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# Fire Properties of Heat-Resistant Polymers

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## LIST OF SYMBOLS AND ACRONYMS

крс	Thermal inertia
t <sub>ign</sub>	Time to sustained ignition
Tign	Temperature at ignition
ASTM	American Society for Testing and Materials
BPA	Bisphenol-A
BPC-PC	Polycarbonate of bisphenol-C
CAS	Chemical Abstracts Service
CFR	Code of Federal Regulations
CHF	Critical heat flux
CO	Carbon monoxide
$CO_2$	Carbon dioxide
CR	Combustion residue after burning
EHC	Effective heat of combustion
HRR	Heat release rate
HRR <sub>av</sub>	Average heat release rate
HRR <sub>pk</sub>	Peak heat release rate
ISO	International Standards Organization
MLR	Mass loss rate
PAI	Polyamideimide
PBI	Polybenzimidazole
PC	Polycarbonate of bisphenol-A
PEEK	Polyetheretherketone
PEI	Polyetherimide
PEKK	Polyetherketoneketone
PEN	Polyethylene naphthalate
PI	Polyimide
PPS	Polyphenylene sulfide
PPSU	Polyphenylsulfone
PSU	Polysulfone
SEA	Smoke extinction area
SPR	Smoke-production rate
THR	Total heat released
TRP	Thermal response parameter
TSP	Total smoke production

#### EXECUTIVE SUMMARY

The fire behavior of heat-resistant polymers used in aircraft interiors was measured in a fire (cone) calorimeter for comparison to that of commercial and research engineering thermoplastic polymers. The aircraft polymers tested were polyetherimide, polyamideimide, polyimide, and polyphenylsulfone. The engineering thermoplastics tested were polyphenylene sulfide, polyetheretherketone, polyetherketoneketone, polyethylene naphthalate, polysulfone, and the polycarbonates of bisphenol-A and bisphenol-C (1,1-dichloro-2,2-bis(4-hydroxyphenyl) ethylene). Fire calorimetry data for the time to ignition, mass loss rate, heat release rate (HRR), and yields of flaming combustion products were collected and used to derive material fire parameters including the critical radiant heat flux for piloted ignition, thermal inertia, heat of gasification, and ignition temperature. The aircraft polymers generated significant amounts of char when burned and exhibited low HRRs compared to engineering thermoplastic polymers. As expected, the critical heat flux for ignition (fire resistance) of the polymers increases with thermal stability (heat resistance) as indicated by the ignition temperature. When ignited, the rate at which heat is released during burning increases with the mass fraction and heat of combustion of the fuel gases. The rigid molecular architectures of these heat-resistant polymers impart high glass transition temperature, high modulus, and chemical resistance to the polymer, and the low mole fraction of hydrogen in the backbone accounts for the high thermal stability, ignition resistance and large amount of voluminous black char formed during the burning of these polymers. The rigid, low-density char layer reduces heat conduction through the surface and absorbs/reradiates incident energy, which reduces heat transfer to the underlying polymer and lowers the burning rate.

#### ABSTRACT

The fire behavior of heat-resistant engineering and specialty thermoplastic polymerss was measured to set a benchmark for the properties of polymers used in aircraft interiors. Fire (cone) calorimeter tests were conducted on polyetherimide, polyamideimide, polyethylenenaphthalate, polycarbonate, polyphenylenesulfide, polysulfone, bisphenol-A polyetheretherketone, polyetherketoneketone, polyimide, polyphenylsulfone, and the polycarbonate of 1,1-dichloro-2,2bis (4-hydroxyphenyl) ethylene (bisphenol-C). Fire calorimetry data were collected for the time to ignition, mass loss rate, heat release rate (HRR), and yields of flaming combustion products. Fire parameters derived from these data include critical radiant heat flux for piloted ignition, thermal inertia, heat of gasification, and ignition temperature. These thermoplastic polymers generated significant amounts of char when burned and exhibited relatively low HRRs. As expected, the critical heat flux for ignition (fire resistance) of heat-resistant thermoplastic polymers increases with thermal stability (heat resistance) as indicated by the ignition temperature. However, when ignited, the HRR increases with the mass fraction and heat of combustion of the fuel gases.

#### INTRODUCTION

Fatal fires in commercial transport category aircraft can occur during or after flight. In-flight fires typically originate in an inaccessible area containing combustible materials, such as a cargo hold or the space above the cabin compartment. Post-crash cabin fires are more common and usually result from penetration of a jet fuel fire into the cabin compartment followed by ignition and burning of aircraft cabin materials. Reports [1, 2] have documented the initiation and growth of cabin fires in full-scale tests simulating a post-crash fuel fire scenario. The cabin fire begins when flames impinge on, and ignite, interior components. The fire spreads away from the ignition source along the seats, ceiling, and overhead stowage bins, and incomplete combustion products accumulate at the ceiling. Ventilation of the cabin influences the nature and quantity of combustion products and the spread and intensity of the fire. Flashover occurs when the incomplete combustion products near the ceiling spontaneously ignite, spreading the fire to the entire compartment and making escape impossible. The maximum amount of time available for escape from a post-crash cabin fire is therefore limited to the time to flashover. It has been shown [1, 2] that the flaming heat-release rate (HRR) of materials in a compartment such as an aircraft cabin correlates with the time to flashover (escape time) better than any other single fire quantity, so the HRR is considered to be the primary indicator of material fire hazard [3].

Aircraft cabins contain several tons of combustible thermoset resins, thermoplastic polymers, and elastomers in the form of floor panels and carpeting, lower and upper sidewall panels, overhead stowage compartments, dividers, lighting covers and fixtures, passenger seats, galleys, stowage, and emergency equipment [4]. Often, these furnishings are supplemented by entertainment and telecommunication systems in the form of seat-mounted displays, computers, telephones, and facsimile machines, all of which are encased in thermoplastic and contain thermoset or thermoplastic circuit boards and wiring. Exterior to the cabin compartment but within the pressure hull, thermosetting resins and thermoplastic polymers are used in air conditioning ducts, thermal-acoustic insulation bags, jackets for electrical wiring, and as miscellaneous parts, fittings, and fasteners. It is estimated that commercial transport aircraft cabins contain between 1000 and 2500 kg of combustible thermoplastic polymers [4, 5].

Passive fire protection in the form of ultra-fire-resistant materials is a cost-effective approach to improved aircraft fire safety [4]. The long-term goal of the FAA Fire Resistant Materials Program [6] is for order-of-magnitude reductions in the HRR of combustible interior materials to significantly extend the passenger escape time from an aircraft cabin in the event of an external, post-crash, fuel fire [7, 8]. This paper presents reaction-to-fire data for commercial engineering, heat-resistant, and specialty thermoplastic polymers representing the state-of-the-art in fire resistance to establish a benchmark for current and future materials developments.

#### MATERIALS

Commercial engineering, heat-resistant, and specialty polymers selected for this study are listed in table 1 with their Chemical Abstracts Service (CAS) registry numbers, trade names, and the repeat unit chemical structure. The materials tested in this study were unfilled, natural, or virgin materials containing no fire retardant additives, fillers, or fibrous reinforcement obtained from commercial suppliers, distributors, or manufacturers. Samples having dimensions 100 by 100 mm and thicknesses 3.2 mm, 6.35 mm, or 12.5 mm were cut from extruded thermoplastic sheets. Certain samples were not available in 12.5-mm thickness, including polyethylene naphthalate (PEN) (3.2 mm), polyphenylsulfone (PPSU) (6.35 mm), bisphenol-C polycarbonate (BPC-PC) (6.35 mm), and polyetherketoneketone (PEKK) (3.2 mm), as noted in table 1.

Although the natural, unfilled polymers selected for this study represent the spectrum of thermal stability/ignition resistance available commercially, none (with the exception of PPSU, polyamideimide [PAI] and polyetherimide [PEI]) are used in large-area cabin interior components (e.g., window shrouds, passenger service units, and stowage bin door handles) that are required to pass the Title 14 Code of Federal Regulations (CFR) Part 25.853(a-1) HRR test [8]. The PEI used in the aircraft cabin as thermoformed sheet ranges from 1.6 mm to 3.2 mm in thickness and is a siloxane-modified version of the PEI tested in this study. Some of these thermoplastic polymers are used in commercial aircraft cabin parts that are not required to pass the HRR test, including food service trays, windows, air ducts, telecommunication housings, seat parts, and escape chute holders [4].

**Polycarbonate of Bisphenol-A** (**PC**) is an amorphous, transparent thermoplastic polymer widely used for electrical/electronic applications because of a very high impact strength and high modulus of elasticity. The material has a high heat distortion temperature and absorbs almost no moisture. Its strength, impact resistance, and transparency make it an ideal material for certain transparent structural applications [9, 10], but it does not pass the heat-release requirements for the wide-area interior materials specified in 14 CFR 25.853.

**Polyetherimide** (**PEI**) is an amorphous, dark amber, semi-transparent engineering thermoplastic used in high-temperature pump and valve applications in the chemical industry and in medical devices [10, 11]. Aircraft-grade PEI (not tested) is modified with silicone to pass the flaming HRR test for cabin materials specified in 14 CFR 25.853.

**Polysulfone** (**PSU**) is a tough, amorphous thermoplastic polymer that is naturally transparent and light amber in color [9]. PSU was the first commercialized engineering polymer that contained a sulfone moiety. The polymer is molded and extruded to make parts for medical devices, food

processes, chemical process equipment, and automotive parts. Examples include medical trays, food service equipment, microwave cookware, and surgical instrument handles.

**Polyphenylsulfone** (**PPSU**) is an amorphous polymer that was developed for specialty medical devices, such as sterilizable surgical trays, the chemical process industry, and similar applications requiring thermal and hydrolytic stability and chemical inertness. PPSU is also used in commercial aircraft interiors for molded cabin parts and in high-heat automotive applications, such as reflectors, sockets, connectors, and fuse bodies [9–11].

**Polyethylenenaphthalate** (**PEN**) is a semi-crystalline thermoplastic polyester with good gas barrier properties. The bulky 2,6-naphthalenedicarboxylic acid monomer results in a polyester with higher glass transition (heat distortion) temperature and tensile strength than conventional thermoplastic polyester derived from terephthalic acid. PEN is used as a substrate for photographic and magnetic films and as beverage bottles [11].

**Polyamideimide** (**PAI**) is an amorphous polymer that is used in applications requiring strength at high temperatures, creep, wear resistance, and chemical and hydrolytic stability. PAI parts, such as valve plates, bearings, washers, and disk pads, have replaced metal parts in heavy-duty vehicles and engineering equipment in which parts are subjected to high-temperature, high-speed environments. PAI is exceptionally resistant to chemicals and is known for high compressive strength and impact resistance [9–11].

**Polyetheretherketone** (**PEEK**) is a semi-crystalline, high-temperature resistant engineering thermoplastic polymer with good chemical and hydrolytic stability in high heat and corrosive environments, such as medical implants and pump and valve components. It is used in fabricated parts for oilfield drilling equipment [9, 10].

**Polyphenylenesulfide** (**PPS**) is a semi-crystalline, high-temperature resistant polymer with good chemical and hydrolytic stability, electrical insulation properties, and inherent flame resistance. PPS is used in applications such as electronic components, under-the-hood automotive applications, high-pressure liquid chromatography fittings, bearings and rings, and pump and valve components used in oilfield drilling equipment [9, 10].

**Polyimide** (**PI**) is an amorphous polymer that can withstand continuous use at  $250^{\circ}$ C and short periods of time at temperatures as high as  $480^{\circ}$ C. A combination of good electrical properties, high strength, and thermal and radiation resistance makes unfilled PI useful for electrical applications in severe thermal environments [9–11].

**Polybenzimidazole** (**PBI**) is an amorphous polymer that provides wear resistance and loadcarrying capability at higher temperatures than any other unfilled engineering thermoplastic. It has a heat-deflection temperature of 425°C and a continuous service capability of 750°C in inert environments. Known applications of Celazole include high-heat insulator bushings, electrical connectors exposed to temperatures over 250°C, textile fibers for heat/fire resistant clothing, and parts used in manufacturing printed board circuits and semiconductor industry [9–11].

**Polycarbonate of bisphenol-C (BPC-PC)** is an amorphous developmental polymer made from 1,1-dichloro-2,2-bis (4-hydroxyphenyl) ethylene (bisphenol-C/BPC) and is known to be extremely ignition resistant in small flame tests [12–18]. A commercial process for making BPC-PC was

developed by the General Electric Company in the 1970s [15]. The BPC-PC has thermal, optical, and mechanical properties that are indistinguishable from conventional bisphenol-A (BPA) PC, but it has far superior fire performance and lower combustion toxicity [13–18].

**Polyetherketoneketone (PEKK)** is a heat-resistant, semi-crystalline thermoplastic polymer with a glass transition temperature of 160°C and a melting temperature of 305°C. PEKK has a flammability rating of V-0 at 0.8 mm thickness in UL 94 and a limiting oxygen index of 38 (ISO 4589-2). Applications include injection-molded parts with extreme temperature, chemical, abrasion, or flame resistance, and additive manufacturing of metal replacement parts, barrier sheets, and films [9–11].

Material	[CAS Registry Number]	Repeat Unit Chemical Structure
PC ( $T_{\rm g} = 152^{\circ}$ C; $T_{\rm m} = $ N/A)	24936-68-3	-0 $-0$ $-0$ $-0$ $-0$ $-0$ $-0$ $-0$
BPC-PC ( $T_{\rm g} = 168^{\circ}$ C; $T_{\rm m} = $ N/A)	None	
PEEK ( $T_g = 162^{\circ}C; T_m = 324^{\circ}C$ )	29658-26-2	
PPS ( $T_{\rm g} = 85^{\circ}{\rm C}; T_{\rm m} = 280^{\circ}{\rm C}$ )	9016-75-5	— — s—
PSU $(T_{\rm g} = 220^{\circ}{\rm C}; T_{\rm m} = {\rm N/A})$	25135-57-7	$- \swarrow \stackrel{O}{\underset{II}{\overset{II}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}$
PAI ( $T_{\rm g} = 250^{\circ}{\rm C}; T_{\rm m} = {\rm N/A}$ )	31957-38-7	
PEI ( $T_{\rm g} = 216^{\circ}$ C; $T_{\rm m} = 340^{\circ}$ C	61128-46-9	
PEN ( $T_g = 113^{\circ}C; T_m = 272^{\circ}C$ )	25853-85-4	$-0-CH_2CH_2-0-C$
PI ( $T_{\rm g} = 265^{\circ}{\rm C}; T_{\rm m} = {\rm N/A}$ )	26023-21-2	
PPSU ( $T_{\rm g} = 290^{\circ}{\rm C}; T_{\rm m} = {\rm N/A}$ )	25608-64-4	
PBI ( $T_{\rm g} = 425^{\circ}{\rm C}; T_{\rm m} = {\rm N/A}$ )	25928-81-8	
PEKK ( $T_g = 165^{\circ}C; T_m = 384^{\circ}C$ )	54991-67-2	

Table 1. The chemical structure and designated trade names of high-performance polymers

#### METHODS

The fire behavior of the engineering thermoplastics was measured according to a standard method in a fire calorimeter conforming to ASTM E1354 [19], as shown in figure 1. The fire calorimeter continuously measures HRR, specimen mass loss during burning, smoke production, and combustion gas concentrations in the exhaust during the test. The heat released during flaming combustion is calculated from the oxygen depletion of the exhaust gases [20–22].



Figure 1. The cone fire calorimeter

The fire (cone) calorimeter used for these tests uses a conical radiant heater to provide a uniform radiant heat flux to the sample surface. The apparatus and testing procedure have been described in detail by Babrauskas [20, 21] and have been standardized by the American Society for Testing and Materials (ASTM) [19] and the International Standards Organization (ISO) [23]. Square samples (100-by-100 mm) of each material were tested in a horizontal configuration at calibrated cold wall heat fluxes over the range,  $\dot{q}_{ext}^{"} = 10-100 \text{ kW/m}^2$ , representing moderate to severe fire conditions [22, 23]. Polymer samples were 3-, 6-, or 12.5-mm thick (see tables 2 and 3), and piloted ignition was achieved during the test by inserting a spark igniter just above the sample surface at the onset of radiant heating. When flashing or intermittent burning occurred, the igniter was kept in place until stable flaming combustion was observed over the entire sample surface. Samples were thermally thick (unsteady, one-dimensional heat conduction applies) if the time to ignition was less than approximately 10, 30, and 120 seconds for 3-, 6-, and 12.5-mm-thick samples, respectively. The thicker samples at higher heat fluxes nearly fulfilled these conditions (see table 2).

All tests were performed with the retainer edge frame placed above the sample as recommended in the standard test method [19] for heat- and smoke-release rates for materials with a tendency for swelling. The majority of thermoplastic polymers were tested at external radiant heat fluxes of  $\dot{q}''_{ext} = 35, 50, 75$ , and 100 kW/m<sup>2</sup>. PC, PEKK, and PEI were tested over the wider range of heat flux levels: 10–100 kW/m<sup>2</sup>. The time to sustained ignition ( $t_{ig}$ ) was measured, and quantities normalized to the nominal sample surface area exposed to the heat flux, including the HRR, total heat released (THR), and mass loss rate (MLR). The effective heat of combustion ( $H_c$ ), smoke extinction area (SEA), and yields of the carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) per unit mass of material consumed were also recorded during the test.

The polymers listed in table 1 are linear engineering or specialty thermoplastic polymers which, unlike commodity thermoplastics such as nylon, polyester, acrylic, styrenics, and polyolefins, are high-performance materials that are relatively costly.

#### **RESULTS AND DISCUSSION**

#### FIRE CALORIMETER DATA

Table 2 shows data from cone calorimeter measurements at external/radiant heat fluxes  $\dot{q}_{ext}'' = 35$ , 50, 75, and 90 or 100 kW/m<sup>2</sup>. Included in table 2 are  $t_{ig}$ , peak HRR (HRR<sub>pk</sub>), average HRR (HRR<sub>av</sub>), THR, MLR, and  $H_c$  at each incident heat flux for the engineering thermoplastic polymers listed in table 1 during the period of flaming combustion or the first 20 minutes of the test. The overall  $H_c$  values reported in table 2 are calculated as the ratio of the time integrated HRR to the total mass lost during the test. A limited number of replicate tests were conducted for a particular test condition and material, so many of the values in tables 2 and 3 are the result of a single measurement obtained in the cone calorimeter.

POLYMER	Heat Flux	t <sub>ign</sub>	HRR <sub>pk</sub>	HRR <sub>av</sub>	THR	MLR	$H_{\rm c}$
(thickness tested)	$(kW/m^2)$	(s)	$(kW/m^2)$	$(kW/m^2)$	$(MJ/m^2)$	$(g/m^2-s)$	(kJ/g)
,	35	342	322	119	87	3.7	23.7
	50	89	264	111	164	5.3	22.4
PC (12.5 mm)	75	37	7 334 162		248	7.5	24.5
	100	18	437	180	252	11.5	21.8
	35	217	188	44	28	2.2	22.3
	50	86	304	107	139	4.2	24.5
PSU (12.5 mm)	75	28	349	212	265	8.1	26.2
	100	16	325	174	226	7.7	24.9
	35				NI		
DEL(12.5  mm)	50	101	36	19	17.6	1.5	17.9
PEI (12.5 mm)	75	35	131	79	79 113		20.3
	100	19	191	111	167	5.1	19.9
	35	179	395	77	40	6.2	19.7
	50	90	393	91	56	7.2	19.3
PEN (3 IIIII)	75	39	391	92	62	8.0	19.8
	100	23	441	120	71	10.2	20
	35	NI					
DAI(125 mm)	50	246	28	17	11	1.5	9.9
PAI (12.5 mm)	75	50	49	34	38	2.4	15.2
	100	22	113	78	115	2.7	31.2
	35				NI		
PEEK (12.5	50	213	46	14	7	1.2	8
mm)	75	65	133	76	77	3.6	24.3
	100	36	191	115	153	4.5	25.5
	35				NI		
DDS(12.5 mm)	50	175	118	48	49	1.3	16.3
<b>FFS</b> (12.3 mm)	75	53	271	130	156	3.6	11.5
	100	32	332	128	171	4.6	15.1

 Table 2. Summary of ignition, heat release, and heat of combustion data from cone calorimeter at thickness tested (NI = No Ignition)

POLYMER	Heat Flux	t <sub>ign</sub>	HRR <sub>pk</sub>	HRR <sub>av</sub>	THR	MLR	$H_{ m c}$		
(thickness tested)	$(kW/m^2)$	(s)	$(kW/m^2)$	$(kW/m^2)$	$(MJ/m^2)$	(g/m <sup>2</sup> -s)	(kJ/g)		
	35		NI						
DDCU(12.5 mm)	50	111	86	14	47	1.6	26.4		
FFSU (12.3 mm)	75	40	192	83	55	3.1	26.6		
	100	22	261	105	73	7.1	24.4		
PEKK (3 mm)	35	251	101	60	30	3.5	14.6		
	50	86	171	104	48	4.6	22.5		
	75	37	270	154	42	8.5	23.6		
	90	26	333	173	43	11.9	20.9		
DI(12.5 mm)	75	163	30	11	22	3.4	2.2		
PI (12.3 mm)	100	85	107	66	95	7.4	11.6		
DDI(125 mm)	75	215	45	39	27	1.8	21.4		
PBI (12.5 mm)	100	108	55	50	39	2.0	24.5		
PDC DC (6 mm)	50	90	73	28	26	3.3	9.6		
$\mathbf{D}\mathbf{r}\mathbf{C}\mathbf{-r}\mathbf{C}$ (0 mm)	100	14	161	80	48	6.9	11.1		

 Table 2. Summary of ignition, heat release, and heat of combustion data from cone calorimeter (NI = No Ignition) (cont.)

During the cone calorimeter tests, the materials in table 1 typically underwent surface blistering and swelling of the top (exposed) surface with the formation of a gas bubble. Deflation of the gas bubble released volatiles that were ignited by the spark igniter, resulting in flaming combustion. All polymers exhibited flashing (transient ignition) when the sample surface reached the flashpoint temperature and transitioned to sustained ignition when the surface temperature reached the fire point. When sustained flaming combustion had commenced, all materials showed extreme swelling and char formation (intumescence). The height of the conical heater was adjusted during the initial stages of burning to prevent the expanding surface of the charred material from touching the heater and compromising the mass-loss data and to maintain a relatively constant heat flux at the rising surface. Figures 2–4 show HRR histories for the polymers of this study.

Figure 2 shows HRR histories for the engineering thermoplastic polymers PEN, PC, PSU, and PPS at the highest external radiant heat flux,  $\dot{q}_{ext}'' = 100 \text{ kW/m^2}$ . This is the only heat flux at which all thermoplastic polymers listed in table 1 ignited and burned to completion, as evidenced by steady values of  $H_c$  in the last column of table 2. All engineering thermoplastic polymers burned at the lowest heat flux,  $\dot{q}_{ext}'' = 35 \text{ kW/m^2}$ , with the exception of PPS.



Figure 2. HRR histories of heat-resistant engineering polymers at  $\dot{q}''_{ext}$  = 100 kW/m<sup>2</sup>



Figure 3. HRR histories of heat-resistant engineering polymers at  $\dot{q}''_{ext} = 100 \text{ kW/m}^2$ , except for PEKK ( $\dot{q}''_{ext} = 90 \text{ kW/m}^2$ )



Figure 4. HRR histories of heat-resistant specialty polymers at  $\dot{q}''_{ext} = 100 \text{ kW/m}^2$ 

Several of the polymers in table 2 are used in large-area constructions in aircraft interiors because they pass the HRR requirements of 14 CFR 25. These heat-resistant polymers include PEI, PEEK, and PPSU, whose HRR histories at  $\dot{q}_{ext}'' = 100 \text{ kW/m}^2$  are shown in figure 3. These polymers did not exhibit sustained ignition in the cone calorimeter at  $\dot{q}_{ext}'' = 35$  or 50 kW/m<sup>2</sup>. However, all ignited at  $\dot{q}_{ext}'' = 35 \text{ kW/m}^2$  in the vertical 14 CFR 25 fire calorimeter because the impinging premixed methane/air pilot flame forced localized ignition, and upward spread of the subsequent flame added an additional 15–20  $kW/m^2$  to the nominal radiant heat, exceeding the minimum (critical) external heat flux (CHF) for piloted ignition in table 4.

A few of the polymers in table 1 (PI, PBI, BPC-PC) did not ignite at heat fluxes as high as  $\dot{q}_{ext}'' = 50 \text{ kW/m}^2$  or burned with very low intensity (PAI), consistent with a minimum CHF for sustained ignition of approximately 50 kw/m<sup>2</sup> (see table 4). The HRR histories of these ignition-resistant thermoplastic polymers at  $\dot{q}_{ext}'' = 100 \text{ kW/m}^2$  are shown in figure 4.

The HRR curves in figures 2–4 show that, when ignited, the polymers tested in thick (6 mm or 13 mm) sections burned for long periods. Irregularities in the burning intensity are due to the appearance of fissures on the material surface. All materials except BPC-PC show an initial peak early in the HRR history, followed by a broad secondary peak associated with the increase in volume of the sample because of char swelling (intumescence). In PAI, PEEK, and PEI, a solid char was formed with very small surface fissures through which volatile gases were able to escape. Small flames were seen anchored to the surface of PAI, PEEK, PEKK, and PEI at the cracks, unlike PC, PSU, and PPS, which exhibited uniform burning across the surface. The maximum HRR of PAI, PEEK, and PEI was comparable at  $\dot{q}''_{ext} = 50 \text{ kW/m}^2$ , and none of these materials sustained steady-flaming combustion because char swelling caused irregular burning, as shown in the HRR curves. The small surface cracks and high char integrity of the PAI, PEEK, PEKK, and PI in the cone calorimeter tests are responsible for the absence of a single well-defined peak in the HRR history and prolonged unsteady burning. As has been shown [24], time-averaged properties, such as THR, HRR<sub>av</sub>, and EHC, are probably the best parameters for assessing the relative fire performance of heat-resistant polymers.

Because of the extended burning time of these polymers when tested as thick samples, HRR<sub>av</sub> in column 5 of table 2 is the average HRR value for the period of flaming combustion or the first 1200 seconds (20 minutes) after ignition. It can be seen that the HRR of the polymers in table 2 is consistent with thermal stability. Polymers with rigid backbones called ladder polymers (PI, PBI, PAI) have a large number of thermally stable carbon-carbon or carbon-nitrogen double bonds and a paucity of hydrogen atoms capable of terminating volatile fragments. These polymers thermally decompose at a high temperature to solid char and volatile gases with low heats of combustion [5] because of the presence of heteroatoms (O, N, S, Cl). The paucity of hydrogen atoms in the polymer chains reduces the likelihood that backbone scission reactions will terminate by hydrogen transfer and lead to volatile aliphatic fuel fragments. The paucity of H-atoms also increases the likelihood that recombination reactions between aromatic moieties will produce a carbonaceous char, which accumulates in a low-density surface layer that reduces heat conduction to the underlying polymer and absorbs and reradiates incident energy-all of which lower the burning rate. When low-fuel-value atoms, such as nitrogen, oxygen and sulfur, replace carbon and hydrogen in the polymer backbone, the heat of combustion of the thermal decomposition products (fuel gases) is correspondingly reduced.

Table 3 shows the smoke and product yields of flaming combustion at each  $\dot{q}''_{ext}$  tested, including the specific extinction area of SEA, the mass of CO and CO<sub>2</sub> produced by combustion per unit mass of sample (yield) and the residual mass fraction, or combustion residue (CR) remaining after the test, expressed as a percentage of the initial mass.

POLYMER	Heat Flux	SEA	CO	CO <sub>2</sub>	CR
(thickness tested)	(kW/m <sup>2</sup> )	(m <sup>2</sup> /kg)	(kg/kg)	(kg/kg)	(kg/kg)
	35	742	0.04	1.61	0.66
$\mathbf{DC}(12.5 \dots)$	50	627	0.03	1.74	0.40
PC (12.5 mm)	75	856	0.08	2.34	0.29
	100	817	0.24	2.89	0.22
	35	648	0.20	0.49	0.85
$\mathbf{D}\mathbf{SU}(12.5 \text{ mm})$	50	164	0.00	0.01	0.35
PSU (12.3 mm)	75	436	0.07	1.76	0.26
	100	472	0.02	0.92	0.29
	35	NI	NI	NI	NI
DEL(12.5 mm)	50	29	0.04	1.53	0.94
$PEI(12.3\;\mathrm{IIIII})$	75	181	0.04	1.66	0.51
	100	146	0.03	1.79	0.41
PEN (3 mm)	35	374	0.05	1.77	0.53
	50	460	0.06	1.60	0.37
	75	573	0.10	1.88	0.32
	100	618	0.04	1.84	0.24
	35	NI	NI	NI	NI
$\mathbf{D}\mathbf{A}\mathbf{I}$ (12.5 mm)	50	103	0.12	0.96	0.87
FAI (12.3 IIIII)	75	127	0.11	1.29	0.72
	100	129	0.20	6.80	0.49
	35	NI	NI	NI	NI
$\mathbf{DEEV} (12.5 \text{ mm})$	50	270	0.31	2.70	0.97
$\mathbf{FLEK} (12.3 \text{ IIIII})$	75	334	0.06	1.83	0.55
	100	250	0.04	1.83	0.37
	35	NI	NI	NI	NI
DDS(12.5 mm)	50	381	0.03	1.05	0.90
<b>FFS</b> (12.3 mm)	75	340	0.03	0.71	0.37
	100	294	0.02	0.64	0.25
	35	NI	NI	NI	NI
DDCII (3 mm)	50	491	0.02	1.94	0.94
	75	360	0.13	2.32	0.34
	100	405	0.07	1.86	0.33

Table 3. Cone calorimeter data for smoke obscuration and combustion product yields

POLYMER	Heat Flux	SEA	CO	CO <sub>2</sub>	CR
(thickness tested)	$(kW/m^2)$	(m <sup>2</sup> /kg)	(kg/kg)	(kg/kg)	(kg/kg)
	35	161	.04	1.60	0.53
$\mathbf{DEKK}(2 \text{ mm})$	50	270	.05	2.10	0.54
	75	400	.03	2.33	0.59
	90	477	.03	2.00	0.55
PI (12.5 mm)	75	33	0.01	1.36	0.89
	100	29	0.00	1.30	0.59
DDI(12.5 mm)	75	39	0.02	1.14	0.95
PBI (12.5 mm)	100	116	0.00	0.98	0.75
	50	90	0.19	0.83	0.63
DrC-rC (0 IIIII)	100	176	0.12	1.38	0.44

 Table 3. Cone calorimeter data for smoke obscuration and combustion product yields (cont.)

The reported yields of combustion products are for the entire test duration. At the highest heat flux,  $\dot{q}_{ext}' = 100 \text{ kW/m}^2$ , all the polymers, with the exception of PBI, burned vigorously, and the residue at the end of the test consisted mainly of carbonaceous char. The high-residual mass fraction for PBI (93%) at  $\dot{q}_{ext}' = 100 \text{ kW/m}^2$  consisted largely of unburned virgin material. The CO and CO<sub>2</sub> yields have been normalized to the sample mass loss. The SEA described in the standard [19, 23] is the area of smoke particulates in the combustion products per unit mass of polymer burned, and it represents the total visible obscuration caused by smoke. Table 3 shows that the SEA increases as HRR increases with heat flux for all the polymers.

#### EFFECTIVE PROPERTIES AT IGNITION

The time delay before ignition occurs ( $t_{ig}$ ) is an important characteristic of a material in a fire because it controls the flame-spread rate. For a given heat flux, the  $t_{ign}$  depends on many factors, including the thickness, density, and thermal conductivity of the material and the heating conditions (fire environment). The ignition delay time of a material can be expressed in terms of effective material properties that are derived from analytic solutions for transient, one-dimensional heat conduction [25]. The cone calorimeter data were analyzed in this way to determine three such properties: the minimum (critical) external heat flux for sustained ignition CHF; the product of thermal conductivity  $\kappa$ , density  $\rho$ , and heat capacity c, called the thermal inertia ( $\kappa\rho c$ ); and the surface temperature at ignition ( $T_{ign}$ ). The CHF refers to the minimum incident heat flux needed to initiate sustained flaming combustion of a material. The thermal inertia of a material determines how quickly it responds to the external heat flux, with high  $\kappa\rho c$  indicating a slow thermal response to the fire. Equation 1 shows the relationship between  $t_{ig}$  and  $\kappa\rho c$  when a material having surface emissivity,  $\varepsilon$ , is subjected to a constant external heat flux,  $\dot{q}''_{ext}$ , at time t = 0 in an environment at temperature  $T_{\infty}$  [25–28]

$$t_{ign} = \frac{\pi}{4} \kappa \rho c \left[ \frac{T_{ign} - T_{\infty}}{\varepsilon \dot{q}''_{ext} - CHF} \right]^2 \tag{1}$$

Equation 1 can be linearized as,

$$\frac{1}{\sqrt{t_{ien}}} = \frac{\dot{q}_{ext}''}{TRP} - \frac{CHF/\varepsilon}{TRP}$$
(2)

In equation 2, TRP is a fire property called the thermal response parameter [24–26],

$$TRP = \sqrt{\frac{\pi}{4} \kappa \rho c} \left( T_{ign} - T_{\infty} \right) / \varepsilon$$

A plot of  $(t_{ign})^{-1/2}$  versus  $\dot{q}''_{ext}$  is shown in figure 5 for PC. The slope of the linear portion of the curve is equal to the reciprocal of the thermal response parameter (TRP), as shown in equation 2. Table 4 shows the TRP for each polymer in table 1 calculated using equation 2, as shown in figure 5. Tewarson [26, 27] has described TRP as an effective material property that collectively expresses the effect of thermal inertia and ignition temperature. Values for TRP and CHF have been reported for a large number of polymers and fiber-reinforced polymer composites [26–28]. These data suggest that most thermally stable, heat-resistant polymers have TRP values between 400 and 650 kW-s<sup>1/2</sup>/m<sup>2</sup>. Literature values of TRP for polycarbonate range from 331 [26] to 455 kW-s<sup>1/2</sup>/m<sup>2</sup> [28] whereas CHF ranges from 15–20 kW/m<sup>2</sup>, compared to 433 kW-s<sup>1/2</sup>/m<sup>2</sup> and 17 kW/m<sup>2</sup> from this study in table 4.

A series of tests were performed in the cone calorimeter for PC at decreasing heat fluxes from 100 kW/m<sup>2</sup> to 10 kW/m<sup>2</sup> to obtain the lowest measurable heat flux at which ignition occurred within 20 minutes (CHF). The minimum external heat flux to cause ignition can be obtained experimentally by successively exposing samples of the material to decreasing incident heat flux until a flux is found at which there is no ignition within the (arbitrary) maximum test duration of 20 minutes [19, 20]. Figure 5 shows the plot of this ignition data for PC, in which the CHF is defined to be the value of  $\dot{q}''_{ext}$  midway between the lowest value at which ignition is observed and the highest value at which ignition is not observed (i.e., when  $t_{ign}^{-1/2} = 0$ ). This value (CHF) was found to be between 15 and 18 kW/m<sup>2</sup> by the bracketing procedure in figure 5. Such an approach can be time consuming and may not be feasible when only a limited quantity of material is available.



Figure 5. CHF of PC by bracketing procedure

An alternative to the ASTM [19] and ISO [23] method of determining CHF by a bracketing procedure is shown in figure 6. This is the asymptotic method of Safronava, et. al. [29], in which a plot of  $t_{ign}$  versus  $\dot{q}_{ext}''$  weighted for  $t_{ign}$  to emphasize thermally thin behavior near ignition is fit to equation 3 using ( $\rho cb/\overline{h}$ ) and CHF as adjustable parameters, with  $\overline{h}$  the linearized surface heat transfer coefficient:

$$t_{ign} = \frac{\rho cb}{\overline{h}} \ln \left[ \frac{\varepsilon \dot{q}_{ext}''}{\varepsilon \dot{q}_{ext}'' - CHF} \right]$$
(3)

Equation 3 is based on the assumption that the sample is approximately uniform in temperature (thermally thin), as  $\dot{q}_{ext}^{"} \rightarrow$  CHF and  $t_{ign} \rightarrow \infty$ . Figure 6 shows a plot of the ignition data for PC, PSU, PEI, and PEKK with the nonlinear least squares regression line of equation 3 forced through the data points. Values of CHF for the polymers of this study obtained by this procedure are given in table 4. These same fits give  $\bar{h} \approx 30\text{-}40 \text{ W/m}^2\text{-}\text{K}$  for the coefficient of convective and reradiation heat losses, which is reasonable considering the convective component alone is  $h_c = 20 \text{ W/m}^2\text{-}\text{K}$  at the high ignition temperatures of these polymers. It can be seen that CHF for ignition of PC in table 4 by the asymptotic procedure, CHF = 17 kW/m<sup>2</sup>, agrees well with the value obtained by the bracketing procedure (see figure 5). Moreover, the CHF of the other polymers are consistent with the minimum heat flux at which a measurable HRR is observed (see table 2).



Figure 6. CHF for PC, PSU, PEI, and PEKK by asymptotic procedure using equation 3 (The vertical dashed line is the asymptote at  $\dot{q}_{ext}^{"}$  = CHF.)

The ignition temperature of the polymer is defined as the surface temperature  $T_s$  at ignition. The net heat flux at the surface, neglecting heat transfer into the solid and pyrolysis, is the difference between the incident heat flux and the heat losses by convection and reradiation,

$$\dot{q}_{net}'' = 0 = \varepsilon \dot{q}_{ext}'' - \dot{q}_{rr}'' - \dot{q}_{cond}'' = CHF - \varepsilon \sigma \left(T_s^4 - T_{\infty}^4\right) - h_c \left(T_s - T_{\infty}\right)$$
(4)

In equation 4,  $\sigma$  is the Stefan-Boltzmann radiation constant and  $h_c$  is the surface convective heat transfer coefficient. The surface temperatures at ignition  $T_{ign}$  in table 4 were calculated by iteration of equation 4 with  $\dot{q}''_{net} = 0$  and  $\varepsilon \dot{q}''_{ext} = CHF$  in table 4, assuming  $h_c = 20 \text{ kW/m}^2$  [22] and  $\varepsilon = 0.95$  [30]. These computed ignition temperatures are in good agreement with direct measurements of the surface temperatures at ignition of these polymers in a fire calorimeter [31] and mass loss/heat generation rates in thermal analysis experiments [32]. However, the ignition temperature is not a thermodynamic property like the reversible glass transition ( $T_g$ ) and melting temperatures ( $T_m$ ) in table 1. A critical surface temperature at ignition are a critical fuel/air mixture at the heated surface or a critical combustion energy density in the gas phase [31]. These chemical processes in the gas phase can be included in the surface energy balance at the onset of flaming combustion when thermal penetration into the surface layer by conduction is included in the energy balance,

$$-\kappa \left(\frac{dT}{dx}\right)_{x=0} = \dot{q}_{cond}'' = \varepsilon \dot{q}_{ext}'' - \dot{q}_{conv}'' - \dot{q}_{rr}'' - \dot{m}'' L_g$$
<sup>(5)</sup>

In equation 5,  $-\kappa (dT/dx)_{x=0} = \dot{q}''_{cond}$  is the net heat flux entering the polymer of thermal conductivity  $\kappa$  by conduction at the heated surface x = 0,  $\dot{m}''$  is the mass flux of thermal decomposition products (fuel gases) into the air, and  $L_g$  is the heat absorbed to thermally decompose and vaporize (gasify)

the solid polymer. At incipient ignition,  $\varepsilon \dot{q}''_{ext} = \dot{q}''_{conv} + \dot{q}''_{rr} = CHF$ , so the net heat flux at ignition of the fuel/air mixture when pyrolysis of the solid is taken into account is,

$$\dot{q}_{cond}^{\prime\prime} = -\dot{m}^{\prime\prime} L_g \tag{6}$$

The minimum (critical) mass flux for sustained ignition is  $-\dot{m}''_{cr} = MLR^*$  and the minimum HRR is HRR<sup>\*</sup> =  $-\dot{m}''_{cr}H_c$  [31], so the critical heat flux for ignition of the fuel/air mixture is,

$$\left(\dot{q}_{cond}''\right)_{cr} = CHF^* = MLR^*L_g = \frac{HRR^*}{H_c/L_g} = \frac{HRR^*}{HRP}$$
(7)

Figure 7 shows a graph of the critical heat flux for gas phase ignition (CHF\* of equation 7) versus the critical heat flux for condensed phase ignition (CHF in table 4), with CHF\* computed from gas phase properties, MLR\* H 3 g/m<sup>2</sup>-s and HRR\* H 66 kW/m<sup>2</sup> for each of these polymers measured separately [32], with the condensed phase properties  $L_g$  and HRP from table 4. It can be seen that the critical heat flux for ignition of the gas phase is relatively constant at CHF\* =  $18 \pm 5$  kW/m<sup>2</sup> and independent of  $T_{ign}$  (i.e., CHF) of the condensed phase.



Figure 7. Critical heat flux for ignition of gas phase (CHF\*) versus critical heat flux for ignition of condensed phase (CHF) for heat-resistant polymers

#### EFFECTIVE MATERIAL PROPERTIES OF BURNING

Once ignition is sustained in the cone calorimeter, and a flame is established on the surface, an additional heat flux from the flame is added into the energy balance, which for sustained flaming combustion becomes,

$$\dot{Q}'' = \dot{m}'' H_c = \frac{H_c}{H_g} \left( \varepsilon \dot{q}_{ext}'' + \dot{q}_{fl}'' - \dot{q}_{rr}'' - \dot{q}_{cond}'' \right)$$
(8)

In equation 8,  $\dot{q}''_{fl}$  is the heat flux from the flame to the surface of the sample,  $\dot{q}''_{rr}$  is the heat loss by reradiation from the surface, and  $\dot{q}''_{cond}$  is the heat lost by conduction from the surface into the sample, of which an amount,  $\dot{m}'' L_g$ , is consumed to heat and decomposes the solid and vaporizes the thermal decomposition products. The rate of vaporization is given by the mass loss rate per unit area of the sample  $\dot{m}''$  and is dependent on the magnitude of the net heat flux. To determine  $L_g$ , the mass flux from the burning surface ( $\dot{m}''$ ) is plotted versus external heat flux ( $\dot{q}''_{ext}$ ), and  $L_g$ is obtained as the reciprocal slope of the best fit line, assuming the flame heat flux to the surface and heat losses from the surface by reradiation and conduction are constant. The method for PC, PSU, and PEI is shown in figure 8, which is a plot of the peak mass flux versus the incident/external heat flux  $\dot{q}''_{ext}$ . The heats of gasification estimated by this method for the polymers of this study are listed in column 7 of table 4 and are typical of high-performance polymers [28].



Figure 8. Mass flux versus incident heat flux for PC, PSU, and PEI

The  $\Delta h_c$  (kJ/g) in table 4 are the heats of complete combustion of the volatiles produced by these charring polymers obtained from microscale combustion calorimetry [28, 33]. The effective heat

of combustion measured in the cone calorimeter,  $H_{c,}$ , is less than this theoretical value because combustion is incomplete when soot, CO, and unburned hydrocarbons are released during burning. Hydrocarbon polymers that vaporize completely without forming much soot, such as PMMA, polyoxymethylene, and polyethylene, usually exhibit relatively complete flaming combustion. In this study, the combustion efficiency,  $\chi$ , was calculated from the ratio of the effective heat of flaming combustion,  $H_c$ , measured in the cone calorimeter during the period of flaming and the theoretical heat of complete combustion of the pyrolysis gases,  $\Delta h_c$ , measured in the microscale combustion calorimeter [33] (i.e.,  $\chi = H_c/\Delta h_c$ ). The average  $H_c$  at  $\dot{q}''_{ext} = 75$  and 100 kW/m<sup>2</sup> and the flaming combustion efficiency,  $\chi$ , and  $\Delta h_c$  for the polymers of this study are listed in the last three columns of table 4.

Motorial	CHF	$\frac{\text{TRP}}{(\text{kWs}^{1/2}/\text{m}^2)}$	$T_{ig}$		UDD	$L_{\rm g}$	$H_{\rm c}$	$\Delta h_{\rm c}$	~
DC	(K W/III )	111 )	$(\mathbf{C})$	K S)		(KJ/g)	(KJ/g)	(KJ/g)	$\chi$
PC	1 /	433	424	1.50	4.9	4.7	23.2	28.1	0.8
PEKK	28	452	493	1.07	4.4	4.5	19.9	19.5	1
PEN	33	483	536	1.14	3.0	6.7	19.9	18.1	≈ 1
PSU	34	351	543	0.58	3.8	6.7	25.6	25.6	1
PEI	35	352	551	0.57	2.6	7.7	20.1	24.7	0.8
BPC-PC	39	309	578	0.40	4.4	1.6	7.1	11.6	0.6
PI	43	829	603	2.62	3.1	3.7	11.6	15.6	0.7
PBI	44	892	609	2.97	3.9	5.5	21.4	26.5	0.8
PPSU	48	423	632	0.62	4.5	5.7	25.5	23.1	≈ 1
PEEK	49	509	637	0.88	4.5	5.6	24.9	26.8	0.9
PPS	49	494	637	0.83	2.0	6.6	13.3	27.7	0.5
PAI	50	334	643	0.37	2.9	8.0	23.2	16.5	≈ 1

Table 4. Effective material properties derived from cone calorimeter data

Table 4 shows that the thermal decomposition products from these heat-resistant polymers burn relatively completely ( $\chi$  H 1) in the well-ventilated diffusion flame of a fire calorimeter, so the fire resistance of these polymers can be ascribed to high thermal stability that increases the ignition temperature, critical heat flux, and char yield—all of which reduce the burning rate.

#### CONCLUSIONS

Heat-resistant thermoplastic polymers like those in this study contain rigid ladder-like structures in the polymer backbone that restrict thermally-induced molecular motions that lead to chemical bond breaking (thermal decomposition) until high temperatures. The paucity of hydrogen atoms in the polymer chains reduces the likelihood that backbone scission reactions will terminate by hydrogen transfer and lead to volatile fuel fragments, and increases the likelihood that recombination reactions between hydrogen-deficient moieties will produce aromatic char and nonaromatic fuel gases, as indicated by the low SEA of the most thermally stable polymers PAI, PI, PBI, and PEI. When low-fuel-value atoms, such as nitrogen, oxygen, and sulfur, replace carbon and hydrogen in the polymer backbone, the heat of combustion of the thermal decomposition products (fuel gases) is correspondingly reduced. The minimum/critical external heat flux for piloted ignition (CHF) increases with the thermal decomposition temperature of the solid polymer, which is a kinetic property responsible for heat resistance. Ignition of the fuel/air mixture at the CHF is a gas phase phenomenon that is independent of the thermal stability of the solid but depends on the thermodynamic properties of the solid,  $L_g$  and  $H_c$ . When ignited, the rigid, low-density char layer reduces heat conduction through the surface due to its low thermal conductivity and its ability to absorb and reradiate incident energy, which minimizes heat transfer to the underlying polymer and lowers the burning rate.

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