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Review of Smoke Toxicity of Fiber-Polymer Composites Used in Aircraft

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I. Introduction

A SAFETY concern with the use of fiber-polymer composites in aircraft, rotorcraft, and spacecraft is their smoke toxicity in the event of fire. Composites produce smoke that consist of a potentially toxic mix of combustion gases, airborne fiber fragments, and char (soot) particles. The fiber and char particles suspended in smoke are ultrafine, typically 0.3–3 μm in size. With the growing use of composite materials in both airframe structures and aircraft cabins, there is a need for the aviation industry to better understand the toxic potency of the smoke and the health problems caused by smoke inhalation. The purpose of this paper is to review the current state of knowledge in the smoke toxicity of aircraft composite materials.

The fire properties and flammability of the composite materials used in aircraft, most notably graphite fiber-epoxy used in airframes and glass fiber-phenolic used in cabins, have been thoroughly evaluated [1–17]. Fire reaction properties of graphite-epoxy and glass-phenolic composites, including their time to ignition, heat release rate, limiting oxygen index, and flame spread rate, have been determined for a diverse range of fire conditions. The fire reaction properties of other aerospace composite materials have also been determined, including graphite-bismaleimide, glass-epoxy, and aramid-epoxy [12,18–21]. Although a wealth of information and scientific data is available on the fire performance and flammability of aircraft composite materials, much remains unknown about the toxicity and health hazards of the smoke these materials produce in the event of an aircraft fire.

Several aircraft fires involving composite materials have raised concerns about smoke toxicity from the fumes, char, and fiber fragments. One of the earliest incidents occurred in 1990 when an accident investigation team from the Royal Air Force attended the crash site in Denmark of a burnt out Harrier GR5. The fuselage and wings of the aircraft contained graphite-epoxy composite. Many in the team suffered health problems that varied in severity from eye and skin irritations to severe breathing difficulties [22–24]. These health problems occurred even though protective clothing, masks, and goggles were worn. In another incident, 22 firefighters were hospitalized after extinguishing a fire on a U.S. Air Force F-117A Nighthawk stealth fighter, which contains a large amount of composite material. The firefighters suffered nausea, headaches, eye soreness, skin irritation, and labored breathing when exposed to the smoke from the burning aircraft.

It has been speculated that the health problems are caused by the release of ultrasmall fragments of fiber, which are believed to pierce the skin causing irritation, adhere to the eyes causing soreness, and cause breathing difficulties when inhaled [25]. Smoke and fumes released during combustion of the organic matrix also contribute to the health complaints. Other health hazards have been attributed to composites in fire, including airborne fibers behaving as so-called microscopic poison darts that deposit toxins in the respiratory system [26]. However, many of the explanations for the health problems are speculative and not based on clinical studies or laboratory research. Furthermore, the delayed and long-term health problems from smoke inhalation are not well understood. Despite the numerous incidents of health problems experienced by people exposed to burning composites, medical researchers, toxicologists, and the aviation industry have paid scant attention to the health effects of smoke produced by composite materials. The growing use of composites in aircraft where passengers and crew will be exposed to smoke in the event of fire underpins the need to better understand the toxicity and health effects of smoke inhalation.

Chaturvedi and Sanders [27] reviewed published research into the smoke toxicity of aircraft materials, but they did not focus on composite materials. Furthermore, the review by Chaturvedi and Sanders was published in the mid-1990s and, since then, a great deal of new work has been published on smoke toxicity of aircraft composites. Other reviews into the smoke toxicity of composites have been published [28–30], although without considering the combined effects of the combustion gases, fiber fragments, and char particles.

This paper presents a review of published research into the toxicity and health effects of the combustion gases, fiber fragments, and char particles within the smoke plume of fiber-polymer composite materials used in aircraft, rotorcraft, and spacecraft. An overview of the smoke properties of aerospace composite materials is presented, with emphasis given to the factors controlling the density of the smoke plume. The N-gas model for calculating the toxic potency of combustion gases is described as an analytical method for assessing the smoke lethality of composites. Toxicology and epidemiology

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studies into the inhalation of fiber fragments and soot particles are reviewed. Most attention is given to the toxicity of graphite and glass fibers because of their use in aircraft composite materials, although the toxicity of aramid fibers used in some aircraft components is also considered. Based on this review, gaps in our understanding of the toxicity and heath effects of smoke from burning composites are identified, and topics requiring further research are suggested in the attempt to increase the fire safety of composite materials when used in aircraft.

II. Smoke Density of Composite Materials

The smoke plume from a burning composite is a mix of small fiber fragments, ultrafine char particles, and combustion gases, and it is these materials that are the potential health hazard. The density (or "thickness") of smoke is determined mainly by the airborne concentrations of these materials. Smoke density has long been recognized as critical to aircraft safety because thick, blinding smoke reduces visibility and increases the cabin escape time for passengers and crew. The smoke properties of a variety of composite materials, including those used in aircraft, have been determined in laboratory tests [1,31]. The test apparatus most often used to measure smoke density is the cone calorimeter [32], although the Ohio State University calorimeter [33] and National Bureau of Standards smoke chamber [34] are also used. Laboratory tests using these instruments are useful for ranking materials in terms of their relative smoke density values, although it is not possible to accurately scale up the smoke density values measured with such apparatus on a small material test piece to the smoke released by a large composite component in an actual aircraft fire. This requires large-scale tests performed inside aircraft cabins containing composite materials, and only a few such studies have been reported (e.g., [35–39]).

Table 1 gives smoke density values for various aerospace composite materials with different polymer matrices. The smoke value is not an inherent fire property of the material, but depends on the combustion conditions (e.g,. heat flux, oxygen level, presence or absence of flame, etc.) and the test conditions under which the smoke density was measured (e.g., test method, specimen geometry, etc.). The values given in Table 1 are expressed as the smoke extinction area (SEA, m^2/kg), which is a measure of the smoke density having units of square meters of smoke particulate scattering surface per kilogram of material burned. The SEA values were measured at the heat flux of 50 kW/m^2, which heats the composite surface to about 700°C. The smoke density from the graphite-epoxy composite used in airframes is high compared to the other materials. There are other thermoset resins (e.g., polyimide) and thermoplastics [e.g., polyethersulfone (PES), polyetheretherketone (PEEK)] that produce less smoke than graphite-epoxy because of their higher char yield when matrix decomposition occurs, although they are more expensive.

An examination of the published data reveals that smoke density is dependent on a variety of factors, including the volume fractions and types of polymer and fiber reinforcement in the composite, the heat flux (or temperature) and oxygen content of the fire, and the mode of combustion (flaming or smoldering). It is difficult to make too many general statements about the smoke density based on the available data, although some observations can be made. Firstly, the smoke density increases with the volume fraction of polymer in the composite. This is expected considering that the polymer matrix contributes more to smoke production via combustion gases and char particles than the fiber reinforcement. Secondly, smoke density usually (but not always) increases with the temperature of the fire due to an increase in the release rate of combustion gases and char particles. Lastly, the ability of the polymer to transform into solid carboneaceous char that is retained in the material has a major influence on the smoke yield. The greater the mass fraction of polymer that is converted into char, the less that can be released as gas, thereby reducing the smoke density.

Smoke density may also be considered an indirect measure of the toxic potency of the fumes. Although there is not necessarily a direct correlation between the density and the toxicity of smoke, the smoke density is still an indirect measure of the concentration of potentially hazardous gases and airborne particles. For example, Fig. 1 compares the smoke density (expressed as smoke extinction area) with the concentrations of carbon monoxide (CO) and carbon dioxide (CO_2) released from a composite material over the duration of a fire. The curves in Fig. 1 show a strong correlation between the smoke density and the amounts of CO and CO_2 present in the smoke. The sudden increase in the smoke density is accompanied by a corresponding rise in the CO and CO_2 concentrations. The concentrations of the smoke and gases then remain relatively constant with time until the composite is completely decomposed. However, not all composites exhibit such a strong relationship between smoke density and CO and CO_2.

III. Toxicity of Combustion Gases in Smoke

The main cause of death in most aircraft fires is the inhalation of toxic gases released by the aircraft materials, rather than heat from the fire. The gas that generally has the greatest individual hazard is carbon monoxide. Chaturvedi and Sanders [27] report that postmortem blood samples taken from 360 people who died in aircraft fires showed carbohemoglobin saturation levels high enough to impair performance. The amount of CO produced by a burning composite material depends on the composition of the organic constituents, the fire temperature, and the oxygen availability; but even very low levels of CO can cause incapacitation or death. Death in humans will occur within 1 h when the CO concentration in air reaches about 1500 ppm. In addition to CO, other toxic gases have been measured inside aircraft cabins during fire, including hydrogen chloride, hydrogen cyanide, hydrogen fluoride, and high concentrations of graphite dioxide (CO_2) [38,39].

A large amount of data has been published on the concentrations of CO and CO_2 inside the smoke plume of composite materials [4,6,7,9,14,19,40–43]. The yields of CO and CO_2 gases from a wide variety of aerospace composite materials with thermoset (e.g., epoxy, phenolic, bismaleimide, phthalonitrile) or thermoplastic matrix [e.g., PEEK and polyphenylene sulphide (PPS)] composites

Table 1 Smoke density values for aerospace composite materials

Polymer matrix[a]	Fiber reinforcement[b]	SEA, m^2/kg[c]	Reference
Epoxy	Graphite	1232	[37]
Cyanate ester	Glass	898	[38]
PPS (polyphenylene sulfide)	Glass	690	[38]
Bismaleimide	Glass	546	[38]
Polyetherketoneketone	Graphite	274	[38]
Phenolic	Glass	268	[29]
PMR-15 polyimide	Glass	170	[38]
Phenolic	Graphite	156	[39]
PES (polyethersulfone)	Graphite	145	[38]
PEEK (polyetheretherketone)	Graphite	69	[38]

[a]Volume fraction of the polymer matrix is different between materials, although most within the range of 0.4–0.5.
[b]Data are present for composites reinforced with graphite or glass fibers, although the fiber type does not significantly affect the smoke density value.
[c]SEA measured at the heat flux of 50 kW/m^2.

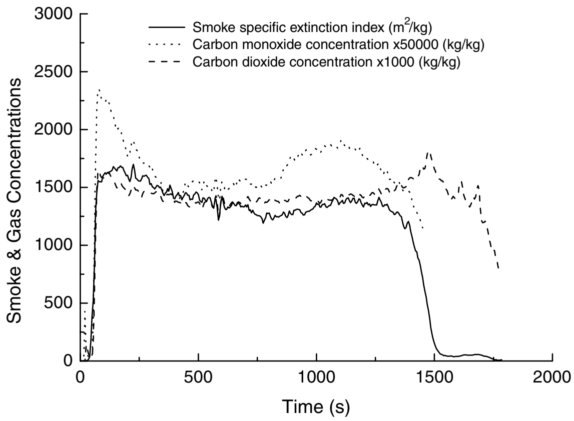

Fig. 1 Trends in smoke density (SEA) and CO and CO_2 concentrations during the flaming combustion of a fiber-polymer composite exposed to a constant heat flux of 50 kW/m^2.

have been determined for a range of fire test conditions. Typical concentrations of these gases measured for a medium intensity fire (heat flux of 50 kW/m^2) are given in Table 2. The concentrations of CO and CO_2 vary considerably between the materials, with the graphite-epoxy composites used in airframes releasing relatively large amounts, whereas the glass-phenolic materials used in cabins producing smaller amounts.

It is generally observed that the concentration of CO in the smoke plume drops with an increase in the char yield of the polymer used for the matrix phase, as shown in Fig. 2. This is due to a greater mass of polymer being retained as solid char rather than released as volatile gases (including CO and CO_2). The yields of gases such as CO and CO_2 are also dependent on the type of combustion. For example, Hunter and Forsdyke [42] determined that a glass fiber-phenolic composite (similar to that used in aircraft cabins) released about 50 ppm CO and 300 ppm CO_2 when decomposition occurred by nonflaming combustion. However, when the same material decomposed via flaming combustion, the gas concentrations increased substantially to 100 ppm CO and 5000 ppm CO_2 due to the higher decomposition reaction rate of the phenolic matrix. Therefore, suppressing flaming combustion may be an effective method for reducing the release of CO and CO_2.

In addition to CO and CO_2, aircraft composite materials release a large number of heavier organic volatile compounds that may have a large impact on the toxic potency of the smoke. However, few studies have analyzed the complete composition of the gases from aerospace composites, and much remains unknown about their toxic potency [44–46]. The lack of information on the types and amounts of gases released by aerospace composite materials is a major deficiency in understanding the toxic potency and potential health hazards of these materials in the event of fire. Complete chemical analysis of all the compounds released by composite materials is a difficult and very time-consuming task, which is a key reason why studies are rarely performed. The few studies that have been performed reveal that the composites used in aircraft release many types of potentially toxic gases. For example, Vogt [44] detected over 100 different volatile compounds produced in the thermal decomposition of graphite-epoxy composites used in airframes, whereas Tewarson and Macaione [9] found a large variety of gases in the smoke from the glass-phenolic composites used in aircraft cabins, including toluene, methane, acetone, propanol, propane, benzene, and various aromatic compounds. Lipscomb et al. [46] identified 90 different gases released by a burning graphite/bismaleimide composite, several of which are known to be mutagenic or carcinogenic in laboratory mice. Quinoline was one of the main combustion gases, and this compound is known to damage DNA and alter the functions of the retina, optic nerves, cardiovascular system, and central nervous system. The smoke also contained toluidine that can cause health problems such as methemoglobinemia, and also contained N-hydroxymethylcarbazole that is a mutagen.

Smoke toxicity can be increased considerably when composites are reinforced with organic fibers, such as aramid, rather than graphite or glass fibers. Aramid fibers are increasingly being used in damage tolerant aircraft structures needing high impact resistance or vibration damping properties, such as helicopter motor casings. Aramid fibers release CO, CO_2, HCN, nitrogen oxides, and various organic compounds [47–49]. The combination of gases released by aramid fibers and the polymer matrix can increase considerably the gas concentration of a composite material, although the toxicity and composition of the combustion gases released by aramid fiber composites used in aircraft have not been studied in detail.

Composite materials used in aircraft may contain polymers that are chemically modified or blended with flame retardant additives to delay ignition and reduce flammability [1]. The yields of combustion gases from flame retardant composites can be much less than the untreated material, particularly when the additive promotes char formation. These additives slow thermal decomposition of the composite material and thereby reduce the smoke density and gas concentration. However, some flame retardants can greatly increase the smoke density. Despite the growing use and variety of flame retardants used in composites, few studies into the toxicity of combustion gases from flame retardant composites have been reported. It is well known that brominated polymers release dioxins and dibenzofurans, whereas chlorinated polymers produce hydrogen chloride, dibenzo-p-dioxins, and related dioxin volatile compounds [50]. High levels of dioxins can cause chloracne and are potent modulators of cellular growth and differentiation, particularly of epithelial tissues, that can promote cancer. However, the toxicity and health effects of the flame retardants used in aerospace composites are not well understood.

IV. N-Gas Model for Smoke Toxic Potency

Experimental smoke toxicity tests are an expensive and time-consuming approach to assess the safety of composite materials used in aircraft. Several models have been developed to calculate the toxic dose of single or multiple gases generated by fire which reduces the need for tests [51–56]. The models can estimate, with varying degrees of accuracy, the concentration of gases needed to cause incapacitation and/or death. Levin and colleagues developed a mathematical approach to calculate smoke toxicity, which is called the N-gas model [57–62]. The model eliminates the need for an exhaustive experimental testing program, which often involves laboratory animals such as mice, rats, and guinea pigs. The model is based on the assumption that a small number N of gas types in smoke account for a large percentage of the toxic potency. That is, the model

Table 2 Graphite monoxide and graphite dioxide yields for aerospace and nonaerospace composite materials

Polymer matrix[a]	Fiber reinforcement[b]	CO yield, kg/kg[c]	CO_2 yield, kg/kg	Reference
Phenolic	Glass	0.016	1.18	[10]
Polyester	Glass	0.036	1.74	[10]
Epoxy	Graphite	0.042	1.62	[37]
Vinyl ester	Glass	0.046	1.74	[10]
Cyanate ester	Glass	0.105	0.58	[40]

[a]Volume fraction of the polymer matrix is different between materials, although most within the range of 0.4–0.5.
[b]Data are present for composites reinforced with graphite or glass fibers, although the fiber type does not affect significantly the yield values of CO and CO_2.
[c]Gas concentrations measured at the heat flux of 50 kW/m^2.

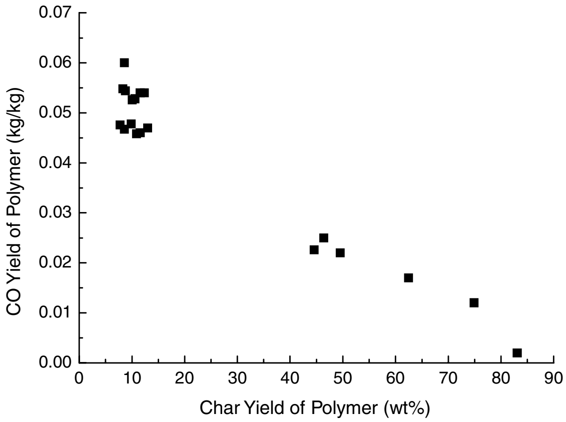

Fig. 2 Relationship between char yield and CO yield for several thermoset polymers.

assumes that only a few gases are toxic, and any other gases present in the smoke are not hazardous because their concentration is very low. The effects of gases that occur in moderate or trace amounts within the smoke plume of a burning composite are not considered important and are ignored in the N-gas model. As mentioned, the epoxies, phenolics, and other polymers used in aircraft composites release a large number of different gases, several of which are known to be toxic at high concentrations, but the N-gas model only considers the most common gases. Despite this assumption, the N-gas model has proven accurate in calculating the toxicity of many combustible materials including a wide range of polymers.

To use the model, a sample of the test material must first be thermally decomposed using a bench-scale smoke method, such as the National Institute of Standards and Technology radiant panel or National Institute of Building Sciences toxic hazard tests. The gas concentrations in the smoke are measured by chemical analysis techniques, and the data are then used to calculate the smoke toxicity using the N-gas model. The six-gas model considers the toxicity of six gases commonly found in smoke (CO, CO_2, O_2, HCN, HCl, and HBr) and is expressed by the empirical equation

$$\text{N-gas value} = \frac{m[\mathrm{CO}]}{[\mathrm{CO_2}] - b} + \frac{21 - [\mathrm{O_2}]}{21 - LC_{50}(\mathrm{O_2})} + \frac{[\mathrm{HCN}]}{LC_{50}\mathrm{HCN}} + \frac{[\mathrm{HCl}]}{LC_{50}\mathrm{HCl}} + \frac{[\mathrm{HBr}]}{LC_{50}(\mathrm{HBr})}$$

where LC_{50} is the toxic potency of the gas, which must be experimentally measured in animal smoke tests. The numbers in brackets indicate the concentrations of the CO, CO_2, HCN, HCl, and HBr gases (in parts per million) and O_2 (in percent) present in the smoke, and m and b are empirical constants. When the mass of burnt material generates a sufficient amount of combustion gases to produce an N-gas value of about 1, then the smoke toxic potency is high enough to cause some animals to die when exposed to the smoke plume. When the N-gas value is above $\sim$1.3 then it is highly likely that all the animals will die. When the value is below 0.8 then the gas concentrations are sufficiently low that it is predicted that all the animals will survive smoke exposure.

The benefit of the model is that, by knowing the concentrations and the LC_{50} values of a few gas types, it is then possible to calculate the toxicity (defined by N-gas value) for the smoke. The N-gas model has been shown to correctly predict the level of smoke toxicity for a variety of materials (e.g., wood, plastics) and should be applicable to aircraft composites, provided the gas concentrations in the smoke are known. However, the accuracy of the N-gas model in the prediction of the smoke toxicity for polymer composite materials has not been assessed, and is a topic worthy of further research and analysis to reduce the need for a large number of smoke toxicity tests on aircraft composite materials.

V. Toxicity of Fibers

A. Fibers in Smoke

The aviation industry is concerned with the release of fibrous particles from composites into the smoke plume. Serious health problems with the inhalation of asbestos and other toxic mineral fibers are causing concern about the possible hazards of the graphite, glass, and aramid fibers used in aircraft composite materials. However, the toxicity of airborne fibers inside the smoke plume of burning aircraft composite materials is not well known. Medical research has shown that the concentration and size of mineral fibers (such as asbestos and silica) are critical parameters in controlling their toxicity. The toxic potency generally increases with the fiber concentration and when the fiber particle size is within a narrow range (usually in the micron size range). Several studies have measured the concentration and sizes of fiber particles in the smoke plume of burning composite materials, and the key findings have been reviewed by Gandhi et al. [28]. The studies measured the amount and size of fibers released from burning graphite-epoxy composites [63–68]. Very little information is available on the release of fibers from other types of graphite composites (e.g., with a polymer matrix of bismaleimide, PPS, etc.) and glass-phenolic composites where the results may be different. Further work in the measurement of fibers inside the smoke released from the different types of composite materials used in aircraft is needed.

Measurements of the fiber content in the smoke plume of burning graphite-epoxy composites have shown large variations, with values as low as 1% and as high as 23% of the fibers being released into the plume [63,65,66]. This variation occurs because the release of fibers depends on several factors, including the fiber architecture (e.g., unidirectional, woven, stitched), original fiber length, char yield of the polymer matrix, and ablative properties of the composite. Other factors also contribute to the release of fibers, including the fire temperature, flame turbulence, and wind speed. A key factor is the degree of pulverization to the composite caused by crash landing, which crushes the fibers into small fragments, assisting their release into the smoke plume. In one large-scale study, a 45 kg aircraft composite component was burnt within a jet fuel pool fire for 20 min [62]. Filters suspended in the smoke plume were used to collect airborne graphite fibers, and the average concentration was under 0.14 fibers/cm^3 of smoke. This fiber concentration is below the maximum allowable level of fiber exposure specified by health organizations in many countries.

Another critical issue with the release of fibers from burning composites is their size. Airborne fibers within a certain size range can be easily inhaled and deposited in the respiratory system, whereas large fibers are less hazardous because they are not easily inhaled. Table 3 and Fig. 3 show the ability of humans to inhale particles with different aerodynamic size ranges. Airborne fibers have irregular shapes, and their size is therefore expressed in terms of an equivalent aerodynamic diameter d_a, which is defined in terms of the diameter of an equivalent spherical particle that has the same terminal velocity as the fiber. Fibers with an aerodynamic diameter greater than about 50 μm are usually not inhaled because they quickly fall from the smoke plume under their own weight. Any particle with an aerodynamic diameter greater than $\sim$50 μm that is inhaled is long enough to be trapped in the nose and throat, and then rejected by sneezing or coughing. Therefore, relatively large fibers ($d_a > 50$ μm) in the smoke of a burning aircraft composite are unlikely to be inhaled. The likelihood of inhaling fibers is much greater in the aerodynamic size range of $\sim$7 to 50 μm because they remain suspended in the smoke plume for a longer time than larger particles. When fibers in this size range are inhaled, they are deposited in the nose, throat, and other upper regions of the respiratory system, although, as with larger particles, they are often quickly rejected. The fiber size range in smoke that poses the greatest risk is between $\sim$0.7 and 7 μm because the particles can be easily inhaled deep into the respiratory system with little chance of being rejected.

The diameter of graphite fibers used in composite materials is typically 7–10 μm, which is slightly too large to be inhaled deep into the respiratory system. However, the diameter of graphite fibers can

Table 3 Effect of fiber size on inhalation

Aerodynamic diameter	Effect
>50 μm	Usually not in air long enough to be inhaled.
~7–50 μm	Particles in this size range are often large enough to be caught by nose and throat and are often ejected by coughing or sneezing. Usually filtered out by the nose, although can be deposited in cilia or airways.
0.7–7 μm (respirable dust)	This particle size range presents the greatest hazard. They are small enough to reach the lungs when inhaled, yet large enough to remain in the lungs when we breathe out. Deposited in the lower bronchioles and alveoli.
<0.5 μm	Usually remain airborne and are exhaled.

be reduced in fire by oxidation and fibrillation to a size that can be easily inhaled. Fibers inside the smoke plume occur in different forms, ranging from single filaments to fragments that can contain up to several hundred filaments bound together by char or resin. An analysis of graphite fibers collected in the smoke plume of burning graphite/epoxy composites has revealed that the mean fiber diameter is under 7 μm, which is within the respiratory range [28]. Figure 4 shows a distribution plot giving the range of fiber diameters collected from the smoke of a graphite/epoxy laminate. Included in the figure is the range of original fiber diameters before fire testing, and this was between 5 and 7.5 μm. It is seen that the diameter of graphite fibers inside the smoke plume is between 1.5 and 7.5 μm, with about 60% of the total fiber population being small enough to be inhaled deep into the lungs. However, the fibers are often much longer than they are wide, and their length is often sufficient to stop them being easily inhaled.

The diameter of glass fibers used in composites is about 12 μm, which is above the critical size range of 0.7–7 μm that can be inhaled deep into the respiratory system. Unlike graphite fiber, the diameter of glass fiber is not reduced in a fire because oxidation or fibrillation does not occur. However, the sizes of glass fibers in smoke have not been measured experimentally in fire tests to confirm that their size is not within the critical size range of inhalation.

B. Toxicity of Graphite Fibers

The toxicity of graphite fibers has been studied extensively [69–79]. Most toxicological and epidemiological studies focus on the occupational health of industry workers who manufacture graphite fibers. In these studies, the health effects of inhaling virgin fibers have been evaluated. However, the toxicity of fibers released from a burning composite may be substantially different than virgin fibers because they are contaminated with various solid combustion products, including char and other organic residuals of the polymer matrix. The health problems associated with inhaling contaminated graphite fibers is not as well understood as for virgin graphite fibers, and this is an issue that fails to attract much attention from the medical research community. Despite this, toxicology studies performed on graphite dust and virgin fibers provide insights into the potential health problems of inhaling graphite fibers from burning composite materials.

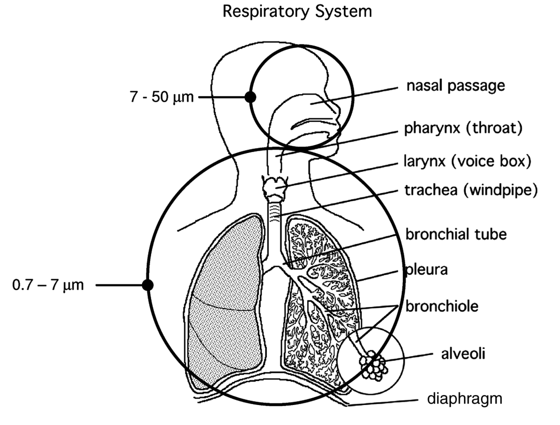

Fig. 3 Schematic of the human pulmonary system. Locations where fiber particles of different aerodynamic diameters can reach are indicated.

1. *Effect of Fiber Dosage and Exposure Time*

A few toxicology studies have been performed using laboratory animals to determine the safe exposure limits and the health effects of inhaling high doses of virgin graphite fibers [71,74–78]. The studies have examined the respiratory responses of animals exposed to high doses of graphite fiber (>40 fibers/cm^3 in air), which is much higher than the fiber concentrations measured in the smoke plume of burning composite materials (<1 fiber/cm^3). Thomson et al. [74] exposed laboratory rats to airborne graphite fibers at concentrations of 40, 60, or 80 fibers/cm^3 for 1 h each day over a nine-day period. The graphite fibers were 3.5 μm long and 3.5 μm in diameter, which is about the average diameter of airborne graphite fibers in a smoke plume. Postmortem examination of lung tissue taken from euthanized animals was performed by Thomson et al. at different times between 1 and 14 days after fiber exposure, and no signs were found of pulmonary infection or damage. Furthermore, no graphite fibers were observed in the lung tissue, presumably because the fibers were too long to be inhaled deep into the respiratory system. Warheit et al. [75] also studied the respiratory response of animals when exposed to high concentrations of graphite fibers suspended in air. In this study, rats were exposed to doses ranging from 50 to 90 fibers/cm^3 for times between one and five days. The graphite fibers were 1–4 μm wide and 10–60 μm long. The exposure caused inflammation of the lung tissue, although the reaction was not permanent, with the inflammation subsiding within 10 days of the final exposure. It is important to note that, although the inhalation caused a short-term reaction, as mentioned, the toxicity tests were performed at dose levels well in excess of the fiber content measured in the smoke plume of a burning graphite-epoxy composite.

The effect of exposure time to graphite fibers on the respiratory system has also been investigated in laboratory tests using animals [71,75,78]. The exposure times used in the toxicity studies were much longer (ranging from several hours to many days) than the times that passengers, crew, and firefighters are exposed to the smoke of aircraft fires. Holt and Horne [78] exposed guinea pigs to graphite fiber dust for 104 h and did not observe any significant health problems. Owen et al. [71] and Waritz et al. [76] performed respiratory studies on rats exposed to graphite fibers for 6 h per day for five days each week over a 16 week period. No changes to the lung function response were detected. These studies indicate that breathing problems are not experienced by laboratory animals after exposure times and fiber dose levels that are much higher than in an aircraft fire.

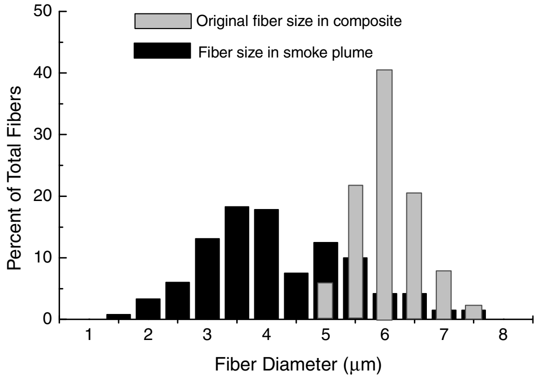

Fig. 4 Histogram showing the variation in fiber diameter before and after fire testing of a graphite/epoxy composite. Reproduced from Gandhi et al. [28].

Several studies have investigated the physiological responses of the respiratory system to the inhalation of graphite and graphite-polymer dust particles. Owen et al. [71] euthanized rats immediately after exposure to a high dose of graphite fibers over a long period, and then performed a postmortem examination of the brain, lungs, esophagus, stomach, duodenum, jejunum, ileum, colon, nasal turbinates, larynx, trachea, and lymph nodes. No damage to any of these organs or tissues was observed. Histologic examination of the lung tissue revealed the presence of graphite particles that were coated with alveolar macrophages, which indicated the body's self-defense mechanism worked by phagocytosis to dissolve the fibers. A in vivo toxicity study by Zhang et al. [77] confirmed this observation. The study by Zhang et al. involved intratracheal injection of a liquid suspension of graphite fibers or graphite fiber-polymer dust directly into the lungs of laboratory mice. Most of the fibers had a diameter under 5 μm and the medium length was 37.5 μm. Postmortem examination of lavage cells extracted from the lungs at different times after the injection revealed that the fibers persisted for at least one month. However no fibers were found in the lungs for periods longer than about one month, and it is believed that the fibers and dust particles were dissolved in the lungs by macrophages. Zhang et al. did not observe any adverse reactions to the graphite, and concluded that they are biologically inert at the high dose level and small particle size range studied.

Martin et al. [72] also studied the inhalation toxicity of graphite-polymer composite dust particles. Martin performed the study in vitro using rabbit alveolar macrophages as a measure of toxicity and in vivo using direct intratracheal injection into the lungs of rats. The toxicity of five types of graphite fiber composites were investigated: four types of graphite-epoxy and one type of graphite-PEEK. These materials are typical of the composites used in aircraft. The composites differed in the type of graphite fiber (polyacrionitrile or pitch-based) and type of epoxy resin (cured with an amine or aromatic amide reactive agent). The composites were pulverized into dust particles to an aerodynamic diameter of 1.1–1.9 μm before being ingested by the animals. It was found that the type of graphite fiber had no significant effect on toxicity, although the type of epoxy matrix had a major influence. It was discovered that composites containing the epoxy matrix cured with the aromatic amine-curing agent had the highest cytoxicity, although the reason for this is not known. A significant increase in the amount of alveolar macrophages and neutrophils were observed in samples of the lung tissue taken from animals exposed to the amine-cured epoxy composite. However, the infection was not lethal, and the graphite-epoxy dust was found to be much less toxic than known fibrous carcinogens such as quartz dust. Martin et al. [72] suggest that dust particles from graphite/epoxy composites cured with an aromatic amide agent have the potential to cause biologic effects in the human lung, although the types and extent of acute lung damage that may occur are not known.

2. *Graphite Fibers in Smoke*

Only a few studies have assessed the toxicity of graphite fibers in the smoke plume of burning composite materials. Whitehead et al. [80] exposed laboratory rats to the smoke released from burning graphite-epoxy composite and monitored changes to their respiratory response. The composite was ground into a fine powder before burning to ensure a high dose of fibers in the smoke. Analysis of the smoke revealed the presence of various combustion gases, including CO, CO_2, SO_2, and nitrogen oxides, as well as graphite fibers with a median diameter of 1.6 μm. The smoke was hazardous enough to cause several rats to asphyxiate during the test. The lung function of the surviving rats was studied over a seven-day period following the smoke exposure. Inflammation of lung tissue was diagnosed, although Whitehead and colleagues believe that this was a typical reaction to severe smoke inhalation rather than a health problem unique to the inhalation of smoke from a graphite-epoxy composite material. No sign of more serious lung damage was found, such as hemorrhaging or acute lung injury.

Castiostro [81] assessed the smoke toxicity of burning graphite-epoxy materials to determine the conditions that cause incapacitation and death inside an aircraft during fire. The toxicity test was designed to replicate the smoke conditions inside an aircraft by having the ratio of the composite sample weight to smoke chamber volume scaled to a similar ratio as the composite panel weight to cabin volume in a large aircraft. The respiratory and cardiac responses of rats were monitored when exposed to the smoke, and the concentration of their blood enzymes was measured to provide an indication of tissue necrosis in the respiratory, neural, and cardiovascular systems and in the liver and kidneys. In addition, the delay in reaction time of the animals due to smoke inhalation was measured. To measure the reaction time, rats were conditioned to jump on a pole to avoid a mild electric shock passing through a metal grid on the cage floor to the smoke chamber. Before the toxicity test, the rats were trained to jump given a light or sound signal that warned them the gird was about to be electrified. The time delay in jumping onto the poles after the warning was used by Castiostro as a measure of the loss of avoidance response of the animals. When the rats were exposed to the smoke from a burning graphite-epoxy composite, their avoidance and escape responses were seriously affected and most of the animals died after about 16 min. An autopsy revealed extensive pulmonary edema and kidney damage consistent with the inhalation of a lethal dose of toxic smoke. However, the testing did not identify the combustion gases or graphite fibers or combination of both that was responsible for the delayed responses and death of the animals.

Kimmel et al. [82] used guinea pigs to evaluate the toxic potency of smoke released by a graphite-epoxy composite. The gases in the smoke were mostly CO_2 and CO, with small amounts of NO_2 and SO_2. Kimmel et al. found the breathing response of the guinea pigs was not affected until the smoke density rose above a critical level, at which time the animals experienced labored breathing similar to acute asthma. Not surprisingly, the difficulty in breathing increased with smoke density and, at the highest level used in the test, the animals suffered convulsions. Kimmel et al. found that filtering out the airborne graphite particles in the smoke before exposing the animals moderated the adverse reactions, but did not eliminate the breathing problems. This suggests that breathing problems are caused by both the solid particles (fibers, char) and the combustion gases in the smoke plume, and not by a single component. It was observed that breathing returned to normal when the animals were given fresh air, however, the recovery was short-lived for several guinea pigs who suffered recurring bouts of labored breathing. The implications of this study for humans are not conclusive, but obviously severe breathing problems will be experienced when exposed to the smoke of graphite-epoxy composites due to the combustion gases and fibers.

In summary, the toxicology studies performed to date have found no major health problems associated with inhaling graphite fibers or graphite-polymer composite dust. Most of the studies were performed using fiber dose levels and exposure times far in excess of those expected in a smoke plume from a burning composite aircraft structure, which suggests that acute lung injury and other long-term respiratory problems should not be experienced from inhaling graphite fibers during an aircraft fire. However, no epidemiological data are available on the long-term health problems that may arise from inhaling smoke from composite materials containing graphite fibers that are contaminated with char and other solid degradation products from the polymer matrix. A variety of hazardous compounds have been detected on the surface of graphite fibers following fire, including aromatic compounds, phenols, and polycyclic aromatic hydrographites, which can be carcinogenic [45]. Therefore, contaminated fibers may possess different toxicological properties than virgin graphite fibers but, as yet, a thorough analysis of their health effects has not been performed.

3. *Toxicity of Glass Fibers*

The health effects from inhaling glass fibers used in aircraft cabin composite fittings have also been studied, and as with graphite fibers, most of the toxicology studies have been performed on virgin fibers rather than fibers contaminated with combustion products released in fire. A large number of toxicology and epidemiology studies have been performed on the inhalation of virgin glass fibers, and all found no serious adverse health effects [83–90]. These studies were performed using fiber doses and exposure times that are much higher than for an aircraft fire. For example, Hesterberg et al. [84] forced laboratory rats to inhale different doses (3, 16, or 30 mg/m^3) of short glass fibers for 6 h per day, five days per week, over 24 months. This long-term exposure caused inflammation of the lung tissue, although this subsided when exposure to the fibers was stopped. Examination of the lung tissue did not reveal evidence of acute lung injury, and the study concluded that respirable glass fibers do not represent a significant hazard for lung disease in humans.

A reason for glass fibers not being a serious health hazard is they are rapidly dissolved by alveoli macrophages, particularly when under 10–20 μm [83,85,89]. For example, Eastes and Hadley [85] showed that a 1-μm-diam fiber of glass wool dissolves in a rat lung within about 50 days, whereas complete dissolution by macrophages of chrysotile fibers and crocidolite asbestos fibers of the same size takes 7 and 52 years, respectively. Another important reason for the low health risk of glass fibers is that they rarely penetrate further than the upper respiratory system because of their large diameter, whereas asbestos fibers are smaller and can therefore reach deeper into the lungs. In 1997, the World Health Organization, through the International Agency for Research on Cancer, concluded that glass fibers are not carcinogenic. However, no research has been reported on the health problems experienced with inhaling contaminated glass fibers from a burning composite material. Although the fibers themselves are not hazardous, the combustion products adhering to their surface may be toxic and this is an issue requiring further investigation.

4. *Toxicity of Aramid Fibers*

The health problems associated with inhaling aramid fibers used in aircraft composite materials have not been extensively studied. Aramid fibers decompose between 500 and 550°C [91,92], which is below the temperature of many postcrash aircraft fires. A large percentage (~60%) of the fiber mass is converted into solid char at high temperatures, which can be inhaled. The inhalation toxicity of charred aramid fibers has not been investigated. Searl [87] investigated the effect of inhaling virgin aramid fiber on rats, and found that macrophages rapidly cleared these fibers from the lungs and therefore did not cause acute damage to the pulmonary system.

5. *Toxicity of Char Particles*

The toxicity of the char released by burning composite materials is poorly understood. It is well known that certain graphite-rich materials, such as coal dust, cause long-term health problems when high doses are inhaled over a long period. However, many differences exist between coal dust and char particles in terms of chemical composition and particle size and shape, and therefore it is not possible to extrapolate the toxicological effects of coal to char. Graphite black has a similar composition to many types of char produced by aromatic polymers, however, the particle size is much smaller (typically 10–800 nm). Studies have shown that exposure to graphite black dust, particularly at high concentrations over a long period, causes pulmonary fibrosis, bronchitis, and emphysema, although it is not considered to be carcinogenic [93]. Purser [50] reports that char particles released from burning composites can contain carcinogens, such as polyaromatic hydrographites, dibenzodioxins, and dibenzofurans, or free radicals that are formed by the thermal decomposition of certain polymers. These compounds may condense onto or be absorbed by the char particles and then inhaled along with combustion gases and fiber fragments in an aircraft fire. However, until laboratory research into the inhalation toxicity of char in the smoke plume of burning aircraft composite materials is performed, then it is not possible to assume it is not hazardous.

VI. Conclusions

An overview of the health hazards with the smoke released from burning aircraft composite materials has been presented. People have suffered a variety of health problems when exposed to the smoke from burning composites, which vary in severity from skin and eye irritation to severe coughing and respiratory problems that have required short-stay hospitalization. The health problems suffered from smoke inhalation are usually quickly alleviated when the person is removed from the scene of the fire and exposed to fresh air. As yet, no human deaths or long-term health problems have been attributed to smoke inhalation from composites in aircraft fires, although much remains unknown about the toxic potency of the combustion gases, fiber fragments, and char particles in the smoke.

A considerable amount of experimental (animal) research has been conducted into the toxicity of the primary combustion gases produced by composite materials, such as CO, CO_2, HCN, HCl, and NO_2. However, the polymers commonly used in aircraft composites also release a variety of more complex organic compounds, and the toxicity and toxic interactions of many of these gases are not well understood. More research is required into the toxic potency of the combustion gases and their associated acute health problems. Fibers released from burning composite materials may also pose a health hazard. Graphite, glass, and aramid fibers do not appear to cause long-term health problems at the concentrations found in smoke. However, most studies into the toxicity of graphite and glass have been performed using virgin fibers. The fibers and char particles within smoke are often coated with free radicals and organic compounds, some of which may be toxic when inhaled. Again, further research into the toxic potency and health problems when exposed to contaminated fibers and char particles is required. With the growing use of composites in civil and military aircraft, it is essential that the health hazards associated with the smoke are fully evaluated to ensure their safe use. In addition, ongoing development of new composite materials with low smoke toxicity is obviously essential [94–97].

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