Flammability of Polymer Composites

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16. Abstract

The flammability and mechanical properties of fiber-reinforced thermoset resin structural composites were evaluated. Processing characteristics, thermal stability, and flammability of the neat resins were measured using rheology, thermogravimetry, and pyrolysis-combustion flow calorimetry, respectively. Structural laminates were fabricated from liquid resins and woven glass fabric by vacuum-assisted resin transfer molding. Single-layer specimens (lamina) were prepared for fire testing using a hand lay-up technique. Mechanical properties of the laminates were measured in three-point bending. Fire behavior of the lamina and laminates was measured according to Title 14 Code of Federal Regulations 25.853(a-1) and Military Standard MIL-STD-2031. Results for flammability, fire performance, and mechanical properties of these composites are presented in this report.

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LIST OF SYMBOLS, ACRONYMS, AND ABBREVIATIONS

BPA	Bisphenol A
BPC	Bisphenol C
CE	Cyanate ester
CFR	Code of Federal Regulations
FAA	Federal Aviation Administration
HR	Heat release
HRR	Heat release rate
MDA	Methylenedianiline
MIL-STD	Military standard
η_c	Heat release capacity
OSU	Ohio State University calorimeter
PCFC	Pyrolysis-combustion flow calorimeter
psi	Pounds per square inch
T_{ig}	Time to ignition
U.S.	United States
VARTM	Vacuum-assisted resin transfer molding

EXECUTIVE SUMMARY

The flammability and mechanical properties of fiber-reinforced thermoset resin structural composites were evaluated. The processing characteristics, thermal stability, and flammability of the neat resins were measured using rheology, thermogravimetry, and pyrolysis-combustion flow calorimetry, respectively. Structural laminates were fabricated from liquid resins and woven glass fabric by vacuum-assisted resin transfer molding. Single-layer specimens (lamina) were prepared for fire testing using a hand lay-up technique. The mechanical properties of the laminates were measured in a three-point bending test. Fire behavior of the lamina and laminates was measured according to Title 14 Code of Federal Regulations 25.853(a-1) and Military Standard MIL-STD-2031. The results for flammability, fire performance, and mechanical properties of these composites are presented in this report.

1. INTRODUCTION.

There is a need for fire-safe decorative panels for aircraft cabin interiors and fire-safe structural composites for warships and submarines. The Federal Aviation Administration (FAA) and the United States (U.S.) Navy have evaluated thermoset resins for these purposes. Recently, both agencies have evaluated polymers based on 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethene (BPC) due to their excellent fire properties. FAA-funded research has investigated these materials as candidate materials for aircraft interiors [1 and 2]. The BPC can be used to synthesize thermoplastics and thermosets [3 and 4] by the same chemical routes used for 4,4[1] dihydroxy-2,2-diphenyl propane (BPA). Studies on the BPA and BPC epoxy show that substituting the dichloroethylene group of BPC for the isopropylidene group of BPA can significantly change the burning characteristics of the polymer while preserving the mechanical properties [5-7]. Previous studies by the U.S. Navy [8 and 9] showed the cyanate ester (CE) of BPC (BPCCE) to have excellent fire properties, and it is one of the few organic matrix materials to pass the Military Standard (MIL-STD)-2031 in a composite form. This report compares the fire and mechanical performance of BPC thermoset resin composites to their BPA analogs, a developmental silicone resin composite, and a commercial, toughened epoxy resin aerospace composite for structural applications.

CEs are of interest due to their facile-processing characteristics and additional cure mechanism that produces no volatiles [10]. They are also of interest due to their high strength, thermal stability, and high char yield when burned [11-15]. The BPC version of this polymer is desirable for applications where extreme fire resistance is required. FAA studies on the BPC-containing polymers indicated very good fire performance due to the low fuel value of the evolved gases during thermal degradation and high char yield. The decomposition mechanism for BPC-containing polymers, according to Ramirez [16], involves dehydrochlorination and rearrangement to a phenyl acetylene, which then cyclizes to form a highly aromatic, thermally stable char structure. The combination of halogen free-radical scavenging by hydrogen chloride in the gas phase along with copious char formations make BPC polymers ideal for composite applications where fire safety is a consideration.

2. EXPERIMENTAL.

2.1 MATERIALS.

All materials were used as-received from the manufacturer without further modification other than curing the liquid resins. Gases used were 99.999% pure and were obtained from Welco-CGI Gas Technologies, LLC. Figure 1 shows the structures for the unreacted BPA and BPCCE and epoxies.
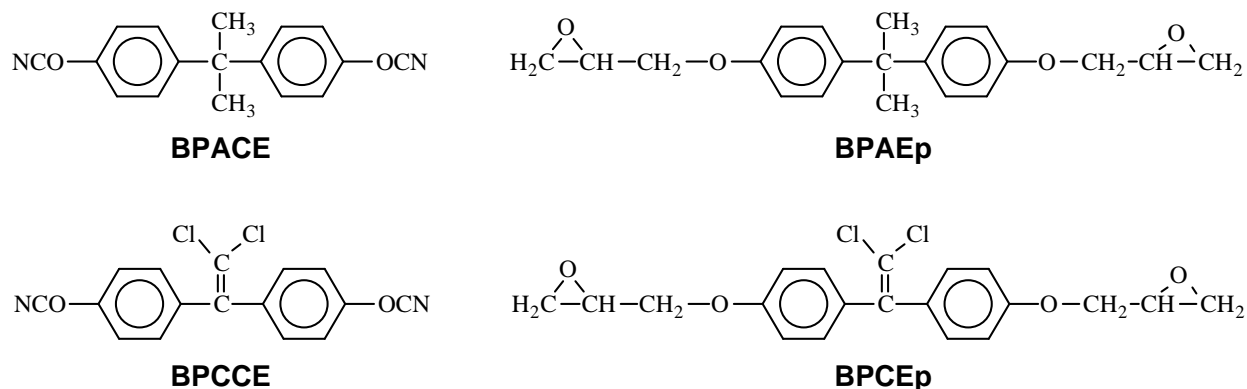
EP = Epoxy

Figure 1. Structures of the Unreacted Resins

In this study, the CEs were thermally cured without a catalyst, which involves cyclotrimerization of three cyanate groups to form the crosslinked cyanurate network [10]. The epoxy resins were cured with the addition of 1% by weight of an ethyl methyl imidazole catalyst (EMI-24) and cured by an anionic ring-opening polymerization [17]. The epoxy was also reacted with methylenedianiline (MDA) in a stoichiometric amount to produce an epoxy-amine network [18 and 19].

Two commercial resin systems were examined in this study. A toughened, low-viscosity, two-part silicone resin (0-3015 DEV Sample, Dow Corning Corporation) was cured with 0.5 weight percent catalyst (0-3030 DEV Sample, Dow Corning Corporation). A commercial, toughened, carbon fiber-reinforced aerospace epoxy composite (UD T800S/3900, Toray Composites America, Inc.) obtained as a cured, 16-ply, quasi-isotropic laminate fabricated by Integrated Technologies, Inc., Everett, WA, was tested as-received.

2.2 SAMPLE PREPARATION.

Vacuum-assisted resin transfer molding (VARTM) was used to fabricate composite panels for this study. A cylindrical pressure vessel outfitted with thermocouples, valves, and heaters was constructed as shown in figure 2. An excess of liquid resin was heated (if necessary), degassed, and added to the preheated pressure vessel through the top. The apparatus was then sealed, connected to the preheated tool already in the heated press, and pressurized with 5-20 pounds per square inch (psi) of nitrogen to force the resin out of the vessel and into the tool.

The tool used was a large, flat, Teflon®-coated aluminum plate outfitted with compression fittings for the resin infusion and vacuum connections. The composite panels were prepared by stacking 18 layers of glass fabric (Style 3783, 8HS weave, 16.15 oz/yd^2) on the plate, which gave a cured panel thickness of approximately 6 mm (~1/4 inch). The perimeter of the aluminum plate was fitted with high-temperature tacky tape. A Teflon-coated release fabric was placed over the top of the stacked glass and a high-temperature vacuum bag was placed over that and was used to seal the tool assembly (figure 2). The panels then had a 500-mm (20-inch) mercury vacuum pulled to aid the resin infusion and minimize voids in the composite matrix. After the resin completely wetted the glass, the press was closed and set to 150 psi for the remainder of the cure.

Samples were cured in a large, heated press (manufactured by PHI), per the cure schedule suggested by the manufacturer of the respective resins.
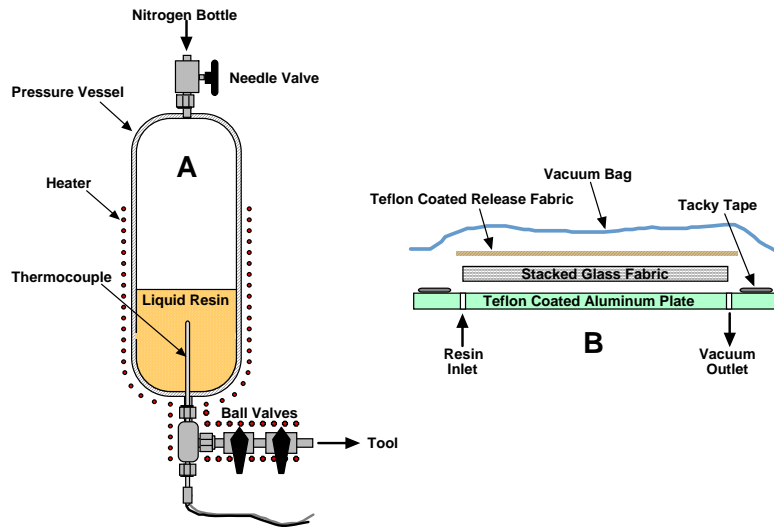

Figure 2. Schematic of VARTM Apparatus (A) Pressure Vessel (B) Tool

The lowest possible temperature was used for the resin infusion step to ensure the sample did not cure too quickly while keeping the resin viscosity low. Once the resin was completely infused with the glass inside the press, the samples were heated to curing temperatures. Several different resins were used to prepare large and small panels for comparing the flammability and mechanical strengths. All the samples were prepared using approximately the same method.

After the composite panels were cured in the press, they were removed from the tool and vacuum bag. The samples were then postcured in a large convection oven to ensure completion of the cure. Samples for all the tests were cut on a table saw using a diamond-tipped saw blade, which produced straight and smooth cuts that minimized edge effects in the mechanical tests. Samples for the mechanical tests were taken from the visibly nicest section of the cured composite panels to ensure a minimum of voids. The VARTM setup described earlier worked fairly well. The pressure forced the resin into the tool, and the vacuum helped pull it through the stacked glass fabric. A squeegee was used to expedite the resin infusion, which made sure all the glass was wetted and a uniform resin front moved across the tool and sample. Once the resin had completely covered the stacked glass, the press was closed and the temperature was increased to effect cure. The resulting panels were uniform and had resin volume fractions ranging from 28.9% to 44.2%, with an average of 37.8%. Panel sections containing visible voids were avoided when cutting samples for the mechanical tests.

2.3 RHEOLOGY.

Isothermal viscosities of liquid resins were measured as the complex viscosity on a rheometer (RDA II, Rheometrics Scientific) using 50-mm (2-inch) parallel plates with a 0.5-mm (0.020-inch) gap at a strain of 10% in dynamic time sweep mode at 1 Hz in the temperature range of 25° to 100°C.

2.4 FLAMMABILITY.

A pyrolysis-combustion flow calorimeter (PCFC) was used to screen resins for flammability in this study [20-22]. In the PCFC test, approximately 5 mg of the cured resin sample is weighed in a ceramic sample cup, which is placed on a platform with an embedded thermocouple and heated at 1°C/s under nitrogen to a maximum sample temperature of 900°C. The volatile thermal decomposition products are purged from the sample chamber and combined with excess oxygen in a 900°C combustor to affect complete oxidation. Water is scrubbed from the combustion gas stream, and the heat release rate (HRR) is calculated from the oxygen depletion and the flow rate measurements [23 and 24]. The primary flammability characteristic determined in the test is the heat release capacity, η_c [25 and 26], which is the maximum HRR divided by the sample mass and heating rate.

2.5 MECHANICAL PROPERTIES.

Flexural strength and stiffness of composite laminates were determined in a three-point bending test on a universal testing machine (Model 4400, Series 1125, Instron Corporation) using a 5-kN load cell according to ASTM D 790-95a [27]. Dimensions of the sample bars for all flexural tests measured approximately 6 by 12 by 150 mm (0.24 by 0.47 by 6 inches). Dimensions for the aerospace epoxy composite were approximately 3 by 12 by 150 mm (0.12 by 0.47 by 6 inches). The three-point bend fixture had rollers with a 6-mm radius, and the span length was set to 100 mm. A crosshead speed of 2.8 mm/min (0.11 inch/min) was used for all tests. To obtain an average value, five duplicate tests were performed for each sample.

2.6 FIRE CALORIMETRY (14 CFR 25.853).

The HRR was measured in the Ohio State University calorimeter (OSU) according to FAA Title 14 Code of Federal Regulations (CFR) Part 25.853(a-1) [28]. The OSU is a bench-scale fire calorimeter that requires a 15- by 15-cm (6- by 6-inch) vertically mounted sample. After thermal equilibration for 1 minute in a holding chamber, the specimen is inserted into the test chamber where it is exposed to a 35-kW/m^2 radiant heat flux with a pilot flame impinging on the lower sample surface. Samples tested using the OSU were either single-ply glass lamina prepared by using a hand lay-up technique, as routinely used to screen resins for fire performance [29 and 30]; or structural laminates prepared by VARTM, as required by the U.S. Navy [31]; or obtained from suppliers.

2.7 FIRE CALORIMETRY (ASTM E 1354).

The cone calorimeter (ASTM E 1354) [32] was used to test fire performance per MIL-STD-2031 [33] at radiant heat fluxes of 25, 50, 75, and 100-kW/m^2. MIL-STD-2031 fire response parameters include the peak and average HRRs (kW/m^2) and the time to ignition (T_{ig}) (seconds) as well as the type and amount of combustion gases produced at a 25-kW/m^2 incident heat flux. Due to the limited amount of samples, only the BPCCE was tested at the MIL-STD-2031 heat fluxes. All other samples discussed in this report were only tested at a radiant heat flux of 50 kW/m^2.

3. RESULTS AND DISCUSSION.

3.1 RHEOLOGY.

Resin viscosities varied over a wide range. Several common resins were tested for comparison to literature values and were found to be within the reported ranges [34]. The BPACE and BPCCE resins are crystalline at room temperature and have melting points of 92° and 75°C, respectively, as determined by differential scanning calorimetry. Once the resin is melted, it remains liquid until a nucleation site is introduced. The recrystallization of the BPACE is rapid and exothermic, while the BPCCE is slow, on the order of days. The liquid resins have very different viscosities. The BPACE has a very low viscosity, while the BPCCE is fairly viscous at room temperature. Figure 3 shows a plot of the resin viscosity as a function of set point temperature.
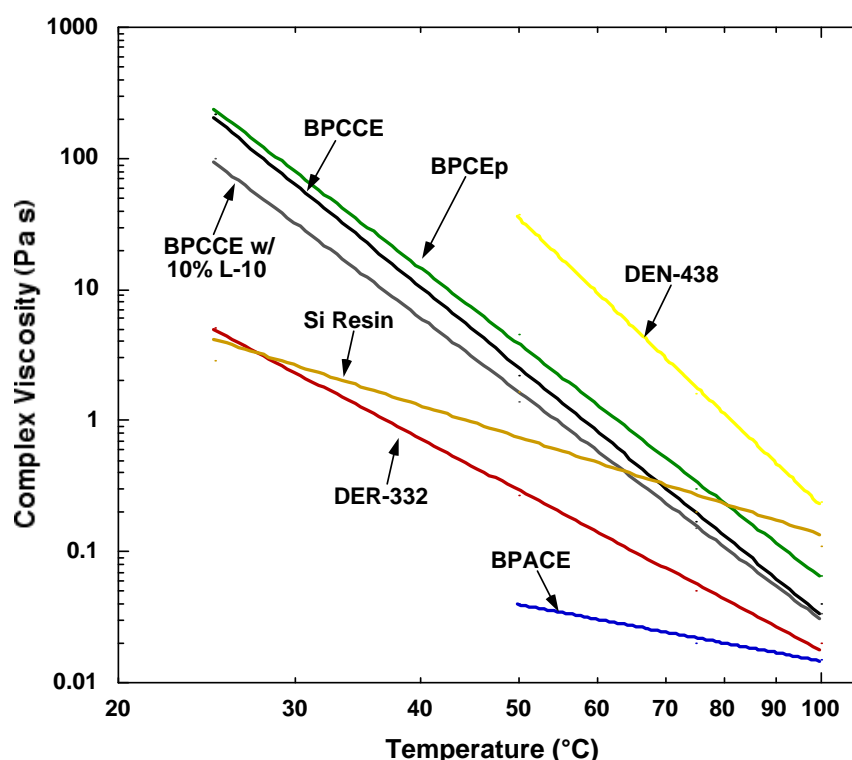
Figure 3. Viscosity of Several Thermoset Resins as a Function of Temperature

The viscosity of the BPCCE fell in the middle of the resins tested. Adding 10% of bisphenol F CE (L-10, Vantico) reduced the viscosity of the BPCCE by more than a factor of two. Values for the viscosity of the BPACE at 25°C could not be obtained due to the sample recrystallizing, and the viscosity of the Dow Chemical Company epoxy novolac resin (DEN-438) at 25°C was too high and was out of the range of the transducer. The silicone resin was tested without the addition of the hardener to prevent curing during the test.

3.2 FLAMMABILITY.

Thermogravimetry shows the effect on thermal stability with the substitution of the dichloroethene for the isopropylidene group in the epoxy and CE. Both the onset and peak decomposition temperatures are lowered with the inclusion of the dicloroethyl group, as shown in table 1. However, there is a boost in the char yield and a decrease in the rate of heat release (HR) and the heat of combustion of the evolved gases found by PCFC, also shown in table 1. The BPCCE is among the least flammable of the materials tested in this study and the many plastics that have been tested by PCFC [35].

Table 1. Small-Scale Thermal Analysis and Flammability Results

	TGA-10°C/min			PCFC		
Resin	Onset (°C)	Tp (°C)	Char (%)	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)
BPC Epoxy	342	345	46.8	766	6.2	39.9
BPA Epoxy + MDA	373	384	16.2	618	23.8	12.7
BPA Epoxy	411	432	9.5	502	24.8	7.1
BPA CE	428	440	41.9	341	14.8	42.4
Aerospace Epoxy*	374	403	73.3	96	6.8	72.2
Silicone Resin	490	543	77.4	85	8.9	77.5
BPCCE	422	437	55.1	10	1.2	61.5

*Composite used in analysis   Tp = Peak pyrolysis temperature
TGA = Thermal gravimetric analysis   K = Kelvin

3.3 MECHANICAL PROPERTIES.

The flexural test results, according to ASTM D 790-95a for the 18-ply laminates, are shown in table 2. All values listed are the average of five duplicate tests, unless otherwise indicated. All samples tested had similar flexural strengths. Sample failures occurred by a combination of tension and compression except for the resin-rich sample of BPC epoxy, which failed by shear. The aerospace composite sample was tested as-received from the manufacturer at a thickness of 3 mm and having carbon fiber reinforcement. All other samples had a thickness of approximately 6 mm and continuous glass fiber reinforcement.

Table 2. Flexural Strengths of Laminates

	Mechanical Properties—3-Point Flex Test		
Resin	Yield Stress (MPa)	Yield Strain (%)	Flexural Modulus (GPa)
Aerospace Epoxy*	795.7	1.83	46.7
BPA Epoxy	622.4	2.31	28.8
BPACE	571.3	1.84	31.7
BPCCE	519.6	2.22	26.0
BPA Epoxy + MDA	502.0	1.63	31.8

Table 2. Flexural Strengths of Laminates (Continued)

Resin	Mechanical Properties—3-Point Flex Test		
	Yield Stress (MPa)	Yield Strain (%)	Flexural Modulus (GPa)
BPC Epoxy**	486.1	2.10	24.8
Silicone Resin	222.5	1.14	23.5

*Sample was tested as received in 3-mm thickness
**Result from a single test due to a limited amount of sample
MPa = Mega Pascals
GPa = Giga Pascals

3.4 FIRE CALORIMETRY (14 CFR 25.853).

The BPCCE composites showed very good fire performance when compared to the BPACE and epoxy panels. The BPCCE easily passed the required 65-kW/m^2 peak HRR at 5 minutes and the 65-kW-min /m^2 total HR in 2 minutes (65/65) as both single- and 18-ply laminates, while the epoxies did not, as shown in table 3. The single-ply samples showed good response and separation in the test. A range of peak HR values were obtained with the lowest being the two BPC materials and the silicone resin.

Table 3. Heat Release Data From the OSU, 14 CFR 25.853(a-1)

Resin	OSU at 35-kW/m^2 Irradiance					
	Single-Ply Lamina			Multiple-Ply Laminates		
	Peak HRR (kW/m^2)	2-min Total HR (kW/m^2 min)	Char* (%)	Peak HRR (kW/m^2)	2-min Total HR (kW-min/m^2)	5-min Total HR (kW-min/m^2)
BPA Epoxy + MDA	88	26	5.6	216	-11	350
BPA Epoxy	111	44	1.9	168	-13	324
Aerospace Epoxy	NA	NA	NA	146	83	342
BPACE	72	28	16.3	139	-18	171
BPC Epoxy	48	28	14.1	102	-3	201
BPCCE	13	13	26.8	11	-13	-14
Silicone Resin	33	12	NA	0	-0.6	-1

*Char yield based on resin fraction
NA = Not available

Figure 4 shows the HRRs for the first 3 minutes of the 14 CFR 25.853 test. The BPCCE has a near-zero peak HRR and negligible HR. The silicone resin also performed very well in the single-ply configuration. The char yield listed in column 4 of table 3 is based on the resin fraction of the composite and was obtained by subtracting the weight of the glass from the sample weight measured before and after the test. The aerospace composite was received as a cured laminate and could not be tested in the single-ply configuration.
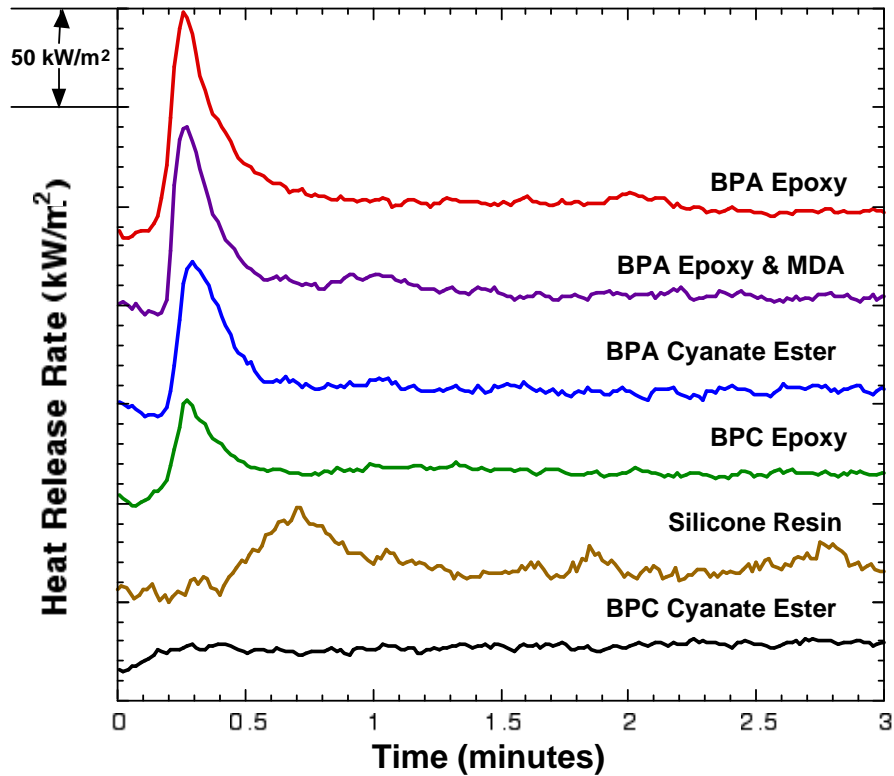
Figure 4. Heat Release Rates of Single-Ply Composite Panels in the OSU at 35 kW/m^2

All the composite laminates showed good performance early in the test up to about 2 minutes. After that, the impinging pilot flame ignited all the samples, excluding the BPCCE and silicone resin. Once the samples ignited, they burned readily for the remainder of the test. The values for the 18-ply polymer composites in table 3 are the 14 CFR Part 25 values for maximum HRR during the first 5 minutes and the average HR during the first 2 minutes, as listed in 14 CFR 25.853(a-1). The last column of data is the 5-minute total HR. This shows that after the samples ignited at approximately 2 minutes they released a considerable amount of heat. The long delay to ignition can be attributed to the sample thickness. Single-ply samples tested in the OSU were less than 0.5 mm thick, whereas the structural composite panels were approximately 6 mm thick and, therefore, took longer to reach the ignition temperature. The 2-minute average is expressed as a negative number, because the samples remove heat from the system before ignition. This is due to the OSU measuring HR by a temperature rise method. Although all the structural composite samples, except for the aerospace composite, passed the 2-minute average HRR requirement, all but the BPCCE and silicone resin failed the criteria for the peak HRR within 5 minutes.

The OSU is not a research instrument. It is mainly used for production qualification and FAA certification of large surface area cabin materials in commercial aircraft. Some of the structural composites were a larger fire load than the test method was designed for, and the tests were stopped before the samples were done flaming.

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3.5 FIRE CALORIMETRY (ASTM E 1354).

Few organic resin composite materials pass the MIL-STD-2031 due to the severity of the test and the high-performance requirements. Consequently, MIL-STD-2031 tests in the cone calorimeter were only performed on the BPCCE. All other laminates were tested in the cone calorimeter at a radiant heat flux of 50 kW/m^2. The results from these tests are shown in table 4.

Table 4. Multiple-Ply Laminate Heat Release Data From the Cone Calorimeter at 50 kW/m^2

Resin	Cone Calorimeter at 50-kW/m^2 Irradiance				
	Peak HRR (kW/m^2)	Avg. HRR (kW/m^2)	Total HR (MJ/m^2)	t_{ig} (s)	Char* (%)
Aerospace Epoxy	302	182.0	29.3	61	NA
BPA Epoxy	155	77.5	36.4	102	24.5
BPACE	118	24.2	13.3	129	52.1
BPA Epoxy + MDA	107	77.9	33.6	110	40.0
BPC Epoxy	77	51.0	26.9	74	44.3
Silicone Resin	74	47.9	23.0	259	82.7
BPCCE	8	-2.4	0.3	NI	62.4

*Based on resin fraction of composite   NI = No ignition
MJ = Mega Joules   NA = Not available

All samples ignited and burned completely at a 50-kW/m^2 heat flux with the exception of the BPCCE, as shown in figure 5. The BPCCE had no ignition during the 10-minute exposure to the radiant heat flux. There was some variation in the results due to nonuniformity of each sample; however, the burning character of each material was completely different. The BPA epoxy ignited and burned steadily for about 4 minutes with a large flame that gradually went out. The BPA/MDA epoxy sample ignited, burned with a steady increase in the HRR, then decreased. The BPC epoxy ignited, burned steadily, then rapidly increased, shooting flames out the sides of the holder and up and around the cone heater. The flames rapidly died down and the sample continued to flicker until about 9 minutes into the test. The BPACE ignited and burned steadily through small jets distributed uniformly over the surface, then gradually decreased until it flickered and eventually extinguished at 8 minutes into the test. The BPCCE sample gradually turned black with slight off-gassing above, and eventually below, the sample holder. The average HRR of the BPCCE is expressed as a negative number due to the sample not igniting and evolving mostly noncombustible gases. The results in table 4 for peak HRR correspond to the first peak after ignition. Peaks occurring later in the test, for some materials, were larger due to heat reradiating from the back of the samples as the thermal wave passed through them. The BPC epoxy performance must be weighted when compared to the others due to a 7% to 15% larger resin fraction in the resulting composite. The resin's high flammability can be attributed to the large aliphatic groups between aromatic rings. Since there was a limited supply of the BPC epoxy, only one sample was prepared and tested. The silicone resin took almost 5 minutes to ignite then burned steadily with a low HRR until it diminished and self-extinguished about 10 minutes later. The aerospace composite ignited in about 1 minute, burned rapidly for about 2 minutes, and self-extinguished within 5 minutes.
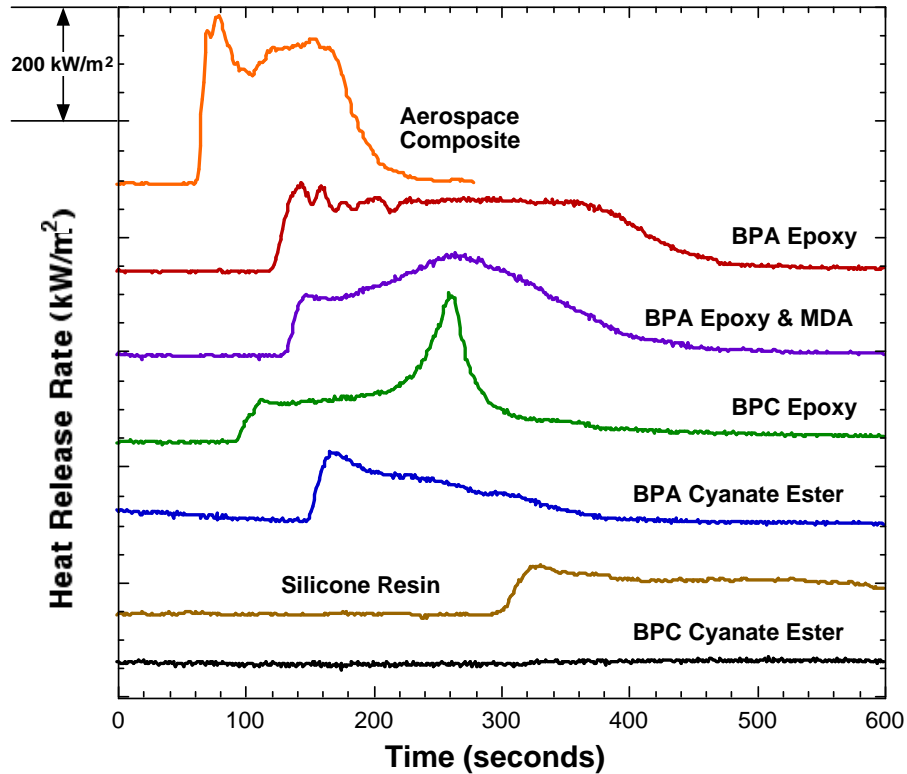
Figure 5. Heat Release Rates of the Multiple-Ply Composite Panels in Cone Calorimeter at 50 kW/m^2

The BPCCE structural composites were also tested at 75- and 100-kW/m^2 heat fluxes. The results for the peak HRR and the T_{ig} were almost identical to those obtained by Koo [8]. Results at 100 kW/m^2 for the T_{ig} was 145 seconds, and the peak HRR was 48.1 kW/m^2. The BPCCE samples performed better under a 100-kW/m^2 heat flux than the other samples at a 50-kW/m^2 heat flux. The residual BPCCE samples still retained some strength after the 100-kW/m^2 test.

4. CONCLUSIONS.

It has been demonstrated that high flexural strengths, similar to those of epoxies, can be achieved with the bisphenol-C (BPC) cynate ester (CE) when prepared using vacuum-assisted resin transfer molding. This study showed the BPCCE glass fiber-reinforced laminates had comparable mechanical properties to epoxy resin laminates in contrast to previous results.

The BPCCE resin satisfies the fire performance requirements for both large surface area decorative panels in commercial aircraft and structural polymer composites for United States Navy ships and submarines as an unmodified resin containing no fillers or additives to reduce flammability, improve mechanical properties, or enhance processing characteristics.

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