhalogen fire-smart polymers rely equally on heat resistance (R_T) and fuel replacement (μ) to achieve fire resistance by molecular design. Table 6 contains data for the mass fraction of BPA polyarylate in the BPA-BHDB copolyarylates along with the thermal combustion properties measured by microscale combustion calorimetry (MCC).

Table 6. Mass Fraction of BHDB Arylate in BHDB-BPA Copolyarylates Along With Thermal Combustion Properties

Mass Fraction BHDB Arylate in BHDB-BPA Copolyarylate	HRC (J/g.K)	Total HR (kJ/g)	T_{max} (°C)	Char Yield (Weight %)
1.00	65	7.5	520	45
0.87	65	7.5	479	42
0.78	74	8.9	482	40
0.70	81	10.8	483	37
0.53	148	12.3	501	37
0.41	159	12.8	508	34
0.27	165	12.9	508	33
0.23	166	13.2	520	32
0.21	169	13.0	522	33
0.14	237	13.1	508	31
0.12	272	15.9	512	26
0.07	317	16.2	529	29
0.00	456	17.7	526	26

Table 7 contains data for the mass fraction of BHDB polyarylate in the BHDB poly(arylate-co-phosponates) along with the thermal combustion properties measured by MCC.

Table 7. Mass Fraction of BHDB Arylate in Poly(Arylate-Co-Phosphonate) Along With Thermal Combustion Properties

Mass Fraction BHDB Arylate in Poly(arylate-co-Phosphonate)	HRC (J/g-K)	Total HR (J/g-K)	T_{max} (°C)	Char Yield (Weight %)
1.00	65	6.0	520	45
0.77	48	4.6	515	50
0.58	41	5.3	480	56
0.47	36	5.1	490	54
0.40	40	4.7	485	57
0.23	59	8.0	480	55
0.00	80	9.5	470	52

The data in tables 6 and 7 show that the minimum HRC is associated with the maximum char yield, suggesting that fuel replacement by charring is the main mechanism of fire resistance for the BHDB-based polymers and copolymers. The copolymer data can be analyzed to determine the effect of the different moieties on char formation using rules of mixtures with an interaction term [29].

$$\mu = \phi_a\mu_a + \phi_b\mu_b + \lambda(\phi_a\phi_b)^{1/2}(\mu_a + \mu_b)/2 \qquad (4)$$

In equation 4, μ_a, μ_b, and ϕ_a, ϕ_b are the char yields and mass fractions of components *a* and *b*, respectively (e.g., BHDB and BPA arylates, or BHDB-arylate and BHDB-phosphonate), and λ is a parameter characterizing the sign and magnitude of the interaction between the *a* and *b* moieties. If there are no specific interactions between *a* and *b*, then $\lambda = 0$, and equation 4 becomes the simple rule of mixtures in which the component effects are additive

$$\mu = \phi_a\mu_a + \phi_b\mu_b \tag{5}$$

A positive (synergistic) interaction between the *a* and *b* moieties produces more char than the weighted sum of the individual contributions and is characterized by $\lambda > 0$. A negative (antagonistic) interaction produces less char than expected from the weighted sum of the contributions and is characterized by $\lambda < 0$. Figure 8 is a plot of equation 4 for the case where $\phi_a + \phi_b = 1$ and $\mu_a = 2\mu_b$. The char yield of the mixture is divided by the char yield of component B to give the reduced char yield, μ/μ_b, which is plotted versus ϕ_a in figure 8 for the three possible interactions: antagonism ($\lambda < 0$), ideal behavior/no interaction ($\lambda = 0$), and synergism ($\lambda > 0$).

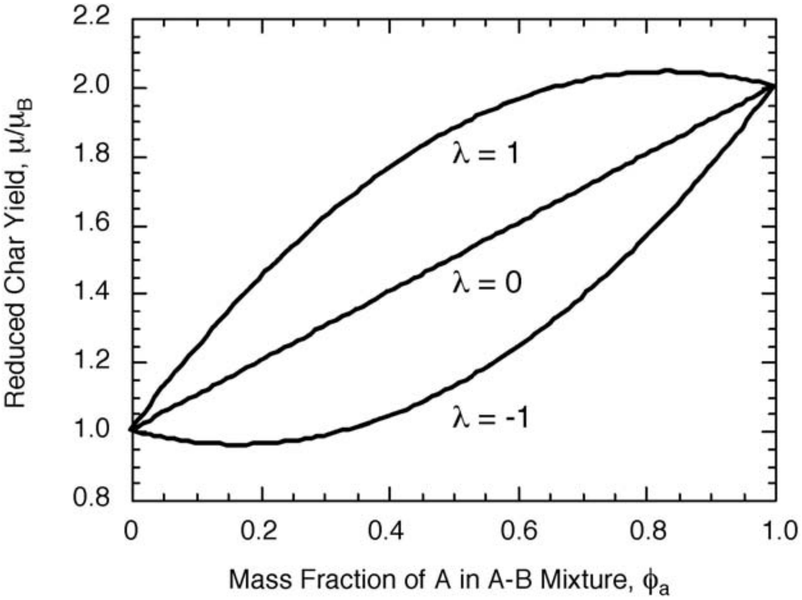


Figure 8. Reduced Char Yield Versus Mass Fraction of Component A in A + B System Showing Synergism ($\lambda = 1$), Ideal Behavior ($\lambda = 0$), and Antagonism ($\lambda = -1$)

Figure 9 is a plot of the mass fraction of char in table 6 versus the mass fraction of BHDB in the BHDB-BPA copolyarylate. It is clear that a straight line captures the data very well, indicating that BHDB and BPA act independently (ideally) so that the char yield is additive as per equation 5.

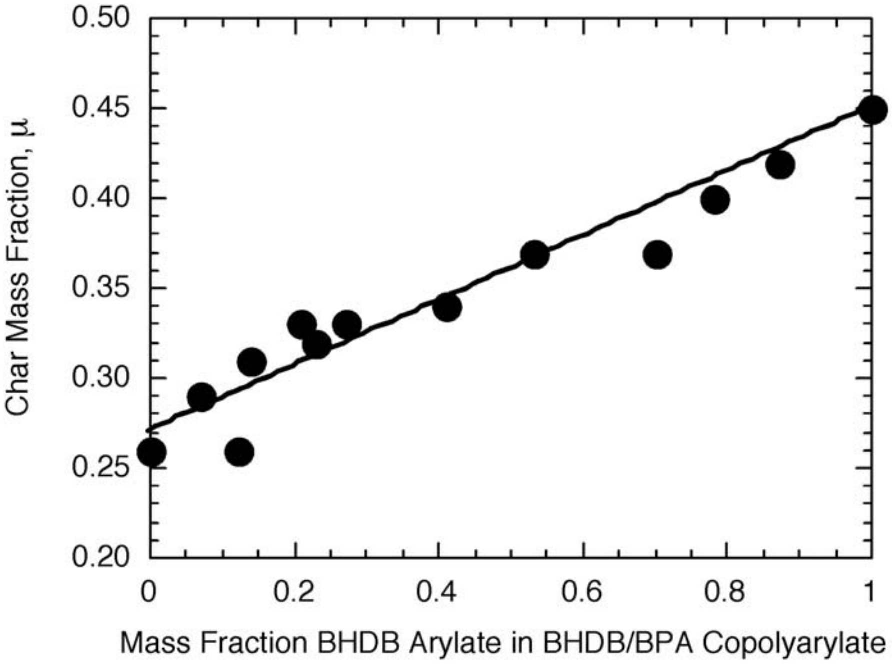


Figure 9. Char Mass Fraction Versus BHDB Arylate Mass Fraction in BHDB-BPA Copolyarylate
(Solid line is ideal (additive) behavior.)

Figure 10 is a plot of the char mass fraction in table 7 versus the arylate mass fraction in BHDB poly(arylate-co-phosphonates). The char yield data (solid circles) shows a maximum in the vicinity of 45% BHDB arylate, which is a positive deviation from ideal/rule of mixtures behavior (dashed line) with respect to char formation. The solid line in figure 10 is the linear first-order interaction model (equation 4) that was fit to the data with an interaction parameter $\lambda = 1.2$. Thus, the BHDB arylate and phosphonate moieties in combination produce more char than each acting separately and synergism is observed with respect to char formation.

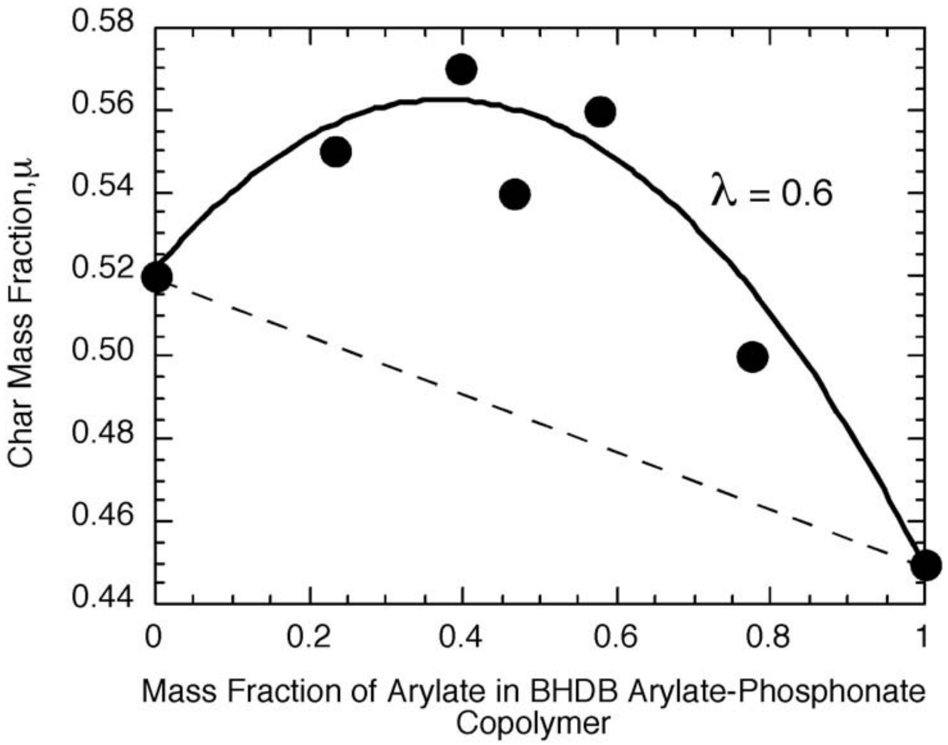


Figure 10. Mass Fraction of Char Versus Mass Fraction of Arylate in BHDB Poly(Arylate-Co-Phosphonates)
(Solid circles are data, dashed line is additive, and solid line is equation 4 with $\lambda = 0.6$.)

Because the BHDB polymers are research materials available only in gram quantities, the peak HRR in 14 CFR Part 25 could not be measured. Instead, the correlation between the peak HRR in 14 CFR Part 25 testing of aircraft cabin materials and the HRC of the same materials measured in the MCC plotted in figure 11 was used to estimate a peak HRR < 50 kW/m^2 for the BHDB polyarylate, BHDB polyphosphonate, and the equimolar BHDB poly(arylate-co-phosphonate) using the values in table 3.

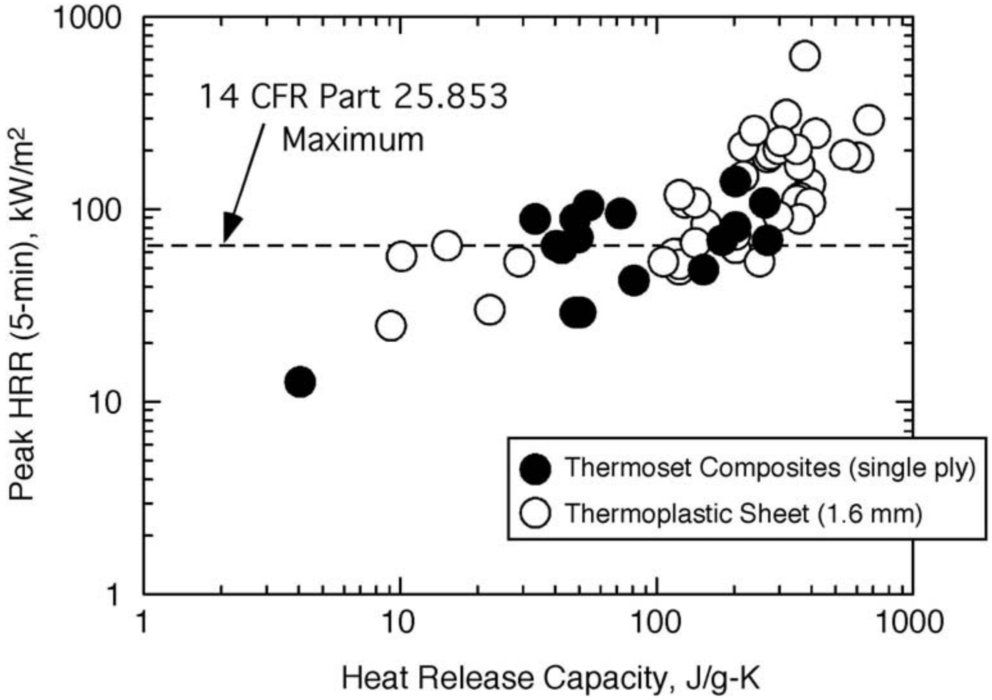
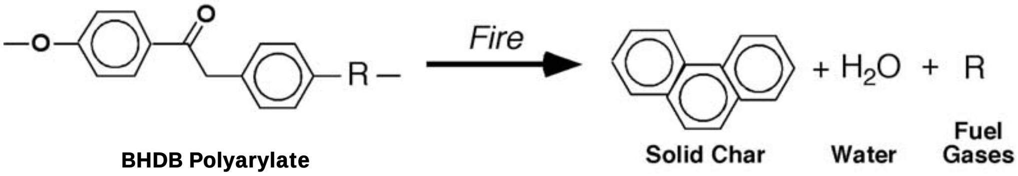


Figure 11. Peak HRR in 14 CFR Part 25 Versus HRC Measured in MCC for Aircraft Cabin Materials

SUMMARY

Nonhalogen strategies for a fireproof aircraft cabin are reviewed in light of pending environmental restrictions on plastics. A parametric decomposition of the HRR in 14 CFR Part 25 according to the component mechanisms of fire resistance: flame inhibition, fuel replacement, heat resistance, and intumescence, accounts for the fire performance of nonhalogen plastics that are suitable for large-area aircraft cabin materials. A combination of fire resistance mechanisms acting simultaneously or synergistically is particularly effective as demonstrated by the fire-smart polyestercarbonates and the BHDB-polyarylates and poly(arylate-co-phosphonates), the latter reacting to fire according to the following scheme:



Consequently, ultra-fire-resistant, nonhalogen, fire-smart polymers based on BHDB will have chemical moieties, R, that have strong positive interaction with BHDB to enhance char formation ($\lambda > 0$ in equation 4) and have low heat of combustion/low fuel value.

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