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ATSB RESEARCH AND ANALYSIS REPORT

Aviation Safety Research Grant – B2004/0046

Final

Fire Safety of Advanced Composites for Aircraft

A.P. Mouritz

School of Aerospace, Mechanical & Manufacturing Engineering, RMIT University

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Abstract

Fire contributes to aircraft accidents and many fatalities. The growing use of polymer composite materials in aircraft has the potential to increase the fire hazard due to the flammable nature of the organic matrix.

This report assesses the fire hazard of current and next-generation polymer composites for aircraft, and identifies those materials with improved flammability resistance. A comprehensive review of the scientific literature was performed to develop a database on the fire properties of a large number of polymer composite materials. For both aircraft cabin materials and aircraft structural materials the following fire properties were considered in the determination of fire safety: time-to-ignition, limiting oxygen index, peak heat release rate, average heat release rate, total heat release, flame spread rate, smoke, and combustion gases. The data is presented as performance tables which rank the composite materials in order from best to worst.

The composite most often used in pressurised aircraft cabins is glass/phenolic, and the database shows that this material has excellent fire reaction performance and that very few next-generation composites display superior properties. The most used structural composite is carbon/epoxy, and this material has poor fire resistance and can pose a serious fire hazard. A number of advanced structural composites with superior fire properties are identified, including materials with high temperature thermoset polymer, thermoplastic or inorganic polymer matrices.

EXECUTIVE SUMMARY

Fire contributes to aircraft accidents and many fatalities. The growing use of polymer composite materials in aircraft has the potential to increase the fire hazard due to the flammable nature of the organic matrix.

The polymer composite most often used in the external structures of aircraft is carbon/epoxy, which is a flammable material that easily ignites and burns when exposed to fire. A large percentage of the cabin interior of wide-bodied passenger aircraft is made using composite materials, mostly glass/phenolic. Phenolic composites have good flammability, but newer materials are being developed that offer the promise of increasing the fire safety of aircraft cabins. In fact, a large number of new composite materials are being developed for cabins and external structures that have the potential to increase the fire safety of aircraft, but a detailed analysis of the fire performance of these materials against conventional materials now used in aircraft has not been performed. Such an evaluation will provide a clear indication of the potential improvements in fire safety by using new fire resistant composites in aircraft.

This report assesses the fire hazard of current and next-generation polymer composites for aircraft, and identifies those materials with improved flammability resistance. A comprehensive review of the scientific literature was performed to develop a database on the fire properties of a large number of polymer composite materials. For both aircraft cabin materials and aircraft structural materials the following fire properties were considered in the determination of fire safety: time-to-ignition, limiting oxygen index, peak heat release rate, average heat release rate, total heat release, flame spread rate, smoke, and combustion gases. The data is presented as performance tables which rank the composite materials in order from best to worst.

The composite most often used in pressurised aircraft cabins is glass/phenolic, and the database shows that this material has excellent fire reaction performance¹ and that very few next-generation composites display superior properties. The most used structural composite is carbon/epoxy, and this material has poor fire resistance and can pose a serious fire hazard. A number of advanced structural composites with superior fire properties are identified, including materials with high temperature thermoset polymer, thermoplastic or inorganic polymer matrices.

¹ Fire reaction performance is a measure of a material's resistance to combustion as determined by a range of parameters such as time-to-ignition, heat release rates, limiting oxygen index, etc.

Fire is a major safety hazard for civil, commercial and military aircraft. In-flight fire is ranked at the fourth highest known contributing cause of fatalities arising from accidents involving commercial jet aircraft ². The Federal Aviation Administration (FAA) believes that if aircraft accident rates continue at a constant rate, then death due to fire will increase at 4% per annum in-line with the growth in air passenger traffic ³.

Without careful management and strict safety regulations, the risk of aircraft fires could increase with the growing use of fibre reinforced polymer composite materials in aircraft. Many polymer composites rapidly ignite when exposed to fire and generate high amounts of heat, blinding smoke and choking fumes. The careful selection of fire resistant composite materials is essential to aircraft safety.

This report and associated website are designed to allow aviation safety authorities, aerospace design engineers, fire safety engineers and aircraft operators to better understand and evaluate the flammability and fire properties of polymer composite materials. The website contains a comprehensive database on the fire properties of polymer composites. The data is presented as a series of 'fire performance tables' that rank the fire properties of composites from best to worst.

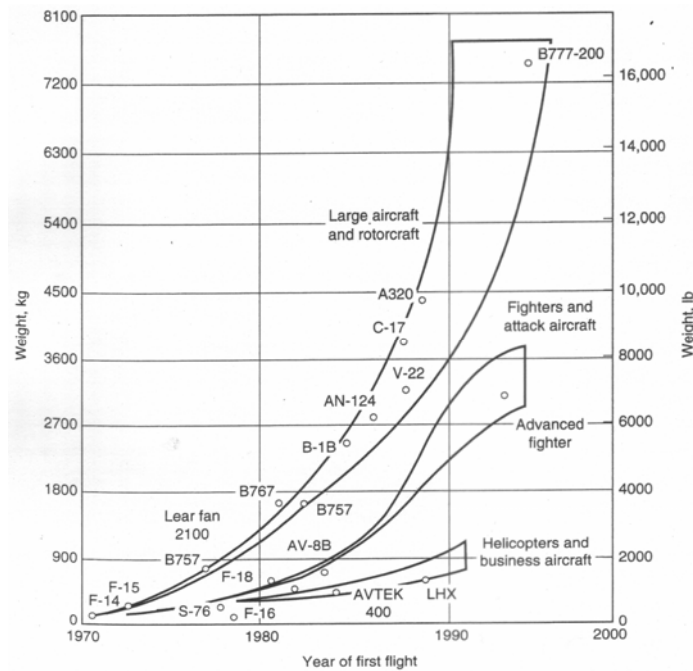
² Boeing 2005, *Statistical summary of commercial jet airplane accidents – worldwide operations 1959-2004*, Seattle, Washington, US, p. 18 [This report excludes airplanes manufactured in the Confederation of Independent States – the former Soviet Union].

³ Federal Aviation Administration (US) website
<<http://www.fire.tc.faa.gov/research/summary.stm>> viewed 10 April 2006.

2.1 Composite applications in aircraft

The amount of polymer composite material used in aircraft and helicopters has risen dramatically since the 1970s. The rapid growth in the use of composites in large civil aircraft, military aircraft and rotorcraft is shown in figure 1. In all three classes of aircraft the use of composites has increased many-fold over the past thirty years, and this trend is set to continue as these materials continue to replace aluminium and other aerospace alloys in primary structures and control surfaces.

Figure 1: Composite aircraft structure by weight



Source: M. Wilhelm, 'Aircraft applications', ASM Handbook, Vol 21: Composites, ASM International, 2001

The value of aircraft components made using composite materials in 2004 is estimated at over \$130 billion. The market value is expected to grow in coming years provided, among other things, composites do not pose an increased fire safety hazard to aircraft. Boeing and Airbus – the two largest aerospace companies – expect the amount of composites used in their aircraft to increase in the next 10 to 15 years. The percentage of the structure of large passenger aircraft made using composites is currently 5 to 10%, although this is projected to increase to over 20% and possibly higher. Both the new A380 and B787 aircraft will make extensive use of composite materials. The use of composites in cabins is expected to increase with their growing use in passenger electronics and telecommunications equipment.

The growth in the usage of composites is due to several factors, most notably:

- light weight
- high specific stiffness and specific strength

- fatigue endurance
- design flexibility
- corrosion resistance.

There are many varieties of composite materials used in aircraft, although the two most common types are:

Glass reinforced phenolic composites that are used extensively in aircraft cabins. Phenolic composites are used as either a single skin laminate or as a sandwich material that consists of thin glass/phenolic face skins over a Nomex honeycomb core. Phenolic composites account for 80%-90% of the interior furnishings of modern passenger aircraft. These composites are used in ceiling panels, interior wall panels, partitions, galley structures, large cabinet walls, structural flooring and overhead stowage bins. An important reason for the extensive use of phenolic composites inside cabins is their low flammability and good fire resistance.

Carbon reinforced epoxy composites are used in aircraft structures including fuselage, wing and tail fin components, control surfaces and doors. As with phenolic composites, epoxy composites are used as either carbon/epoxy laminates or sandwich materials containing carbon/epoxy skins and a Nomex or aluminium honeycomb core. Most types of carbon/epoxy laminates used in aircraft structures are flammable and readily decompose when exposed to heat and fire.

Flame retardant epoxies and other fire-resistant polymers are being used increasingly in carbon fibre composite aircraft structures; however these materials are often much more expensive and may not have the same mechanical performance as conventional aerospace-grade epoxies.

The data presented in this report compares the fire performance properties of a wide variety of polymer composite materials against the benchmarks of the glass/phenolic and carbon/epoxy materials currently used in aircraft.

2.2 Fire hazard to aircraft

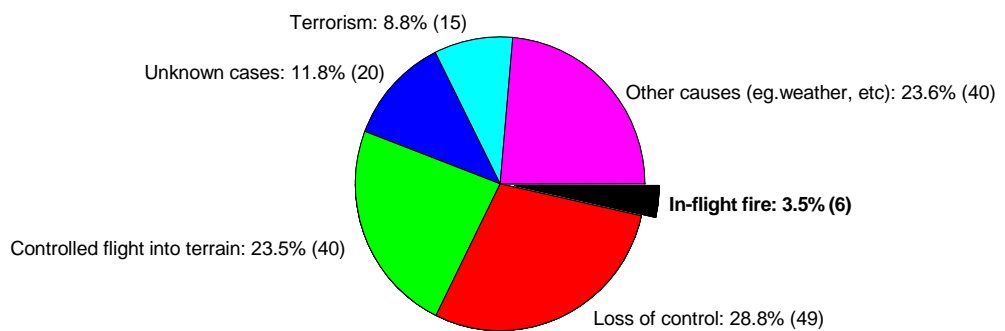
Aircraft fire safety is a high priority with aviation safety authorities and, of course, the flying public. A major hazard with the use of many types of polymer composite materials in aircraft cabins and structures is their flammability. When composites are exposed to high temperatures (typically above 300-400°C) the organic matrix decomposes with the release of heat, smoke, soot and toxic volatiles. Organic fibres used to reinforce composites, such as aramid and polyethylene, also decompose and contribute to the generation of heat, smoke and fumes. Composites also soften, creep and distort when heated to moderate temperature (>100-200°C), and damage caused by the heat and flame can cause distortion, buckling and failure of load-bearing structures. The heat, smoke and gases released by a burning composite and the degradation in structural integrity can quickly jeopardise the safety of an aircraft. The susceptibility of many conventional composites to fire has been the key issue in curtailing their use in many aircraft applications.

Aircraft fires are extremely hazardous because there is little time to combat and extinguish the fire before the crew and passengers are in danger. The hazard is extremely severe in the event of cabin flashover, which may occur within several minutes without the use of appropriate fire resistant materials. As a guide, when fire occurs in the cargo-hold, the pilots have about two minutes to extinguish the flames. If it takes longer than this, the fire will often grow too large to extinguish using on-

board fire-suppression systems. If the aircraft has an extinguishable fire, the pilots have about 14 minutes to land/ditch and evacuate before the risk of incapacitation from smoke and fumes.

The pie-chart in figure 2 shows the causes of fatal wide-body passenger aircraft accidents over a ten-year period (from 1987 to 1996). Over this time there were 180 accidents, but only six (or 3.5%) of these were caused by fire. During this period, in-flight fire was the tenth most common cause of aircraft accidents. Fire is a rare event because of the strict fire safety regulations and effective flame suppression systems in aircraft⁴.

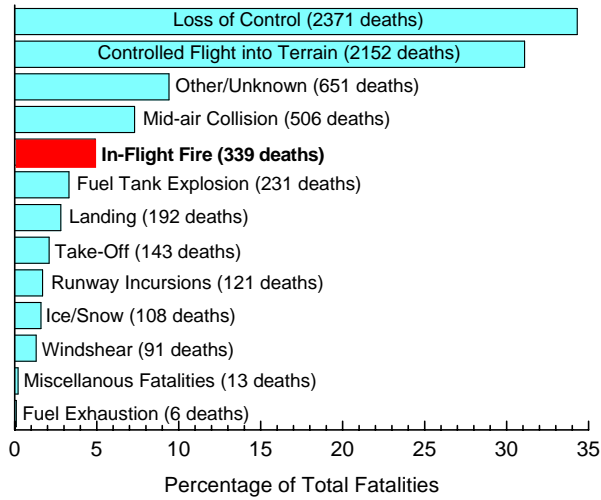
Figure 2: Causes of fatal wide-body passenger aircraft accidents between 1987 and 1996; the number for the different causes is shown in brackets (source FAA)



Despite the relatively small number of aircraft accidents caused by fire, another telling statistic is that fire is the fourth highest cause of fatalities (excluding accidents due to unknown causes). Figure 3 gives a breakdown of the causes of aircraft fatalities between 1992 and 2001 when 339 people were killed (4.9% of all fatalities) by in-flight fire. These statistics highlight the danger that in-flight fire poses to aircraft safety, and the tragically high death toll it can cause.

⁴ Data used in this section and presented in Figures 2 and 3 was sourced from the FAA website in May 2003 <<http://www.faa.gov>>.

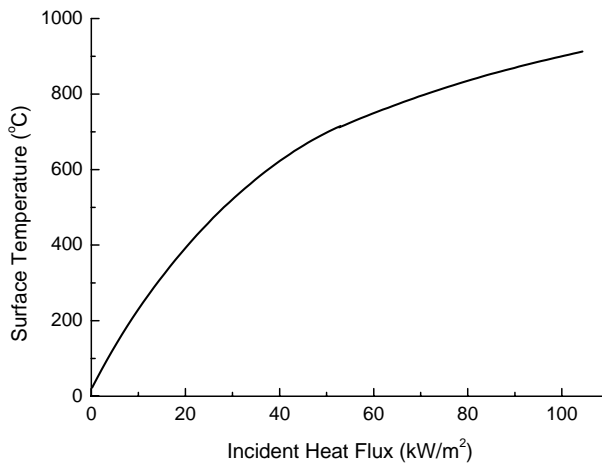
Figure 3: Fatalities resulting from passenger aircraft accidents between 1992 and 2001; the number of fatalities for the different causes of accidents is shown in brackets (source FAA)



It is common practice by fire scientists to quantify the intensity of a fire by the radiant heat flux rather than flame temperature. Figure 4 shows the relationship between heat flux and temperature at the hot surface of a polymeric material. There is an approximate relationship between fire type and heat flux, and examples are:

- small smouldering fire: 2-10 kW/m²
- trash can fire: 10-50 kW/m²
- cabin fire: 50-100 kW/m²
- post-flashover cabin fire: >100 kW/m²
- jet fuel fire: 150-200 kW/m².

Figure 4: Relationship between heat flux and surface temperature of a polymer material



2.3 FAA fire safety regulations

The FAA determines the fire safety regulations on the materials used in US designed and manufactured civil aircraft. These regulations are generally applied across the global aviation sector, including within Australia. Aircraft fires fall into three categories: ramp, in-flight and post-crash. Ramp fires occur when an aircraft is parked at the terminal ramp, and the incidence of fire in this state is very low. The fire hazard is much more common during flight, such as occurred to Swissair 111 on 2 September 1988⁵, or, in particular, post-crash. For this reason, the FAA regulations consider the fire, smoke and toxicity properties of cabin materials for a post-crash fire scenario. The scenario dictates that passengers must be able to escape a large, wide-body aircraft within five minutes of a crash landing without being incapacitated, injured or hindered by heat, toxic fumes or smoke released from combustion of the cabin materials.

All non-metallic materials used inside the pressure vessel of commercial aircraft are subject to the FAA flammability regulations. There are several fire tests mandated by the FAA to assess the flammability and fire performance of materials, and these are specified in FAR 25.853. The key fire properties considered by FAR 25.853 are total heat release, heat release rate and smoke emission. The FAA sets performance limits for heat and smoke on cabin materials to delay cabin flashover and thereby increase the escape time for passengers. Cabin flashover is a fire event characterised by ignition of the hot smoky layer below the cabin ceiling that contains incomplete combustion products released by the burning and smouldering cabin materials. When flashover occurs the cabin temperature rises rapidly, the flames spread rapidly, and the chances of survival for passengers and crew are virtually non-existent. The FAA also specifies other fire regulations for ignition resistance and flame propagation using the traditional Bunsen burner test.

The FAA mandates that the heat release properties of non-metallic materials must be measured using the Ohio State University calorimeter test operated at a heat flux of 35 kW/m², as described in ASTM E906. As part of the safety regulations, the test material is required to have a total heat release of less than or equal to 65 kW/m² over two minutes and a peak heat release rate of less than or equal to 65 kW/m² over the five minute duration of the test. These specifications are used to ensure a cabin material does not contribute to the growth and spread of a fire during the first five minutes following a crash landing.

The FAA requires that the smoke properties of non-metallic materials be measured using the NBS Smoke Chamber according to ASTM E662. The material is required to have a smoke specific optical density (D_s) value of less than or equal to 200 at four minutes.

Further information on the fire safety regulations can be found in FAR 25.853, and McLean et al. (2004) provide a review of the different test methods.

⁵ Swissair Flight 111 was a regular passenger flight which departed New York for Geneva Switzerland on 2 September 1998. The aircraft was destroyed by fire and crashed into the ocean off the coast of Nova Scotia with the loss of all on board. The investigation report is available from the Transportation Safety Board of Canada's website
<<http://www.tsb.gc.ca/en/reports/air/1998/a98h0003/a98h0003.asp>>.

The intention of the database is to provide aviation safety authorities, aerospace design engineers, fire safety engineers and aircraft operators with the necessary information so they better understand and can compare the relative flammability and fire properties among polymer composite materials.

A large number of materials are considered in the database – as listed in Tables 1 and 2. The database considers both current and potentially next-generation composites for aircraft cabins and structures. The advanced materials in the database include composites with high temperature thermoset, thermoplastic and inorganic polymer matrices. Composites reinforced with glass, carbon, aramid and polyethylene fibres are considered. However, the database does not include fire property data for composites that contain modified flame retardant polymers, such as halogenated polymers, phosphorus-containing polymers or nanopolymer composites. While these materials are being used now in aircraft construction, and will be used increasingly in future aircraft, they are not included in the database because their properties are highly dependent on the type and amount of flame retardant which makes it difficult to include in a database that is designed to be easy-to-use.

The database considers the following fire properties of aircraft composite materials:

- time-to-ignition
- limiting oxygen index
- peak heat release rate
- average heat release rate
- total heat release
- flame spread rate
- smoke
- combustion gases.

Fire safety regulations mandated by the FAA only consider several fire properties; but this database considers additional properties to provide a more comprehensive assessment and ranking of the fire performance of aircraft composites.

The information provided in the database was sourced from a comprehensive review of the scientific literature on the fire reaction properties of composite materials. The scientific articles and reports from which the data was drawn are listed in the tables, and referenced in the resources section of this report and the website. As much data was collected from the literature as possible: however, for some properties only a limited amount of information is available. In particular, the tables for properties such as flame spread rate and combustion gases is limited due to the paucity of published information. There is a wealth of other information available in ‘closed’ or confidential papers and reports. Unfortunately, however, this fire data cannot be presented in the database.

The fire properties of composite materials depend on several factors: the type of material, the fire conditions, and the test method used to measure the property. Material properties that affect fire performance include the polymer content and type of fibre reinforcement. The polymer content of the composites in the database is not given, and it does differ among materials. The volume content of polymer in

the composite materials considered in the database ranges from 40% to 60%. The burning conditions, such as heat flux, oxygen level, the presence or absence of flame, as well as the test conditions, including test chamber volume, ventilation and specimen geometry, affect the fire performance. As a consequence, accurately describing the fire performance of a composite material and comparing it directly against other materials can be difficult and problematic. The burning conditions and test conditions for each fire property presented in the database was kept constant to allow more reliable comparisons to be made among materials. The database only considers the fire performance properties of composite laminates, and not sandwich composite materials because there is insufficient data in the scientific literature on their fire properties. Furthermore, the effects of paints and decorative surface films on the fire hazard of composites are not considered.

An important aspect of the database is that fire property data generated by the cone calorimeter test is given for only one incident heat flux level: 50 kW/m². This heat flux generates a maximum temperature at a polymer composite surface of about 700°C, and is roughly equivalent to a medium intensity aircraft cabin fire. This heat flux was selected because most of the fire data available for composite materials is for fire testing performed at 50 kW/m². The fire performance of aircraft composites exposed to other fire conditions; that is, heat flux levels other than 50 kW/m², are not considered. While the fire properties of most composites are dependent on heat flux, it is generally true that the rankings in the fire performance among materials do not change substantially with heat flux.

3.1 Aircraft composites

A wide variety of composite materials are being developed and evaluated for future use in aircraft. This includes composites with high-temperature thermoset polymers, thermoplastics, nanopolymer composites, and inorganic polymers as the matrix phase. It also includes composites with organic fibre reinforcement (eg. aramid, ultra-high molecular weight (UHMW) polyethylene). Unfortunately, not every type of advanced composite has been evaluated for its fire performance.

Tables 1 and 2 list the composites that are considered in the database. The tables consider separately those composites for use in pressurised aircraft cabins, which it is assumed are reinforced with glass fibres, separately from materials used in aircraft structures, which it is assumed contain carbon, aramid or UHMW polyethylene fibres.

The tables give the approximate cost of the polymers used in the composites, although these are subject to change. It is important to note that these costs should be considered as approximate and not as highly accurate figures. When no cost is given this indicates that even an approximate cost could not be found, which is the situation for most polymers still under development or not widely used. The tables also indicate whether the composite is currently used in aircraft or has potential (next-generation) applications. Several composites are included in the database that were used in early-generation aircraft (eg. polyesters), but are no longer in use. Some composites that have no foreseeable use in aircraft are included in the database for completeness of the information.

Table 1: List of aircraft cabin materials (and other composites) examined in the fire database. The benchmark composite material used in aircraft cabins is glass/phenolic.

Polymer matrix	Fibre Reinforcement	Polymer Cost (aud/kg)	Use			
			Current	Potential	Past	None
Phenolic	Glass	2.0	X			
Cyanate ester	Glass			X		
Phthalonitrile	Glass			X		
PMR-15 polyimide	Glass	1900.0		X		
PPS (polyphenylenesulfide)	Glass	30.0		X		
PET (poly(butylene terephthalate))	Glass	2.8		X		
PEKK (polyetherketoneketone)	Glass	83.0		X		
Phenolic-siloxane	Glass			X		
Polyester	Glass	1.0			X	
Bismaleimide	Glass	5.0		X		
Epoxy	Glass	3.4				X
Vinyl ester	Glass	1.5				X
Polyaromatic melamine	Glass			X		
Phenolic-polyester	Glass			X		
Geopolymer*	Carbon			x		

* Data on the fire performance of geopolymer glass composites is not available. However, the data for geopolymer carbon materials can be used as an indication because the performance is not affected significantly by the type of fibre reinforcement.

Table 2: List of aircraft structural materials (and other composites) examined in the fire database. The benchmark composite material used in aircraft structures is carbon/epoxy.

Polymer matrix	Fibre Reinforcement	Polymer Cost (aud/kg)	Use			
			Current	Potential	Past	None
Epoxy	Carbon	3.4	X			
Geopolymer	Carbon			X		
PES (polyethersulfone)	Carbon	18.0		X		
PEEK (polyetheretherketone)	Carbon	85.0	X			
PEKK (polyetherketoneketone)	Carbon	83.0		X		
Polyacrylsulfone	Carbon			X		
Polyphenyl sulphone	Carbon	30.0				
Phenolic	Carbon	2.0	X			
Phenolic-novolac	Carbon					X
Phthalonitrile	Carbon			X		
Bismaleimide	Carbon	5.0	X			
Phenolic	Aramid	2.0				X
Vinyl ester	Aramid	1.5				X
Epoxy	Aramid	3.4	X			
Polyurethane	Aramid	5.5				X
Epoxy	Polyethylene	3.4				X
Vinyl ester	Polyethylene	1.5				X
Phenolic	Polyethylene	2.0				X

4.1 Time-to-ignition of aircraft composite materials

Time-to-ignition is the period of time that a combustible material can withstand exposure to a constant radiant heat flux before igniting and undergoing sustained flaming combustion. More simply, it is the time taken for a material to start burning.

The ignition time can be used as a rough measure of the flammability resistance of a material. Obviously, it is desirable to use materials with long ignition times in high fire risk applications. Extending the time-to-ignition value reduces the fire hazard of a composite material used in an aircraft. The unit for time-to-ignition is seconds (sec).

4.1.1 Aircraft cabin composites: time-to-ignition

Table 3 gives the ranking of time-to-ignition values for twenty-six fibreglass composites when exposed to the same heat flux (50 kW/m²). The materials are ranked from the composite with the longest ignition time (geopolymer matrix material) to the composite with the shortest time (polyester matrix material).

4.1.2 Aircraft structural composites: time-to-ignition

Table 4 gives the ranking of time-to-ignition values for various structural composite materials. As with the table for aircraft cabin materials, the composites are ranked from the most resistant to the least resistant to ignition. The time-to-ignition value for carbon/epoxy composites used in aircraft structures is in the range of 60 to 100 seconds when exposed to a heat flux of 50 kW/m². The value for this composite is taken to be 79 ± 7 seconds.

Many structural composite materials possess much better resistance to ignition than carbon/epoxy. Geopolymer and phthalonitrile matrix composites have excellent ignition resistance, and the FAA is evaluating these materials as next-generation fire-resistant aircraft materials. Many varieties of thermoplastic matrix materials (eg. PEEK, PEKK, PES) have superior ignition resistance, with ignition times from about 2 to 4 times longer than carbon/epoxy. However the high cost of processing these materials can be a limitation for many structural applications. Furthermore, many of these composites do not have the mechanical properties (stiffness, strength, fatigue endurance) and/or environmental durability needed for structural applications. High-temperature thermosetting matrix composites (eg. phenolic, bismaleimide) also exhibit superior times to ignition.

Most composites containing aramid or polyethylene fibres have inferior ignition resistance to carbon/epoxy. This is because the organic fibres decompose in fire and thereby contribute to the ignition process.

Table 3: Performance table for ignition times for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	Time-to-ignition (secs)	Normalised ignition resistance	Reference source
1	Geopolymer	Does not ignite	Infinity	Lyon et al. (1997)
2	Phthalonitrile	530	3.63	Koo et al. (2000)
3	Phenolic-polyester	349	2.39	Koo et al. (2000)
4	Phenolic-siloxane	307	2.10	Koo et al. (2000)
5	PPS (polyphenylenesulfide)	244	1.67	Lyon et al. (1977)
6	Polyimide	175	1.20	Sastri et al. (1997)
7	PMR-15 polyimide	172	1.18	Lyon et al. (1997)
8	Phenolic	146 ± 27	1.00	
9	Bismaleimide	141	0.97	Lyon et al. (1997)
10	Epoxy	105	0.72	Sastri et al. (1998)
11	Vinyl ester	92	0.63	Brown & Mathys (1997)
12	Epoxy	88	0.60	Scudamore (1994)
13	Vinyl Ester	78	0.53	Lyon et al. (1997)
14	Polyester	78	0.53	Brown & Mathys (1997)
15	Polyester	77	0.53	Lyon et al. (1997)
16	Vinyl ester	74	0.51	Sastri et al. (1997)
17	Polyester	62	0.42	Scudamore (1994)
18	Cyanate ester	58	0.40	Lyon et al. (1997)
19	Epoxy	50	0.34	Lyon et al. (1997)
20	Vinyl ester	44	0.30	Egglestone & Turley (1994)
21	Vinyl ester	42	0.29	Egglestone & Turley (1994)
22	PET (poly(butylene terephthalate))	42	0.29	Casu et al. (1998)
23	Polyester	41	0.28	Egglestone & Turley (1994)
24	Epoxy	35	0.24	Mouritz (2005)
25	Polyester	26	0.18	Kandola et al. (2002)
26	Polyester	25	0.17	Mouritz (2005)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

Table 4: Performance table for ignition times for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	Time-to-ignition (secs)	Normalised ignition resistance	Reference source
1	Geopolymer	Does not ignite	Infinity	Lyon et al. (1997)
2	Phenolic*	418	5.29	Brown et al. (1994)
3	Phthalonitrile	337	4.27	Koo et al. (2000)
4	PEEK (polyetheretherketone)	307	3.88	Lyon et al. (1997)
5	Phenolic	295	3.73	Hshieh & Beeson (1997)
6	PEKK (polyetherketoneketone)	223	2.82	Lyon et al. (1997)
7	Phenolic	195	2.47	Sorathia et al. (1994)
8	Polyarylene	175	2.22	Lyon et al. (1997)
9	PES (polyethersulfone)	173	2.19	Lyon et al. (1997)
10	Phenolic	163	2.06	Sorathia et al. (1994)
11	Phenolic*	140	1.77	Hshieh & Beeson (1997)
12	Phenolic	129	1.63	Sorathia et al. (1994)
13	Bismaleimide	126	1.59	Brown (1987)
14	Polyacrylsulfone	122	1.54	Lyon et al. (1997)
15	Epoxy	79 ± 7	1.00	
16	Vinyl ester*	73	0.92	Brown et al. (1994)
17	Vinyl ester [#]	29	0.37	Brown et al. (1994)
18	Epoxy [#]	24	0.30	Brown et al. (1994)
19	Phenolic [#]	20	0.25	Brown et al. (1994)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.2 Limiting oxygen index of aircraft composite materials

The limiting oxygen index (LOI) is often used to quantify the flammability of composite materials. The LOI is defined as the minimum percentage of oxygen in the fire environment needed to sustain flaming combustion. Therefore, the LOI may be considered as a measure of the ease of extinguishment of a burning material. An increasing LOI value means that a greater concentration of oxygen is required to maintain combustion of a material after it has ignited. When the oxygen content falls below the critical LOI value for a material, it will not ignite or continue burning because there is insufficient oxygen for the combustion process. It is desirable for materials to have a high LOI value to minimise the potential fire hazard.

The LOI is experimentally determined in a test that involves subjecting a sample material to an ignition flame in atmospheres having different concentrations of oxygen, and from this determining the minimum oxygen content that allows the sample to burn with a candle-like flame. This value is taken to be the critical LOI value for the material.

The test is performed according to ASTM D2863, ISO 4589-2 and NES 714⁶. Unfortunately the method does not test the sample in a realistic fire environment, and therefore the LOI index cannot be used to accurately quantify the fire behaviour of a material. However, the oxygen index value is often used to rank the relative flammability of polymer composite materials.

4.2.1 Aircraft cabin composites: limiting oxygen index

The amount of published information on the limiting oxygen index value for composite materials is extremely limited, and therefore it is not possible to develop a comprehensive performance table for this fire reaction property. Table 5 shows that glass/phenolic composites have a high LOI value (54 ± 2), and is ranked second highest. Only the bismaleimide matrix composite has a superior LOI index, although it is only marginally higher than the phenolic composite. The other materials have LOI values that are vastly inferior to the phenolic composite.

Composites with highly stable or aromatic polymers have higher index values, which includes the glass/phenolic used in aircraft cabins. It is generally recognised that the LOI values for polymers and polymer composites increase with their ability to yield char in a fire. This is because the formation of char occurs at the expense of combustible volatiles, which in turn increases the oxygen level required to sustain flaming combustion.

Table 5: Performance table for limiting oxygen index values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	LOI	Relative Improvement	Reference source
1	Bismaleimide	60	1.11	Kourtides et al. (1979)
2	Phenolic	54 ± 2	1.00	
3	Polyaromatic melamine	42	0.78	Kourtides et al. (1979)
4	Epoxy	38	0.70	Tewarson & Macaione (1993)
5	Epoxy	27	0.50	Kourtides et al. (1979)
6	Polyester	23	0.43	Tewarson & Macaione (1993)
7	PET (poly(butylene terephthalate))	22	0.41	Casu et al. (1998)
8	Polyester	19	0.35	Kandola et al. (2002)

4.2.2 Aircraft structural composites: limiting oxygen index

The LOI value for carbon/epoxy is 41, and there are several high temperature thermoplastic and thermoset polymer composites that show superior performance. The three best performing composites (with polyether sulphone, polyphenyl sulphone, phenolic-novolac) are expensive, low commodity materials that have little chance of being used in future aircraft structures unless their cost is reduced substantially, their ease of processing is improved, and their mechanical properties are increased. Carbon/bismaleimide is currently used in aircraft structures exposed

⁶ ASTM is the American Society for Testing and Materials
 ISO is the International Standards Organization
 NES is National Engineering Standards (superceded by ASTM)

to high temperature, although it's LOI value is only slightly higher than carbon/epoxy.

Table 6: Performance table for limiting oxygen index values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	LOI	Relative improvement	Reference source
1	Polyether sulphone	54	1.32	Kourtides (1984)
2	Polyphenyl sulphone	52	1.27	Kourtides (1984)
3	Phenolic-novolac	50	1.22	Kourtides (1984)
4	Bismaleimide	47	1.15	Kourtides (1984)
5	Phenolic	46	1.12	Kourtides (1984)
6	Epoxy	41	1.00	Kourtides (1984)
7	Phenolic*	28	0.68	Tewarson & Macaione (1993)
8	Polyurethane*	19	0.46	Kutty et al (1993)

* Aramid fibre reinforcement

4.3 Peak heat release rate of aircraft composite materials

The peak heat release rate (PHRR) is defined as the maximum rate that a composite material releases heat when exposed to fire. The PHRR usually lasts for a very short duration of time (typically less than a few seconds). Despite the transient nature of this property, PHRR is generally considered one of the best indicators of the flammability of a material.

Materials with large PHRR values are usually highly flammable, and make a greater contribution to the growth and spread of fire. Composite materials that possess low values for peak heat release rate are often suitable in high fire risk applications to minimise the growth and spread of fire.

The unit for peak heat release rate is thermal energy per surface area of the material (J/m^2).

The PHRR values given in tables 7 and 8 were measured using the cone calorimeter technique at an incident heat flux of 50 kW/m^2 . It is important to note that the FAA requires the PHRR to be measured using the Ohio State University (OSU) calorimeter operated at a heat flux of 35 kW/m^2 . Data from cone calorimeter testing is presented because a much larger number of PHRR results are available using this technique. It is expected that the order of ranking given in the tables would be similar were the OSU calorimeter used for the measurements.

4.3.1 Aircraft cabin composites: peak heat release rate

Table 7 below shows the ranking for twenty-six fibreglass composite materials from the lowest to highest PHRR value. The average PHRR value for the glass/phenolic composites is $73 \pm 15 \text{ kJ/m}^2$, and is ranked as the fifth best material. As with the performance ranking for time-to-ignition of cabin materials, there are only a few composites that perform better than the phenolic material (table 3). The materials with improved PHRR properties are several high temperature thermoset and

thermoplastic composites. The fibreglass composites containing phthalonitrile, PPS or polyimide have low PHRR values. The composite displaying the best performance is a cyanate ester laminate, which has a PHRR value over six times lower than the phenolic material. However, a second type of glass/cyanate ester (ranked 7) had a PHRR value nearly twice that of the phenolic material. This difference arises because of the many different types of cyanate ester composites, which can exhibit substantially different fire properties.

Table 7: Performance table for peak heat release rate values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	PHRR (kw/m ²)	Improvement Factor	Reference source
1	Cyanate ester	11	6.60	Koo et al. (2000)
2	Phthalonitrile	34	2.10	Koo et al. (2000)
3	PMR-15 polyimide	40	1.80	Lyon et al. (1997)
4	PPS (polyphenylenesulfide)	48	1.50	Lyon et al. (1997)
5	Phenolic	73 ± 15	1.00	
6	Phenolic-siloxane	77	0.95	Koo et al. (2000)
7	Cyanate ester	130	0.56	Lyon et al. (1997)
8	Polyester	159	0.46	Scudamore (1994)
9	Polyester	164	0.45	Brown & Mathys (1997)
10	Bismaleimide	176	0.41	Lyon et al. (1997)
11	Epoxy	178	0.41	Sastri et al. (1997)
12	Vinyl ester	180	0.41	Brown & Mathys (1997)
13	Polyester	198	0.37	Lyon et al. (1997)
14	Vinyl ester	199	0.37	Sorathia et al. (1993)
15	Vinyl ester	222	0.33	Lyon et al. (1997)
16	Epoxy	294	0.25	Lyon et al. (1997)
17	Polyester	333	0.22	Egglestone & Turley (1994)
18	Vinyl ester	333	0.22	Egglestone & Turley (1994)
19	Vinyl ester	343	0.21	Egglestone & Turley (1994)
20	Polyester	346	0.21	Gibson & Hume (1995)
21	Vinyl ester	361	0.20	Gibson & Hume (1995)
22	Epoxy	363	0.20	Scudamore (1994)
23	Polyester	451	0.16	Kandola et al. (2002)
24	Polyester	477	0.15	Kandola et al. (2002)
25	Epoxy	571	0.13	Gibson & Hume (1995)
26	PET (poly(butylene terephthalate))	1490	0.05	Casu et al. (1998)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.3.2 Aircraft structural composites: peak heat release rate

The PHRR value for carbon/epoxy composites used in aircraft structures is 240 ± 24 kJ/m². This is a relatively high value, and places this composite near the bottom of the performance table. The structural composite displaying the best performance is the geopolymer material, which did not release any heat because it did not decompose. Several types of high temperature thermoplastic composites (PES,

PEEK, PEKK) have PHRR values 10 to 20 times lower than the epoxy composite. The high temperature thermoset composites (phenolic, phthalonitrile) also have low PHRR values.

Table 8: Performance table for peak heat release rate values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	PHRR (kw/m ²)	Improvement factor	Reference source
1	Geopolymer	0	Infinity	Lyon et al. (1997)
2	PES (polyethersulfone)	11	21.8	Lyon et al. (1997)
3	PEEK (polyetheretherketone)	14	17.1	Lyon et al. (1997)
4	PEKK (polyetherketoneketone)	21	11.4	Lyon et al. (1997)
5	Polyacrylsulfone	24	10.0	Lyon et al. (1997)
6	Phenolic	37	6.5	Sorathia et al. (1994)
7	Phenolic	48	5.0	Hshieh & Beeson (1997)
8	Phthalonitrile	55	4.4	Koo et al. (2000)
9	Phenolic*	85	2.8	Hshieh & Beeson (1997)
10	Phenolic*	89	2.7	Brown et al. (1994)
11	Phenolic [#]	98	2.4	Sorathia et al. (1994)
12	Phenolic*	163	1.5	Sorathia et al. (1994)
13	Epoxy	171	1.4	Lyon et al. (1997)
14	Vinyl ester*	184	1.3	Brown et al. (1994)
15	Phenolic [#]	186	1.3	Brown et al. (1994)
16	Epoxy*	207	1.2	Brown et al. (1994)
17	Epoxy	240 ± 24	1.0	
18	Epoxy [#]	608	0.4	Brown et al. (1994)
19	Vinyl ester [#]	812	0.3	Brown et al. (1994)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.4 Average heat release rate of aircraft composite materials

Heat release rate (HRR) is the single most important fire reaction property of polymer composites because the heat released by decomposing materials can contribute to the growth and spread of fire. No other reaction property has such a dominant influence on the fire behaviour of composites. Furthermore, several other reaction properties, such as surface spread of flame, smoke generation and CO emission, are dependant on or related to the HRR. Therefore, using materials with low heat release rate values can reduce the fire hazard of aircraft composites.

This section of the database compares the average heat release rate values of composite materials. As opposed to the PHRR value, which occurs over a very short duration of time (usually less than a few seconds), the average HRR is the total heat released averaged over a combustion period of five minutes, and is considered a reliable measure of the heat contribution to a sustained fire.

The units for average heat release rate is thermal energy per surface area of the material (J/m^2).

4.4.1 Aircraft cabin composites: average heat release rate

Table 9 shows average heat release rate values for twenty-one fibreglass composite materials. The glass/phenolic is ranked with the seventh lowest heat release rate. Several high temperature thermoset composites (phthalonitrile, polyimide) and PPS have average heat release rate values that are more than twice as low as the phenolic material. These materials were also highly ranked in terms of ignition resistance and low peak heat release rate.

4.4.2 Aircraft structural composites: average heat release rate

The carbon/epoxy used as the benchmark for structural aircraft composites has one of the highest average heat release rate values ($139 \pm 18 \text{ kW}/\text{m}^2$) of the thirteen materials listed in table 10. As with the other fire properties, the geopolymer composites displayed the best performance. The high temperature thermoplastic composites show exceptionally low heat release rate values, with improvement factors of between about 14 and 23. Several thermally stable thermoset composites, most notably the phthalonitrile material, also possess lower average heat release rate values than carbon/epoxy.

Table 9: Performance table for average heat release rate values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	Average heat release rate (kJ/m^2)	Improvement factor	Reference resource
1	PMR-15 polyimide	27	2.33	Lyon et al. (1997)
2	PPS (polyphenylenesulfide)	28	2.25	Lyon et al. (1997)
3	Phenolic-polyester	30	2.10	Koo et al. (2000)
4	Phthalonitrile	32	1.97	Koo et al. (2000)
5	Phenolic-siloxane	54	1.17	Koo et al. (2000)
6	PPS (polyphenylenesulfide)	55	1.15	Brown (1987)
7	Phenolic	63 ± 4	1.00	
8	Cyanate ester	71	0.89	Lyon et al. (1997)
9	PPS (polyphenylenesulfide)	90	0.70	Brown (1987)
10	Polyester	120	0.53	Lyon et al. (1997)
11	Polyester	126	0.50	Brown & Mathys (1997)
12	Epoxy	135	0.47	Lyon et al. (1997)
13	Vinyl ester	140	0.45	Brown & Mathys (1997)
14	Polyester	142	0.44	Gibson & Hume (1995)
15	Polyester	150	0.42	Egglestone & Turley (1994)
16	Vinyl ester	158	0.40	Lyon et al. (1997)
17	Bismaleimide	161	0.39	Lyon et al. (1997)
18	Vinyl ester	168	0.38	Gibson & Hume (1995)
19	Vinyl ester	173	0.36	Egglestone & Turley (1994)
20	Epoxy	174	0.36	Gibson & Hume (1995)
21	Vinyl ester	203	0.31	Egglestone & Turley (1994)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of $50 \text{ kW}/\text{m}^2$.

Table 10: Performance table for average heat release rate values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	Average heat release rate (kJ/m ²)	Improvement factor	Reference resource
1	Geopolymer	0	Infinity	Lyon et al. (1997)
2	PES (polyethersulfone)	6	23.2	Lyon et al. (1997)
3	PEEK (polyetheretherketone)	8	17.4	Lyon et al. (1997)
4	PEKK (Polyetherketoneketone)	10	13.9	Lyon et al. (1997)
5	Phthalonitrile	32	4.3	Koo et al. (2000)
6	Phenolic*	79	1.8	Brown et al. (1994)
7	Epoxy*	97	1.4	Brown et al. (1994)
8	Bismaleimide	110	1.3	Brown (1987)
9	Vinyl ester*	110	1.3	Brown et al. (1994)
10	Phenolic [#]	136	1.0	Brown et al. (1994)
11	Epoxy	139 ± 18	1.0	
12	Epoxy [#]	304	0.5	Brown et al. (1994)
13	Vinyl ester [#]	350	0.4	Brown et al. (1994)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.5 Total heat release of aircraft composite materials

Total heat release, as the name implies, is the total amount of thermal energy released from a decomposing composite material. The lower the total heat release the less the material will contribute to the temperature of a fire.

While the peak and average heat release rate values of a composite material are considered good measures of its flammability and fire hazard, the total heat release is also a good parameter to evaluate the contribution a material will make to the development of fire. In general, materials that possess low peak and average heat release rates also (as would be expected) have a low total heat release.

The total heat release is measured using the oxygen consumption cone calorimeter technique (ASTM F1550; AS/NZS 3837:1998). This is the same technique used to measure time-to-ignition, average heat release rate, peak heat release rate, and smoke specific extinction area. The technique uses samples of the test material that are 100 mm x 100 mm in size and up to 50 mm thick. While this is a relatively small sample size compared with the scale of aircraft structures, it is considered by the fire science community as reliable for assessing the total heat release by a material. It is important to note that the total heat release value measured by the cone calorimeter cannot be scaled-up to determine the total heat evolved in the burning of the large composite aircraft part. Instead, the value can only be used for comparison and ranking purposes among different materials tested under identical conditions.

The unit for total heat release is Joules (J).

4.5.1 Aircraft cabin composites: total heat release

The amount of available data on the total heat release of fibreglass composites is limited, and from the few composites that are considered the glass/phenolic shows the best performance (table 11). This material exhibits a total heat release value that is much lower than the glass/polyimide and glass/PPS composites that were superior in other fire properties, such as time-to-ignition and peak heat release rate.

Table 11: Performance table for total heat release values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	Total heat release (mj)	Improvement factor	Reference resource
1	Phenolic	10	1.00	Brown & Mathys (1997)
2	Vinyl ester	21	0.48	Lyon et al. (1997)
3	PMR-15 polyimide	21	0.48	Lyon et al. (1997)
4	Vinyl ester	25	0.40	Lyon et al. (1997)
5	Polyester	27	0.37	Kandola et al. (2002)
6	Polyester	33	0.30	Brown & Mathys (1997)
7	PPS (polyphenylenesulfide)	39	0.26	Lyon et al. (1997)
8	Vinyl ester	44	0.23	Brown & Mathys (1997)
9	Cyanate ester	49	0.20	Lyon et al. (1997)
10	Bismaleimide	60	0.17	Lyon et al. (1997)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.5.2 Aircraft structural composites: total heat release

The rankings for total heat release for structural composite materials are shown in table 12. The geopolymer and several thermoplastic composites possess heat release values that are much lower than the carbon/epoxy, and this superior performance is also observed with other fire properties.

Table 12: Performance table for total heat release values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	Total heat release (mj)	Improvement factor	Reference resource
1	Geopolymer	0	Infinity	Lyon et al. (1997)
2	PAS (Polyacrylsulfone)	1	13.50	Lyon et al. (1997)
3	PEEK (polyetheretherketone)	3	4.50	Lyon et al. (1997)
4	PES (polyethersulfone)	3	4.50	Lyon et al. (1997)
5	Epoxy	13.5 ± 1.8	1.00	
6	PEKK (polyetherketoneketone)	15	0.90	Lyon et al. (1997)
7	Phenolic	19	0.71	Sorathia et al. (1994)
8	Phenolic*	28	0.48	Brown et al. (1994)
9	Phenolic*	57	0.24	Sorathia et al. (1994)
10	Vinyl ester*	65	0.21	Brown et al. (1994)
11	Epoxy*	67	0.20	Brown et al. (1994)
12	Epoxy [#]	99	0.14	Brown et al. (1994)
13	Vinyl ester [#]	104	0.13	Brown et al. (1994)
14	Phenolic [#]	107	0.13	Sorathia et al. (1994)
15	Phenolic [#]	114	0.12	Brown et al. (1994)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.6 Flame spread rate of aircraft composite materials

The speed at which flames spread over the surface of a combustible material is a critical factor determining the growth and spread of fire. Due to the high flammability of many composites, there is a serious safety concern that flames will quickly spread through an aircraft and thereby make it extremely difficult to contain and extinguish a fire.

The flame spread of composite materials can be determined using several experimental techniques, with the most common being the radiant panel flame spread test (ASTM D3675). This test basically involves exposing a flat composite panel inclined at an angle of 45° to a radiant heater operated at a constant heat flux. The composite panel ignites at the upper edge, and the speed at which the flame front travels down the specimen surface is measured during testing. In this respect, the radiant panel flame spread test is unrealistic because the flame front is required to travel downwards, whereas in actual fires it is the more rapid upward movement of flames that is responsible for the spread of fire. Despite this, it is a standard test for determining the flame spread properties of composites and other combustible materials.

The speed at which flames spread over the surface of a composite material is defined by the 'flame spread index'. The lower this value the slower will flames spread over a surface.

4.6.1 Aircraft cabin composites: flame spread rate

Data on the flame spread rate of fibreglass composites is very limited. The small amount of data reveals that phenolic laminates have good resistance to flame spread, and this is another outstanding fire reaction property of these materials that makes them suited for high fire risk applications. In addition to the phenolic composite, the table shows that fibreglass composites with a polyimide or high-temperature thermoplastic (eg. PEKK, PPS) matrix have superior resistance to flame spread.

Table 13: Performance table for flame spread index values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	Flame spread index	Improvement factor	Reference source
1	PMR-15 polyimide	2.0	2.70	Sorathia et al. (1993)
2	Polyimide	2.5	2.16	Sorathia et al. (1993)
3	PEKK (polyetherketoneketone)	3.0	1.80	Sorathia et al. (1993)
4	Phenolic	5.4 ± 1.4	1.00	
5	PPS (polyphenylenesulfide)	7.0	0.77	Sorathia et al. (1993)
6	Epoxy	11.0	0.49	Sorathia et al. (1991)
7	Bismaleimide	18.0	0.30	Sorathia et al (1991)
8	Vinyl ester	27.0	0.20	Sorathia et al (1991)

The flame spread rate index values were measured according to ASTM E162.

4.6.2 Aircraft structural composites: flame spread rate

The carbon/epoxy composite has one of the worst flame spread index values. Several high temperature thermoplastic composites have lower flame spread rates, particularly the PEEK matrix material that has index value over 3.5 times lower than carbon/epoxy. The carbon/phenolic composite also has a lower index value than carbon/epoxy.

Table 14: Performance table for flame spread index rate values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	Flame spread index	Improvement factor	Reference source
1	PEEK (polyetheretherketone)	3	3.67	Sorathia et al. (1993)
2	PPS (polyphenylenesulfide)	7	1.57	
3	Phenolic	8	1.38	Sorathia et al. (1994)
4	PAS (Polyacrylsulfone)	8	1.38	Sorathia et al. (1993)
5	PES (polyethersulfone)	10	1.10	Sorathia et al. (1993)
6	Epoxy	11	1.00	
7	Phenolic*	30	0.37	Sorathia et al. (1994)
8	Phenolic [#]	48	0.23	Sorathia et al. (1994)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The flame spread rate index values were measured according to ASTM E162.

4.7 Smoke release of aircraft composite materials

One of the main safety concerns with polymer composites is the generation of dense smoke caused by fire. Smoke is defined by the ASTM Fire Standards Committee as a visible ‘airborne suspension of solid and liquid particles evolved when a material undergoes pyrolysis and combustion’. The particles suspended in smoke are ultra-fine; being typically 0.3 to 3 microns in size. The quantity and size of smoke particles is determined by the chemical composition of the material, char yield and the nature of the combustion process, with flaming, pyrolysis and smouldering conditions affecting smoke. The smoke produced by a burning composite is a mix of small fragments of fibre and ultra-fine carbon (soot) particles.

While the short-term exposure of people to smoke released from a burning composite is usually not considered a serious health hazard, the smoke can be extremely dense and thereby reduce visibility, cause disorientation for passengers and crew, and make it difficult to fight the fire.

Smoke formation is not an inherent fire property of a material. The level of smoke measured in a test depends on the burning condition (eg. heat flux, oxygen level, the presence or absence of flame) as well as the test conditions (eg. test chamber volume, ventilation, specimen geometry, etc). As a consequence, the amount of smoke produced by a composite material can be described in several ways.

Two parameters most often used to quantify smoke density are the specific extinction area (SEA) and maximum specific optical density (D_{\max}). The SEA is a measure of how effectively a given mass of flammable volatiles released by a combustible material is converted into smoke, and is often used to quantitatively define the smoke density. D_{\max} is a dimensionless number that is directly related to the lack of visibility through smoke. The higher the D_{\max} number the higher the maximum density of smoke produced by a decomposing material. The FAA requires non-metallic materials used inside pressurised aircraft cabins to have a D_{\max} value less than or equal to 200 at four minutes.

4.7.1 Aircraft cabin composites: smoke

Phenolic glass composite produces much less smoke, both in terms of SEA and D_{\max} , compared to many other composite materials, as seen in tables 15 & 16, which is one of the main reasons for their use in aircraft cabins. In addition to phenolic resins, other highly aromatic thermoset polymers (eg. polyimides, phthalonitrile) and several high temperature thermoplastics have low smoke emission.

Polymers with aliphatic backbones, or those that are largely aliphatic and oxygenated, have a tendency to yield low levels of smoke, while polyenic polymers and those with pendant aromatic groups generally produce more smoke. Polymers with high thermal stability or which form small amounts of flammable pyrolyzates generally produce little visible smoke. Increasing char formation is one way of minimising the yield of pyrolyzates and hence smoke production. For this reason, composites containing resins that yield a high amount of char, such as phenolics and polyimides, generate less smoke.

The production of char can also reduce the smoke density by impeding the release of ultra-small fragments of fibre into the smoke. It has been shown that the continuous char structure formed in high char yield composites is effective in eliminating the hazardous release of fibres into a smoke plume.

It is important to note that the smoke released from a burning composite is dependent on a variety of factors, including the amount and type of resin and fibre reinforcement together with the heat flux of the fire, and therefore the rankings in the tables may change (to some extent) under different fire conditions.

Table 15: Performance table for smoke specific extinction area (SEA) values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	SEA (m ² /kg)	Improvement factor	Reference source
1	PMR-15 polyimide	170	1.60	Lyon et al. (1997)
2	Phenolic	268 ± 116	1.00	
3	Polyester	378	0.71	Lyon et al. (1997)
4	Bismaleimide	546	0.49	Lyon et al. (1997)
5	PPS (polyphenylenesulfide)	690	0.39	Lyon et al. (1997)
6	Vinyl ester	861	0.31	Lyon et al. (1997)
7	Epoxy	870	0.31	Scudamore (1994)
8	Cyanate ester	898	0.30	Lyon et al. (1997)
9	Polyester	975	0.27	Scudamore (1994)
10	Polyester	1090	0.25	Egglestone & Turley (1994)
11	Vinyl ester	1190	0.22	Egglestone & Turley (1994)
12	Polyester	1256	0.21	Brown & Mathys (1997)
13	Vinyl ester	1441	0.19	Brown & Mathys (1997)
14	Vinyl ester	1539	0.17	Egglestone & Turley (1994)
15	Epoxy	1683	0.16	Lyon et al. (1977)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

Table 16: Performance table for maximum smoke specific optical density (D_{max}) values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	D _{max}	Improvement factor	Reference source
1	Phthalonitrile	1	28.00	Sastri et al. (1997)
2	PEKK (polyetherketoneketone)	4	7.00	Sorathia et al. (1993)
3	Polyimide	15	2.00	Sastri et al. (1997)
4	PMR-15 polyimide	16	1.75	Sorathia et al. (1993)
5	Phenolic	28	1.00	
6	PPS (polyphenylenesulfide)	87	0.32	Sorathia et al. (1993)
7	Bismaleimide	130	0.22	Sorathia et al (1991)
8	Epoxy	165	0.17	Sastri et al. (1997)
9	Epoxy	180	0.16	Sorathia et al. (1991)
10	Vinyl ester	310	0.09	Sorathia & Beck (1996)
11	Vinyl ester	576	0.05	Sastri et al. (1997)

The specific optical density values were measured using the NBS smoke chamber (ASTM E662).

4.7.2 Aircraft structural composites: smoke

The data presented in the tables below show that carbon/epoxy is one of the worst materials for the production of smoke. This material has the worst ranking for SEA and one of the lowest for D_{max}. There are many composite materials that yield much lower amounts of smoke, and this is due to their ability to yield higher amounts of char during the decomposition process.

Table 17: Performance table for smoke specific extinction area (SEA) values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	SEA (m ² /kg)	Improvement factor	Reference source
1	Geopolymer	0	Infinity	Lyon et al. (1977)
2	PEEK (polyetheretherketone)	69	17.9	Lyon et al. (1977)
3	PES (polyethersulfone)	145	8.5	Lyon et al. (1977)
4	Phenolic	156	7.9	Sorathia et al. (1994)
5	PEKK (polyetherketoneketone)	274	4.5	Lyon et al. (1977)
6	Phenolic	294	4.2	Sorathia et al. (1994)
7	Phenolic*	403	3.1	Brown et al. (1994)
8	Phenolic [#]	589	2.1	Brown et al. (1994)
9	Vinyl ester [#]	792	1.6	Brown et al. (1994)
10	Epoxy [#]	808	1.5	Brown et al. (1994)
11	Epoxy*	860	1.4	Brown et al. (1994)
12	Vinyl ester*	888	1.4	Brown et al. (1994)
13	Epoxy	1232	1.0	Mouritz (2005)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

Table 18: Performance table for smoke specific optical density (D_{max}) values for structural composite materials. (All materials reinforced with carbon fibres unless otherwise indicated).

Ranking	Polymer matrix	D _{max}	Improvement factor	Reference source
1	PEEK (polyetheretherketone)	1	173.0	Sorathia et al. (1993)
2	Polyacrylsulfone	3	58.0	Sorathia et al. (1993)
3	PES (polyethersulfone)	5	35.0	Sorathia et al. (1993)
4	Phenolic	13	13.0	Sorathia et al. (1994)
5	Phenolic*	62	3.0	Sorathia et al. (1994)
6	Epoxy	173	1.0	
7	Phenolic [#]	241	0.7	Sorathia et al. (1994)

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

The specific optical density values were measured using the NBS smoke chamber (ASTM E662).

4.8 Gas release of aircraft composite materials

Toxic gases produced in a cabin fire are one of the most serious hazards. It is estimated that 40% of post-crash fire fatalities are caused by smoke and toxic combustion products from burning cabin materials and jet fuel. It is well recognised that the main direct cause of death in fires is the toxicity of combustion products, and the gas that often has the greatest individual hazard is carbon monoxide (CO).

The amount of CO produced by a burning composite depends on the composition of the polymer matrix and (if present) organic fibres, the temperature of the fire, and

oxygen availability; but even very low levels of CO can cause incapacitation or death. Death in humans will occur within one hour when the CO level in air reaches about 1500 ppm. In comparison, the CO₂ content must exceed 100,000 ppm for death to occur within the same time. In addition to CO, a variety of other toxic gases or cariogenic volatiles can be produced during combustion of composite materials.

A composite material can release a large number of different types of gases. For example, phenolic laminates produce CO, CO₂, toluene, methane, acetone, propanol, propane, benzene, benzaldehyde and higher molecular weight aromatic compounds. Other corrosive and toxic gases can also be given off, including HCl, HCN and aromatic halogenated species. Carbon/epoxy composites can produce over 100 different gases. Most studies of the combustion gases released by burning composite materials focus only on carbon monoxide and carbon dioxide, and ignore other gases despite their potential hazards.

4.8.1 Aircraft cabin composites: carbon monoxide and carbon dioxide

Tables 19 and 20 show the rankings from best to worst in the generation of carbon monoxide and carbon dioxide gases when composite materials are thermally degraded. The yields of carbon monoxide and carbon dioxide are expressed by the mass of gas produced (in kg) per mass of composite material consumed (in kg). As an example, it is seen that the phenolic composite yields 0.0155 kg/kg of carbon monoxide. This means that 0.0155 kg of CO is produced for every kilogram of the phenolic composite that is degraded in fire.

It is seen that of the eight fibreglass composites for which gas data could be found in the scientific literature, the phenolic composite produced the lowest amount of carbon monoxide and is ranked fourth lowest in the generation of carbon dioxide. Of these two gases, carbon monoxide is the more lethal, indicating that the glass/phenolic material presently used in aircraft cabins is the least hazardous of the materials listed in the table. In fact, the data reveals that the phenolic composite produces less than half the amount of carbon monoxide as the next best material (glass/polyester). It is seen that certain types of advanced thermoset polymers, such as cyanate ester, phenolic/polyester and phenolic/siloxane, yield small amounts of carbon dioxide but release relatively large amounts of carbon monoxide.

Table 19: Performance table for carbon monoxide yields values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	Carbon monoxide yield (kg/kg)	Improvement factor	Reference source
1	Phenolic	0.0155	1.00	Brown & Mathys (1997)
2	Polyester	0.036	0.43	Brown & Mathys (1997)
3	Vinyl ester	0.0464	0.33	Brown & Mathys (1997)
4	Polyester	0.060	0.26	Kandola et al. (2002)
5	Polyester	0.060	0.26	Kandola et al. (2002)
6	Phenolic-siloxane	0.089	0.17	Koo et al. (2000)
7	Cyanate ester	0.105	0.15	Koo et al. (2000)
8	Phenolic-polyester	0.121	0.13	Koo et al. (2000)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

Table 20: Performance table for carbon dioxide yields values for cabin composite materials. (All of the materials are reinforced with glass fibres).

Ranking	Polymer matrix	Carbon dioxide yield (kg/kg)	Improvement factor	Reference source
1	Cyanate ester	0.577	2.05	Koo et al. (2000)
2	Phenolic-polyester	0.580	2.03	Koo et al. (2000)
3	Phenolic-siloxane	0.701	1.68	Koo et al. (2000)
4	Phenolic	1.180	1.00	Brown & Mathys (1997)
5	Polyester	1.570	0.75	Kandola et al. (2002)
6	Vinyl ester	1.740	0.68	Brown & Mathys (1997)
7	Polyester	1.740	0.68	Brown & Mathys (1997)
8	Polyester	1.830	0.64	Kandola et al. (2002)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

4.8.2 Aircraft structural composites: carbon monoxide and carbon dioxide

The amount of carbon monoxide and carbon dioxide gases produced by burning carbon/epoxy is relatively high compared to many other structural composites. However, this should not pose a major hazard provided the structures are external to the pressure vessel of the aircraft.

Table 21: Performance table for carbon monoxide yields values for structural composite materials.

Ranking	Polymer matrix	Fibre reinforcement	Carbon monoxide yield (kg/kg)	Improvement factor	Reference source
1	Phenolic	Aramid	0.0079	5.30	Brown et al. (1994)
2	Phenolic	Polyethylene	0.0222	1.89	Brown et al. (1994)
3	Epoxy	Aramid	0.0239	1.75	Brown et al. (1994)
4	Vinyl ester	Aramid	0.0243	1.72	Brown et al. (1994)
5	Epoxy	Polyethylene	0.0343	1.22	Brown et al. (1994)
6	Vinyl ester	Polyethylene	0.0367	1.14	Brown et al. (1994)
7	Epoxy	Carbon	0.0419	1.00	Mouritz (2005)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

Table 22: Performance table for carbon dioxide yields values for structural composite materials.

Ranking	Polymer matrix	Fibre reinforcement	Carbon dioxide yield (kg/kg)	Improvement factor	Reference source
1	Vinyl ester	Aramid	1.19	1.55	Brown et al. (1994)
2	Epoxy	Aramid	1.29	1.43	Brown et al. (1994)
3	Phenolic	Aramid	1.61	1.15	Brown et al. (1994)
4	Epoxy	Carbon	1.62	1.14	Mouritz (2005)
5	Vinyl ester	Polyethylene	1.85	1.00	Brown et al. (1994)
6	Epoxy	Polyethylene	1.93	0.96	Brown et al. (1994)
7	Phenolic	Polyethylene	2.19	0.84	Brown et al. (1994)

The time-to-ignition values were measured using the cone calorimeter technique (ASTM D1354) at an incident heat flux of 50 kW/m².

This section of the database gives a summary of the fire performance of the composites against the benchmark materials of glass/phenolic for aircraft cabins and carbon/epoxy for aircraft structures. The tables presented below are designed to allow a quick and easy comparison to be made among materials, and further information can be found in the database for the individual fire properties.

The relative performance of the composites are ranked using the following:

- indicates that the fire property of the composite is more than 100% better than the bench-mark material
- indicates that the fire property of the composite is between 10% and 100% better than the bench-mark material
- indicates that the fire property of the composite is about the same (within 10%) as the bench-mark material
- indicates the that the fire property of the composite is 10% to 100% worse than the bench-mark material
- indicates that the fire property of the composite is more than 100% worse than the bench-mark material.

The abbreviations for the fire properties are:

- t_i = time-to-ignition
- LOI = limiting oxygen index
- PHRR = peak heat release rate
- AHRR = average heat release rate
- THR = total heat release
- FSR = flame spread rate index
- SEA = smoke specific extinction area
- D_{\max} = maximum specific optical smoke density
- CO = carbon monoxide yield
- CO₂ = carbon dioxide yield.

Table 23: Summary of the fire performance of the composite materials compared to glass/phenolic for application to aircraft cabins. All the composites are reinforced with fibreglass.

Polymer matrix	t _i	LOI	PHRR	AHRR	THR	FSR	SEA	D _{max}	CO	CO ₂
Geopolymer	✓✓		✓✓	✓✓	✓✓					
Phthalonitrile	✓✓		✓✓	✓✓				✓✓		
Phenolic-polyester	✓✓			✓✓					☒☒	✓✓
PMR-15 polyimide	✓		✓	✓✓	☒☒	✓✓	✓	✓		
Phenolic-siloxane	✓✓		○	✓					☒☒	✓
PEKK (polyetherketoneketone)						✓		✓✓		
Phenolic	○	○	○	○	○	○	○	○	○	○
Cyanate ester	☒☒		✓✓	☒	☒☒		☒☒		☒☒	✓✓
PPS (polyphenylenesulfide)	✓		✓	✓	☒☒	☒	☒☒	☒☒		
Bismaleimide	○	✓	☒☒	☒☒	☒☒	☒☒	☒	☒☒		
PET (poly(butylene terephthalate))	☒	☒☒	☒☒							
Polyester	☒☒	☒	☒☒	☒☒	☒☒		☒☒		☒☒	☒
Vinyl ester	☒☒		☒☒	☒☒	☒☒	☒☒	☒☒	☒☒	☒☒	☒
Epoxy	☒☒	☒	☒☒	☒☒		☒☒	☒☒	☒☒		
Polyaromatic melamine		☒								

Table 24: Summary of the fire performance of the composite materials compared to carbon/epoxy for application to aircraft structures. All the composites are reinforced with carbon unless otherwise stated.

Polymer Matrix	t _i	LOI	PHRR	AHRR	THR	FSR	SEA	D _{max}	CO	CO ₂
Geopolymer	✓✓		✓✓	✓✓	✓✓		✓✓			
PES (polyethersulfone)	✓✓		✓✓	✓✓	✓✓	✓✓	✓✓	✓✓		
PEEK (polyetheretherketone)	✓✓		✓✓	✓✓	✓✓	✓✓	✓✓	✓✓		
PAS (polyacrylsulfone)	✓		✓✓		✓✓	✓		✓✓		
PEKK (polyetherketoneketone)	✓✓		✓✓	✓✓	○		✓✓			
Phthalonitrile	✓✓		✓✓	✓✓						
Polyphenyl sulphone		✓	✓✓							
Phenolic	✓✓		✓✓		☒	✓	✓✓	✓✓		
Phenolic-novolac		✓								
Bismaleimide	✓	✓		✓						
Phenolic*	✓✓	☒	✓✓	✓✓	☒☒	☒☒	✓✓	✓✓	✓✓	○
Vinyl ester*	☒		✓		☒☒		✓		✓	✓
Epoxy*			✓	✓	☒☒		✓		✓	
Epoxy	○	○	○	○	○	○	○	○	○	○
Polyurethane*		☒								✓
Epoxy [#]	☒☒		☒☒	☒☒	☒☒		✓		✓	☒
Vinyl ester [#]	☒☒		☒☒	☒☒	☒☒		✓		✓	☒
Phenolic [#]	☒☒		✓	○	☒☒	☒☒	✓✓	☒	✓	☒

* Aramid fibre reinforcement

Polyethylene fibre reinforcement

There are several excellent articles that provide a general background to the fire properties of polymers and polymer composite materials. These articles include:

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Kandola, BK & Horrocks, AR 2002, 'Composites' in *Fire Retardant Materials*, ed. AR Horrocks and D Price, Woodhead Publishing, Cambridge, pp.182-203.

McLean, B, Glicksberg, S & Coulliard, K 2004, 'Qualification and certification of a new aerospace material with FAA fire property requirements', *SAMPE Journal*, vol. 40, (Sept/Oct) pp. 6-12.

Price, D, Anthony, G & Carty, P 2002, 'Introduction: polymer combustion, condensed phase pyrolysis and smoke formation', in *Fire Retardant Materials*, ed. A.R. Horrocks and D. Price, Woodhead Publishing, Cambridge, pp.1-30.

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