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Fire Response of Geopolymer Structural Composites

Richard E. Lyon

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16. Abstract

The fire response of a potassium aluminosilicate matrix (geopolymer) carbon fiber composite was measured and the results compared to organic matrix composites being used for infrastructure and transportation applications. At irradiance levels of 50 kW/m^2, typical of the heat flux in a well developed fire, glass- or carbon-reinforced polyester, vinylester, epoxy, bismaleimde, cyanate ester, polyimide, phenolic, and engineering thermoplastic laminates ignited readily and released appreciable heat and smoke, while carbon-fiber reinforced geopolymer composites did not ignite, burn, or release any smoke even after extended heat flux exposure. The geopolymer matrix carbon fiber composite retains sixty-three percent of its original 245 MPa flexural strength after a simulated large fire exposure.

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INTRODUCTION

The Federal Aviation Administration has recently initiated a research program to develop low-cost, environmentally friendly, fire resistant matrix materials for use in aircraft composites and cabin interior applications[1]. Although significant progress has been made in recent years to develop new, high temperature, thermoxidatively stable fibers from boron, silicon carbide, and ceramics[2], parallel work on high temperature/fire resistant matrix materials to bind the fibers has not kept pace. At the present time, affordable, low-temperature processable matrix materials for fire resistant composites are unavailable since most organic polymers soften and ignite at temperatures of 400-600°C which are characteristic of fuel fire exposure conditions. The flammability requirement for new materials is that they withstand a 50 kW/m^2 incident heat flux characteristic of a fully developed aviation fuel fire penetrating a cabin opening without propagating the fire into the cabin compartment[3]. The goal of the program is to eliminate cabin fire as cause of death in aircraft accidents. However, voluntary adoption of the new materials technology by aircraft and cabin manufacturers requires that it be cost effective to install and use, so it is expected that these new aircraft materials will be broadly applicable in transportation and infrastructure where a high degree of intrinsic fire resistance is needed at low to moderate cost. A new, low-cost, inorganic polymer derived from the naturally occurring geological materials – silica and alumina – offers a potential solution for some of the low heat release resin matrix applications.

MATERIALS

The geopolymer matrix resin being evaluated for structural composites is a potassium aluminosilicate, or poly(sialate-siloxo), with the general chemical structure

$$K_n \{-(SiO_2)_z - AlO_2\}_n \bullet wH_2O \tag{1}$$

where, z >> n. This particular resin hardens to an amorphous or glassy material at moderate temperatures and is one of a family of inorganic geopolymer materials described previously[4,5]. Cross-ply [0/90] composites were fabricated by hand rolling the deaerated, caustic aqueous liquid resin into a flat weave carbon fabric (3K Tow, Amoco T-300 fiber, 5.7 oz/yd^2) and air drying 30 seconds at 80°C to remove residual moisture and develop tack. Approximately 25 plies were then cut, stacked, and cured in a vacuum bag at 80°C in a heated press with 0.3 MPa pressure for three hours. The panels were then removed from the vacuum bag and dried for an additional 12 hours at 80°C or until constant weight was achieved. Final thickness of the cross-ply laminates was a uniform 5.6 mm and the density was 1.85 g/cm^3. Hand impregnation and layup resulted in a fiber volume fraction of about 45 percent. Visual inspection of the cut edges revealed that the laminates were substantially free of large bubbles, but immersion density measurements indicated a void content of several percent.

Organic matrix cross-ply laminates of polyester (PE), vinylester (VE), epoxy (EP), cyanate ester (CE), bismaleimide (BMI), PMR-15 polyimide (PI), and phenolic (PH) thermoset resins as well as thermoplastic polyphenylene sulfide (PPS), polyetheretherketone (PEEK), polyetherketoneketone

(PEKK), polyarylsulfone (PAS), and polyethersulfone (PES) resin matrices were prepared from commercial S-glass, E-glass, or carbon fabric prepregs. The details of material composition and fabrication have been described elsewhere[6-8]. Some of the phenolic laminates were hand impregnated[9] and contained only about 34 percent fiber volume compared to a nominal 60 percent fiber volume for all of the commercial prepreg materials. The density of these cured laminates ranged from about 1.55 to about 1.98 g/cm^3 at the nominal 60 percent carbon volume and glass fiber loading, respectively.

METHODS

IGNITABILITY, HEAT RELEASE, AND SMOKE (ASTM E-1354).

Peak heat release rate, 300-second average heat release rate, total heat release, mass loss during burning, ignitability (time-to-ignition), and the specific extinction area of smoke produced were measured in an oxygen consumption calorimeter employing a conical radiant heater to provide 50 kW/m^2 of radiant energy to the surface of a 10- by 10-cm sample having a nominal thickness of 6 mm. The sample is positioned horizontally on a weighing device with a spark igniter 2.54 cm above the surface to ignite combustible vapors (piloted ignition). The mass flowrate of air past the burning sample is measured as well as the amount of oxygen consumed from the air stream by the combustion process and these measurements are used to calculate the heat release rate (HRR) of the burning material using a factor of 13.1 kJ of heat produced per gram of oxygen consumed[10].

FLAME SPREAD INDEX (ASTM E-162-83).

Flame spread across a surface is one measure of the propensity of a material to propagate a fire. Downward flame spread was measured after ignition of a 15- by 46-cm sample by a radiant heat source. Only the combustible organic matrix composites were tested in this procedure as the geopolymer sample would not support flaming combustion.

RESIDUAL FLEXURAL STRENGTH (ASTM D-790).

Specimens were tested for flexural strength before and after the fire test to determine the residual strength of the composite panels after fire exposure. Specimens having dimensions 7.6 cm by 7.6 cm were exposed to a 25 kW/m^2 radiant heat source for a duration of 20 minutes according to ASTM E-662 protocol for smoke generation in a flaming mode. The panels were reclaimed and 5 coupons, 1.27 cm wide by 7.6 cm long were cut from each for flexural testing on a universal testing machine. The geopolymer composites were not subjected to the ASTM E-662 protocol because they would not burn. Instead a more severe test was used wherein panels were exposed to an 800°C oxidizing environment for 60 minutes[11], which is the equivalent of a 75 kW/m^2 radiant energy exposure in air compared to the 25 kW/m^2 exposure for the organic matrix composites. The original sample thickness was used to calculate the residual flexural strength for all samples after the fire test.

RESULTS AND DISCUSSION

Table 1 summarizes all of the cone calorimeter data for the composite specimens. Individual values for percent weight loss during the fire test, time to ignition, peak heat release rate, 300-second average heat release rate, total heat released per unit area, and specific extinction area of smoke are reported for each material. Average values of these fire parameters were calculated for families of the organic materials grouped together according to chemistry (condensation/ phenolics, addition/thermosets), physical properties (engineering thermoplastics), or end-use applications (high temperature/advanced thermosets). It is seen that this somewhat arbitrary grouping leads to variations within groups which can be greater than the variation between groups. However, the averages are fairly representative of each type of material, and it is clear that the geopolymer composite is noncombustible while all of the organic polymer matrix composites support flaming combustion. It was noted that the geopolymer resin became white (crystallized) after fire exposure but did not ignite or smoke even after ten minutes in the cone calorimeter.

It is important to try to understand how or if the fire parameters in table 1, measured in a small scale bench test, relate to the actual fire hazard of a composite material in the use environment. This is a very difficult task and it is important to realize that no single parameter will provide the best estimation of the fire hazard of a material because the hazard depends to a large extent on where and how the material is used (e.g., enclosed space, open space, structural, nonstructural, etc.).

It has been suggested that heat release rate of a material measured in small scale tests under simulated radiant exposure conditions is the single most important parameter in characterizing the hazard of a material in a fire[12]. Recently, it was shown that a combined parameter which is the ratio of the peak heat release rate to the time to ignition, also known as the flame propagation index (FPI) or flashover parameter, is a more accurate predictor of time to flashover in both room and aircraft compartment fires because it more accurately accounts for thickness effects of the material[13]:

$$Flame\ Propagation\ Index\ (FPI) = \frac{Peak\ Heat\ \mathrm{Re}lease\ Rate\ (kW/m^2)}{Time\ to\ ignition\ (\mathrm{sec}onds)} \qquad (2)$$

Flashover is a phenomenon unique to compartment fires where incomplete combustion products accumulate at the ceiling and ignite causing total involvement of the compartment materials and signaling the end to human survivability. Consequently, in a compartment fire the *time to flashover* is the time available for escape and this is the single most important factor in determining the fire hazard of a material or set of materials in a compartment fire. The Federal Aviation Administration has used the time to flashover of materials in aircraft cabin tests as the basis for a heat release and heat release rate acceptance criteria for cabin materials for commercial aircraft [1]. Figure 1 shows the calculated time to flashover of the 6-mm-thick composite material groups from table 1 if they were used as wall linings in an 8- x 12-ft room which is 8 feet high.

TABLE 1. FIRE CALORIMETRY DATA FOR CROSS-PLY LAMINATES AT 50 KW/M^2 IRRADIANCE[6-8]

RESIN	FIBER	Weight Loss	Time to Ignition	Peak HRR	300s Average HRR	Total Heat Release	Smoke
		%	Seconds	kW/m^2	kW/m^2	MJ/m^2	m^2/kg
Isophthalic polyester	Glass	–	77	198	120	–	378
Vinyl Ester	Glass	–	78	222	158	–	861
Vinyl Ester	Glass	26	74	119	78	25	1721
Epoxy	Glass	–	105	178	98	30	580
Epoxy	Glass	19	18	40	2	29	566
Epoxy	Glass	28	49	181	108	39	1753
Epoxy	Glass	22	50	294	135	43	1683
Epoxy	Carbon	24	94	171	93	–	–
THERMOSETS		**24**	**68**	**175**	**99**	**33**	**1077**
Cyanate Ester	Glass	22	58	130	71	49	898
PMR-15 Polyimide	Glass	11	175	40	27	21	170
Bismaleimide	Glass	25	141	176	161	60	546
ADVANCED THERMOSETS		**19**	**124**	**115**	**86**	**43**	**538**
Phenolic	Glass	–	210	47	38	14	176
Phenolic	Glass	12	214	81	40	17	83
Phenolic	Glass	6	238	82	73	15	75
Phenolic	Glass	10	180	190	139	43	71
Phenolic	Glass	3	313	132	22	12	143
Phenolic	Carbon	28	104	177	112	50	253
Phenolic	Carbon	9	187	71	41	14	194
PHENOLICS		**11**	**206**	**111**	**66**	**23**	**142**
Polyphenylenesulfide	Glass	13	244	48	28	39	690
Polyphenylenesulfide	Carbon	16	173	94	70	26	604
Polyarlylsulfone	Carbon	3	122	24	8	1	79
Polyethersulfone	Carbon	–	172	11	6	3	145
Polyetheretherketone	Carbon	2	307	14	8	3	69
Polyetherketoneketone	Carbon	6	223	21	10	15	274
ENGINEERING PLASTICS		**8**	**207**	**35**	**22**	**15**	**310**
geopolymer	Carbon	**0**	**∞**	**0**	**0**	**0**	**0**

The equation used to calculate the time to flashover from the peak heat release rate/time to ignition ratio (FPI) from table 1 is[13]

$$\textit{Time to flashover}\ (\text{sec}) = 991 - 629 \log_{10} FPI \tag{3}$$

Equation 3 provided the best fit ($r^2 = 0.94$) to all of the EURIFIC full-scale fire test data [14] for 13 different lining materials obtained according to ISO 9705 corner wall/room fire test using the

100/300 ignition option (100 kW fire for 10 minutes + 300 kW fire for an additional 10 minutes) in the corner of a 3.6-m-long x 2.4-m-wide by 2.4-m-high room. For comparison to the predicted behavior of the composite materials in figure 1, materials in the ISO 9705 test with 10-12 minute flashover times include a melamine high pressure laminate on noncombustible board, steel faced polymeric foam with mineral wool backing, fire-retardant PVC on gypsum wallboard, fire retardant particle board, and a fire retardant textile on gypsum wallboard.

The calculated values for time-to-flashover of organic and geopolymer composites in a full-scale room test shown in figure 1 provide a qualitative ranking of the fire hazard of these materials in a compartment. The engineering thermoplastics are predicted not to reach flashover during the 20-minute ignition period but could generate appreciable smoke, while the geopolymer composite will never ignite, reach flashover, or generate any smoke in a compartment fire. It is possible that the actual time to flashover of the continuous fiber reinforced composite laminates listed in table 1 would be significantly different from the calculated values displayed in figure 1 and full-scale validation tests of these materials are planned.

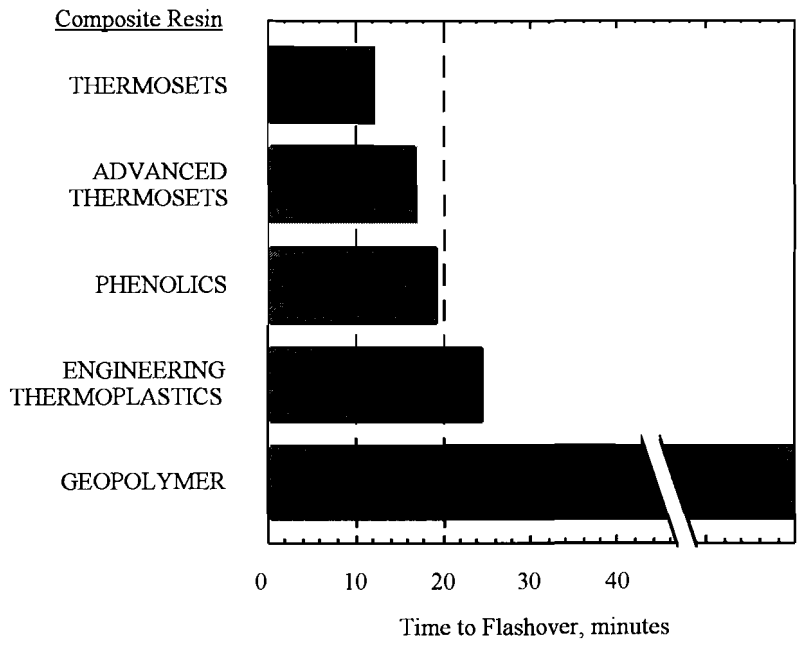

FIGURE 1. PREDICTED TIME TO FLASHOVER IN ISO 9705 CORNER/ROOM FIRE TEST WITH VARIOUS STRUCTURAL COMPOSITES AS WALL MATERIALS

The flame spread index provides a relative measure of the speed at which the flame front of a burning composite travels. Consequently the flame spread index provides a qualitative ranking of the rate of fire growth in an open environment. Figure 2 shows a plot of the ratio of the peak heat release rate/time to ignition (FPI) from table 1 for selected materials which were also tested for flame spread index. The correlation is seen to be very good between the flame propagation index determined in the bench scale cone calorimeter test and the measured ASTM E-162 flame spread index for these cross-ply composite laminates. According to this plot the geopolymer composite

would have a flame spread index of zero, indicating that the geopolymer composite would be an excellent fire barrier.

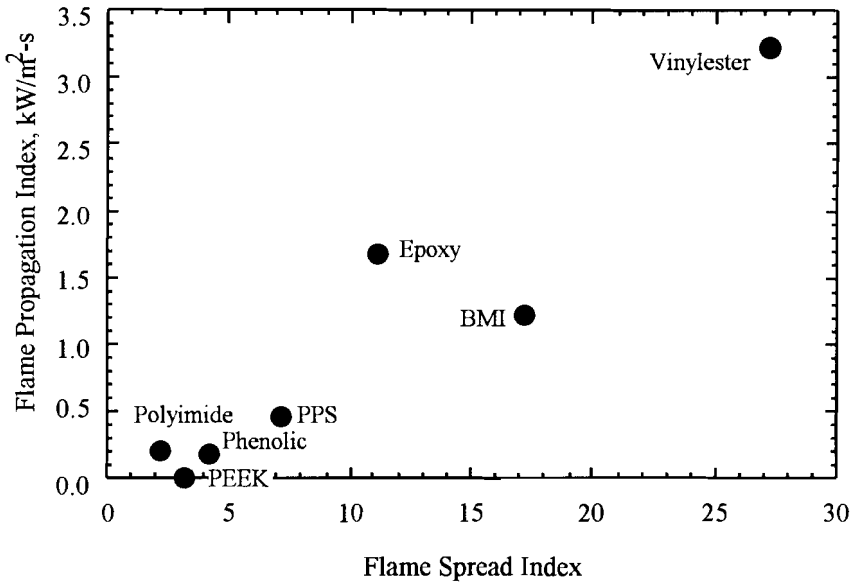

FIGURE 2. FLAME PROPAGATION INDEX AT 50 KW/M^2 INCIDENT FLUX *VERSUS* FLAME SPREAD INDEX FOR A NUMBER OF GLASS-REINFORCED ORGANIC POLYMER COMPOSITES

Perhaps the most important fire response parameter for structural applications is the residual strength of the composite after fire exposure. Comparison of the composite resin categories on the basis of percent residual flexural strength retained after the fire exposure is shown in figure 3. The values represent a combined average for the thermoset (vinylester, epoxy), advanced thermoset (BMI, PI), phenolic, and engineering thermoplastic (PPS, PEEK). As mentioned previously, the carbon fiber reinforced geopolymer cross-ply laminate was subjected to a much more severe thermal environment (800°C/75 kW/m^2) than the organic composites but still retains 63 percent of its original 245 MPa flexural strength. By way of comparison the original flexural strength of the carbon fiber reinforced phenolic resin cross-ply laminate was 283 MPa.

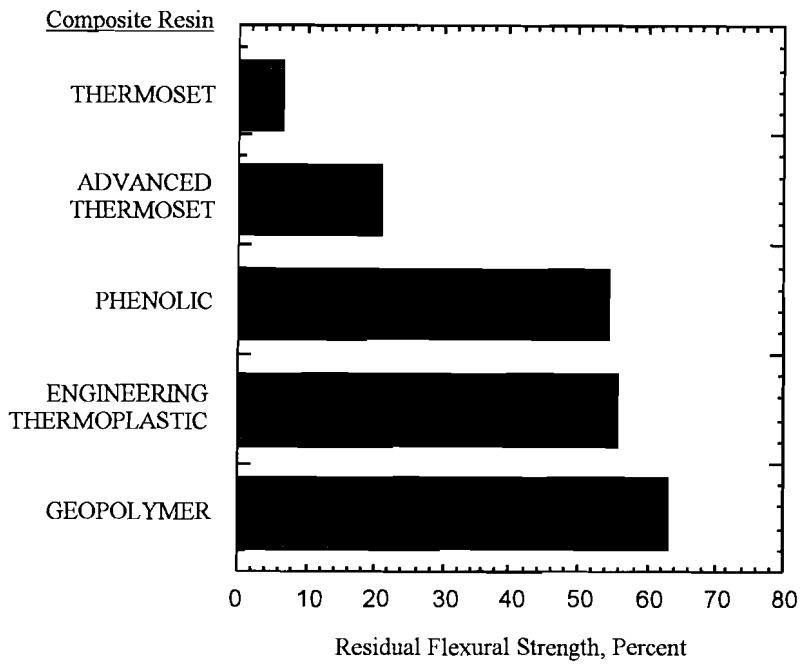

FIGURE 3. RESIDUAL FLEXURAL STRENGTH OF CROSS-PLY LAMINATES AFTER FIRE EXPOSURE

Table 2 compares some thermomechanical properties of fiber reinforced concrete [19,20], structural steel [20,21], a 7000-series aluminum [22] used in aircraft structures, and the Geopolymer-carbon fiber composite laminate [8]. Maximum temperature capability is defined as the temperature in air at which Young's modulus falls to one-half of its room temperature value. The Geopolymer-carbon fiber composite, even in the prototype configuration tested, significantly outperforms fiber reinforced concrete with regard to flexural strength and surpasses concrete and structural steel in temperature capability. It is hypothesized that the observed ≈800°C temperature capability of the GEOPOLYMER composite in air is the result of protection of the carbon fibers from oxidation by surface chemical reactions with the aluminosilicate matrix at elevated temperature.

Specific flexural strength is the flexural strength of the material divided by the bulk density and is the figure of merit for weight-sensitive applications such as aircraft and surface transportation vehicles. The Geopolymer composite is superior to all of the materials listed including aircraft-grade aluminum, with respect to specific strength. The inorganic Geopolymer resin composite is comparable in strength to polymer matrix composites but is entirely non-combustible. Figure 4 shows the relationship between specific strength and approximate materials cost for the materials listed in table 2. It is clear that cost increases exponentially with specific strength. However, the higher cost of materials used in air and ground transportation vehicles is offset by fuel savings over the operating life of the vehicle. The cost of the prototype Geopolymer composite is presently on the order of fifty dollars per pound–ninety-eight percent of which is the cost of the intermediate-modulus carbon fabric which comprises a nominal sixty percent of the composite volume. The Geopolymer resin itself costs about two dollars per kilogram.

CONCLUSIONS

Carbon fiber reinforced potassium aluminosilicate resin (geopolymer) composites are non-combustible structural materials which are suitable for composite material applications where a high degree of fire resistance is needed at low to moderate cost. Carbon fabric reinforced geopolymer cross-ply laminates fabricated at 80°C have comparable strength to fabric reinforced organic resin composites and better strength retention after fire exposure. It is anticipated that loadbearing capability during fire exposure, where temperatures reach several hundred degrees centigrade, will be significantly higher than organic resin composites which soften and lose nearly all of their compressive strength at these temperatures.

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