MATERIALS AND FIRE THREAT

by

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Polymer research is producing new materials with exceptional properties, and products made with these materials may well replace many conventional products. Fiber-reinforced polymer composites offer the U.S. military the potential for significant reductions in weight and signatures. Current seaborne applications of composite materials in the U.S. Navy include sonar bow domes and windows, and coastal minehunter MHC-51 hulls (1). The U.S. Navy is also evaluating composite materials for both primary and secondary load-bearing structures such as foundations, deckhouses, and hulls; machinery components such as composite piping, valves, centrifugal pumps, and heat exchangers; and auxiliary or support items such as gratings, stanchions, ventilation ducts, and screens. This new interest in composite materials is due to increased need for a corrosion-free, lightweight, and affordable low-cost alternative to metallic components. The U.S. Army is evaluating composite combat vehicles and the U.S. Air Force has taken the lead in transitioning composite technology to military advantage as evidenced by superior performance of the Stealth Fighter.

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Weight savings and resulting fuel efficiency are driving the use of advanced lightweight materials by airframe manufacturers and other civil transportation industries. The Federal Aviation Administration is evaluating advanced thermoplastics and composite materials for aircraft interiors, airframe, skins, and other structural applications. Boeing projections for the structural weight fraction of polymer composites in subsonic commercial airplanes show increases in use from about seven percent currently to about 20 percent over the next fifteen years. The Infrastructure industry is evaluating continuous fiber composites for wrapping of concrete columns to reinforce new construction, damaged bridges, and buildings in earthquake prone areas. Bridges and highways in the United States are degrading due to the corrosion of steel reinforced concrete caused by salty water and deicing compounds (2). A number of research programs have been initiated to study the feasibility of using continuous glass, carbon, and aramid fiber polymer composites to replace the steel rebar in concrete bridges and highways. Furthermore, the inherent corrosion resistance of composite material systems can significantly reduce maintenance and life cycle costs of U.S. infrastructure and off-shore oil platforms. Historically, composite products constructed of glass fiber reinforced plastic (GRP) have been used in onshore oil and gas operations for over 30 years. Early applications included storage tanks and low pressure pipes. In recent years, some companies made extensive use of GRP pipe for onshore hydrocarbon gathering, transmission lines, downhole tubing products, and platform structures. Production from deep water (over 2,000 feet) petroleum reservoirs in the North Sea, west coast of Africa, and Gulf of Mexico is expected to become an important source for new development in the 21^{st} century (3). Composite components could help accelerate production from deep water by providing solutions which are both practical and economical. Current and potential composites related applications for ships, submarines, and aircraft cabin interior are shown in Figure 1.

However, the organic resins that comprise up to 50 percent by weight of composite structures present safety problems in the event of exposure to a fire source. At a recent "Composites for Surface Ships and Submarines Workshop" conducted on May 22-23, 1995 and coordinated by Naval Sea Systems Command (NAVSEA, Dr. E. Camponeschi), Office of Naval Research (ONR, J.

Gagorik), and Naval Surface Warfare Center, Carderock Division (NSWC/CD, J. Beach), it was concluded that a significant technical issue which has limited composite use on board Naval ships and submarines is the combustible nature, and hence, the fire, smoke, and toxicity of organic matrix based composite materials. In a list of prioritized needs, fire threat ranked as one of the top concerns among technical issues which included lower cost, benefit impact analysis, acceptance process, education and training, environmental effects/disposal, structural analysis/joints, electromagnetics, weapon effects, and large scale validation.

Many Federal agencies with fire performance responsibilities are affected by advances in polymer and materials science. These agencies have responsibilities which include the development of new materials, ascertaining their performance and the benefits or hazards that result, and providing the basis for procurement. Applications range from public safety to national security. To address this problem, and to maximize the "bang" of shrinking federal research budgets, several government agencies in August 1993, created the Interagency Working Group on Fire and Materials (IWGFM). The goal was to implement a coordinated, long range, national research effort to understand the fire and thermal behavior of polymeric materials and composites, and develop advanced materials with improved performance. This group is described in greater detail later in this paper.

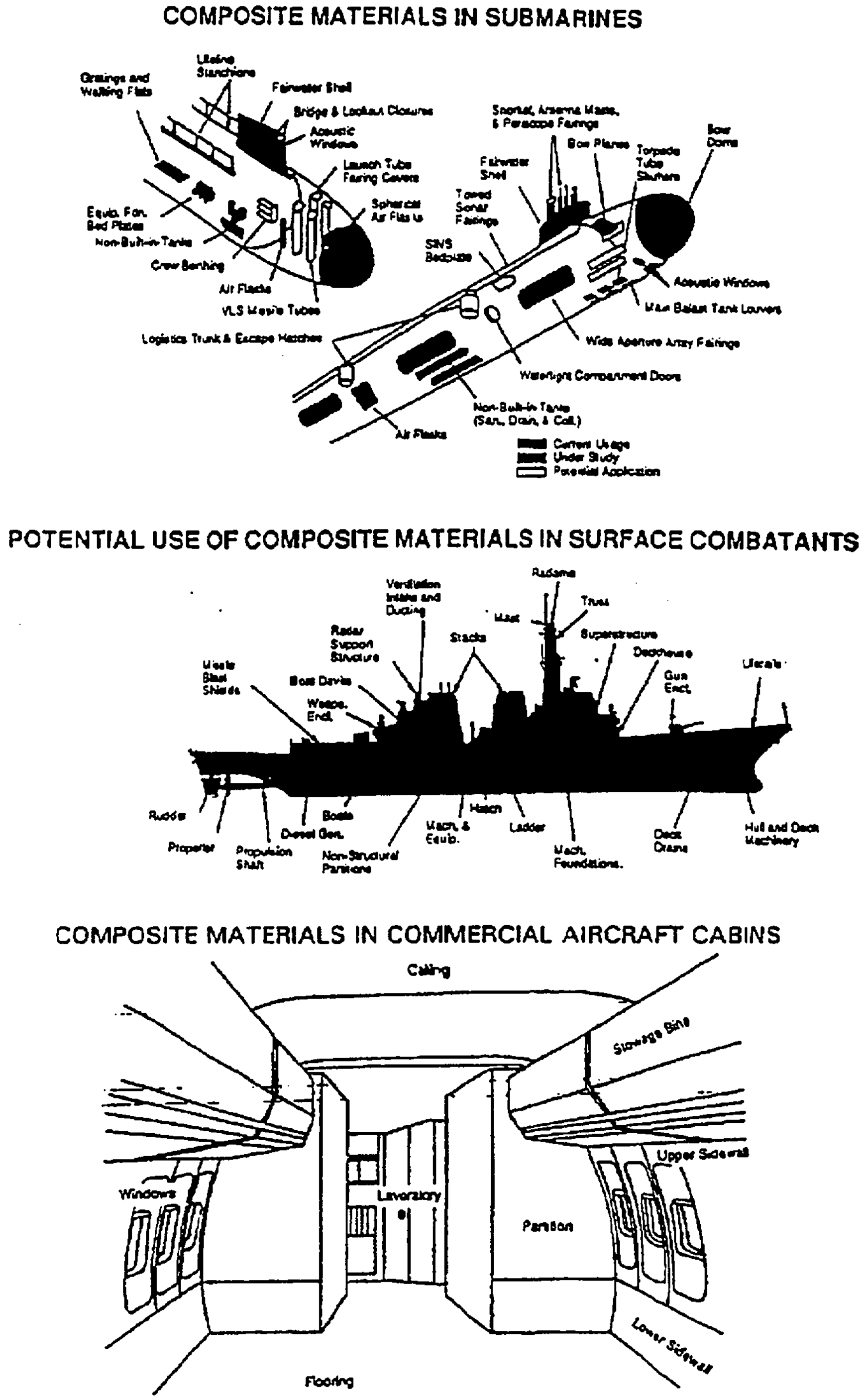

Figure 1. Current and potential applications of composite materials.

MATERIAL RESPONSE TO FIRE

Fire threats can come from many sources in various levels of severity. In an aircraft carrier, the major source of combustibles is jet fuel. In a machinery compartment, it can be lube oil or hydraulic fluid. In an engine compartment, it may be an ignition of fuel or lubricant. In a combat vehicle, it can be a propellant from on board missile storage. In a civil aircraft, it may be a fuel fire penetrating the fuselage after an accident. On an off-shore oil platform, it may be a high pressure gas jet fire. Fire consequences of polymers, plastics, and composites can be divided into four major components; a) Fire Growth; b) Habitability; c) Residual Strength and Structural Integrity; and d) Fire Extinguishment. These are described below.

Fire Growth

Polymers, plastics, and fiber reinforced composite materials when heated in a fire evolve combustible gases, ignite, release heat, and propagate the flame front. In a compartment fire, the phenomenon known as flashover presents a sudden increase in hazard. Flashover occurs when the thermal environment in a space is sufficiently intense that all combustibles ignite, rapidly accelerating the rate of heat release from the fire, and signaling the end to human survivability.

For every fire situation, there is a maximum fire size that can be tolerated before the people are harmed and/or the facility is lost. This fire size is best characterized by a critical rate of heat re-

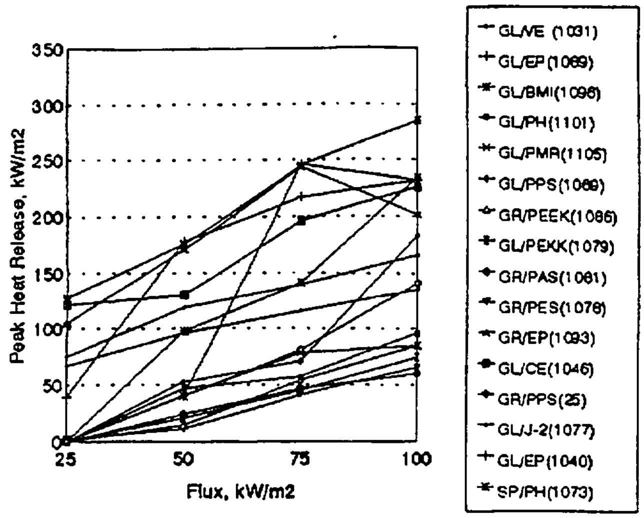

Figure 2. PHR vs. Flux for selected composite materials.

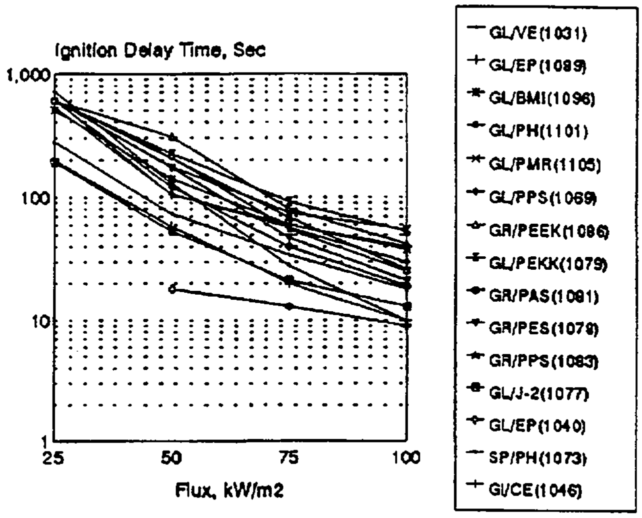

Figure 3. Ignitability of selected composite materials.

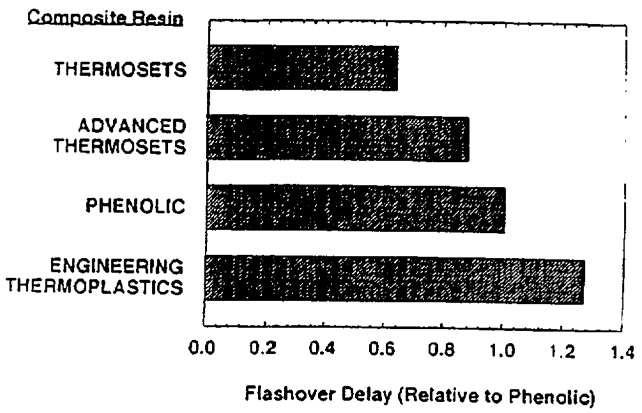

Figure 4. Flashover delay (relative to phenolic) in ISO 9705 corner/room fire test.

lease. This is a function of such variables as the ease of ignition, burning rate of the contained materials, thermal properties of the materials of which the compartment is constructed, and the available air supply. Thus, "acceptable" performance of a material or product will vary among its uses, and no single flammability test is able to characterize a product by itself. Instead, the performance test data are used as input to a calculation of fire hazard.

It has been suggested that the 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 (4). The oxygen consumption cone calorimeter is a small scale test method which can be used to generate material fire behavior properties and related to one quarter scale or a full scale fire. This small scale test method (sample size 10 x10 cm) has been accepted in the Navy as MIL-STD-2031 (SH), and nationally and internationally as ASTM E 1354, NFPA 264, and ISO 5660. The Lateral Ignition and Flame Spread apparatus (LIFT, ASTM E 1321, ISO 5658) provides additional information to complement cone calorimeter data. Figures 2 and 3 show the results for peak heat release rate and ignitability for selected conventional and advanced thermosets and thermoplastics materials at various heat fluxes of 25, 50, 75, and 100 kW/m^2 (5). These thermal insults correspond to a small Class A fire, a large trash can fire, a significant room fire, and a oil pool fire. The material flammability characterization was performed to identify composites that would meet or compare favorably with the MIL-STD-2031. The thermoset materials evaluated included vinyl esters, epoxies, bismaleimides, modified bismaleimides, phenolics, and polyimides. Thermoplastic materials evaluated included polyphenylenesulfide (PPS), polyetheretherketone (PEEK), polyethersulfone (PES), polyarylsulfone (PAS), and polyetherketoneketone (PEKK).

It is important to understand how or if the fire parameters derived from a small scale bench tests 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, non-structural etc.).

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. Several attempts have been made to correlate the time to flashover in an enclosure fire with bench scale flammability parameters measured for the wall or lining materials. For example, a combined parameter which is the ratio of the peak rate of heat release to the time to ignition of a small sample (ASTM E1354) provides reasonable correlation of time to flashover data for a wide range of lining materials in ISO 9705 full scale room fire test (6). ISO 9705 is a corner wall/room fire test which uses the 100/300 ignition option (100 kW fire for 10 minutes plus 300 kW fire for an additional 10 minutes) in the corner of a 2.4 m x 3.6 m (8 ft x 12 ft) room which is 2.4 m (8 ft) high. Figure 4 compares predicted time to flashover in the ISO 9705 room fire test with 6 mm thick glass or carbon fiber reinforced polymer-based composite materials.

Flashover delay has been normalized to the value for carbon fiber reinforced phenolic composites to provide a relative ranking of the fire safety of typical thermoset (epoxy, vinyl ester, polyester), advanced thermosets (bismaeimide, cyanate), and advanced thermoplastic (polyetheretherketone, polyphenylenesulfide, polysulfone) resin systems when used as walls or lining materials in habitable enclosures. The FAA has used this time to flashover criterion to distinguish between safe and unsafe cabin materials for commercial aircraft (7).

A more fundamentally-based approach is to treat the polymeric material as a source of fuel as opposed to a source of potential heat release. Fuel sources can then be included in dominant physics based computational models which have shown significant promise in predicting the heat fluxes (8) and effects of differing fuels (9) on fire environments. Application of this approach requires a more thorough understanding of material decomposition mechanisms, supported by an improved experimental knowledge base for the fire performance of materials.

Habitability

Combustion gas generation is defined as the gases evolved from materials during the process of combustion. The most common gases evolved during combustion are carbon monoxide and carbon dioxide; and to a lesser extent, hydrogen chloride (HCL), hydrogen cyanide (HCN), and others, depending upon the chemistry of the matrix resin of a given composite material. Most fatalities in fires are caused by the inhalation of carbon monoxide. The Committee on Fire Toxicology of the National Academy of Science has concluded (10) that as a basis for judging or regulating materials performance in a fire, combustion product toxicity data must be used only within the context of fire hazard assessment. The committee asserted that smoke toxicity is best obtained with animal exposure methods for purposes of predicting the fire hazard of materials. One such test method, validated against real scale fires, is NFPA 269.

All combustibles, including polymers and polymer composites, give off smoke when they burn. Smoke affects visibility and hinders the ability of the occupants to escape, and of fire fighters to locate and suppress the fire. Smoke density is influenced by the degree of ventilation. ASTM E-662 test method covers the determination of specific optical density of smoke generated by solid materials. Measurement is made of the attenuation of a light beam by smoke accumulating within a closed chamber due to non-flaming pyrolytic decomposition and flaming combustion.

Residual Strength and Structural Integrity

Polymer matrix composite structures show stiffness reduction during thermal exposure and exhibit a significant loss of load bearing capability from melting or devitrification of the matrix resin at elevated temperatures. Since the buckling strength of a composite plate is proportional to its stiffness, the loss in load bearing capability during and after fire exposure depends to a large extent on the thermal stability of the composite matrix resin. Tests have shown strength reduction as great as 50 percent at temperatures as low as 121°C (250°F) for glass reinforced vinylester composites. In a recent study

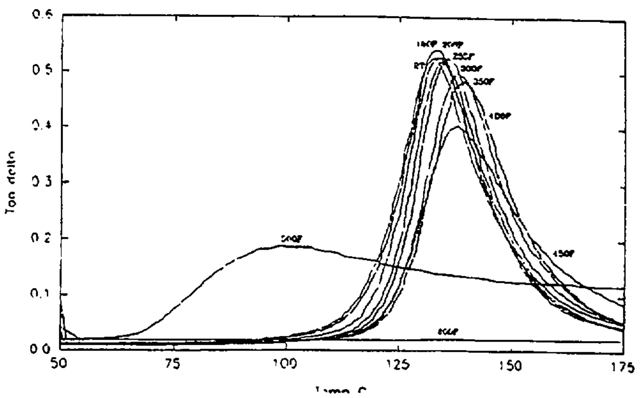

Figure 5. P326PC; Tan delta for previously isothermally exposed glass/vinyl ester panels.

(11), glass reinforced vinylester composites were exposed to isothermal aging for eight hours at temperatures up to 288°C (550°F). After cooling back to room temperature, these samples were then subjected to dynamic mechanical thermal analysis (DMTA) to assess thermal damage sustained from isothermal exposure. At temperature conditions of room temperature and upto 232°C (450°F), the isothermal aging of composite panels revealed reversible thermal damage. The 260°C (500°F) dynamic mechanical thermal analysis scan, shown in Figure 5, indicates chemical breakdown of the vinyl ester moiety of a composite panel and the resin loses characteristic viscoelastic behavior even after the panel has been cooled to room temperature. This is the threshold temperature for irreversible thermal damage under these conditions of isothermal aging for glass/vinylester composite.

The inherent chemical nature and complexity of polymer matrix composite materials do not lend themselves to easy analytical prediction of their behavior when exposed to a high heat flux from a fire source. Composites exhibit anisotropic heat transfer. They selectively burn, produce smoke, release heat, chemically degrade, produce char and delaminate.

NSWC/CD has initiated a program focused on the issue of residual strength and structural integrity of composite structures. The program initially studied fire-damaged (cold) composite panels for residual strength (12). Studies were also conducted to assess the heat transfer through the thickness of composites during thermal exposure and determine the loss of residual strength in isothermally heated samples (13). Under a research contract funded by the Advanced Research Project Agency (ARPA) in 1990, Milke and Vizzini (14) from the University of Maryland formulated a three dimensional heat transfer model to characterize the thermal response of an anisotropic composite laminate. Under the Submarine Technology Exploratory Development Program, Prof. Richard Corlette of the University of Washington developed a test apparatus to determine the residual strength of composites using an environmentally controlled fire chamber (15).

With support from G. Remmers and J. Kelly of the ONR Submarine and Materials Technology Program, Prof. M. Tuttle at the University of Washington has been tasked to comprehensively model the behavior of fire impacted composite structures. The goal is to produce analytical models that can predict the structural behavior of composites during fire as well as the post fire mechanical performance. When completed, these models can be provided to naval architects to aid in the design of full scale fire-tolerant composite structures. The methodology will require integration of thermal distribution (fire), viscoelastic behavior (polymer matrix), and thermomechanical (structural) mathematical models into an existing finite element analysis model (ABAQUS).

To experimentally validate ABAQUS models for fire tolerance and residual structural performance, NSWC/CD has designed, fabricated, and instrumented a Structural Fire Survivability Test Chamber (16). This facility is capable of loading a six foot composite structural beam in flexural mode under different fire scenarios. This chamber will be instrumented with strain gages; extensometers; thermocouples; hydraulic or pneumatic loading mechanisms and load cell; multi-purpose framework to perform structural tests in tension, compression, or flexural mode; multipurpose heating arrangement with radiant heaters and circulating air heaters to simulate isothermal or distributed thermal loads; and video and other inspection and analytical equipment. When completed, this Structural Fire Survivability Test Chamber will serve as a national resource for structural testing of composite prototypes under a variety of fire conditions.

Fire Extinguishment

Existing fire extinguishment agents have been found to be satisfactory for military applications. However, fiber reinforced composites pose unique challenges in fire fighting doctrine. Typically, glass reinforced composites tend to protect the adjacent compartments due to high thermal capacitance, slow through thickness burning, and insulative characteristics of delaminated and intumesced materials. However, this may retain thermal energy inside which could result in reflash after the fire has been put out. At elevated temperatures, ignition of the material requires less oxygen. During fire extinguishment, composites should be cooled below the temperature corresponding to an oxygen temperature index of 21 to prevent reignition.

There is a general lack of knowledge regarding the extinguishment of burning composite materials and the special hazards to fire fighters. Only the military and National Aeronautics and Space Administration (NASA) have done detailed studies of what gases are released in composite fires. (17). Recent experience by composite aircraft accident investigators, who experienced sore eyes and throats despite damping down the accident scene with liquids and wearing protective clothing, masks, and goggles, require further attention.

FIRE SAFETY OF MATERIALS

The projected growth in commercial air traffic over the next decade combined with the uniform accident rate over the past decade translates into a nearly passenger aircraft accident each week, on average, by the year 2010. Twenty percent of these accidents will involve death by fire according to current statistics. Compounding the problem of a higher number of accidents is the increased fire load in future aircraft cabins in the form of passenger electronics and telecommunications equipment. Future aircraft will require significant reductions in materials flammability to maintain even current cabin and airframe fire loads The recent move in Europe to eliminate all halogen containing materials and chemicals as potential ozone depletors indicates a need to develop halogen free fire safe materials. Halogenated polymers and polymers modified with halogenated additives are highly resistant to ignition, particularly in synergistic combination with other additives. However, once ignited, combustion of halogenated materials produce toxic acid gases (hydrogen chloride, HCL; hydrogen fluoride, HF; hydrogen bromide, HBr) which cause respiratory and eye irritation of passengers and corrosion of the aluminum airframe and electronic components (18).

A survey of commercially available materials and comparison of flammability data for various thermoset and thermoplastics composites show that phenolic based composite materials offer benefits in cost effective fire performance over many existing polymer based composites (19). Phenolic resins have the inherent characteristics of low flammability, less smoke, low flame spread, high ignition delay (more difficult to burn), low peak heat release rate, and high oxygen index. Also, phenolic composites (thermoset) char during fire exposure due to high degree of cross linking. The char tends to insulate the core of composite structure and thus render less structural damage.

However, most phenolic resins cure via polycondensation reactions with the evolution of water yielding a weaker resin matrix with high void content. Hence, current fiber reinforced phenolic composites are generally unsuitable for primary structural applications. For semi structural applications, phenolics make a good choice for large scale evaluation.

In 1995, the FAA initiated a long range Fire Research Program with the goal of eliminating fire as a cause of death in aircraft accidents. Fire Safe Materials is a program component which seeks to discover the fundamental relationships between the composition and structure of materials and their behavior in fires to enable the design of a totally fire resistant cabin for future commercial aircraft (20). This program has set interim materials fire performance goals which include no piloted ignition of cabin materials for 15 minutes when tested in a horizontal orientation at 35 kW/m^2 irradiance in accordance with ASTM E1354-92; peak heat release rate to be less than 25 kW/m^2, and two minute total heat to be less than 25 kW/m^2-min for cabin materials tested at 50 kW/m^2 irradiance. Full scale cabin fire performance goal is to demonstrate survivable aircraft cabin conditions for 10-15 minutes in post crash fuel fires. No flashover or incapacitation from combustion gases for at least 15 minutes in full scale aircraft cabin fire tests is required by the FAA under quiescent wind conditions.

These fire safety goals will be pursued by synthesis and characterization of new materials such as polybenzoxazines, nanoscale inorganic reinforcement, environmentally friendly inorganic-organic polymer hybrids from silica and glycols, low cost routes to polychlorophosphazene-based elastomers for seat cushions and sealants, new cyanate ester monomers leading to addition cured triazine resins, and fire safe polymeric materials containing no halogens or heteroatoms based on soluble oligomeric and polymeric alkyne-functionalized polyphenylenes and fullerenes.

THERMAL/FIRE BARRIERS (FIRE HARDENING)

The main conclusion from the extensive fire testing conducted by NSWC/CD is that unprotected composite systems cannot meet the stringent fire requirements specified for interior spaces of U.S. Navy ships or submarines. Military vessels must perform their mission even when damaged, and must survive the fire for sufficient periods of time to carry out rescue missions. Fire barriers are needed to prevent or sufficiently delay composite materials from contributing to the spread of a fire to ensure personnel safety, enable fire fighting and retard conditions that would promote flashover.

Over the past 5-10 years, NSWC/CD has conducted extensive studies on the performance of a wide variety of fire barriers to fire harden polymer matrix composite systems. Composite systems selected for studies included glass/vinyl ester, and glass and graphite reinforced epoxy. A total of 22 fire barrier systems were evaluated in these studies (21-22). Fire barriers evaluated included ceramic fabric, ceramic coating, water and solvent based intumescent coatings, a hybrid of ceramic and an intumescent coating, silicone foam, phenolic skin, ablative sheet, endothermic mat, intumescent mat, and glass mat. All configurations were tested for flammability characteristics. These included flame spread index, smoke generation, heat release rate, ignitability, and residual strength. Selected fire/thermal barrier treatments with a glass/vinyl ester composite were also evaluated for fire endurance (ASTM E-119 Fire Curve) and propensity to flashover (Navy Quarter Scale Flashover Test).

Data show that glass mat, intumescent mat and a water based intumescent/ceramic coating were the most effective of the numerous fire barrier treatments evaluated in these studies. Using either of these fire barrier treatments, a glass reinforced vinyl ester composite system met the ignitability and peak heat release requirements of MIL-STD-2031 at all radiant heat fluxes of 25, 50, 75, and 100 kW/m^2. An intumescent/ceramic coating with a glass/vinyl ester composite system was selected for and passed the Navy quarter-scale flashover test. The intumescent mat/glass-vinyl ester system and glass mat/vinyl ester system were selected for and met the ASTM E-119 Fire Curve endurance requirements with an average backside temperature of less than 232°C (450°F) for a period of 30-60 minutes. These fire barrier treatments have further advantages in that they can be in-situ fabricated during composite processing, thereby reducing the cost of installation and increasing their durability.

THE INTERAGENCY WORKING GROUP ON FIRE AND MATERIALS

Several Federal agencies have long recognized the importance of fire and materials that are able to withstand the threat of fire, both in terms of not burning themselves, and in terms of providing thermal protection. In August 1993, an assemblage of Federal Scientists and engineers formed the Interagency Working Group on Fire and materials (IWGFM) with the following mission:

To implement a coordinated, long-range, national research effort to understand the fire and thermal behavior of materials and develop advanced materials with improved performance. The agencies participating in the Working Group have mutual interest in fire and materials and will support cooperative research through the sharing of information and resources with the ultimate goal of improving human survivability and protecting property in severe thermal environments.

IWGFM activity is directed by a Steering Committee. The current membership of the Steering Committee is: Richard Gann, NIST, Chairman; Richard Lyon, FAA; Louis Nash, USCG; Patricia Pettit, Air Force; Russell Skocypec, SNL; Usman Sorathia, Navy; and Robert Friedman, NASA.

Within this mission, the Group intends to:

- Develop uniform guidelines for fire performance evaluation of materials for consideration by government agencies;
- Provide a mechanism to coordinate and communicate among government, industry, and university research activities;
- Analyze current research, development and technology in light of present and projected National needs;
- Advance defense/civilian agency dual-use objectives; and
- Promote research and development of advanced fire-safe materials by strengthening the case for more government and industrial funding.

To meet these objectives, the Working Group has established five thrusts. The titles, leaders, and intended functions are as follows:

Advanced Materials and Processing

Leader: Richard Lyon, Federal Aviation Administration
Deputy Leader: Takashi Kashiwagi, National Institute of Standards and Technology

Identification and evaluation of commercial fire- and heat-resistant materials.

Research and development of new resins, films, foams, coatings, additives and composites with significantly improved fire safety and high temperature thermal performance.

Research on process engineering needed to ensure manufacturability of advanced materials and facilitate recycling efforts.

Fire and Thermal Property Testing

Leader: Usman Sorathia, Naval Surface Warfare Center
Deputy Leader: Louis Gritzo, Sandia National Laboratory

"Encyclopedia" of currently used fire test methods and their uses.

Basis for broad Federal use of a consistent set of measurements to be used in uniformly specifying materials and products for use in environments at risk from fire or high temperatures.

Identification and measurement of thermal and mechanical properties of materials needed for modeling flammability, heat transmission, and structural performance at elevated temperatures.

Research on, development of methodologies for, and provision of guidance on:

- scaling from bench- to real-scale
- realistic bench-scale measurement methods,
- measurement techniques for fire environments and materials properties in those environments, and
- structural performance of load-bearing structures during and after defined fire or thermal insults.

Data Base for Materials' Fire and Thermal Properties

Leader: Richard G. Gann, National Institute of Standards and Technology
Deputy Leader: Vacant

Format for a broad, searchable matrix of data from diverse tests for a range of materials fire and thermal behavior and properties.

Creation and maintenance of such a data base in a manner that users have ready access.

Criteria and an evaluation protocol for candidate data, followed by a mechanism for adding data to the set.

Fire and Thermal Response Modeling

Leader: Vernon Nicolette, Sandia National Laboratories
Deputy Leader: David Aldis, Department of Energy

Identification of available fire and thermal response modeling tools (software) that exist and compilation of current modeling research and development to promote collaboration among agencies.

Development and advancement of models to understand the behavior of solid materials in complex systems in fire environments and other adverse thermal environments:

- Characterization of the fire environments that materials must withstand,
- Interaction of the fire environment with a material,
- Flammability, heat transmission, and structural performance in a fire or at elevated temperatures, and
- Production of enthalpy and combustion products from burning materials.

Predictive capabilities for relating materials/product data from small-scale screening tests to real-scale performance.

Health and Environmental Response

Leader: Douglas Nelson, U.S. Air Force
Deputy Leader: Vacant

Compilation and assessment of the hazards of burning, burned, and exploded advanced materials/composites.

Research and exchange of information to:

- Expand the knowledge base to support the development of safe procedures for mishap responses,
- Determine unusual aspects of the extinguishment of advanced materials, and
- Assess the environmental safety and health issues associated with fire-damaged materials.

Several of these projects are now underway. The work will impact across the Federal government by collaborative research and development efforts between various agencies and their laboratories and show benefits for private sector by coordinated exchange of technical and regulatory information. The membership in the Working Group is open to representatives of all Federal agencies. Most of the planned projects will be developed jointly with appropriate and interested corporations. Interested parties should contact the authors at the above address.

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