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Flame retardant aircraft epoxy resins containing phosphorus[☆]

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Abstract

As part of a program to develop fire resistant exterior composite structures for future subsonic commercial and general aviation aircraft, flame retardant epoxy resins are under investigation. Epoxies and their curing agents (aromatic diamines) containing phosphorus were synthesized and used to prepare epoxy formulations. Phosphorus was incorporated within the backbone of the epoxy resin and not used as an additive. The resulting cured neat epoxy formulations were characterized by thermogravimetric analysis, propane torch test, elemental analysis, microscale combustion calorimetry, and fire calorimetry. Several formulations showed excellent flame retardation with phosphorous contents as low as 1.5% by weight. The fracture toughness and compressive strength of several cured formulations showed no detrimental effect due to phosphorus content. The chemistry and properties of these new epoxy formulations are discussed.

Keywords: Fire retardant; Structural epoxy resins; Phosphorus containing epoxies

1. Introduction

The use of composite structures in both commercial and general aviation aircraft has been increasing primarily because of the advantages composites offer over metal (e.g. lower weight, better fatigue performance, no corrosion, better design flexibility, etc.). The new Airbus A380 is expected to have about 22% of the structural weight in composites. About 50% of the structural weight of the new Boeing 787 is proposed to be composites, including for the first time a composite fuselage and wings in a large commercial airliner. Currently no fire resistance requirements exist for exterior polymer composite structures on airplanes. However, the aircraft manufacturer will be required to demonstrate that polymer structural composites provide equivalent safety to the current material system (aluminum alloy). The primary hazards during aircraft fires are heat, smoke, and toxic gas. In a severe aircraft fire, life-threatening levels of these hazards are produced by cabin flashover, the time to which is largely governed by the rate of heat release of the materials in the fire. Other concerns in a carbon fiber composite fire include the potential release of electrically conductive small carbon fibers that can cause damage to electrical equipment and health problems (from inhalation). However, a study [1,2] reported in 1980 concluded that it was unlikely severe damage to electrical equipment would result from an accidental release of carbon fibers from an aircraft fire. A recent paper [3] discussed the concern about potential health hazards from the exposure to airborne carbon fibers released from a burning airplane containing carbon fiber composite parts. This paper [3] concluded that at the present time there is no evidence linking airborne carbon fibers to any unusual health hazard.

The use of phosphorus (P) as a flame retardant, particularly in epoxy resins, has been widely studied and is the subject of recent review articles [4–6]. A 3 year BRITE-EURAM Program was conducted in the European Community to develop new structural materials with improved fire resistance, reduced smoke and toxicity [7].

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This effort concentrated on the use of bis(3-aminophenyl)-methylphosphine oxide as a curing agent for epoxies [8–10]. Extensive composite evaluation was carried out and several published articles evolved from this work (Refs. [8–10]). Bis(3-aminophenyl)methylphosphine oxide had been used previously as a curing agent for epoxies [11,12]. Phosphorus when incorporated in polymers as an additive or reactive comonomer is known to impart fire retardation by condensed phase and gas phase mechanisms [9]. In the condensed phase P catalyzes char formation which protects the underlying material from heat and acts a barrier to the release of fuel gases from the surface. When acting in the condensed phase as a char catalyst, P retards the spread of fire with minimal release of toxic gases [13]. In the gas phase P acts as a flame poison with PO species participating in a kinetic mechanism that is analogous to that of halogens in flames [14,15]. Gas phase activity is indicated by low heats of flaming combustion, the production of visible smoke and mineral acids (halogens), and high yields of carbon monoxide as consequence of the incomplete combustion of the fuel gases in the flame. Phosphorus has been incorporated into polymeric materials both as an additive and as part of the polymeric chain. Additives are normally more economical but tend to leach out, and have a negative impact on processability and mechanical properties. Cured epoxy resins have a high concentration of hydroxyl (OH) groups and therefore, P-containing flame retardant compounds are particularly effective because P tends to react with OH groups [4–6,8–10].

The intent of this work was to identify reactive organophosphorus compounds that could be incorporated into existing 177 °C (350 °F) cured epoxy formulations to provide fire resistant structural composites with little or no compromise in processing, handling, physical, and mechanical properties. The work reported herein concerns the initial research to identify promising epoxide- and amine-functional organophosphorus compounds by screening cured epoxy formulations for flammability and mechanical properties at the lab and bench scale.

2. Experimental

2.1. Materials

N,*N*,*N*′,*N*′-Tetraglycidyl-4,4′-methylenedianiline (TGMDA), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (cycloaliphatic epoxy, Araldite CY 179), and 4,4′-diaminodiphenylsulphone (DDS) were obtained from commercial sources and used as received. Phosphorus oxychloride, phenylphosphonic dichloride, phenyl dichlorophosphate, and triethylamine were purchased from a commercial source and distilled prior to use. All other chemicals were purchased from commercial sources and used without further purification.

2.2. Characterization

^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) Spectra were obtained on a Bruker 300 NMR Spectrometer. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer. Melting points were determined by DSC (heating rate of 10 °C/min, recorded at the onset and peak of the endotherm). Dynamic thermogravimetric analysis (TGA) was performed on a Seiko 200/220 instrument on cured formulations at a heating rate of 2.5 °C/min in nitrogen at a flow rate of 15 cm^3/min. Char yields were determined by TGA from the mass of the residue remaining at 800 °C. Epoxy equivalent weights (E.E.W.) were determined using the hydrogen bromide method [16]. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Liquid chromatography/mass spectroscopy (HPLC/MS) data was collected on a Waters 2695 Separations module interfaced with a Waters Integrity™ System Thermabeam Mass Detector.

2.3. Synthesis

2.3.1. Synthesis of bis(4-nitrophenyl)methylphosphonate

A 1 l 3-neck round-bottom flask fitted with a mechanical stirrer, an addition funnel, and a condenser was charged with 4-nitrophenol (102.9 g, 0.74 mol), triethylamine (103 ml, 75 g, 0.74 mol), and tetrahydrofuran (THF, 250 ml). The solution was cooled with an ice-water bath. A solution of methylphosphonic dichloride (49 g, 0.37 mol) in 200 ml of THF was added dropwise over a period of 30 min. The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was poured into 1 l of stirred water and the resulting precipitate was collected by vacuum filtration. The solid was dried in a vacuum oven at 55 °C for 4 h to give 103.86 g (83%) of tan crystalline solid, mp of 120–122 °C (lit. mp 121.5–122.5 °C) [17] by DSC. ^{1}H NMR (DMSO) ppm: [2.05, 2.22] (s, 3H, methyl), 7.49 (d, 4H), 8.27 (d, 4H). ^{31}P NMR (DMSO) ppm: 27.4. HPLC/MS: 1 peak, $m/z = 337$.

2.3.2. Synthesis of bis(4-aminophenyl)methylphosphonate *1*

A large Parr™ bottle was charged with bis(4-nitrophenyl)methylphosphonate (40.32 g, 0.1192 mol), anhydrous methanol (150 ml), and 5% Pd/C (0.2976 g). The bottle was shaken on a hydrogenator for 14 h under 40 psi of H_2. The reaction mixture was filtered to remove the catalyst and the filtrate was concentrated to give a yellow oil. To the oil was added 150 ml of isopropanol and a pale yellow solid formed upon standing. The solid was collected and dried in a vacuum oven at 75 °C to give 28.6 g (86%), mp of 118–121 °C. ^{1}H NMR(DMSO) ppm: [1.60, 1.66] (s, 3H, methyl), 5.07 (s, 4H, amine), 6.49 (d, 4H), 6.81 (d, 4H). ^{31}P NMR (DMSO) ppm: 25.1. HPLC/MS: 1 peak, $m/z = 277$.

2.3.3. Other diamines *2* and *3*

Bis(3-aminophenyl)methylphosphine oxide **2** (mp 148–

151 °C, lit. 146–149 °C) [9] and bis(4-aminophenyl)phenylphosphine oxide **3** (mp 264–266 °C, lit. 264–265 °C) [18] were prepared following literature procedures.

*2.3.4. Synthesis of diglycidylmethylphosphonate **4***

A 500 ml 3-neck round-bottom flask fitted with an addition funnel, a mechanical stirrer, and a condenser was charged with glycidol (28.14 g, 0.3762 mol), toluene (200 ml), and triethylamine (38.07 g, 0.3762 mol). The clear solution was cooled with an ice-water bath. A solution of methylphosphonic dichloride (23.73 g, 0.1785 mol) in toluene (100 ml) was added dropwise through the addition funnel. The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was filtered to remove triethylamine hydrochloride and the filter cake was washed with 100 ml of toluene. The filtrate was concentrated on a rotary evaporator to give a brown viscous liquid. The liquid was placed under vacuum at 85 °C for 1 h with stirring to remove toluene and excess glycidol. (Yield 34.2 g, 87%). ^{1}H NMR ($CDCl_3$) ppm: [1.45, 1.50] (3H, methyl group), [2.56, 2.74] (4H), 3.13 (2H), [3.81, 4.20] (4H). ^{13}C NMR ($CDCl_3$) ppm: 9.8, 10.2 (methyl), 44.0, 50.0, 65.8. ^{31}P NMR ($CDCl_3$) ppm: 32.5. Anal. Calcd for $C_7H_{13}O_5P$: C, 40.39%; H, 6.30%; P, 14.88%. Found: C, 39.00%; H, 6.85%; P, 11.98%. (E.E.W. 124, theoretical E.E.W. 104).

2.3.5. Other epoxy synthesis

Diglycidylphenylphosphonate **5** (E.E.W. 182, theoretical E.E.W. 135) (Anal. Calcd for $C_{12}H_{15}O_5P$: C, 53.34; H, 5.60; P, 11.46. Found: C, 52.41; H, 5.30; P, 10.99.) [19], diglycidylphenylphosphate **6** (E.E.W. 198, theoretical E.E.W. 143) [20], triglycidylphosphate **7** (E.E.W. 212, theoretical E.E.W. 83) [21], and triglycidylphosphate **8** (E.E.W. 117, theoretical E.E.W. 89) [22] were prepared following literature procedures.

*2.3.6. Synthesis of diethylphenylphosphonate **9***

A 100 ml round-bottom flask equipped with a magnetic stirrer was charged with ethanol (40 ml, 31.8 g, 0.69 mol) and triethylamine (20 ml, 14.5 g, 0.14 mol). The solution was cooled with an ice-water bath. Phenylphosphonic dichloride (10 ml, 13.8 g, 0.07 mol) was added dropwise through an addition funnel. The reaction mixture was stirred for 14 h and then filtered to remove the resulting salt. The filtrate was concentrated on a rotary evaporator to give 13.66 g (91%) of a clear liquid. ^{1}H NMR ($CDCl_3$) ppm: 1.25 (t, 6H), 4.03 (m, 4H), 7.4 (m, 3H), 7.71 (m, 2H).

2.4. Cured neat resin plaque preparation

Circular neat resin plaques approximately 4.5 cm in diameter and 0.4 cm thick were prepared by mixing epoxy compounds with 80% of the stoichiometric amount of the curing agent at room temperature. The formulations were heated to and maintained at ~90 °C with periodic stirring for 1–2 h until homogeneous. The formulations were then degassed for 15–20 min in a vacuum oven at ~90 °C and subsequently cured for 4 h at 100 °C followed by a 2 h post-cure at 177 °C. Except for formulations containing diamine **3**, transparent plaques were obtained.

2.5. Flammability testing

2.5.1. Flame resistance

A flame resistance test was conducted by placing a cured epoxy specimen approximately 1.5 cm × 1.5 cm × 0.4 cm in a propane torch flame at a 45° angle for 5–10 s and noting the time required for the sample to self-extinguish upon removal from the flame. Initially the burn test consisted of placing a piece of the cured resin plaque in the flame of a propane torch for 5 s. As work progressed, the time in the propane torch flame was increased to 10 s. No noticeable difference was detected between 5 and 10 s burns with specimens from the same plaque.

2.5.2. Microscale combustibility

In a pyrolysis combustion flow calorimeter, 5 mg samples of cured epoxy formulations were heated to 900 °C at a heating rate of 1 °C/s in a stream of nitrogen flowing at 80 cm^3/min. The volatile, anaerobic thermal degradation products in the nitrogen gas stream are mixed with a 20 cm^3/min stream of pure oxygen prior to entering a 1000 °C combustion furnace. Measured during the test is the heat release rate dQ/dt (W) and sample temperature as a function of time at constant heating rate [23,24]. The specific heat release rate HRR (W/g) is obtained by dividing dQ/dt at each point in time by the initial sample mass. The heat of combustion of the fuel gases per unit mass of initial sample HR (J/g) is obtained by time-integration of HRR over the entire test. The char fraction, μ, is obtained by weighing the sample before and after the test. A derived quantity, the heat release capacity HRC (J/g K) is obtained by dividing the maximum value of the specific heat release rate by the heating rate in the test. The heat release capacity is a molecular level flammability parameter that is a good predictor of flame resistance and fire behavior when only research quantities are available for testing. Three to five samples were tested for each resin formulation. Reproducibility of the test for homogeneous samples is about ±8%.

2.5.3. Ohio State University rate of heat release test

Heat release rates (HRR) in flaming combustion were measured on cured single-ply fiberglass reinforced specimens using a modification of ASTM E-906 [25] as specified by 14 CFR Part 25 Appendix F. In this study the Ohio State University Rate of Heat Release (OSU) apparatus was modified to measure heat release rate and total heat release by oxygen consumption calorimetry simultaneous with the standard FAA method. A 15 cm × 15 cm sheet of style 7781 fiberglass was hand impregnated with epoxy formulations containing 0.5 parts per hundred parts resin (phr) of a

BF_3-piperazine catalyst. The resin impregnated ply was cured in a Carver press under contact pressure for 1 h at 149 °C and post cured free standing for 1 h at 177 °C. Two specimens were tested per each resin formulation.

2.5.4. Cone calorimetry

A cone calorimeter at 50 kW/m^2 external heat flux was used to test cured neat resin plaques having dimenions of approximate 8.9 cm × 8.9 cm × 0.6 cm in flaming combustion. Testing was carried out according to a standard procedure ASTM 1354 [26]. Three plaques were tested per resin formulation.

2.6. Mechanical properties

2.6.1. Plane strain fracture toughness

Single-edge notched bend (SENB) specimens were tested following ASTM D 5045-99 [27]. Cured epoxy formulations having dimensions of approximately 1.27 cm × 6.35 cm × 0.64 cm were cut from a neat resin plaque. A crack was initiated with a razor blade [28] and the specimens were tested at a crosshead speed of 0.51 mm/min on a Korros Data test stand equipped with a 0.5 kN (45.5 kg) load cell. Three to five specimens of each resin formulation were tested at room temperature.

2.6.2. Compressive properties

Compression testing as conducted on cured cylindrical specimens 1.8 cm diameter by 3.8 cm high using a modification of ASTM D695 [29]. Testing was done on an MTS test stand with a 490 kN load cell. Two extensiometers with 2.5 cm gauge lengths were used to measure strain for the modulus calculations. Four specimens of each resin formulation were tested at room temperature.

2.7. Moisture uptake

Cured epoxy specimens were dried in a vacuum oven at 100 °C for 12 h to a constant weight and then placed in a closed chamber saturated with water vapor at ambient (room) temperature. The specimens were weighed again after 90 days in the moist environment to determine moisture uptake. Three specimens were used per formulation tested.

3. Results and discussion

3.1. Synthesis

The P-containing compounds in this study are known compounds and where possible, were prepared following literature procedures. The compounds were characterized with ^1H, ^{13}C and ^{31}P NMR, HPLC/MS, elemental analysis, E.E.W., and melting point where applicable.

3.1.1. Diamines

Reaction schemes for the syntheis of the organophosphorus diamines are shown in Scheme 1. Bis(4-aminophenyl)methylphosphonate **1** was prepared by reacting 4-nitrophenol with methylphosphonic dichloride to yield bis(4-nitrophenyl)methylphosphonate, that was subsequently reduced to the diamine. Likewise, bis(3-aminophenyl)methylphosphine oxide **2** [12] was prepared through the nitration of diphenylmethylphosphine oxide followed by the reduction of the dinitro compound to the diamine.

Bis(4-aminophenyl)phenylphosphine oxide **3** [30] (mp 264–266 °C, lit. 264–265 °C) [18] was prepared in four steps following literature procedures with an overall yield of 35%. First, 4-bromoaniline was protected with a STABASE group (1,1,4,4-tetramethyldisilyl azacylopentyl) to give 1-bromo-4-(1,1,4,4-tetramethyldisilyazacylopentyl) benzene in 70% overall purified yield [18]. The protected bromoaniline was then reacted with dichlorophenylphosphine in the presence of *n*-butyl lithium/tetrahydrofuran to give phenylbis[4-(1,1,4,4-tetramethyldisilyazacylopentyl)phenyl]phosphine in 71% yield [18]. The STABASE protecting group was removed in methanol in the presence of *p*-toluenesulfonic acid monohydrate to give bis(4-aminophenyl)phenylphosphine which was then oxidized with 30% hydrogen peroxide to give bis(4-aminophenyl)phenylphosphine oxide **3** in 75% yield [30].

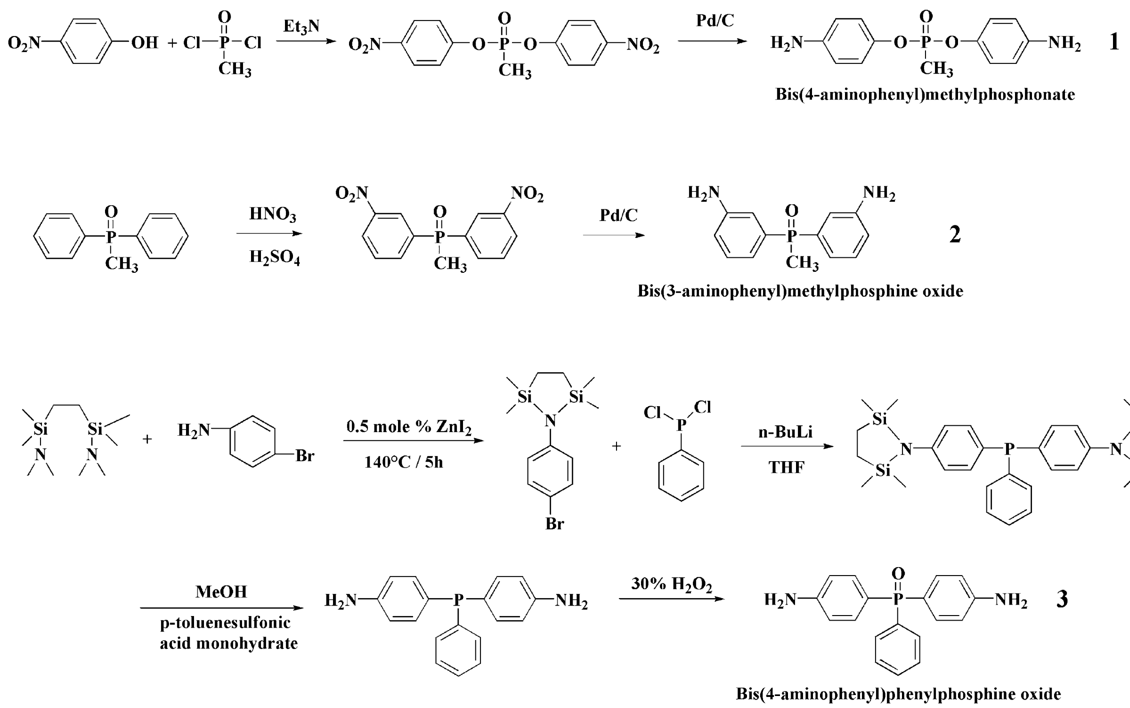
3.1.2. Epoxides

The organophosphorus epoxy compounds **4–8** were prepared from the reaction of glycidol with the corresponding chlorophosphorus compound (methyl and phenyl phosphonic dichloride, dichlorophenyl phosphate, phosphorus trichloride, and phosphorus oxychloride) in the presence of triethylamine as shown in Scheme 2. Epoxy equivalent weights, determined using the hydrogen bromide method, varied significantly from the theoretical values. This is common for epoxies because of impurities such as dimers, trimers, 1,2-glycols, etc. that are present.

3.2. Model compound study of chemical reactivity

Some concern existed about whether the glycidyl functionality could be cleaved at the P–oxygen bond by an amine during curing. To resolve this issue diethylphenylphosphonate **9** was synthesized to use as a model compound to study this potentially detrimental reaction.

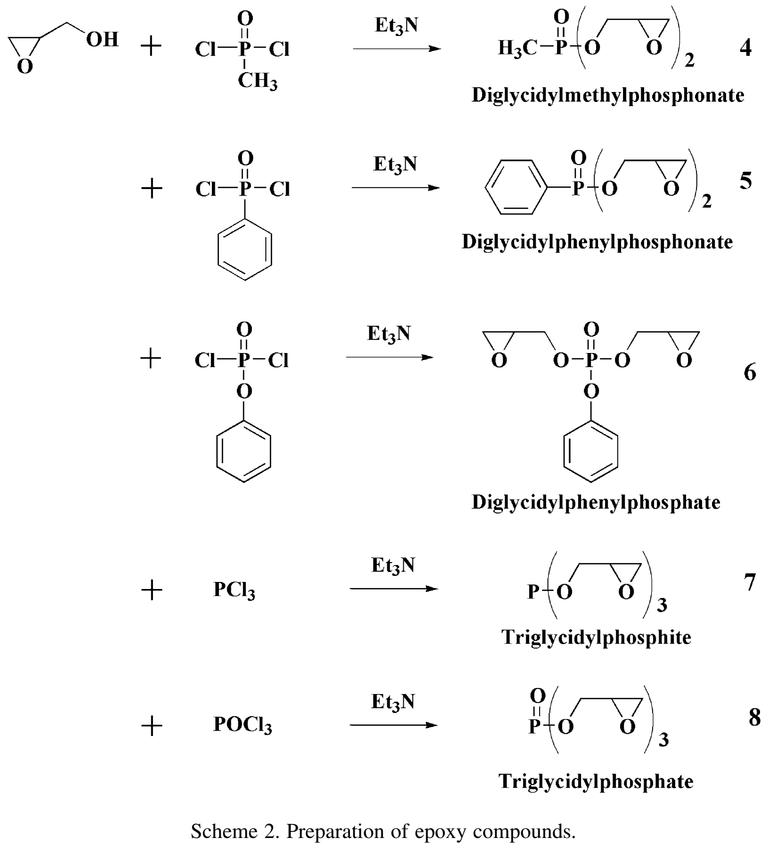
A stoichiometric solution of compound **9** and DDS was stirred at room temperature and subsequently heated. Aliquots were removed after 19 h at room temperature, 2.5 h at 70 °C, 3 h at 100 °C and 1.5 h at 125 °C. The aliquots were analyzed by HPLC and no evidence of reaction between the phosphate ester and the diamine was observed.



Scheme 1. Preparation of diamines.

3.3. Cured neat resin plaques

Commercial aerospace structural epoxy formulations contain TGMDA as the base epoxy and DDS as the curing agent and are polymerized (cured) at 177 °C. These formulations also generally contain additional components such as a thermoplastic toughening agent, diepoxy, and in some cases, a catalyst. The following formulations are



Scheme 2. Preparation of epoxy compounds.

modifications of the commercial aerospace epoxy in which P is introducted at low loading levels ($<5\%$ w/w) using reactive compounds **1–3** and reactive compounds **4–8** as partial replacement for the amine curing agent DDS and epoxy resin TGMDA, respectively. Formulation **F1**, as shown in Table 1, is the control (base) formulation in which TGMDA is cured with an 80% stoichiometric amount of DDS to compare properties with the P-containing epoxy formulations. All samples were cured for 4 h at 100 °C and post-cured for 2 h at 177 °C.

*3.3.1. Formulations with phosphorus-containing diamines **F2–F6***

Formulations **F2–F4** have P-containing diamines **1–3** in place of DDS respectively resulting in cured samples having calculated P contents (by weight) of approximately 4.0%. The cured plaques of formulations **F2** and **F3** were transparent, reddish-brown while **F4** was an opaque yellow. The apparent viscosity of the uncured **F4** formulation was much higher than that observed with the other formulations. Formulations **F5** and **F6** contain a smaller amount of diamine **1** to determine the minimum P content necessary for the specimen to extinguish immediately after removal from the propane torch flame.

*3.3.2. Formulations with phosphorus-containing epoxides **F7–F21***

Epoxy formulations were also prepared where P was introduced via epoxy compounds. These formulations were prepared using only DDS as the curing agent and are listed in Table 2. Formulations **F7–F9** contained diglycidylmethylphosphonate **4** in amounts ranging from 10 to 33 phr as shown in Table 4 resulting in cured specimens having P contents ranging from 0.87 to 3.3%. Formulations **F10–F12** were prepared using diglycidylphenylphosphonate **5** in concentrations ranging from 10 to 40 phr. Diglycidylphenylphosphate **6** was used to prepare formulations **F13–F15** with 3.2, 2.3 and 1.4% P respectively. Triglycidylphosphite **7** was also evaluated in cured epoxy formulations. A cycloaliphatic epoxy at a concentration of 20 phr was used as a partial replacement for TGMDA in **F16** and **F17**. This diepoxy is used to help solubilize the DDS but it is also used in epoxy formulations (generally with boron trifluoride (BF_3) catalyst) to improve handleability (tack and outtime). However, a BF_3 catalyst was not used in these formulations. Triglycidylphosphite **7** [$P(OR)_3$] appeared to be more reactive (advancing cure) than the other P containing epoxies evaluated in this work. A small amount of gel was observed during the mixing and degassing of the epoxy formulation. This is not unexpected because phosphines [PR_3] are frequently used as a catalyst in epoxy resins. Formulations **F18–F21** contain triglycidylphosphate **8** with P contents ranging from 0.8 to 3.1%. The cycloaliphatic epoxy mentioned above was not used in these formulations.

3.4. Moisture uptake

A study was conducted to determine the moisture uptake of the cured epoxy formulations. Water absorption is known to lower the glass transition temperature and reduce the mechanical properties. The cured resin plaques were first dried in a vacuum oven to remove any absorbed moisture and subjected to a high humidity atmosphere for 90 days at ambient temperature. As shown in Table 3, the baseline material **F1** had an average water uptake of 2.6% which is similar to commercial 177 °C systems. Formulation **F11** containing 20 phr epoxy **5** (phosphonate) had a slightly higher water uptake of 2.9% while formulation **F20** containing 20 phr epoxy **8** (phosphate) had a water uptake of 4.3%. No firm conclusions can be drawn from this limited data set.

3.5. Neat resin mechanical properties

Neat resin mechanical properties were determined on several formulations containing P epoxies. Single-edge notched bend specimens were prepared and tested for select formulations to evaluate the effect of incorporating the P-containing compounds on K_{1c}. Table 4 lists plane–strain fracture toughness values for selected formulations ranged from 0.47 to 0.79 MPa $m^{1/2}$. The values obtained for formulations **F2**, **F8**, **F11**, and **F20** were essentially the same as measured for **F1** (TGMDA/DDS) while the fracture toughness of **F14** was significantly lower.

Table 5 lists compression moduli formulations containing 20 phr P epoxy (**F11**, **F14**, and **F20**). Compressive moduli ranged from 3.12 to 4.54 GPa for the P-containing epoxies, which is significantly higher than the baseline

Table 1
Flame resistance of phosphorus diamine formulations

Formulation	TGMDA (phr)	Diamine, amount	P (%)	Char (%)[a]	Flame test[b]
F1	100	DDS, 48 phr	0	25	Sustained burn
F2	100	**1**, 54 phr	3.9	31	Extinguished immediately
F3	100	**2**, 47 phr	4.0	23	Extinguished immediately
F4	100	**3**, 37 phr	3.7	24	Extinguished immediately
F5	100	DDS, 36 phr; **1**, 14 phr	0.9	30	2 s Burn
F6	100	DDS, 24 phr; **1**, 27 phr	1.7	31	Extinguished immediately

[a] Char fraction in nitrogen at 800 °C, TGA heating rate 2.5 °C/min.

[b] Sample placed in propane torch flame for 5 s and removed.

Table 2
Flame resistances of phosphorus epoxy formulations

Formulation[a]	TGMDA (phr)	P Epoxy (phr)	P (%)	Char[b] (%)	Flame test[c]
F7	67	**4**, 33	3.3	35	Extinguished immediately
F8	80	**4**, 20	2.1	28	Extinguished immediately
F9	90	**4**, 10	0.9[d]	31	2 s Burn
F10	60	**5**, 40	3.2	36	Extinguished immediately
F11	80	**5**, 20	1.5[d]	34	Extinguished immediately
F12	90	**5**, 10	0.8	33	2 s Burn
F13	60	**6**, 40	3.2	44	Extinguished immediately
F14	70	**6**, 30	2.3	41	Extinguished immediately
F15	80	**6**, 20	1.4[d]	37	Extinguished immediately
F16	60[e]	**7**, 20	1.6[d]	35	Extinguished immediately
F17	60[e]	**7**, 10	0.9	–	~1 s Burn
F18	60	**8**, 40	3.1	42	Extinguished immediately
F19	70	**8**, 30	2.4	42	Extinguished immediately
F20	80	**8**, 20	1.5	37	Extinguished immediately
F21	90	**8**, 10	0.8	–	~1 s Burn

[a] Cured with 80% stoichiometric amount of DDS.
[b] At 800 °C under nitrogen, TGA heating rate 2.5 °C/min.
[c] Sample placed in propane torch flame for 10 s and removed.
[d] Result from elemental analysis.
[e] Contains 20 phr cycloaliphatic diepoxy.

formulation **F1**. The ultimate compression strength ranged from 188 to 214 MPa. Formulations **F11** and **F20** had compression strengths similar to **F1** while formulation **F14** was lower. The reduction in fracture toughness observed with **F14** relative to **F1** could exclude epoxy **6** from consideration for use in structural epoxy formulations even though this compound showed a high efficiency in reducing flammability relative to the other P-epoxies studied.

3.6. Chemical characterization

Elemental analysis was performed on cured formulations **F9**, **F11**, **F14**, **F16** and **F20** to verify the amount of P in the samples. The results are listed in Table 6 and show good agreement between found and theoretical values in the cured epoxies. For the samples tested, the % P found by elemental analysis was slightly lower than the amount calculated based on the weight of P containing epoxy used in the formulation.

3.7. Flammability

3.7.1. Flame resistance

Results for flame resistance of the P-containing diamine formulations are presented in Table 1. Formulation **F1** which contained no P had a char yield of 25% at 800 °C in N_2 and exhibited self-sustained burning in air after removal of the flame. Formulations **F2–F4** showed intumescense and extinguished immediately after being removed from the flame with little visible smoke. Formulation **F2** which containing diamine **1** (phosphonate) gave a char yield of 31% at 800 °C in N_2, which is higher than formulations **F3** and **F4** which had char yields similar to the baseline compound **F1**. Formulation **F5** containing diamine **1** and 0.9% P burned for approximately 2 s after removal from the propane torch flame. Formulation **F6** contained 50% diamine **1** resulting in a P content of 1.7%. The cured **F6** specimen extinguished immediately after removal from the flame. Char yields at 800 °C in N_2 were the same (30–31%) for all formulations containing diamine **1**.

Results for flame resistance of the P-containing epoxide formulations are presented in Table 2. Formulations **F7** and **F8** extinguished immediately upon removal from the propane torch flame while **F9**, having less than 1% P, burned for approximately 2 s. The three specimens all showed good intumescense and very little visible smoke. A char yield of 35% at 800 °C was obtained for specimen **F7**. Both **F10** and **F11**, with 3.2 and 1.6% P content respectively, extinguished immediately upon removal from the propane torch flame and exhibited intumescense

Table 3
Average water uptake of cured epoxy formulations

Formulation	P (% w/w)	Water uptake (% w/w)
F1	0	2.6
F11	1.5	2.9
F20	1.6	4.3

Table 4
Plane–strain fracture toughness

Formulation	Fracture toughness (MPa $m^{1/2}$ ± 1 SD)
F1	0.62 ± 0.04
F2	0.68 ± 0.04
F8	0.79 ± 0.05
F11	0.64 ± 0.13
F14	0.47 ± 0.09
F20	0.54 ± 0.05

Table 5
Compression properties of cured resin formulations

Formulation	P (%)	Compression modulus (GPa)	Ultimate compressive strength (MPa)
F1	0	3.12±0.02	196±14
F11	1.5[a]	4.54±0.06	214±4
F14	1.4[a]	3.50±0.03	188±2
F20	1.5	4.35±0.01	213±1

[a] Result from elemental analysis.

and low smoke. Formulation **F12** with 0.8% P burned for approximately 2 s upon removal from the flame but showed good intumescense. As seen with previous specimens, a minimal P content of 1–1.5% appeared to be necessary to obtain acceptable fire retardation. Char yields at 800 °C for formulations **F10–F12** ranged from 33 to 36% and were slightly higher than observed from the corresponding samples containing diglycidylmethylphosphonate **4**. The increased char yields from formulations containing epoxy **5** presumably are from the phenyl ring contributing to the char.

Formulations **F13–F15** extinguished immediately upon removal from the propane torch flame with low smoke and very good intumescense. Char yields for samples containing epoxy **6** at 800 °C were higher than observed for formulations containing epoxy **5**. Formulation **F13** had the highest char yield of all the samples tested at 44%. Formulation **F16** containing 1.6% P extinguished immediately after removal from the propane torch flame and showed good intumescense and low smoke. **F17**, which contained less than 1% P, burned for 1 s upon removal from the propane torch flame with moderate intumescense. The char yield of **F16** at 800 °C was 35%. Formulations containing epoxy **8** all extinguished immediately except for **F21** which contained 0.8% P. No increase in char yield was observed between sample **F19** with 2.4% P and **F18** with 3.1% P suggesting a maximum char yield had been obtained for formulations containing epoxy **8**.

3.7.2. Combustibility

Rapid screening of organophosphorus compounds for combustibility was conducted using pyrolysis combustion flow calorimetry (PCFC). The PCFC uses oxygen consumption calorimetry to measure the rate and amount of heat produced by complete combustion of the fuel gases generated during controlled pyrolysis of a milligram sized sample. Microscale combustion calorimetry data are shown graphically in Figs. 1–6. The coefficient of variation for samples **F8**, **F9**, and **F16** taken from the same sample was unusually high at 33% suggesting inhomogeneity at the 5 mg level of the test specimen. All other samples had coefficient of variation <5%.

Fig. 1 is a stack plot of specific heat release rate versus temperature for the TGMDA/DDS control **F1** as well as epoxy formulations **F7** and **F10** containing 3% P incorporated as epoxides **4** and **5**, respectively. Also plotted in Fig. 1 is the specific heat release rate data for laboratory formulations containing 3% P incorporated as epoxies **6** and **8**. Each heat release rate curve is the average of between 3 and 5 individual measurements. Curves have been shifted vertically to avoid overlapping data but the specific heat release rate scale is unchanged and is indicated by the included arrow. Two heat release rate peaks are observed for the TGMDA/DDS control, one at 395 °C and another at 425 °C. The incorporation of 3% P into the polymer backbone as epoxides **4**, **5**, **6**, and **8** shifts these peaks to lower temperature by about 30 °C and reduces the height and area under the curves by a factor of 2. Fig. 1 shows that thermal degradation (fuel generation) begins earlier in the heating history for P-containing epoxy formulations but less fuel (combustion heat) is generated over the course of heating.

A two step thermal degradation process occurring at roughly the same temperatures as indicated in Fig. 1 for the TGMDA/DDS control has been observed for TGMDA/diglycidylether of bisphenol-A (DGEBA) epoxide mixtures

Table 6
Elemental analyses of selected epoxy formulations after curing

Formulation		%**C**	%**H**	%**N**	%**P**
F9	Theoretical	64.84	6.37	7.66	1.01
	Found	64.25	6.13	7.73	0.87
F11	Theoretical	64.59	6.24	7.15	1.59
	Found	61.42	6.39	6.99	1.49
F14	Theoretical	64.20	6.19	7.16	1.49
	Found	62.96	6.24	7.10	1.37
F16	Theoretical	62.36	6.33	6.36	1.65
	Found	60.54	6.48	6.29	1.57
F20	Theoretical	62.02	6.28	6.34	1.57
	Found	61.47	6.62	6.13	1.55

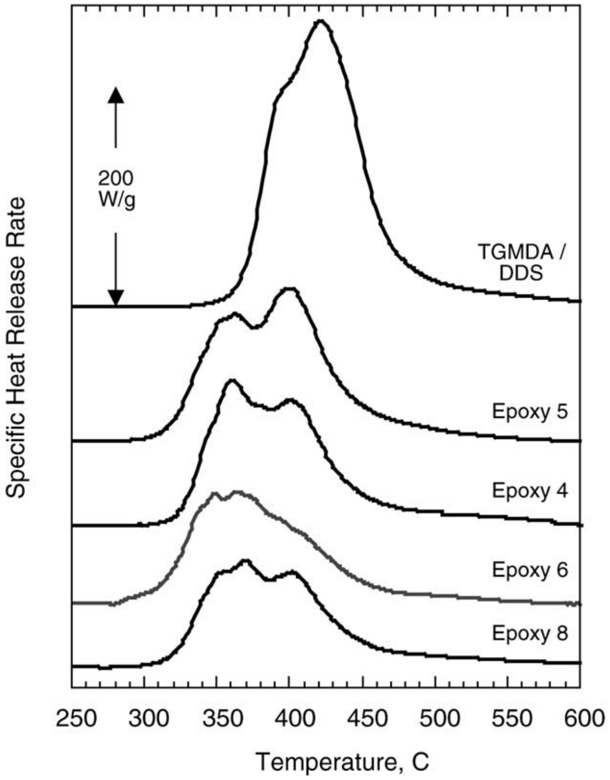


Fig. 1. Plot of specific heat release rate versus temperature for TGMDA/DDS control and epoxy formulations containing 3% phosphorus incorporated as epoxides **4**, **5**, **6**, and **8**.

(1:1) cured with diamine **2** [9]. When diamine **2** was used as the curing agent the decomposition peaks shifted to lower temperatures by roughly the same amount as observed for the heat release rate peaks of the P-containing epoxies in Fig. 1. Based on thermal and evolved gas analyses of these systems it has been suggested [9,10] that the low temperature process, which is exothermic and involved a large mass loss (60%), was due to dehydration, random scission and formation of a char precursor. The high temperature process, which is endothermic and involved less mass loss (20%), was attributed to further decomposition (carbonization) of the char precursor to a thermally stable aromatic structure. These same general processes are probably operative in the present systems. A mechanistic interpretation P-catalyzed charring based on pyrolysis (fuel generation) kinetics [31] is proposed as follows.

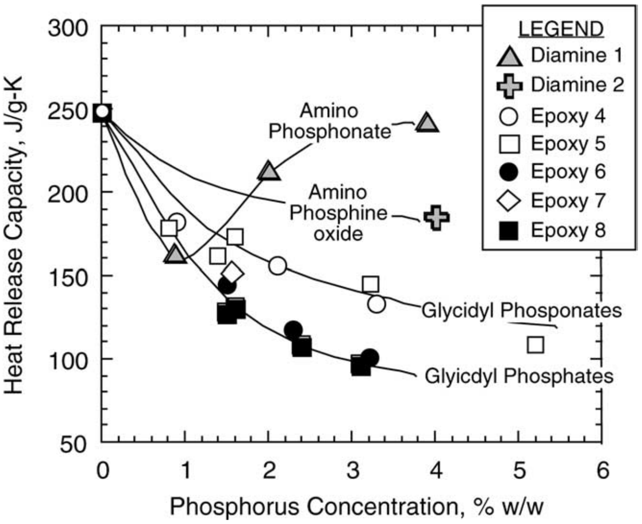


Fig. 2. Plot of heat release capacity versus phosphorus concentration for epoxy formulations containing diamine **1** and **2**, and epoxides **4**, **5**, **6**, **7**, and **8**.

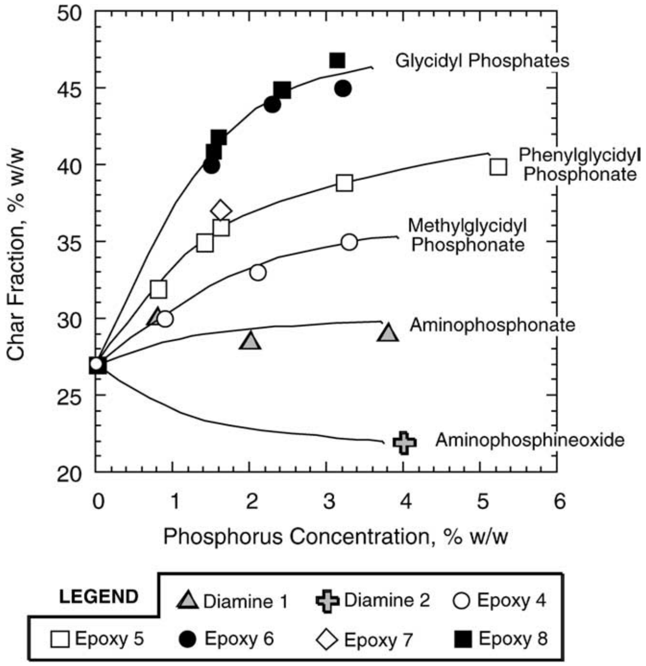


Fig. 3. Plot of anaerobic char fraction versus phosphorus concentration for epoxy formulations containing diamine **1** and **2**, and epoxides **4**, **5**, **6**, **7**, and **8**.

The maximum value of the specific heat release rate for each of the compounds in Fig. 1 divided by the heating rate in the test (1 K/s) is the heat release capacity (HRC) of the

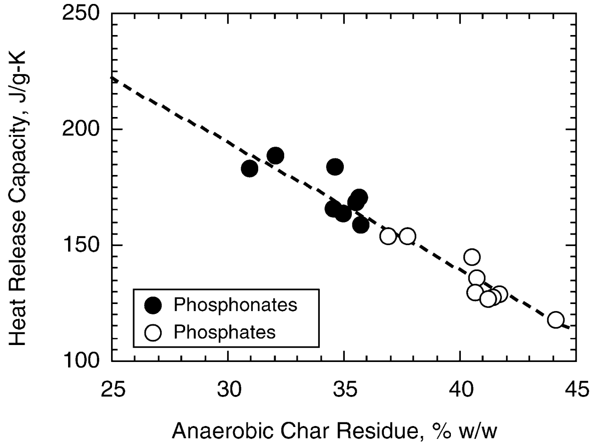


Fig. 4. Plot of heat release capacity versus anaerobic char fraction for epoxy formulations containing 1.5% phosphorus as epoxides **4**, **5**, **6**, and **8**.

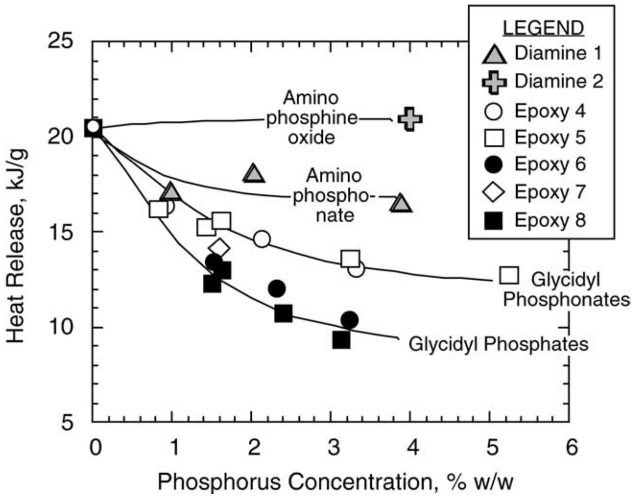


Fig. 5. Plot of heat release versus phosphorus concentration for epoxy formulations containing diamine **1** and **2**, and epoxides **4**, **5**, **6**, **7**, and **8**.

compound plotted in Fig. 2. For the compounds in Fig. 1 these heat release capacities are 260 J/g K for the TGMDA/DDS control and 140, 130, 100, and 95 J/g K for the formulations containing epoxides **5**, **4**, **6**, and **8**, respectively (Fig. 2). HRC is related to the decomposition kinetics and combustion parameters of the sample [31,32].

$$\mathrm{HRC}=\frac{h_c(1-\mu)}{eRT_p^2/E_a}\approx\frac{h_c(1-\mu)}{\Delta T_p} \tag{1}$$

In Eq. (1), μ is the anaerobic char fraction, $(1-\mu)$ is the fuel fraction, h_c (J/g) is the heat of combustion of the fuel gases, E_a (J/mol) is the activation energy for pyrolysis T_p (K) is the temperature at peak mass loss/fuel generation/thermal decomposition rate and e and R are the natural number and gas constant, respectively, and

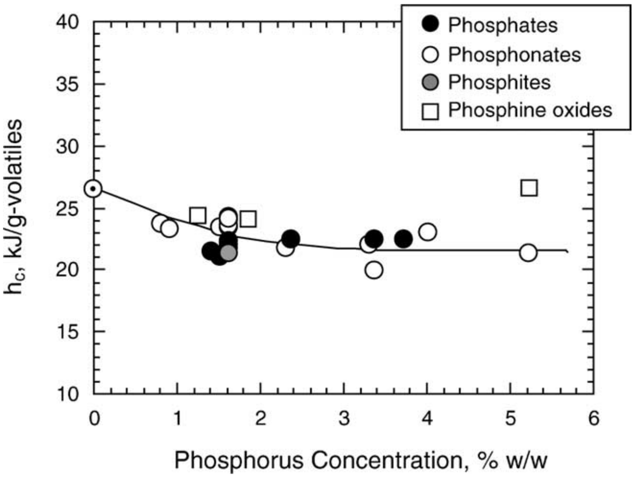


Fig. 6. Heat of complete combustion of volatiles versus phosphorus concentration for epoxides and diamines grouped by phosphorus oxidation state.

$$\Delta T_p=\frac{eRT_p^2}{E_a} \tag{2}$$

is the temperature interval over which the majority of pyrolysis (fuel generation) occurs. The data in Fig. 1 are representative of all of the epoxy formulations reported in this paper with respect to the temperatures over which heat is released (fuel is generated) during a constant rate of temperature rise. Fig. 1 shows that the width of the specific heat release rate peak at half of the maximum peak height is $\Delta T_p\approx 80$ K at $T_p\approx 410$ °C (683 K) for the TGMDA/DDS control and $\Delta T_p\approx 100$ K at $T_p\approx 380$ °C (653 K) for the epoxy formulations containing 3% P. From these data a rough estimate of the activation energy for pyrolysis is computed from Eq. (2), $E_a=eR(683\ \mathrm{K})^2/80\ \mathrm{K}=132$ kJ/mol for the TGMDA control and $E_a=eR(653\ \mathrm{K})^2/100\ \mathrm{K}=96$ kJ/mol for the epoxy formulations containing 3% P. Thus, P reduces both the temperature and activation energy for pyrolysis, as would occur for a catalytic mechanism.

Fig. 2 is a plot of heat release capacity (HRC) versus P concentration for diamines **1** and **2** as well as epoxides **4–8**. Fig. 2 shows that the efficiency of P in reducing HRC is glycidyl phosphate > glycidyl phosphite ≈ glycidyl phosphonate > aminophosphonate > aminophosphine oxide. The efficiency of P in reducing HRC is in the same general order as the oxidation state of P in the starting epoxide or amine compound, i.e. $PO_4>:PO_3\approx RPO_3>R_3PO$. The aminophosphonate **1** appears to exhibit anomalous behavior in that HRC shows a minimum at about 1% P and increases at higher P concentration. A flammability minimum at about 2% P has been observed in TGMDA/DDS epoxies cured with diamine **2** [9] when tested for limiting oxygen index (LOI) [33] which was attributed to low crosslink density, curing inhibition, or a transition from condensed phase to gas phase activity at high P concentration the latter being, presumably, less effective at reducing the LOI. The trends in the data of Fig. 2 result from variations in the chemical composition and concentration of P-containing epoxies and their effects on HRC.

Fig. 3 is a plot of anaerobic char fraction versus P concentration for the P-containing diamines and epoxides as components of a TGMDA/DDS epoxy formulation. Because the TGMDA/DDS is an aromatic, highly crosslinked system the char fraction is appreciable (27%) even without the addition of P-compounds. The efficiency of P in char formation is seen to follow the same oxidation-state hierarchy observed for HRC, i.e. glycidyl phosphates > glycidyl phosphites ≈ glycidyl phosphonates > aminophosphonates > aminophosphine oxide. A catalytic mechanism of solid state P activity that is related to the oxidation state of the P is indicated by the fact that the additional char mass is several times the mass of P. These data obtained on 5 mg samples are the molecular-level response of the epoxy formulations to controlled heating and do not reflect the macroscopic effects observed in flame tests or fires in which char may act as a heat and/or mass transfer barrier (Section 3.7.1 and Section 3.7.3).

Fig. 4 is a plot of the heat release capacity versus anaerobic char fraction for P-containing epoxies for which the P concentration is 1.5 ± 0.2%. It is clear from Fig. 4 that the anaerobic char fraction μ is highly correlated ($R=0.93$) with combustibility/HRC as per Eq. (1) and that glycidyl phosphates are more efficient char promoters than glycidyl phosphonates at a particular P concentration (1.5% w/w in this plot).

Fig. 5 is a plot of specific heat release (total heat of complete combustion of volatile fuel per unit original mass of sample) HR versus P concentration for the diamines and epoxides of this study. The same general ranking is observed for the reduction in HR with regard to P efficiency, i.e. glycidyl phosphate > glycidyl phosphite ≈ glycidyl phosphonate > aminophosphonate > aminophosphine oxide. Although the amount of heat generated per unit mass of epoxy by combustion of the fuel gases decreases with increasing P concentration, this is primarily the result of a reduction in the fuel fraction rather than the heat of combustion of the volatiles (h_c in Eq. (1)). The heat of combustion of the volatiles was calculated as $h_c = \mathrm{HR}/(1-\mu)$ from the data in Fig. 5 (HR) and the data in Fig. 3 (μ) for all of the samples tested for combustibility. Fig. 6 shows the results of these calculations as h_c versus P concentration grouped by P compound. The slight reduction in h_c may be associated with P but it is independent of P concentration above 1.5% w/w. All of the data falls within the relatively narrow range $h_c = 23.2 \pm 1.8$ kJ/g with no systematic variation related to chemical composition of the P-containing compound or the anaerobic char fraction.

3.7.3. Fire behavior

Average peak heat release rates (HRR) and average heat release at 2 min according to 14 CFR Part 25 Appendix F are reported in Table 7 for selected specimens. FAA allowable values are a peak HRR of 65 kW/m^2 over a 5 min test and 65 kW min/m^2 total heat release at 2 min. HRR requirements for exterior composites do not exist at the time of writing. This test procedure is used to certify large-area components in the passenger compartment of a commercial airplane. The OSU test was carried out for screening purposes only. Formulation **G1** which contained no P has an average peak HRR of 97 kW/m^2 which is well above the FAA allowable value for large-area materials used in aircraft cabin interiors. Specimens **G2**–**G3** contain epoxy **5** with P contents ranging from 1.5 to 3.4%. **G2** (1.5% P) and **G3** (3.4% P) show lower peak HRR relative to **G1** of 72 and 51 kW/m^2, respectively. Specimens **G4** and **G5** contain epoxy **8** with P contents of 1.6 and 3.4%, respectively. The heat release rate values for these two specimens were similar at 65 and 63 kW/m^2. The results show that flaming heat release rate of TGMDA/DDS epoxy is reduced by approximately the same factor as heat release capacity (Fig. 2) when P is incorporated at the levels examined. The single ply specimens tested in the OSU fire calorimeter are thin and burn quickly to completion so that charring has little effect beyond reducing the fuel fraction as per the combustibility test (see 4.2.2). Thick specimens provide sufficient mass for copious char formation that can act as a barrier to heat and mass transfer.

Fig. 7 shows cone calorimeter data for 6-mm thick samples of **F1**, **F11**, and **F20** tested at an external heat flux of 50 kW/m^2 in a cone calorimeter according to standard methods [27]. Intumescence began immediately after ignition of formulations **F11** and **F20** containing 1.5% P as epoxides **5** and **8**, producing a voluminous char that reduced the heat release rate to near zero for 1–2 min into the test. In contrast, very little intumescence was observed for the TGMDA/DDS control, **F1**. The intumescent char layer on **F11** and **F20** bursts open at 150 and 220 s, respectively, releasing trapped fuel gases in a violent deflagration. This intumescence at 1.5% P is probably responsible for the ignition resistance to a brief (10 s) flame exposure shown in Tables 1 and 2.

The total integrated heat release rate obtained from oxygen consumption measurements made during the the fire calorimetry tests (OSU and cone) is the effective heat of flaming combustion (HOC). Flaming combustion is never completely (100%) efficient due to the finite residence time of the fuel/air mixture in the combustion zone of the flame which leads to soot formation and incomplete combustion products such as carbon monoxide and unburned hydrocarbons. Combustion is less efficient when gas-phase-active flame retardants are released into the flame during burning. The efficiency of flaming combustion χ is calculated by dividing the effective heat of flaming combustion by the heat of complete combustion of the volatiles from the microcalorimeter tests of the same formulation, i.e. $\chi = \mathrm{HOC}/h_c$. If P is released from the epoxy during burning and enters the

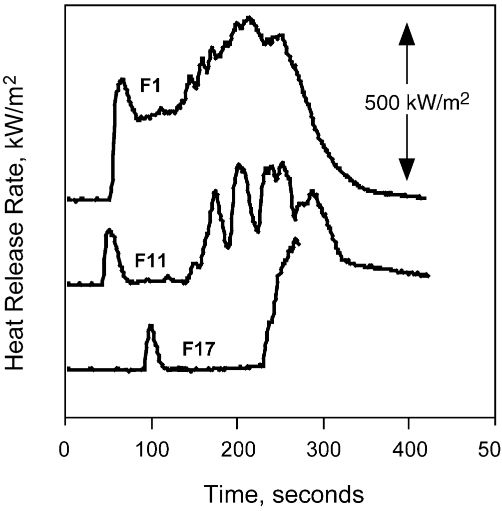


Fig. 7. Fire (cone) calorimeter data at 50 kW/m^2 external heat flux for formulations **F1** (TGMDA/DDS control), **F11** (1.5% P), and **F17** (1.5% P). Complete suppression of heat release rate is observed for **F11** and **F17** for 1–2 min after ignition.

Table 7
OSU test results on single cured epoxy glass ply

Formulation[a]	TGMDA (phr)	P-epoxy (phr)	P (%)	Average peak HRR (kW/m^2)	Average HR (2-min) ($kW\text{-}min/m^2$)
G1	100	–	0	97	29
G2	80	**5**, 20	1.5	72	21
G3	60	**5**, 40	3.4	51	15
G4	80	**8**, 20	1.6	65	18
G5	60	**8**, 40	3.4	63	14

Cured with 80% stoichiometric amount of DDS.

[a] Contain 0.5 phr BF_3-piperazine.

gas phase to inhibit combustion in the flame, then the flaming combustion efficiency should decrease when P is present. The average effective heat of combustion from 40 individual tests of epoxy formulations over a range of P concentration from 0–5% w/w in flaming combustion was HOC = 16.4 ± 2.4 kJ/g. The heat of complete combustion obtained from microcalorimeter tests of the same 40 formulations is $h_c = 23.2 \pm 1.8$ kJ/g with no systematic variation with chemical composition of the P compound. Consequently, the average combustion efficiency for TGDDM/DDS epoxy formulations containing 0–5% w/w P is $\chi = \text{HOC}/h_c = (16.4 \pm 2.4\ \text{kJ/g})/(23.2 \pm 1.8\ \text{kJ/g}) = 0.7 \pm 0.1$. The individual data are shown in Fig. 8 and identified by P-compound as phosphates (open circles), phosphonates (solid circles) or not applicable (e.g. TGMDA/DDS) or not available (N/A) at the time of writing (grey circles). A flaming combustion efficiency of 70% ($\chi = 0.7$) is typical of polymers that generate a lot of smoke during burning, as was the case for these epoxies. There is no discernable effect of P concentration in the solid on the combustion efficiency in the flame within the error of the measurements and calculation indicated by dashed lines in Fig. 8. This data supports the conclusion that P incorporated as P-containing epoxides and diamines (Figs. 3, 4, and 6–8) acts primarily in the condensed phase by promoting char formation. Phosphorus is highly efficient in this regard as the mass of char produced is several times the mass of P incorporated into the polymer. The effect of char at the molecular level is to reduce the amount of combustible fuel.

4. Summary

Phosphorus-containing epoxy formulations were studied as part of a program to develop technology leading to fire retardant exterior structural resins. Phosphorus was introduced as either part of the diamine curing agent or part of an epoxy compound in a typical aerospace epoxy, TGMDA/DDS. The diamines included both phosphonate and phosphine oxide structures while the epoxide compounds included phosphates, phosphite, phosphonates.

Flame resistance, microscale combustibility, and fire behavior were used to assess flammability of P-containing epoxy and diamine formulations. Flame resistance is observed at a P concentration of 1.5% by weight. Fire resistance is observed at P concentration of about 3% by weight, above which TGMDA/DDS epoxies pass the FAA heat release rate test for large area aircraft cabin interior components.

Flaming combustion efficiency was used as a global measure of gas phase activity but did not indicate that P had any significant effect on flame chemistry for the compounds studied. Instead, flammability reduction was attributed to the promotion of charring by P in the condensed phase. Phosphorus appears to act as a catalyst for char formation, i.e. P promotes char but is not consumed in the chemical reactions that form char. Catalytic activity is indicated by (1) the several-fold increase in char mass per unit mass of incorporated P; (2) lowering of the temperature and activation energy for thermal decomposition; (3) saturation of charring at higher P loadings, typically > 3%. The activity of P as a char catalyst is in the same order as the oxidation state of P in the diamine or epoxide, i.e. organophosphate (PO_4) > organophosphite ($:PO_3$) ≈ organo phosphonate (RPO_3) > organophosphine oxide (R_3PO).

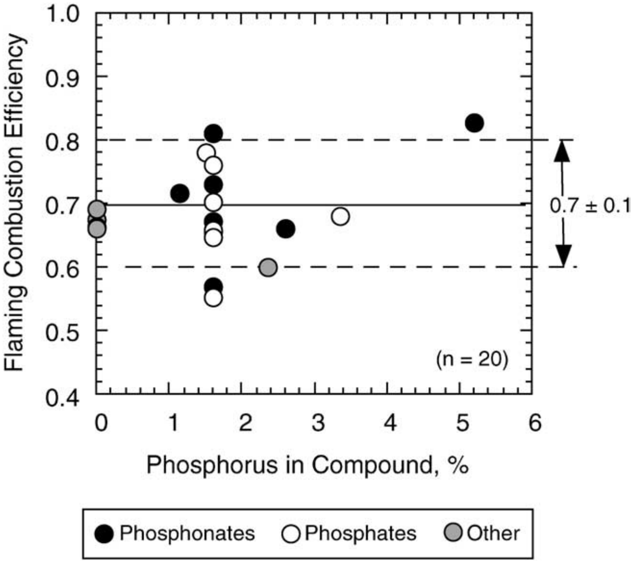


Fig. 8. Plot of flaming combustion efficiency versus phosphorus concentration for TGMDA/DDS control and epoxy formulations containing epoxides **4**, **5**, **6**, and **8**.

This hierarchy could indicate that the active catalyst for char formation is a P oxide or P acid.

Phosphorus incorporated as a reactive component (diamine or glycidylether) into a TGMDA/DDS aerospace epoxy at an effective level for flame resistance ($\sim$1.5% P) has no effect on fracture toughness, compressive strength or compressive modulus with the exception of diglycidylphenylphosphate, which had lower fracture toughness.

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