The Decomposition Behavior of Thermoset Carbon Fiber Epoxy Composites in the Fire Environment

Alexander L. Brown
Sandia National Labs
PO Box 5800
MS 1135
Albuquerque, NM 87185-1135
albrown@sandia.gov

Abstract
Carbon fiber composite materials are increasingly being used in the design and fabrication of transportation vehicles. In particular, the aviation industry is increasing transitioning from metals to this class of composites due to the high strength and low weight of the materials. Most aviation structural composites are thermoset, meaning they require thermal processing to harden the epoxy. In the event of a fire, they will behave significantly different than the metals they replace. Because they are not homogeneous, they also differ significantly from homogeneous solid combustibles. Sandia National Laboratories is motivated to study burning composites because we maintain experimental and modeling capabilities for assessing transportation safety. Understanding the thermal environment created by transportation fires is therefore paramount. This type of focus is not typical of the general literature on these materials in the fire environment. A serious issue with the majority of fire performance data found in the open literature is that the length and mass scales are generally orders of magnitude below those used in vehicle design. With a non-traditional perspective on composite fires, Sandia has performed several test series. Together with a review of the work from other institutions as found in the literature, this report presents a phenomenological overview of the relevant work on the behavior of composite materials in a fire environment.

Introduction
Carbon fiber composites are being used extensively in the design and manufacture of modern aircraft. The low weight coupled with high strength and durability of the materials makes them desirable for extensive use throughout the aircraft. Some general information on composites is available in the literature [1,2]. These composites generally consist of a binder and a fiber. The binder is usually a resin or glue that will set once the part is formed. The binder provides rigidity and strength to the composite matrix. Two of the more common classes of binders used in airframes are thermoset epoxies and bismaleimide resins. Bismaleimides in particular exhibit improved resistance to thermal damage under normal aviation environments. Strength, weight, and thermal resistance are three of the most significant considerations in selection of these materials.

From the perspective of a fire involving these materials, the chemical constituency of the binder is important, but often difficult to understand in detail because the exact formula of each grade of epoxy is a differentiating factor in the manufacturing process. These are proprietary, and not normally divulged. Epoxy resins often have a fundamental resin repeating unit of \( [C_{18}H_{20}O_3]_n \)
(diglycidyl ether of Bisphenol A, or DGEBA), and hardeners often consist of compounds with amine groups that are the active unit that promotes cross-linking of the polymer. Aromatic polyamine hardeners do not set at room temperatures, and are therefore good candidates for thermoset epoxies. Hardeners come in a variety of forms, but may have constituencies like C₆H₄N₂, which is representative of the common m-phenylenediamine hardener \[3\]. Catalytic curing without the use of a chemical hardener is also possible \[1\]. Bismaleimide resin may be similar in elemental constituency, with a repeating unit of \([C_{21}H_{16}2(NO₂)]_n\). Both of these binder materials contain aromatic ring structures, which would be expected to enhance the soot formation pathway among the volatile products of pyrolysis when compared to more common fuels consisting primarily of aliphatic compounds. Often, common compounds as described above are used for the main formulation, but trace materials are included in the matrix to mitigate flammability or for other performance reasons. These may also be proprietary.

Carbon fibers are chosen because they are strong compared to other common fibers, and are typically manufactured by processing polymer strands through a series of reactions consisting of oxidation and charring steps. The manufacturing process yields strands of high carbon content. They have high tensile strength (~3GPa) \[2\], and are pliable such that they can be formed in a variety of shapes. Fibers can be from various sources, and may be different thicknesses and strengths. They are marketed typically in two forms frequently used by the design industry. The first is as a tape, which is a sheet of binder impregnated unidirectional fibers. The second is an epoxy impregnated woven sheet. Weaves can come in a variety of patterns. Fibers can be acquired at varying thicknesses in coated laminate sheets termed ‘prepreg’. Uncured impregnated sheets are typically sold with tightly controlled epoxy to carbon fractions, generally around 35% epoxy and 65% carbon fiber.

Manufacture of parts from these raw materials is also an important consideration. Raw tacky single-layer sheets are often stacked with similar sheets to form layered composites of varying thickness. It is a common practice to rotate the fiber orientation at varying sub-layers, as this has been shown to enhance the general strength of the product. Thermoset resins are cured in a variety of ways, with two more common being in a bag-pressed autoclave, or in a thermal press. The curing process is in a press or pressurized vessel to help induce the removal of air bubbles from within the composite layers to enhance the strength. As the uncured material heats, the binder becomes mobile, so cured composites may have slightly lower binder content than the source prepreg with small amounts of binder escaping along the edges of the manufactured part. Lay-up is typically a manual process, resulting in some potential variability. Aircraft use many shapes and forms of composite materials. Panels for skins are frequently used. Sandwich configurations with any of a number of light-weight secondary internal materials may also be found on designed parts. Structural members can be custom shapes to fit design requirements.

Significant fire testing has been performed previously on these types of materials with various objectives in mind. There have also been efforts to describe the fire behavior of composites through modeling. If one considers all fiber/binder composite materials, the literature is extensive. Three fairly recent reviews detail some broad accomplishments in this regard \[1,4,5\]. Narrowing the scope to just carbon fiber epoxy materials, there is a much more modest amount of literature on fire behavior.
Being organic in nature, the above described composites are expected to be flammable and to burn in a fire environment. This is not to say that under normal operation that there is an increased risk related to these materials. Rather, in an abnormal and/or accidental environment the aircraft material may become a contributor to the thermal output from a fire event.

Sandia as an institution maintains two principal objectives relative to these materials in a fire. First, we need to understand the behavior of these materials in fires to understand the consequences of transportation fires for safety studies. Second, to further this goal we desire to be able to model the combustion and fire behavior of composites in fire environments. This paper is a review paper on the topic of thermoset carbon fiber epoxy fires, with an emphasis on recent findings by the author and colleagues, distinguishing features of carbon fiber epoxy materials, and technology gaps that have been identified in this area of study.

Sections below organize reports containing some of the experimental observations and studies that contribute to the understanding of carbon fiber epoxy fire behavior from previous research by topic. There have been many historical tests, and there is a lot of information generally available. Quintiere et al. (2007) [6] present data on many of these sub-headings for one type of carbon fiber epoxy, and is not necessarily mentioned in each section as having relevant data unless the data are particularly unique or revealing. Other reports are narrower in scope, and are therefore specifically commented on in the appropriate section. Scope is generally limited to studies that focus on carbon fiber epoxy materials, or to papers that clearly exhibit significant findings on the behavior of this class of materials in a fire environment.

**Binder Reactions**

There are a lot of types of binders that fit the sub-category of epoxy, and there are many studies on the decomposition of binder materials in the polymer literature. In a fire, the pyrolysis process typically ensues resulting in yield of a combustible gas and a solid char. Several types of experiments are generally found in the context of binder reactions. Thermogravametric Analysis (TGA), Differential Thermal Analysis (DTA) and cone calorimetry are the most common methods for characterizing pyrolysis. TGA generally yields reaction rates which can be used to develop global decomposition behavior reaction mechanisms. DTA and similar types of experiments describe the heat absorption or emission process during decomposition.

Pyrolysis reactions are typically considered endothermic [7], as deduced from calorimetry and DTA. Gaseous products of the reaction are addressed in a later section. Documented TGA and DTA experiments can be found on binders alone, as well as on binder/fiber combined materials. Examples of such include the work of Chen and Yeh (1996), Kandare et al. (2007), Regnier and Fontaine (2001), Rose et al. (1994), Schartel et al. (2008), and Trick et al. (1997) [8-13]. TGA may be conducted in an inert environment [8-10,12,13], or in an oxidizing environment (normally air) [10,11]. In TGA, one normally finds binder pyrolytic decomposition taking place (temperature range) between 350-600ºC [8,9,11-13].

Cone calorimetry can provide reaction rates, but since samples are typically much larger than in TGA, the instrument is most often used to derive flaming heat release rates (HRR), which is a practical measure of the energy released by the sample material including both pyrolysis and any subsequent reactions such as flaming combustion and surface oxidation. Most of these tests are
found just for laminates, not individual constituents. Extensive data can be found in the work of Brown et al. (1998) and Mouritz (2006) [7,14]. Notably, epoxy is found to be one of the most susceptible binders to fire when compared to others in the studies. Avila et al. (2008) [15] also have extensive data on the binder reactions, but in conjunction with a glass fiber. A recent report by Eibl (2012) [16] employing mostly cone calorimetry suggests that the fiber lay-up influences the substrate burn velocity, heat release rate, and ignition in calorimetry tests. It is therefore concluded that the details of the fiber lay-up are consequential to the way binders decompose and burn.

We have some limited data in the TGA environment, the publication of which is in progress. An example of the type of data we have obtained that are generally consistent with others in the literature is found in Brown et al. (2012) [17]. We also have unpublished cone calorimetry data for several materials. Much of the historical data adequately describe the behavior of these materials. Documentation of these data is in progress.

**Fiber Decomposition**

Carbon fibers can vary in diameter and in constituency based on methods of manufacture. If the range of fibers described in Jiang et al. (2008) [18] can be taken as representative, they are typically around 80% carbon, 15% oxygen, with the balance composed of hydrogen and minor species. A fiber therefore reacts much like other highly carbonaceous materials such as coke, soot, and graphite. High carbon fraction material reaction studies often borrow from each other and use interchangeably reaction rates, etc. Generally speaking, carbon does not pyrolyze, making it a good surface material for very high-temperature applications. It will decompose, but reactions are typically negligible until the temperature exceeds around 700 °C. At these temperatures, the solid carbon will react with gaseous oxidative molecules including OH, O, H₂O, CO₂, as per Acharya and Kuo (2007) [19]. The rocket design community uses carbon materials for thermally resistive component design, and therefore have studied the reaction rates in the interest of being able to determine lifetime in a severe environment. Examples of these include Acharya and Kuo (2007), Bianchi et al. (2011), Klager (1977), and Kuo and Keswani (1985) [19-22].

Jiang et al (2008) evaluating recyclability of fibers noticed increasing carbon ratios, but similar strengths for fibers put through a fluidized bed to remove the binder. They find that the fibers can be recovered through an intermediate intensity pyrolysis process that will consume the binder, but leave the fibers intact. This is evidence that suggests the char formed by the binder may be expected to preferentially oxidize before fibers oxidize in a fire environment.

Further relevant work on carbon oxidation is found in the body of work relating to the oxidation of carbon particles. These studies mostly attempt to uncover the burn rate for the particles. Examples include the work of Blake and Libby (1991), Blake (2002), Chelliah et al (1996), Kassoy and Libby (1982), Libby and Blake (1979), Libby and Blake (1981), and Makino and Law (2009) [23-29]. In a closely related paper with a geometric variation, Makino et al. (2003) evaluate the combustion rate for graphite rods in a high-temperature air flow.

Brown et al. (2011) [30] documents a series of recent tests done at Sandia National Labs where 25-40 kg of varying types of carbon fiber epoxy materials were combusted in an insulated
enclosure. Shape of the composites was also significantly varied. The intent of the tests was to evaluate the capacity for the fibers to burn in an extreme environment, and to explore the peak heat fluxes that could be generated by the burning of carbon fiber epoxy composites. The tests were notable in the duration and in the intensity. Peak fluxes of 200 kW/m² were obtained during flaming and glowing (char and fiber oxidation) phases. The environment exhibited two peaks in intensity (as deduced by the measured heat flux), the first corresponding to flaming combustion, and the second to oxidative reactions (See Figure 1 for an example result). Medtherm radiometers and a bulk metal calorimeter were used to monitor the heat flux during the test. The drop in intensity between the two peaks is presently believed to be due to the lower energy release in the char oxidation phase immediately following flaming combustion when compared to that of the fiber oxidation phase. The duration of the tests was remarkably long, 5-8 hours. Comparable (on a mass basis) wood fire tests were just 1-1.5 hours long. Figure 2 shows some images from one of the tests that illustrate the dynamic behavior of the panel decomposition with time. Notice in particular one panel that fell off the rack and was in good view of the camera as it was decomposing in the top-left part of the opening in the images. This test series achieved 90-98% mass consumption of the initial material, which is suggestive that under ideal conditions it is possible to consume very close to 100% of the carbon fiber epoxy material used in the aircraft design. Pickett et al. (2011) [31] note in contrast that 25-50% mass consumption is typically expected.

The reports on carbon oxidation (including many listed above) suggest minimal reaction until a sustained temperature in the vicinity of 700°C is attained in air. It is therefore not expected that
this type of material will be able to self-sustain glowing fiber combustion unless there is a significant thermal feed-back mechanism that maintains a severe thermal environment.

Figure 2. Video frames from the combustion of 45 kg of carbon fiber epoxy panels at regular half-hour intervals, as time-stamped.

**Heat Transfer**
Heat transfer generally depends on parameters that make up the thermal diffusivity. These include conduction, density, and specific heat capacity. Specific gravity of composites vary, but resins are around 1.25, and carbon fibers are around 1.8, as extracted from various sources (including many listed below in this section). These generally do not change with temperature,
until the resin goes through significant chemical changes such as char formation and decomposition. Fibers and epoxy together have a specific gravity that falls somewhere in-between that of the fiber and epoxy (as a linear product). Specific heat capacity and thermal conductivity are more complex functions, and are described in more detail below.

Because composite materials are heterogeneous, they are more complex in their behavior than most other construction materials like metals that can be well approximated as homogeneous. The thermal properties like conductivity cannot be trivially represented by a classical scalar heat transfer coefficient. A high-fidelity approach to modeling heat transfer in these systems has been demonstrated by Thomas et al (2008) [32], who used finite element modeling to mesh individual fibers in their matrix to evaluate heat transport at the scales at which the materials can be considered homogeneous. This approach is unlikely to be practical at manufactured part scales, and indeed the end of their work was to demonstrate the ability to approximate a conduction tensor from detailed modeling. Also modeling the complex heat transfer in laminate composites, Shokrieh and Abdolvand (2011) [33] compare their model for data from heated panels with embedded thermocouples for glass fiber composites. Their model for the conduction coefficient is directionally and temperature dependent. A polynomial is used to describe the temperature dependence, which presumably does not take into account the variation in conductivity due to char formation (properties only vary by a factor of 3 over a few thousands of degree temperature change). Directional dependence results in as much as a factor of 2 difference in the conduction coefficient in their model. A methods paper by Lattimer and Ouellette (2006) [34] presents a method for determining thermal heat transfer properties along with some relevant data. They focus on glass fiber materials, and show heat capacity and thermal conductivity to be functionally related to temperature. They also present kinetics, and model comparisons. Their data on the directional dependence are on the same order. Milke and Vizzini (1991) [35] predict longitudinal versus transverse conduction, showing nearly a factor of 100 difference in conductivity based on previous data (around 0.5 W/mK to 50 W/mK). They model graphite fibers, potentially explaining the difference with the Shokrieh and Abdolvand (2011) data. The work of Shim et al. (2002) [36] agrees with the Milke and Vizzini (1991) data, showing nearly a factor of 100 directional dependence for carbon fiber composites. Bai and Keller (2009) [37] suggest that there is both a time and temperature property dependence for their glass fiber composites in conductivity, as well as in other parameters. Bai et al. (2008) [38] show data assembled from prior work suggesting that after decomposition the matrix is less conductive, presumably due to the char formation. Chen et al. (1985) [39] also present thermo-physical properties for composites. Specific heat capacities from the literature for appropriate materials range from 800-1700 J/kgK, with the resin having about twice that of the fiber and the matrix heat capacity between those limits. Kalogiannakis et al. (2004) [40] present significant thermal conductivity data for glass and carbon fiber composites, but only in the transverse direction. The bulk of the data suggest that carbon fiber laminates differ significantly from glass fiber laminates in thermal conductivity in the direction of the fibers. The fact that there is a much more pronounced directional dependence on the thermal conductivity for carbon fiber composites appears to be one of the major differences between these and the glass fiber composites.

Conductivity is also complicated by the fact that the fibers have orientation. Fibers are the more conductive medium in the composite. They can be designed in unidirectional or woven layers,
and the layers can be rotated or uniform in directionality. Each potential bulk configuration might be expected to conduct heat differently on a macro-scale.

Based on past work, there is probably a need for more details on the time, temperature, and directional dependent properties for conductivity if one is to adequately model the substrate in a fire. This is especially true for partially decomposed materials. Thermal capacity data exist, and are probably time and temperature dependent. Data on char properties are generally lacking. Partially decomposed material properties are found in some previous work (e.g., Bai et al. (2008) [38]), but are not generally available for a suite of common material variations.

**Pyrolysis Products**

In the context of composite fires, there are not a lot of studies that carefully examine the detailed pyrolysis products from the burning of carbon fiber epoxy materials. In the broader context of binder and resin decomposition, there are more studies available. Two studies are representative of the types of products found in pyrolysis studies. Bradna and Zima (1992) [41] have some of the earliest such combined analysis using gas chromatography and mass spectrometry. They were interested in fingerprinting degraded resins from their products. They list many of the minor species identified in epoxy pyrolysis including many oxygenated compounds. Jiang et al (2007) [42] also looked at soft ionization TG/MS and found mostly aromatics and soot precursors in the products of epoxy pyrolysis. While these two of many studies apparently present contradictory product suites, the differences are not unexpected. Primary products exposed for a short duration and/or a low temperature exposure to the fire environment exhibit more characteristics of the native material. With longer exposure and higher temperatures, the intermediates will continue to react. Final products exhibit less oxygen and more uniformity (more aromatics and CO). These two product suites may be explainable also by the source materials, but the nature of the findings and above explanation are not atypical of what is found in the literature for other decomposing organic materials. Much of the remaining studies (not listed herein) are focused on the products based on minor additives, and consequently are not clearly applicable in a broad sense to existing commercial products.

Several studies are found that use the cone calorimeter to evaluate products. The cone calorimeter classically uses oxygen consumption calorimetry methods to measure the heat release rate, which requires measurements of the CO and CO$_2$ products. Mouritz et al (2006) [7] present extensive CO and CO$_2$ data and conclude that the heat release rate is a good predictor of mass yield. They also conclude that roughly 4% of the original composite mass typically ends up as CO. Brown et al. (1988) [14] show similar data. These are generally flaming products, which explains the difference between the pure pyrolysis products described in the first paragraph when compared with these.

Brown et al. (2011) [30] at Sandia National Labs used an FTIR instrument to measure four product species in the effluent of several large carbon fiber epoxy fires. Water vapor and methane peaked during the first 10-30 minutes as the epoxy was decomposing in a flaming environment. Subsequently, they dropped to nearly zero as the CO and CO$_2$ signals rose during what was presumably char and fiber reaction dominated phases. CO yields were not significantly below that of CO$_2$ at later times, suggestive that there is a significant CO hazard associated with the fiber burning. Smoke obscured the FTIR signal during peak burning. These
data do not add significantly to the body of work in this area, but are interesting and distinctive because they track chronological emissions for larger scale fires.

**Scale Effects**

In general, most of the above described tests are dealing with length scales less than 10 cm, and mass scales less than 1 kg. Aircraft design typically employs orders of magnitude greater amounts of material. One might expect the bulk behavior in a fire to be partially related to the scale of the material. Some work exists at larger scales, and this section lists some of the major findings. It is probable that data at larger scales are not more available because of the prohibitive cost of the testing, and less due to the lack of significant scale-related behavior. As such, there is an inherent value to any data that exist at practical scales.

Pickett et al. (2011) [31] reviews several instances of military mishaps with composite aircraft. A major finding from that review is that the duration in these events is remarkably long. Another is that suppression is very difficult due to what is believed to be deep smoldering within the composite layers. These effects will not necessarily be apparent in data taken using small samples. They conducted a series of tests with square or nearly square panels that ranged from tens to hundreds of centimeters in their primary dimension. Panels were placed in a test frame to impose structural forces during the decomposition for some of the tests. Fires were suppressed, and panels were subsequently examined for post-suppression behavior. They found evidence of deep smoldering in their tests, which might not have been present if smaller panels were used.

Lopez de Santiago et al. (2010) [43] examined quarter-scale skin panels (~50 cm long), and compared their performance to aluminum skins. Panels were exposed to a roughly 1 square meter fuel fire. The objective was to evaluate the safety of internal passenger exposure to radiative flux from the fire. The composites did not burn completely through, whereas aluminum readily melted, exposing the interior of the aircraft to the fire.

Bell (1980) [44] looked at fiber release from a variety of scales from a jet fuel fire. The largest scale tests involved 45 kg of material and a large pool of fuel. At about the same time, Pride (1980) [45] documented details of what appears to be the same test. Whiting et al. (1980) [46] provide additional test documentation. They quantify the nature of the fibers released for diameter and length, and also provide a release fraction. They found appreciable fiber release from the burning of the carbon fiber materials, and were able to detect a wide spread of particles well down-wind of the fire tests.

None of the above efforts (excepting the data in the review of actual mishaps) are at the appropriate scale for most significant aircraft fire events. Recent work at Sandia National Labs categorizes tests by scale with the largest and most relevant including total composite mass greater than 100 kg (see Brown et al (2011) [47]). Observations from work detailed in this section lend to the understanding of such an event. However, there remains significant need for large-scale studies on the behavior of composites at scale since smoldering and re-ignition behavior such as that observed in the work from Pickett et al. (2011) might not be manifest in the more prevalent small-scale tests. Recent work from the Sandia group is building up to larger-scale testing [17, 48].
Swelling
The swelling propensity of carbon fiber epoxy laminates has been observed by many researchers. Plain epoxy alone is inherently intumescent, although not as strongly so as many engineered intumescent materials. Additives might enhance the char formation, which may be a strategy for fire resistive formulations. The more significant swelling normally observed is believed to be due to a combined behavior related to the fiber and the char. As the binder pyrolyzes, the gases internal to the matrix often are unable to escape due to the fiber and char layers. This results in pressurization, which can cause blistering, delamination, and swelling. This complicates modeling efforts, since an internal gas layer will tend to retard the transport of heat between layers when compared to a panel with no gas present. Florio et al. (1991) [49] significantly conclude that the experimentally measured pressure built up in their composite sub-layers during decomposition reached as high as 10 atm for their glass fiber epoxy composites. This finding was subsequently affirmed by Sullivan (1993) [50], who also found significant pressure increases in the sub-layer of composite systems. Quintiere et al. (2007) [6] quantify the volume expansion for their tests to be a factor of 2.2 +/- 0.1. Recent testing at Sandia found greater variability in panel swelling using more samples of varying types [51]. Linear thickness increase was found to be typically 100-200%. On the small coupons, the swelling occurred out to the edges, where combustible gases escaped. In larger-scale testing [48], blistering was also evident, but the edges that were cooler did not necessarily permit escape of the gases. This is suggestive of a length-scale dependency in the way that gases escape from the internal matrix of panels in a fire. The proximity of an edge may change whether gases escape perpendicular or parallel to the panel surface.

It is not well understood what fraction of the swelling is related to blister growth and pressurization, and how much is related to intumescence of the epoxy. There is good evidence for both being contributors. Jetting is often observed in composite burns. Gases will develop a preferred escape pathway, and local flames will set up along the escape path. However at the end of a test, there normally appears to be a somewhat uniform distribution of the fiber layers perpendicular to the panel face. Both potential mechanisms for panel swelling deserve further attention.

Burn-through
Much of the fire testing of carbon fiber epoxy panels found in the literature does not specifically examine the potential for burn-through. Many tests are cut short before this can occur. Other objectives often dominate the motivation for the work, and consequently there is not a lot of information on the nature of the long-term fire and on the potential for the formation of holes.

Carbon fiber materials are very resistive to burn-through in a fire. Simply igniting them does not result in hole formation. The fibers will withstand significant heating. Tearing or significant structural motion is required to create a hole in the short-term. In the long-term, a hole can be formed through oxidative reactions. As already mentioned, Lopez de Santiago et al. (2010) [43] found that a significant fire did not open up a hole in the fiber matrix after 6 minutes. In a similar vein, Bartlett and Stratford (2001) [52] did burn through tests of fiberglass fiber composites, and concluded they were more resistive to burn-through than aluminum. La Delfa et al (2009) [53] show that under compression a sandwich composite of interest will meet a 4 minute burn-through criterion. Recent testing of various types of panels by Sandia has shown
that even under moderate structural loading (~1 MPa) and intense radiative heating (~200 kW/m²) that panels 1-3 mm thick required 20-60 minutes to burn through such that the radiant exposure from the front side penetrated the back side of the panels (Brown et al. (2013) [48]). Figure 3 shows two images of a carbon fiber epoxy panel near burn-through. The study suggests that there may be a strong relationship between panel thickness or fiber orientation relating to this behavior. This is because a thicker panel composed of woven fiber appeared to be disproportionately resistive to burn-through in these tests. These tests were not sufficiently detailed to be able to fully ascribe the differences in behavior to the exact cause.

Structural failures that induce large motion may result in more rapid formation of holes, as the motion can induce puncture holes and tears. Small-scale testing will not exhibit this type of behavior. Since most of the literature testing is at a small scale, this type of behavior has not been documented. More large-scale testing would be required to evaluate this hypothesis.

Figure 3. Two images of a unidirectional carbon fiber epoxy panel approaching burn-through.

Combined Thermal/Structural Effects
An extensive body of work exists on the combined structural and thermal environment. Much of the work is aimed at determining the failure threshold in the combined environment. These tests usually involve small samples under traditional mechanical failure loading with imposed thermal environments. Among the work that is carbon fiber epoxy related, there are examples of studies that look at fairly low temperature environments. Kwon et al. (2006) [54] tested environments under 300ºC, and under compression. Burns et al. (2010) [55] tested to higher temperatures, also in compression. Liu et al. (2011) [56] evaluate the crushing behavior of composite trusses under load up to 260ºC. Compression failure under thermal loading tends to be as indicated by Budiansky and Fleck (1993) [57]. They tested in ambient environments, but conclude that plastic kinking is the dominant mode for compressive failure, which is consistent with the modes
found in the other work. Cao et al. (2009) [58] measured tensile performance at temperatures up to 200ºC.

An alternative approach taken is that of Sorathia et al. (1993) [59], who measured residual strength after mild heating. Mouritz (2003) [60] likewise examines post-fire strength of the laminates, and measures the char layer thickness after exposing panels to a fixed heat flux for a fixed time.

A model was proposed by Mouritz et al. (2004) [61] for post-fire residual strength. They tested a large number of samples, and show good correlation between experimental and modeled strength.

Although they did not test carbon fiber epoxy samples, the glass fiber epoxy work of Elmughrabi et al. (2008) [62] is significant because they examined the thermal heat release rate as a function of stress ranging from near failure point loading under tension to the same under compression. They conclude that there is a minor relationship between heat release rate and the stress imposed on the sample. They speculate that micro-cracking of the epoxy lends to the observation. Expanding on that work at more moderate structural load levels and for larger panels, testing at Sandia National Labs has examined decomposition rates for various panel types under various types of loads [48]. Early flaming decomposition did not clearly depend on structural loading, except for one type of panel, which exhibited back-side burning under the tension tests, but no back-side burning under other loads. Burn rates for the tension tests were significantly higher than for the compression and no force tests because of the difference in the behavior on the back side of the panels. After flaming subsided, all the panels decomposed at a rate that was not related to the residual force imposed.

**Ignition**

Carbon fiber composites will generally ignite when exposed to a sufficiently intense thermal environment. Cone calorimetry yields ignition times, which can be used to compare flammability safety for similar materials. Already detailed reports with extensive data are good resources in this regard, including the more comprehensive studies by Brown et al. (1988) [14] and Mouritz (2006) [7]. Ignition is a difficult phenomenon to use for a fundamental test for characterization of a material. It can be length and time scale dependent, as it locally relates to the combination of fuel, oxidizer, and a heat source. More generically, it also depends on the right conditions existing for propagating an initial flame.

The work of Hubbard et al. (2011) [51] involved peak heat fluxes in the range of 20-30 kW/m². Ignition was not particularly repeatable for some of the tests. In others, an ignition source was provided, in which case ignition was readily achieved. In a later test series, Brown et al (2013) [48] found ignition to be easily achieved for larger panels and higher heat fluxes. Panels will often burn robustly for a time over the entire surface, but also may burn in a regime where the flame dances around the surface presumably due to localized jetting of gases and periodic ignition thereof.

In transportation accidents, ignition is not expected to normally be a significant consideration. Transportation fuels are much more susceptible to ignition, and will likely cause the fire that
ignites the structural material. Thus, the question of whether composites alone ignite may not be particularly relevant except in specific and less common applications.

**Health Effects**

Mouritz and Gibson (2006) [1] review the health hazards of composites in fire. The main concerns relate to several aircraft incidents that resulted in the firefighting response teams complaining of health effects. Response crews experienced significant symptoms that likely were caused by their proximity to the fire. Noxious fumes, soot, and fibers are believed to be the largest potential hazards besides any thermal or structural effects. Rules have been implemented for dealing with such fires that include full body suits and respirators. Though combustion release of microfibers has received the majority of the attention as the cause for such issues, it is not yet generally accepted to be the exclusive cause. The NASA series of large-scale tests previously mentioned focused on product emissions, and largely concluded that aircraft composites in fire would meet fiber release regulatory guidelines [44-46]. In addition to data in Mouritz and Gibson (2006), Lopez de Santiago et al. (2010) [43] measure toxic emissions from panel combustion tests.

![Soot TEM images from intermediate-scale composite fires.](image)

Sampling health related products from composite fires is not a major driver for the work at Sandia National Labs. Any such data has been collected for secondary purposes. In one of the intermediate-scale tests [47], soot samples were taken from the fire plume at early times (5-10 minutes after ignition) corresponding to the heaviest sooting times. Transmission electron microscopy (TEM) analysis of the deposits suggests that the flame products are heavily agglomerated chains of spherical carbon particles. Two images from this test series are found in Figure 4. Spheres varied by about a factor of 2 in size in the samples from two separate tests. This difference is believed to be due to slightly different environmental histories of the agglomerates. Notably, no fibers were found on the collection grid. This is taken as evidence
that fiber emission may not occur until later times after composites have been in a fire environment for an extended period of time.

Summary
This paper reviews past work on the phenomenology of carbon fiber epoxy composite combustion with an emphasis on the fire and thermal related properties, as well as unique characteristic behaviors observed in testing. A major motivation for this review is the assimilation of material that provides experimental evidence relating to capturing phenomenology necessary to model the fire behavior of such fire events. Many papers referenced herein (and also many omitted due to the experimental focus of this paper) attempt to model varying aspects of composite burning. The complexity due to the heterogeneous nature of the material and due to the micro-structure is believed to be one of the biggest challenges with these materials and their thermal behavior. The fact that the materials tend to be structural and that the eminent collapse is not necessarily independent from the burning is also a complicating factor. Swelling of the substrate challenges the modeling. The differing thermal decomposition regime and mechanism for the fibers and epoxy also is a challenge.

Many material properties are available in widely scattered papers throughout the literature. It is difficult to determine at times the source of the composite material, as well as the range of potential material property values given the variety of different industrial sources for carbon fiber epoxy materials. It is therefore risky to take data from one test and apply it to another without ascertaining that the materials are appropriate surrogates.

There are very few larger scale tests that have been documented on composite fires. Those that exist tend to lack detail, as they lack instrumentation or they focus on features besides the behavior of the composites during the test. Some complexity is found in the results of the large-scale tests that cannot necessarily be predicted by current models. One can extrapolate the expected behavior from the testing that has been done at other scales, but without more testing and documentation it will not be possible to fully predict the behavior of these materials in full-scale events. Current work at Sandia National Laboratories is contributing to the understanding of large-scale carbon fiber epoxy composite fires through experimental and modeling efforts.

Acknowledgements
Allen Ricks and Amanda Dodd provided manuscript reviews. Linda Swaving and Tiffany Flores helped generate and format the references. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

References


