Fire Characteristics of Cored Composite Materials for Marine Use

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May 1996

Abstract

A material study was conducted on two types of cored composite materials used in shipbuilding: a GRP/Balsa Cored sandwich and a GRP/PVC Foam Cored sandwich. The two materials were tested in the Cone Calorimeter and the LIFT Apparatus to obtain data on ignitability, heat release rate, mass loss rate, and smoke production. The observed phenomena of delamination, melting and charring of the core materials, and edge effects are discussed in the context of how they affect test results. The ignition data analysis method specified in ASTM E 1321 "Standard Test Method for Determining Material Ignition and Flame Spread Properties" and Janssens' "improved" method of analysis were both used to derive effective material properties of the test materials. These two analysis methods are shown to produce different material property values for critical irradiance for ignition, ignition temperature, and the effective thermal property, $k\rho c$. Material properties derived using Janssens' method are shown to be more consistent between the two test materials and the two different test methods; they were also shown to be better predictors of time to ignition when compared to actual test data. Material properties are used as input to Quintiere's fire growth model in order to evaluate their affect on time to flashover predictions in the ISO 9705 Room/Corner test scenario. Recommendations are made for future testing of cored composite materials, ignition data analysis methods, predictive fire growth models, and other work with composite materials.

Executive Summary

This executive summary provides the reader with an overview of the thesis. A brief discussion of the contents of each chapter of the thesis is included, with the aspects of the material study discussed in more detail. The reader is referred to the individual chapters for more information.

Chapter 2 presents an introduction to marine composites. Resins, reinforcement materials, and core materials are introduced. The intention of this chapter is to introduce the reader to the components used in a marine composite. It is not intended to be an all–inclusive study of composite materials or composite structures. The chapter includes a discussion of applications of composite materials in the marine industry. From small boats to large naval vessels, composites have gained a definite niche in the industry. There has been a renewed interest in composites as a primary shipbuilding material in recent years with the development of High Speed Craft (discussed also in Chapter 3). Chapter 2 closes with a brief introduction to the MARITECH research and development program, which was established by the Department of Defense as an effort to further the development and application of advanced technology (including that of composite materials) to improve industrial competiveness in U.S. shipyards.

Chapter 3 is a review of U.S. and international maritime regulations. The discussion is limited to the regulation of composite materials used in ship structure and components. The U.S. Coast Guard (USCG) is responsible for the development and enforcement of commercial vessel regulations in the United States. The International Maritime Organization (IMO) is responsible for the International Convention for the Safety of Life at Sea, 1974 (SOLAS), which is an international treaty designed to promote safety on international voyages. The recently adopted International Code of Safety for High–Speed Craft (HSC Code) is also discussed in this chapter. An important aspect of the HSC Code with regard to this thesis is the definition and classification of "fire–restricting materials." The IMO has recommended criteria for classifying a surface lining as a fire–restricting material based on the ISO 9705 Room/Corner fire test method.

Chapter 4 provides background information and a review of the fire literature pertinent to the thesis. The Ship Structure Committee (an interagency advisory committee consisting of the USCG, Naval Sea Systems Command, Maritime Administration, American Bureau of Shipping, and the Military Sealift Command) has published a comprehensive document on the "Use of Fiber Reinforced Plastics in the Marine Industry"; this document is discussed. The Military Standard, MIL–STD–2031(SH), "Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used in Hull, Machinery, and Structural Applications Inside Naval Submarines" is discussed, along with other literature on composite materials for naval applications. Work at the National Institute for Standards and Technology (NIST) has focused on fire research for decades. Several useful techical reports have come out of NIST that deal with flammability of composite materials. Recent work at Worcester Polytechnic Institute (WPI) by James Tucker is also of interest. Tucker has completed preliminary development of a heat and mass transfer model for a composite material laminate.

The bulk of Chapter 4 consists of developing the theory for piloted ignition of solid materials. This discussion is merged with an introduction to mathematical models of piloted ignition of solids, particularly as applied to analysis of bench–scale test data. Two such data analysis methods are used in this thesis: (1) the analysis method developed by Quintiere and Harkleroad as standardized in ASTM E 1321, "Standard Test Method for Determining Material Ignition and Flame Spread Properties"; and (2) Janssens' "improved" method of analysis. The latter method is described in detail in this chapter and also in Chapter 6. One important aspect of Janssens' method is that the experimental data is used to determine either semi–infinite solid or "non–thick" (i.e. thermally thin) behavior in the test conditions. This is an important aspect especially when applied to materials such as the cored Glass–Reinforced Plastic (GRP) composites tested in this thesis. For example, with conventional building materials (usually homogeneous solids) the assumption of semi-infinite (thermally thick) behavior in the test conditions is usually valid. Cored composites, however, experience delamination, separation of the GRP facer material from the core, and/or melting of the core material (in the case of the PVC foam core). In this case, it is difficult to evaluate the data based on the semi–infinite assumption, which means the standard data analysis method may not apply. In the small scale tests, edge effects (i.e. escape of pyrolysis gases, edge burning) also may affect test results. These and other peculiarities with the cored composite test materials are discussed further in Chapters 6 and 7.

Chapter 5 describes in detail the two test materials used in this thesis: a GRP/Balsa Cored sandwich composite and a GRP/PVC Foam Cored sandwich composite. Both materials are used in hulls and interior structure in commercial and passenger vessels ranging in length from 24 to 35 meters (80 to 115 feet). The test materials were provided by Westport Shipyard, Inc., of Westport, Washington.

Chapter 6 presents the results and data from cone calorimeter testing (per ASTM E 1354) of the two cored GRP test materials. In the cone calorimeter, a small (100 mm x 100 mm square) material sample is exposed to an external radiant heat source (an electric *cone–shaped* heater). The products of combustion and smoke are received into a exhaust hood above the burning sample and pumped through a series of analyzers which record the oxygen percentage and the percentage CO and CO_2, while a laser beam measures the amount of smoke released. A load cell records the mass of the burning sample throughout the test. The principle theory involved in the calculation of data from the cone calorimeter is that of oxygen consumption calorimetry, which provides a heat release rate for the burning material. A computer and associated software program calculates the data throughout the test.

The cone calorimeter provides data such as the ignitability, heat release rate, effective heat of combustion, mass loss rate, and smoke production for the sample of test material. In addition to the results provided by the computer software, the time–to–ignition data is analyzed in order to derive effective material properties of the material such as the critical heat flux for ignition, $\dot{q}''_{cr}$, ignition temperature, T_{ig}, heat transfer coefficient at ignition, h_{ig}, and the effective thermal property, $k\rho c$. These results can be used to predict how a material will behave in a real fire.

One common ignition data analysis method is the one developed by Quintiere and Harkleroad at NIST. This analysis method is standardized in ASTM E 1321, and is referred to as the "standard method" in this report. This method makes certain assumptions about the material and the apparatus that are valid for most building materials. The major assumption here is that the material behaves as a semi–infinite solid (thermally thick), meaning that ignition occurs before the thermal wave has reached the back surface of the material. This assumption may not apply to the cored composites tested in this thesis. Several factors influence this statement:

- The GRP skin delaminates prior to ignition, forming an air pocket within the laminate and/or between the laminate and the core material.
- The PVC foam core material melts at a relatively low temperature. At particularly low irradiance (external heat flux) levels, this is especially true, as more time is allowed for heat transfer through the GRP skin to the core material prior to ignition.
- Ignoring the delamination factor, the core materials themselves (balsa and PVC foam) may actually insulate the GRP skin enough to make it behave as if it was thermally thin, meaning that the thermal wave has reached the back surface of the GRP skin prior to ignition.

Because of these factors, the improved data analysis method proposed by Janssens may better apply to these types of materials. Janssens' method includes more realistic boundary conditions for the mathematical model used in the correlation of ignition data. Namely, that heat losses from the material are a linear function of surface temperature with a constant convection heat transfer coefficient (h_c), and additionally that surface heat losses are partly radiative, provided that the total heat transfer coefficient (h_{ig}) is used in the calculation of material properties from ignition data rather than h_c. Janssens' method also uses more accurate values for surface emissivity (ϵ) when calculating the ignition temperature. For non–thick materials, Janssens proposes to correlate the ignition data according to the power law,

$$(\dot{q}_e^{"} - \dot{q}_{cr}^{"})t_{ig}^n = C,$$

where C is a constant and n is an exponent between 0.5 and 1. By correlating the ignition data according to this power law, varying the value of n , a determination can be made as to how the material behaves. If the best linear fit to the data occurs with a value of n close to 0.55, the material behaves as a semi–infinite solid. If the value for n is closer to 1, the material behavior is "non–thick" and additional data points at high levels of irradiance (where the material exhibits thermally thick behavior) may be necessary. This discussion is expanded in Chapter 6.

Based on the analysis of ignition data with Janssens' method, the cored GRP materials behave as non–thick. Some justification of this is included in the chapter. First, the thermal penetration depth is evaluated using the equation, $\Delta = 2\sqrt{\alpha t}$, where α is the thermal diffusivity ($k/\rho c_p$) and Δ is the thermal penetration depth. Literature values (for GRP) of the thermal conductivity (k) and specific heat (c_p) are used; the density (ρ) was calculated for the GRP skin. This analysis results in an ignition time (t) of between 7 and 44 seconds, depending on which literature value for k is used. What this means is that where the ignition time for the material was shorter than 44 seconds, the assumption of thermally–thick (semi–infinite solid) behavior may be valid. At higher ignition times, it can be assumed that the material behaves as thermally–thin. In order to justify the possibility that the air pocket (due to delamination) acts to insulate the GRP skin, making it exhibit thermally thin behavior, the Biot number ($\text{Bi} = h\Delta/k$) at the back face of the GRP skin was evaluated. The Biot number compares the relative magnitude of surface convection and internal conduction resistances to heat transfer. A very low Biot number ($\text{Bi} < 0.1$) would indicate that the internal conduction resistance is negligible in comparison to surface convection resistance, indicating that the air pocket acts to insulate the GRP skin. This was the case in this analysis. Likewise, the insulating properties of the Balsa core and the PVC foam core are evident in the fact that their thermal conductivity (k) is less than that of the GRP in both cases.

Chapter 6 presents the material properties for the GRP/Balsa sandwich and the GRP/Foam sandwich materials resulting from analysis of ignitability data based on the both the "standard method" and Janssens' "improved" method. The results from Janssens' method are more consistent between the two test materials and also between the two different bench–scale test methods. Calculated values for the ignition temperature, T_{ig}, and the effective thermal property, $k\rho c$, show a much greater range of difference when calculated using the standard method. $k\rho c$ values calculated using the standard method varied by as much as 95%, while the values obtained using Janssens' method vary by only 20%. The experimental data itself and the thermal penetration depth analysis discussed above seem to indicate that the GRP skin is the primary driving factor involved in the ignition process of these materials, rather than the sandwich composite as a whole. Because of this fact, material properties should be expected to be very similar between the two test materials. As Janssens' method produced more consistent results, and because his method allows the experimental data itself to determine how the material behaves (i.e. either semi–infinite or "non–thick"), it is concluded that this improved data analysis method may better apply to cored composite materials than the existing standard method specified in ASTM E 1321.

Chapter 6 also presents results of the cone calorimeter tests for heat release rate, effective heat of combustion, and smoke production. Some discussion about how edge effects change the heat release rate history is included. For both of the test materials, one test run was conducted without the sample edge frame in place to see how edge effects affected the results.

Chapter 7 presents test results from the LIFT Apparatus (per ASTM E 1321). The Lateral Ignition and Flame spread Test (LIFT) is used for bench–scale ignition and opposed flow flame spread experiments. The LIFT provides data on the ignitability of the test materials (similar to the cone calorimeter in this respect). Much like the analysis carried out in Chapter 6, the LIFT ignition data is analyzed using the two different methods. Normally, the flame spread data obtained from the LIFT is analyzed in order to provide the flame spread parameter (Φ), minimum surface temperature for flame spread ($T_{s,min}$), and minimum heat flux for flame spread ($\dot{q}''_{o,s}$). Unfortunately, it was not possible to derive flame spread properties due to difficulties experienced in obtaining the data. During the flame spread tests, the material exhibited severe edge effects, often igniting the material surface farther down the sample from the original flame front. Also, flame would not propagate down the sample surface under the standard test conditions. It is believed that the fire retardant resin used in the GRP skin may be partly responsible for this. Chapter 10 contains some recommendations for future flame spread testing that may alleviate these conditions and allow accurate flame spread data to be obtained.

Chapter 7 also contains a comparison of ignition data and material properties derived from the LIFT apparatus testing and the cone calorimeter testing. Material properties derived by both analysis methods are evaluated from the standpoint of the Thermal Response Parameter (TRP) described by Tewarson. Using the TRP to predict time to ignition, the material properties derived using Janssens' method are shown to be a better predictor of ignition times than the properties from the standard method.

Chapter 8 covers application of the material properties to a prediction model. A flame spread model developed by Quintiere is used to predict fire growth on the test materials used as a wall lining in an ISO 9705 Room/Corner test scenario. This model has been coded for use on a personal computer. The analysis centers around how the differences in the derived material properties (from the two different data analysis methods) affect the results of the model. The evaluation includes a sensitivity analysis of the model based on variations in the effective thermal property $k\rho c$, total energy per unit area (Q"), and ignition temperature (T_{ig}). This analysis helps to put into perspective how the different ignition data analysis methods ("standard" versus Janssens') will affect the results. The results from the model for time to flashover (1 MW fire size) are evaluated based on the different ranges of input parameters. Time to flashover in the test scenario ranged from 178 seconds to 624 seconds. The model runs using the material properties derived using Janssens' method were more conservative, giving shorter times to flashover. The material properties derived with the standard method gave much longer times to flashover and, in all but one case, the compartment went to flashover only after the burner strength was increased from 100 kW to 300 kW at 10 minutes into the "test".

The IMO has recommended certain criteria for classifying a lining material as "fire–restricting" based on the ISO 9705 Room/Corner test. This thesis provides some useful information for evaluating the use of predictive models using bench–scale test results to screen potential fire–restricting materials for use in high speed craft. It is shown that differences in material properties can greatly affect the results from Quintiere's model. For this reason, it is very important that appropriate data analysis methods be used for deriving these material properties.

Chapter 9 summarizes the conclusions from the material study of the two cored GRP materials. In particular, recommendations are made of how to conduct the experiments and associated data analysis when the materials do not behave like common building materials. Cored composite materials present some particular burning behavior that must be recognized and understood as best as possible in order to derive the most realistic material properties. These peculiarities include delamination, core melting, edge effects due to the small sample size, and apparent thermally thin behavior. As shown in the analysis of the material properties using Quintiere's fire growth model, material properties can greatly affect results of predictive models.

Chapter 10 makes recommendations for future work to be conducted with cored composite materials, with the data analysis methods, and with predictive models. These recommendations include:

- Future Work with the GRP Sandwich Composites
  - Separate the core materials from the GRP skin and test them individually
  - Vary sample size (larger), test orientation (vertical in the cone calorimeter), and method of edge protection.
  - Drill holes in the GRP skin to allow escape of pyrolysis gases. This may alleviate the edge effects due to gases escaping at the edges. It may also prevent delamination.
  - Embed thermocouples within the sandwich composite to obtain a temperature profile throughout the GRP skins and the core.
  - Test the GRP sandwich materials in the full scale, particularly in the Room/Corner test configuration in order to validate the model.
  - Conduct some intermediate scale testing to observe upward flame spread and reduce the edge effects experiences in the small scale.
  - Vary the resin used in the GRP laminate, and the core materials, including thickness of each.
- Future Work with the ignition data analysis methods
  - Conduct more tests with the GRP sandwich materials at high irradiances (50 to 100 kW/m^2) in order to obtain more accurate material properties in the semi–infinite range of burning behavior. This is consistent with the proposed method of Janssens.
- Future Work with the models
  - Obtain data for similar composite materials, and conduct a sensitivity analysis of the model based on derived material properties.
  - Compare with full scale test results.
  - Further develop Tucker's model for heat and mass transfer through a composite exposed to an exterior heat flux. The data obtained from embedded thermocouples in the test materials may help in this development.
- Other Areas for Future Work
  - Conduct structural strength testing of the composite materials before and after exposure to heat and fire. This will help evaluate the material's performance structurally during and after a fire.

- Conduct an evaluation of smoke production properties obtained in the present study. Apply these results to prediction of full scale smoke production. This would be useful to the qualification procedure for fire–restricting materials that the IMO has recommended.
- Continued industry involvement; it is imperative that the U.S. Coast Guard, the maritime industry, and the fire protection engineering sector work together to continue this type of work. Growth in the maritime and fire science sectors would certainly result from continued cooperation and research.

Acknowledgements

Thanks to:

My advisors, Professors Nicholas Dembsey and Jonathan Barnett for their guidance and for putting up with me. Professor Edward Clougherty for his laboratory expertise. The faculty and staff of WPI Center for Firesafety Studies. To Dr. Vytenis Babrauskas for sparking my interest. To Randy Rust of Westport Shipyard for providing the test materials. To Eric Greene, naval architect and composite materials guru; Dr. Robert Asaro of UCSD and the Maritech program. To Tom Ohlemiller of NIST for providing feedback on the test program. To Dr. Marc Janssens of AFPA for his continuing advice. To the U.S. Coast Guard for making this possible; LCDR Tim Cherry, LCDR Rob Holzman, LT Pat Little, and especially LT's P.J. Maguire, Chris Myskowski, and Tony DiSanto for pointing me in the right direction with regard to the regs. To Chris McKeever of the WPI Fire Lab. To Ploss Associates for the occasional use of their computers and copy room. LT John Mauger for all of his time spent assisting me in the fire lab. Finally, and most importantly, to my wife Julia and kids for their love and support, and for putting up with me and all of the all–nighters spent writing this thesis.

Contents

List of Tables

Symbols and Abbreviations

b	ignition correlation parameter, $s^{-1/2}$
Bi	Biot number, $= h_c\Delta/k$
c	specific heat, $J/kg \cdot K$
C	constant, Eq. 4.3
F_n	Froude number
$F_{n,V}$	Volumetric Froude number
g	acceleration of gravity, 9.81 m/s^2
h_c	convective heat transfer coefficient, $W/m^2 \cdot K$
h_{ig}	total heat transfer coefficient at ignition, $kW/m^2 \cdot K$
k	thermal conductivity, $W/m \cdot K$
$k\rho c$	effective thermal property, $(kW/m^2 \cdot K)^2 s$
L	vessel length, m
m	slope, Eq. 4.6
n	exponent, Eq. 4.3
$\dot{q}''_{cr}$	critical irradiance (heat flux) for ignition (modeling parameter), kW/m^2
$\dot{q}''_{e}$	measured incident irradiance, kW/m^2
$\dot{q}''_{o,ig}$	critical irradiance for ignition, kW/m^2
$\dot{q}''_{min}$	minimum irradiance for ignition, kW/m^2
t	time, s

T_{ig}	ignition temperature, K or $^{\circ}C$
$T_{s,min}$	minimum temperature for flame spread, K or $^{\circ}C$
T_{∞}	ambient temperature, K or $^{\circ}C$
V	speed, m/s or knots
∇	vessel's characteristic volume displacement, m^3
α	thermal diffusivity, m^2/s
Δ	thickness, m
ϵ	surface emissivity
Φ	flame heating parameter, kW^2/m^3
ρ	density, kg/m^3
σ	Stefan–Boltzmann constant, $5.67 \times 10^{-11} kW/m^2 \cdot K^4$
ABS	American Bureau of Shipping
ASTM	American Society for Testing and Materials
CFR	Code of Federal Regulations
FRP	fiber reinforced plastic
GRP	glass–fiber reinforced plastic
GT	gross tons
HRR	heat release rate, kW/m^2
HRR-300	average HRR over initial 300 s after ignition
HSC	High Speed Craft
IMO	International Maritime Organization
ISO	International Organization for Standardization
LT	long ton, 2,240 pounds
NBS	National Bureau of Standards
NFPA	National Fire Protection Association

NIST	National Institute of Standards and Technology (formerly NBS)
NVIC	Navigation and Vessel Inspection Circular (USCG)
SEA	Specific Extinction Area, m^2/kg
SM-180	average SEA over initial 180 s after ignition
SM-300	average SEA over ititial 300 s after ignition
SSC	Ship Structure Committee
STDEV	standard deviation
SOLAS	The International Convention for the Safety of Life at Sea, 1974.
THR	total heat energy released
TRP	Thermal Response Parameter, $kWs^{1/2}/m^2$
UL	Underwriters Laboratories
USCG	United States Coast Guard

Chapter 1

Introduction

The use of composites in ship and boat building has become more prevalent in recent decades. Along with the improvements to materials, construction methods, and applications comes an increased responsibility to ensure that vessels are safe for their passengers and crew. Firesafety is just one part of that overall safety concern, but one that is not well understood with regard to how composite materials behave under fire conditions. An inherent problem with composite materials are that they are combustible, where more common ship construction materials such as steel and aluminum are not. If composite materials can be made to withstand certain fire conditions without contributing significantly to the fire, then an acceptable level of safety can be achieved. This thesis work evaluates the performance of a particular type of composite, the cored–composite (or sandwich), under controlled fire conditions.

The first few chapters of this work will introduce the reader to the world of marine composites and regulation. The U.S. Coast Guard (USCG) and the International Maritime Organization (IMO) are working together to allow use of composites in shipbuilding, while maintaining a level of safety for passengers and crews. New regulations are being created that will allow the marine industry to take initiative to improve the technology of modern composite materials and how they are to be used. Rather than choke the industry, these regulations are intended to allow growth.

Chapters 6 and 7 present the results of the material study that was conducted on two types of cored–composites, a GRP/Balsa Core sandwich and a GRP/PVC Foam Core sandwich. The materials were tested in the Cone Calorimeter[1] and the LIFT Apparatus[2]. Material properties such as ignitability, heat release rates, and smoke production are discussed. An "improved" method of ignition data analysis developed by Janssens[3] is discussed in the context of how it applies to fire testing of composite materials, understanding that composite materials are not "typical" building products. Recommendations are made as to how to proceed with further testing of cored–composite materials.

Chapter 8 introduces Quintiere's fire growth model[4] that is used for prediction of full scale fire performance. The performance of building materials in the ISO 9705 Room/Corner test[5] is of interest since it is the standard test method recommended by the IMO for qualifying fire–restricting materials for use in High Speed Craft.[6] The IMO sub–committee on Ship Design and Equipment has received input which considers the use of small–scale (i.e. cone calorimeter) data in conjunction with full scale prediction models to qualify fire restricting materials.

Chapter 9 contains a summary of the thesis work and conclusions. Recommendations for future work in the study of composite materials and fire are made in Chapter 10.

Chapter 2

Composite Materials in the Marine Industry

This chapter presents an introduction to composite materials and their use in the marine industry. It is not intended to be an all–encompassing discussion nor a comprehensive report on composites. Rather, it is intended to introduce the reader to the materials used and some of the applications of composite materials. The discussion will establish a basis for the need to conduct research into non–conventional shipbuilding materials such as composites. The findings will, of course, be applicable to other structures as well. The actual materials used in this study are described in detail in Chapter 5.

For the purposes of this report, a composite material is defined as consisting of a resin matrix reinforced with a fibrous material (i.e. glass, carbon, or polymer). The term “laminate” refers to a multi–layered composite with individual sheets (or plys) bonded together by pressure or heat. A cored composite (or “sandwich composite”) is defined as a core material sandwiched between two laminated composite facings (or “skins”). The two facings of a cored composite provide the required bending and in–plane shear stiffness and carry the axial, bending, and shear loads.[7] Similar to the flanges of an I–beam the facings, separated by the core, resist the bending loads. The core, much like the web of an I–beam, resists the shear loads and help to increase the stiffness of the entire structure by spreading the facings apart.[7] See Figure 5.1 for a schematic of a cored composite.

Composite materials are relatively new to the marine industry, having only come into use within the last 50 years. Traditional shipbuilding materials have been wood, steel, and aluminum. Although larger vessels are constructed primarily of steel, composites are sometimes used in part for ship superstructures[8] and interior components. Glass–fiber reinforced plastics (GRP), one form of fiber reinforced plastics (FRP), were first introduced in the 1940's for use in Navy personnel boats.[9] Since that time, the use of FRP materials have found widespread acceptance in yachts, pleasurecraft, performance craft (i.e. racing boats), and small commercial vessels such as fishing trawlers. The advantages of GRP include improved strength–to–weight ratios, stiffness–to–weight ratios, and corrosion resistance.[8] Interest in the use of composite materials for larger vessels has been increasing in recent years, primarily for high speed passenger craft. However, use of GRP in construction of large ships is limited partly due to problems with hull deflections that may cause problems in propeller shafting and piping arrangements.[9]

A serious problem with composite materials is the fact that they do support combustion. Insulation can help reduce the hazards associated with composite materials exposed to fire[10], but the fact remains that more needs to be understood about their burning behavior before improvements can be made. As compared to wood, some composites behave very well with regard to ignition and flame spread. These properties depend primarily on the type of resin used in the composite. The hazards associated with smoke and toxic products of burning plastics are also a major concern for passengers, as well as corrosivity to electronic components. With regard to smoke production, GRP hull systems generally produce more smoke than similar hulls constructed of wood.[11]

2.1 Resins

Resins are classified as either thermoset or thermoplastic.[12] A thermoset resin will not soften when exposed to heat as a thermoplastic resin does. Thermoset resins, the type used almost exclusively in marine applications, include polyester and epoxy. Their advantages include a wide range of formulations, resistance to high temperatures, good solvent resistance, corrosion resistance (a definite advantage in a marine environment), and good mechanical and electrical properties. Their disadvantages include exothermic reactions during the curing (liquid–to–solid) stage, shrinkage, and creep.[12]

The decision to use a certain type of resin is based on several factors. Epoxy resins provide superior performance with regard to moisture resistance and strength in normal operating environments, but their relative high cost and poor thermal resistance qualities preclude their widespread use for large applications. Polyester resins, on the other hand, are relatively inexpensive, provide good chemical resistance, and are easier to use.[13] The general trend is to use epoxy for smaller vessels, especially wood boats that are often cold-molded (laminated) from thin wood veneers saturated in epoxy resin. Wooden boats made of more traditional planking methods are often coated in epoxy or sheathed with boat cloth wetted out in epoxy. For other applications such as GRP hulls and small commercial vessels made exclusively of GRP materials, polyester resin is most often used. U.S. regulations for commercial vessels require the use of fire retardant resins meeting military specification MIL-R-21607.[14]

2.2 Reinforcement Materials

The most commonly used reinforcement material is fiberglass, which accounts for over 90% of the fibers used in the reinforced plastics industry.[13] Fiberglass is relatively inexpensive and has good strength to weight characteristics.

Polymer fibers, such as Kevlar[1], and other aramid fibers have low weight and high strength properties. Their high cost restricts their use primarily to military applications. Polyester and nylon fibers also fall into the polymer fiber category. Any advantages of polymer fibers usually do not outweigh the cost for most marine applications.[13]

Carbon fibers offer the highest strength and stiffness of all the reinforcement fibers. They also have excellent high temperature performance. As with the polymer fibers, their high cost usually precludes their use to all but the most specialized of applications. Carbon fibers are used more commonly in high performance boats where stiffness and low weight are important.[13]

2.2.1 Reinforcement Construction

Reinforcing fibers are available in several different forms ranging from continuous strands to intricately woven fabrics. The choice of which form to use depends on the layup method and the structural requirements of the laminate. Some applications (for example, car bodies and small boats) use a relatively crude method where a "chopper gun" is used to combine chopped strands of fiber approximately 5 cm (2 in.) in length and resin as the components are sprayed into a mold.[13] It is more difficult to control the final resin/fiber ratio in a method like this. Other layup methods include wetting out fabric, mats, or woven rovings with resin in the mold.

[1] registered trademark of DuPont

Woven composite reinforcements include cloth or woven roving. Cloths are typically lighter in weight (6 to 10 oz/yd^2 or 200 to 340 g/m^2). Woven rovings consist of bundles of continuous strands of fiber (like rope but not twisted) woven in a particular weave pattern. Woven rovings are available in heavier weights (i.e. 24 oz/yd^2 or 815 g/m^2) and are most common in marine applications.[13] It is possible to achieve different directional strengths with woven rovings. They are also more impact resistant than cloth or mats because the fibers are continuously woven.[13]

Reinforcing mats consist of nonwoven random chopped or continuous strands of fiber. Mats can be used to achieve a higher fiber to resin ratio, but their strength characteristics are not as good as a woven fabric due to the random arrangement of fibers and the noncontinuous fibers.[13]

There are other types of reinforcement construction such as knits, omnidirectional and unidirectional, but their use is limited in marine applications.

Most ship and boat construction applications use a combination of chopped strand mat ("CSM") and woven roving. GRP laminates are usually designed for the type of service that the vessel is intended for. The vessel's size and the environment in which it will operate are also factors. The vessel construction plans will usually include a laminate schedule detailing the layup process for each component of the vessel construction.

2.3 Core Materials

2.3.1 Honeycomb

Honeycomb materials include aluminum, aramid paper (Nomex[2]), and phenolic resin impregnated fiberglass.[7] Honeycomb cores have been used extensively in the aircraft industry for many years.[7] Marine applications of honeycomb cores are limited due to the difficulty in bonding to complex geometric shapes and also due to the potential for water absorption. However, it is possible to achieve very lightweight and stiff panels, which may be useful for interior structures and deckplates, although use in these applications is rare. One use for honeycomb cores that has seemed to be very successful is in the manufacture of competitive rowing shells where stiffness and light weight are important. Vespoli USA of New Haven, CT uses an aramid fiber honeycomb core with very thin facings of carbon fiber laminate to construct very light, stiff hulls for their rowing shells.

2.3.2 Plywood

Plywood is sometimes used in areas where local reinforcement is necessary. Areas of thru–hull fittings or other hardware installations sometimes require a plywood core in place of a lower density core material. It is more common to find GRP used as a sheathing material for plywood structures, such as on a bulkhead in a small boat.[13]

[2] registered trademark of DuPont

A thin layer of GRP will be used to protect the plywood from wear and tear, and to apply a moisture resistant barrier.

2.3.3 Thermoset Foams

Thermoset foams such as cellular cellulose acetate, polystyrene, and polyurethane are very light weight (approximately 32 kg/m^3, or 2 lbs/ft^3) and resist water and decay very well.[13] Since thermoset foams have low strength properties and polystyrene is not compatable with polyester resins their use is usually restricted to buoyancy rather than structural applications. Thermoset foams are often used as a foam–in–place material to fill voids in small boat hulls.[13]

2.3.4 PVC Foams

PVC foams are available in two types: cross–linked and linear. The basic difference is that the linear PVC foams contain unique material properties as a result of the non–connected molecular structure. This allows the material to withstand impact loads better than the cross-linked foams and other core materials such as balsa. PVC foams are available in densities as low as 32 kg/m^3 (2 lbs/ft^3).[13]

2.3.5 Balsa

End grain balsa is the most commonly used core material in marine applications.[13] It's low cost coupled with excellent stiffness and bond strength make it a very popular choice among boat builders. One disadvantage of balsa core materials is it's lower resistance to impact forces compared to PVC foam cores, although balsa cored panels generally have higher static strength characteristics.[13] Balsa core materials are available in sheet form for flat panel construction or in a block-cut arrangement with a scrim backing for forming to complex curves.

2.4 Applications in the Marine Industry

Although applications of composite materials reach far beyond the marine industry, for the purposes of this report a brief discussion of the marine uses is included here. Uses in the recreational boating industry are well recognized and established. Canoes, kayaks, sailboats, power boats, and performance craft are all good examples of craft made almost exclusively of composites. Where lightweight construction is an important feature, such as for racing powerboats and sailboats, composites have proven to be very influential to the state of the art of these vessels. Another advantage of FRP or other composite construction, especially in recreational boats, is the ease of repair compared to wood or metal structures.

The first major interest in commercial FRP vessels was in the fishing industry, starting in the late 1960's with the construction of FRP shrimp trawlers.[13] Some of the earlier vessels are still in service today, which provides a testament to the longevity of FRP vessels. Today, approximately 50% of commercial fishing vessels are of FRP construction.[13]

Other commercial uses include deep sea submersibles, navigational aids (buoys), and offshore engineering applications (i.e. offshore drilling platforms and pilings). In lifeboats and utility boats, where longevity and low maintenance are important (primarily for lifeboats, which may sit out of the water in the weather for many years) FRP construction has proven to be very effective and economical.

As with other initiatives in engineering and technology, the military has led research and development of composite materials since World War II.[13] The Navy and Army have integrated several applications of composites into their vehicles, namely small boats, submarines, patrol craft, and minesweepers. Other components, ranging from small equipment brackets to propellers have also proven effective.[13]

The development of passenger ferries over the last two decades has made great strides with regard to speed and economy due to the increased use of composite materials. Due to current regulation in the U.S., the use of composites in the passenger ferry market is limited primarily to relatively small (up to 150 passengers) commuter type vessels. In European countries, there exist some larger passenger and automobile ferries capable of very high speeds.

Presently, there is not much use of composites in larger commercial vessels, although there have been industry studies into building large ships of GRP. In 1971, a feasibility study was made where a 470 foot dry/bulk cargo vessel was evaluated with regard to engineering and economic factors involved in GRP construction. The report, "Feasibility Study of Glass Reinforced Plastic Cargo Ship" by Scott & Sommella, see References [13] and [9], concluded that the state–of–the–art in industry would allow construction of such a vessel, but that long–term durability was a concern. Among the other findings, the fact that U.S. Coast Guard (USCG) fire regulations would not allow construction of such a vessel was of major concern, considering that some significant economic incentive would be necessary to change such regulations.[13] [9] It appears that trends in the maritime industry may have finally reached this incentive point with the present interest in high speed craft.

2.4.1 High Speed Craft

The term "High Speed Craft" (HSC) is sometimes misleading in that it tends to imply some new type of vessel. Actually, high speed craft technology combines age–old technology with newer technology to achieve the goal of getting people and products from one place to another faster and more economically. High speed craft include traditional displacement vessels as well as dynamically supported craft such as hydrofoils and hovercraft. According to "The International Code of Safety for High–Speed Craft"[15], HSC are capable of a maximum speed (m/s) equal to or exceeding:

$$3.7\nabla^{0.1667} \tag{2.1}$$

where, ∇ = displacement corresponding to the design waterline (m^3).

For a vessel with a displacement of 1000 long tons (991.3 m^3 in seawater), this means it would be considered a high speed craft if it was capable of obtaining a maximum speed of 22.7 knots (11.7 m/s). This speed is easily obtainable for conventional displacement type hulls, but there is more to defining a high speed craft than speed alone.

Other engineering characteristics of the craft such as volumetric Froude number[3] and operational considerations are also considered in the definition. The spirit of the HSC code is such that it does form a distinction from conventional ships. The distinction, and the need for a separate code for HSC, result from a different philosophy in managing risk and safety of such vessels. Factors specific to high speed craft such as the speeds involved in operation, the area of operation, the availability of rescue assistance, and the allowance for use of non-conventional shipbuilding materials all come into play.[15] The HSC Code will be discussed in more detail in Chapter 3.

[3]The Froude number, F_n, is a non–dimensional number indicating the relation between a vessel's length and it's speed: $F_n = V/\sqrt{gL}$, where V is the speed, g is the acceleration due to gravity, and L is the vessel length.[16] Volumetric Froude number is a similar term where the vessel's characteristic volume (displacement), ∇, is used in lieu of L, as follows: $F_{n,V} = V/\sqrt{g\nabla^{1/3}}$.

2.4.2 The MARITECH Program

A research and development program run by the Department of Defense's Advanced Research Projects Agency (ARPA) has been in effect since 1994 in order to develop and apply advanced technology to improve industrial competitiveness in U.S. shipyards. The program, called "Maritech", contracts for projects in the categories of (1) advanced shipyard processes and shipboard product technology and (2) near-term ship design construction technology application. What this means is that millions of dollars are being spent in order to improve the technology base of U.S. yards, making them more competitive in the global market. The most recent boost of $18.7 million of federal funds came in the summer of 1995 with projects that include composite ship superstructures, advanced material technology, fast ferry production, and high speed monohull design.[17]

The Maritech program is expected to last at least five years.[17] It stands to significantly improve the knowledge and application of existing and developing technologies which are very important to the future of the economics and capability of U.S. shipyards. It is hoped that the research from the Maritech program, along with studies such as this thesis, will help improve the understanding of how composite materials can be used in ship construction.

Chapter 3

Maritime Regulation and Composite Materials

Current regulations for commercial vessels in the United States generally do not allow the use of composite materials for ships' primary structure. The fact that a shipboard fire provides the occupants with no where to escape seems to make it common sense that the vessel be constructed of non–combustible materials. So it may seem unwise to build an entire ship of a combustible material such as GRP. Yet, with today's technology, advanced materials, and fire suppression systems, it may actually be possible to acheive an acceptable level of safety even when composites are used as the ship's primary structure. Regulations have not reached the point of considering an all-inclusive formula to determine an equivalency to steel construction, but they have reached the point of achieving an acceptable level of safety for certain vessel applications by requiring reduced fire loading, regulating wall linings and furniture, and establishing test procedures for certain ship components.

This chapter will provide a brief review of present regulatory practices in the U.S. and those of the International Maritime Organization (IMO).[1] The emphasis is on the fire safety requirements for composite material construction, and in particular as applicable to High Speed Craft.

3.1 United States Regulations

The Code of Federal Regulations (CFR) regulates the shipping industry in the U.S. The Coast Guard is the primary agency responsible for developing and enforcing these regulations. The CFR at times makes general reference to the requirements of other agency standards such as the American Bureau of Shipping (ABS), National Fire Protection Association (NFPA), Underwriters Laboratories (UL), American Society for Testing and Materials (ASTM), and Lloyds' of London. In addition to the CFR, the Coast Guard periodically releases additional guidance to the industry through "Navigation and Vessel Inspection Circulars" (NVIC). The U.S. Coast Guard is responsible for inspecting and certificating vessels in the U.S., primarily those involved

[1] It would be helpful to have one source for all fire safety regulations, but as with most model building codes, this is not the case. Fire safety requirements are usually buried within the text of such documents. Much of the information in this chapter was obtained from an unpublished paper by David Finnegan and P.J. Maguire at WPI.[18] In the paper, Finnegan and Maguire summarize flammability test requirements and regulations from U.S. and IMO sources. Another useful reference is the Ship Structure Committee Report SSC-360.[13]

in commercial trade or passenger carriers. The Marine Safety Center, located in Washington, D.C., reviews approximately 20,000 machinery, electrical, structural, and stability plans per year.[13][18]

3.1.1 CFR Title 46, Shipping

CFR Title 46, Chapter 1, contains the Coast Guard regulations for vessels under U.S. jurisdiction. Finding the fire safety requirements in this document is sometimes difficult, as they are scattered throughout the many subchapters, which typically separate requirements for vessel types. The CFR requirements generally mirror those found in the International Convention for the Safety of Life at Sea (discussed below) but are sometimes more specific with regard to vessel type. This section summarizes the different subchapters. Although only those regulations that specifically apply to composite materials are discussed here. For more specific information, the reader is referred to the Code of Federal Regulations, Title 46, and the Ship Structure Committee Report SSC-360.[13]

The following is a partial list of subchapters of CFR Title 46 and the vessel types to which they apply:

- Subchapter C - Uninspected Vessels
- Subchapter H - Passenger Vessels ($\geq$ 100 Gross Tons (GT) and $\geq$ 1 passenger for hire)

- Subchapter T - Small Passenger Vessels ($<$ 100 GT and $\leq$ 200 ft (61 m), $\leq$ 150 passengers or $\leq$ 49 overnight passengers)
- Subchapter K - Small Passenger Vessels ($<$ 100 GT and $\leq$ 200 ft (61 m), 151–600 passengers or 50–150 overnight passengers)
- Subchapter K' - Small Passenger Vessels ($<$ 100 GT, $\geq$ 601 passengers or $\geq$ 151 overnight passengers, *or* $>$ 200 ft (61 m))
- Subchapter Q - Shipbuilding Materials
- Subchapter I - Cargo and Miscellaneous Vessels
- Subchapter D - Tank Vessels
- Subchapter I-A - Mobile Offshore Drilling Units

Subchapter C governs uninspected vessels, hence it does not contain stringent requirements for structural items. The regulations in Subchapter C are primarily safety related, such as a requirement to have fire extinguishing equipment on board.

Subchapter H requires that the hull, structural bulkheads, decks, and deckhouses be constructed of steel or other equivalent metal construction. There is no allowance for composite materials or other combustible structural materials.

Subchapter T considers a vessel to display "structural adequacy" if it complies with the standards established by recognized classification societies such as Lloyds' "Rules for the Construction and Classification of Composite and Steel Yachts." With regard to combustibility of structural items, Subchapter T requires that the general construction of the vessel be such as "to minimize fire hazards insofar as reasonable and practicable." This statement can obviously be interpreted in different ways, however the CFR is more specific with some requirements for GRP construction. A vessel made of GRP construction must use fire retardant resins and laminates which have met military specification MIL–R–21607 after 1 year exposure to weather.[14]

Subchapter K and K' are new (effective 11 March 1996), and serve to expand the requirements of Subchapter T, while making the rules more flexible for most Subchapter T boats. One aspect of Subchapter K is that the HSC Code (discussed below) can be used as an equivalency to the requirements of Subchapter T and K, but that if this equivalency is used, the HSC Code should only be applied in its entirety to avoid creating potential regulatory imbalances.[19]

3.1.2 USCG Navigation and Vessel Inspection Circular No. 8–87

The Navigation and Vessel Inspection Circular (NVIC) No. 8–87, titled "Notes on Design, Construction, Inspection and Repair of Fiber Reinforced Plastic (FRP) Vessels", was released by the USCG to disseminate general information relating to good marine practice when dealing with FRP vessels.[20] NVIC 8–87 includes guidance on structural design considerations, plan submittals, construction and fabrication, inspections, and repair of FRP vessels.

Section 1.F of NVIC 8–87 specifies that resins, coatings, paint and sheathing should be fire retardant or made to provide an equivalent degree of fire safety. This section applies to hull, deck, and deckhouses constructed of FRP and wooden vessels with resin gel coats or an FRP sheathing system. Section 1.F.4 specifies fire protection equivalencies for vessels constructed with non–fire retardant resins. These equivalencies include such considerations as protection from ignition sources, the installation of rated fire boundaries, noncombustible surface linings or insulation, and installation of fixed detection and extinguishing systems.[20]

3.2 IMO Requirements for High–Speed Craft

The International Maritime Organization is responsible for the development and promulgation of the "International Convention for the Safety of Life at Sea" (SOLAS). This document contains requirements for the design and construction of vessels engaged on international voyages, including the equipment that should be provided and the conditions for their operation and maintenance. The International Code of Safety for High–Speed Craft (HSC Code) was adopted as Chapter X of SOLAS on 20 May 1994. The HSC Code was adapted from the Code of Safety for Dynamically Supported Craft in response to recognition of the growth, in size and types, of high speed craft. It was written in such a way as to facilitate future research and development of fast sea transportation while maintaining a high degree of safety for passengers and crews. The safety philosophy of the HSC Code is "based on the management and reduction of risk as well as the traditional philosophy of passive protection in the event of an accident."[15] The HSC Code is unique in its overall systems design approach to safety: rather than regulating individual ship components, the code is intended to be applied in its entirety.

The HSC code includes very comprehensive requirements for high speed craft, including stability, structures, machinery, electrical, control, and operational requirements to name only a few. The intent in this section is only to provide a brief review of the fire safety requirements for high speed craft. Chapter 7 of the HSC Code contains extensive fire safety requirements. The requirement most applicable to this work is that of “fire–restricting materials”, defined as materials which comply with the code with respect to:[15]

- low flame spread characteristics
- limit heat flux, due regard being paid to the risk of ignition of furniture in the compartment
- limited rate of heat release, due regard being paid to the risk of fire spread to adjacent compartments
- gas and smoke should not be emitted in quantities that could be dangerous to the occupants of the craft

Although not specifically in the HSC Code, the methods for use in determining the characteristics that qualify a material as “fire–restricting” include the ISO 9705 Full Scale Room Fire Test (room/corner test)[5] and the ISO 5660 (cone calorimeter).[21] The recommendations of the IMO with regard to these test methods have been released as recommended practice via what the IMO calls “assembly resolutions” for adoption by individual countries as they see fit.

HSC Code Paragraph 7.4.1.3 requires that the hull, superstructure, structural bulkheads, decks, deck-houses, and pillars to be constructed on non-combustible materials (i.e. steel). However, the use of other fire–restricting materials may be permitted provided that the requirements of the HSC code (Chapter 7) are met. Paragraph 7.4.1.3 basically allows further growth in the qualification procedures for fire–restricting materials. Currently, the IMO[6] has recommended use of the ISO 9705 room/corner test[5] as a suitable test procedure. Still under development are procedures which may allow use of small scale (cone calorimeter) test data in conjunction with mathematical models to predict full scale performance.[22] The requirements in paragraph 7.4.1.3 also include strength criteria at elevated temperatures for load bearing structural components. Structural compliance will be evaluated using test procedures still be be developed by the IMO.[15]

The IMO's recommended criteria for qualifying a surface material or lining as "fire–restricting" (based on ISO 9705) are:[6][5]

- the time average of the heat release rate (HRR) excluding the ignition source HRR does not exceed 100 kW;
- the maximum HRR (excluding the ignition source HRR) does not exceed 500 kW averaged over any 30 second period of time during the test;
- the time average of the smoke production rate does not exceed 1.4 m^2/s;
- the maximum value of the smoke production rate does not exceed 8.3 m^2/s averaged over any 60 second period of time during the test;
- flame spread must not reach any further down the walls of the test room than

0.5 m from the floor excluding the area which is within 1.2 m from the corner where the ignition source is located; and

- no flaming drops or debris of the test sample may reach the floor of the test room outside the area which is within 1.2 m from the corner where the ignition source is located.

All six of the requirements listed above must be fulfilled in order to qualify as a fire–restricting material. There are no residual strength requirements included in this test procedure. In the HSC Code, structural strength requirements at elevated temperatures must also be met based on procedures still under development by the IMO. An interim standard for measuring smoke and toxic products of combustion also exists as published by the IMO in draft resolution FP 39/19 of the Maritime Safety Committee.

The HSC Code Chapter 7[15] contains additional requirements for fuel systems, ventilation, fire detection and extinguishing systems, protection of special category spaces, fireman's outfits, fixed sprinkler systems, fire barriers, and other fire safety measures. For example, Table 7.4-1 of the HSC Code contains structural fire resistance times for separating bulkheads and decks of passenger craft. The requirements are similar to hourly ratings required by many model building codes. This thesis is primarily concerned with the study of materials that may be considered as fire restricting per IMO's definition, and will not include a review of these other requirements.

Chapter 4

Background Information

This chapter reviews existing literature relevant to this study. While there have been volumes written on the subjects involved, this review will be limited to those most applicable to the study at hand.

4.1 "Use of FRP in the Marine Industry", Technical Report SSC-360

The technical report "Use of Fiber Reinforced Plastics in the Marine Industry"[13] is an extremely comprehensive report on the state of the marine composites industry. Covering the application, materials, design, performance, fabrication, and testing of composite materials, it serves as an excellent reference for designers, builders, and regulators. It also has a brief discussion of the U.S. Coast Guard and American Bureau of Shipping regulations for vessels that use composite materials in their construction.

A chapter on testing contains descriptions of ASTM tests and other specialized tests for composite materials for mechanical and fire properties. It includes requirements for selection of materials used in Naval applications, SOLAS requirements for structural materials in fires, and tables on heat release rates and ignitability data for some composite materials.

4.2 Composites for Naval Applications

This section provides a brief review of some of the literature on fire test methods and experimental studies of composite systems for use in naval ships and submarines. Many of the issues discussed in these documents are applicable to composite material systems in commercial and non–regulated vessels.

4.2.1 Military Standard, MIL–STD–2031(SH)

Military Standard "Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used in Hull, Machinery, and Structural Applications Inside Naval Submarines" (MIL–STD–2031(SH)) establishes the fire and toxicity test methods, requirements, and the qualification procedure for composite materials and composite material systems to allow their use inside naval submarines.[23] The standard acknowledges the fact that no single test method is adequate to evaluate the fire hazard of a particular composite material system, and that fire performance relies not only on the material properties but also on the fire environment to which the material is exposed. Therefore, the standard includes test methods that cover the spectrum ranging from small–scale tests to intermediate scale and large scale tests. The test methods used for qualifying a composite material system for use aboard a naval submarine include the following:[23]

- Oxygen–temperature index (described in MIL–STD–2031(SH), Appendix A)
- Flame spread index (ASTM E 162, Surface Flammability of Materials Using a Radiant Heat Energy Source)
- Ignitability (ASTM E 1354, Cone Calorimeter)
- Heat release (ASTM E 1354, Cone Calorimeter)
- Smoke Obscuration (ASTM E 662, Smoke Chamber)
- Combustion gas generation: CO, CO_2, HCN, HCL (ASTM E 1354, Cone Calorimeter)
- Burn–through fire test (David Taylor Research Center Burn-Through Fire Test, described in MIL–STD–2031(SH), Appendix B)
- Quarter–scale fire test (described in MIL–STD–2031(SH), Appendix C)
- Large scale open environment test (described in MIL–STD–2031(SH), Appendix D)
- Large scale pressurizable fire test (described in MIL–STD-2031(SH), Appendix E)
- N-Gas Model smoke toxicity screening test (described in MIL–STD–2031(SH), Appendix F)

This military standard is a performance–based document, with test acceptance criteria to use in evaluating new equipment and systems for naval submarines. The standard is not intended to create a "pass/fail" requirement for composite materials, but rather to be used as a tool in the overall analysis of such materials and systems.[10]

This military standard is not only important to the design and construction of naval submarines, but the fact that it uses several different fire test methods to qualify composite material systems is a significant effort that may be modeled as a document in regulating the construction of surface ships. For example, the test methods and document structure of MIL–STD–2031(SH) may be applicable to commercial vessel regulation, naval surface vessels (i.e. Coast Guard, Navy, and other military ships), offshore production platforms, or even land–based structures. The development of a document similar to MIL–STD–2031(SH) applicable to commercial vessel regulation would be very valuable to the marine industry.

4.2.2 Fire Barrier Treatments for Composite Structures used in Naval Applications

In a study by Sorathia *et al* some of the test methods described in MIL–STD–2031(SH) were employed to test nine fire barrier systems used to protect composite structures.[10] Fire tests were conducted to evaluate fire barrier systems (ceramic fabric, ceramic coatings, intumescent coatings, hybrid of ceramic and intumescent coatings, silicone foam, and phenolic skin) over composite systems of glass/vinyl ester, graphite/epoxy, graphite/bismaleimide, and graphite/phenolic. The materials were tested with and without the barrier systems applied.[10]

Sorathia *et al* showed that without any fire barrier treatment, all composite systems evaluated failed to meet certain ignitability and peak heat release requirements of MIL–STD–2031(SH). The intumescent coating and a hybrid of intumescent and ceramic coatings were shown to be the most effective fire barrier treatments of the composites in their study.[10]

4.2.3 An Intumescent Resin System for Fire Barrier Protection

Kovar *et al* conducted a study of an intumescent modified phenolic resin system for the U.S. Navy. In "Novel Composite Structures for Shipboard Fire Barriers"[24], they summarize the development and testing of an intumescent composite fire barrier. Rather than simply covering the fire barrier composite material system with an intumescent coating or other fireproofing system (i.e. mineral wool), the resin was preblended with an intumescent additive. A composite which uses this intumescent resin matrix will foam and char when exposed to fire conditions, providing an effective barrier to protect the underlying structure and prevent further spread of flame and smoke production. This creates a load bearing structural composite that will delay the spread of fire and insulate adjacent areas for at least thirty minutes.[24] The significance of the development of this intumescent resin matrix is that it offers an innovative and cost–effective method for fireproofing FRP composite structures in U.S. Navy, Coast Guard, and commercial vessels. The intumescent resin matrix system shows a great improvement over the current practice of using mineral and ceramic wool for fireproofing, which adds weight and can absorb spilled fuels.[24]

4.2.4 Flammability of GRP for Use in Ship Superstructures

Egglestone and Turley have reported test results from the cone calorimeter for several different GRP panels.[8] They tested various resins, including isophthalic polyester, flame retardant polyester, two different vinylesters, and a resole phenolic resin. Test irradiance ranged from 25 to 80 kW/m^2. Their study concluded that the resole phenolic composite laminate had superior flammability resistance compared to the polyester and vinylester resin laminates. The resole phenolic resin laminate had a longer ignition time regardless of irradiance level, produced lower heat release rates, a lower effective heat of combustion, and yielded less smoke.[8] An important finding from this study is that the flame retardant resin did not improve the polyester resin's performance enough to match that of the phenolic resin laminate.

4.3 Work at NIST

The National Institute for Standards and Technology (formerly the National Bureau of Standards) has been on the forefront in the past decade with regard to fire and composite materials research. This section briefly summarizes some of the work that has been conducted at NIST in recent years.

In 1986, Brown *et al* of the National Bureau of Standards completed a literature review[12] which, at the time, was probably the most comprehensive review ever completed. Their goal was to review all of the open literature on fire characteristics of composite materials which may be considered for use in U.S. Navy shipboard installations. Their review presents results of several different fire tests of composite materials, including tests for limiting oxygen index, smoke production, flame spread, fire endurance, differential scanning calorimetry, and thermogravimetric analysis. Unfortunately, it does not include results of more modern standard test methods such as the cone calorimeter[1] and the LIFT apparatus[2]. Their report contains relative rankings of materials based on their review of the existing literature at the time. The rankings include a discussion of the behavior of different resin and reinforcing fiber systems. They conclude with recommendations for test developments and for the future direction of the U.S. Navy's fire evaluation program.[12]

Ohlemiller has completed several studies on composite materials. In his report "Assessing the Flammability of Composite Materials"[25], Ohlemiller has outlined a relatively straightforward approach to testing composite materials. His approach is very similar to what one would take with conventional combustible materials, but he has pointed out some peculiarities that would be experienced with composite materials. In a subsequent paper[26], Ohlemiller *et al* addressed edge effects experienced in small–scale testing of composites by testing larger samples (15 cm square) in the cone calorimeter and using a special water cooled sample frame. This procedure was effective in stopping delamination from spreading beyond the exposed portion of the sample face, keeping pyrolysis gases from escaping at the edges of the sample. Unfortunately, this modified sample frame caused a significant heat sink for the exposed face material, requiring a tedious procedure to account for the heat sink effect.[26]

Ohlemiller and Dolan [27] conducted a material study in the LIFT Apparatus[2] of a honeycomb sandwich panel and a composite armor. Their report provides a useful framework for presentation of the results of a composite materials study. In particular, their report documents the difficulties involved with the testing of composite materials such as delamination, edge effects, and intermittent flaming before ignition.[27]

Brown *et al*[28] conducted a study in which they evaluated the fire performance of several different kinds of composite materials using the cone calorimeter. They derived five parameters to characterize the ignitability and flammability of the materials. These parameters are the minimum external radiant flux required for piloted ignition, a thermal sensitivity index (indicates the burning intensity dependence on external heat flux), the extinction sensitivity index (indicates the propensity for continued flaming combustion without an external heat flux), yield of gaseous products, and an average extinction area normalized to CO_2 yields.[28] They recommended investigating the use of the derived flammability parameters from the cone calorimeter to provide the basic data needed for correlation to large scale compartment fires.[28]

4.4 Tucker's Heat and Mass Transfer Model

A Master's Thesis submitted by James Tucker at WPI presented preliminary development of a three–dimensional heat and mass transfer model for a thermally-thick, laminated, anisotropic, fibrous, charring composite exposed to a radiant flux.[29] Tucker's work also includes a review of previous work in small scale testing of composite materials. Of particular note is the work conducted by the U.S. Navy and Royal Navy where residual strength properties of composites exposed to heat or fire were evaluated, which may have some application to the structural strength criteria discussed in the context of fire restricting materials in Chapter 3.

Tucker's model addresses the decomposition of the composite, as the resin matrix becomes porous. As the composite heats up and undergoes pyrolysis, the model assumes an Arrenhius, temperature–dependent reaction. Tucker includes convection within the composite based on the assumption that local thermal equilibrium between solid and gas pockets is not acheived. This work is significant since, as discussed in subsequent chapters, the materials in the present study experience decomposition and delamination. Tucker's model may be applicable in the future if an attempt is made to model the heat transfer as the composite delaminates, or as the foam core melts.

4.5 Piloted Ignition of Solid Materials

This section includes an introduction to the ignition theories used to reduce and analyze test data obtained in the cone calorimeter and the LIFT apparatus. A distinction is made between the simplified data reduction and analysis methods contained within ASTM E 1321[2] and other methods such as the "improved" method proposed by Janssens.[3]

4.5.1 Ignition as a Gas Phase Phenomenon

As a solid material is exposed to an external radiant heat flux the following must take place for piloted ignition to occur:[30][31]

- heating (surface temperature rises)
- pyrolysis (outgassing of volatiles)
- mixture of pyrolysis gases with air
- a significant energy source exists to ignite the flammable mixture above the material surface (i.e. a spark or pilot flame)
- a significant concentration of fuel (gases) must exist to obtain ignition (achieve a lower flammable limit)
- sustained flaming $\rightarrow$ piloted ignition occurs

Ignition of a solid is a complex phenomenon involving both the condensed phase solid and the gas phase adjacent to the solid. The phenomenon can be simplified, from an analytical perspective, by focusing on the heating of the solid.

Figure 4.1: The relationship between the mass flow rate of pyrolysis gases and surface temperature

If ignition occurs in the gas phase adjacent to the solid surface, how then can we justify evaluating ignition of a solid based on its surface temperature? This can be justified because of the Arrhenius relationship between the mass flow rate of pyrolysis gases and the surface temperature of the solid.[32] Figure 4.1 shows this relationship qualitatively, where a significant increase in the pyrolysis rate occurs over a narrow temperature range around T_{ig}. T_{ig} is the surface temperature required to cause a flow of volatiles sufficient to allow persistent flame at the material surface (ignition of the solid). T_{ig} can then be considered the ignition temperature of the solid in lieu of a complete evaluation of gas phase phenomena.

4.5.2 Mathematical Models of Piloted Ignition

Janssens has presented a comprehensive literature review of ignition theories and mathematical models.[33] Many different ignition models have been proposed. What nearly all of them have in common is the assumption of one or more of the following: [33]

- Heat losses from the sample surface are a linear function of surface temperature.
- Emissivity is equal to one.
- Thermal properties k, ρ, and c are constant regardless of temperature.
- Specimens behave as a semi-infinite solid.

The solid's ignition temperature can be inferred from the thermal equilibrium equation for the surface:[3]

$$\epsilon \dot{q}^{"}_{o,ig} = h_c(T_{ig} - T_\infty) + \epsilon\sigma(T_{ig}^4 - T_\infty^4) \equiv h_{ig}(T_{ig} - T_\infty) \tag{4.1}$$

where the effective ignition temperature (T_{ig}) is experimentally determined from the critical radiant heat flux (irradiance) needed for piloted ignition ($\dot{q}^{"}_{o,ig}$), h_c is the convective heat transfer coefficient, ϵ is surface emissivity, and T_∞ is ambient temperature.

A commonly used ignition model is that of Quintiere and Harkleroad[34] (the method used in ASTM E 1321[2]). This model assumes a semi–infinite solid exposed to a constant net heat flux, with negligible heat losses from the material surface. The experimental results are correlated by the following relationship:[2]

$$\frac{\dot{q}^{"}_{o,ig}}{\dot{q}^{"}_{e}} = F(t) = \begin{cases} b\sqrt{t}, & t \leq t^{*} \\ 1, & t \geq t^{*} \end{cases} \tag{4.2}$$

where, $\dot{q}^{"}_{o,ig}$ is the critical heat flux below which ignition does not occur, $\dot{q}^{"}_{e}$ is the incident heat flux, b is the slope of the associated plot ($b = 2h_{ig}/\sqrt{\pi k \rho c}$, where h_{ig} is the total heat loss coefficient at ignition), t is time to ignition at $\dot{q}^{"}_{e}$, and t^{*} is the characteristic time to reach thermal equilibrium when $\dot{q}^{"}_{o,ig}/\dot{q}^{"}_{e} = 1$ in the test apparatus.

Janssens recommends using the following power law to correlate ignition times.[3] When the best linear fit results from n closer to 0.5, the material behaves as a semi–infinite solid. When the best fit results from n closer to 1, the material behaves as thermally thin.[3]

$$(\dot{q}^{"}_{e} - \dot{q}^{"}_{cr})t^{n}_{ig} = C \tag{4.3}$$

where C is a constant and n is an exponent between 0.5 and 1.

Toal *et al* have correlated piloted ignition data for six materials according to the power law in equation 4.3. They determined a linear relationship between time to ignition and irradiance based on an empirical flux–time product (FTP) as follows:[35]

$$FTP^n = (\dot{q}^" - \dot{q}^"_{cr})^{3/2} t_{ig} \tag{4.4}$$

Silcock and Shields[36] have developed a protocal for analysis of time–to–ignition data. They recommend use of the flux–time product to analyze data from the cone calorimeter and the ISO ignitability apparatus. Their method applies to thermally thick and thin materials by varying the power law index (exponent n) to obtain a best fit to the data.[36]

Ignition phenemenon is relatively well understood, but it must be realized that certain test data correlations do not apply to materials that exhibit "non–thick" behavior (not semi–infinite). Janssens has proposed a method in which the empirical data itself serves to help determine how a material behaves (i.e. as a semi-infinite solid (thermally thick) or "non–thick"). In many cases a material that is physically thick may actually behave as a "non-thick" material when exposed to an external heat flux. A "non-thick" material is defined as that in which the thermal wave reaches the back surface before ignition. Janssens' proposed "improved method"[3] includes an assumption that heat flow in the solid is one-dimensional, which requires that the exposed samples be significantly large so as to minimize edge effects where three–dimensional heat flow would be significant.[3][33] This particular assumption may not be valid if test standards are followed closely with regard to sample size. For example, in the cone calorimeter, the 100 mm square sample may not allow this assumption, especially with test materials that exhibit significant edge effects.

Jannsens[3] recommends correlating ignition data according to equation 4.3, varying n until the best line fit is obtained. If the best fit is for n close to 0.55, the material behaves as a semi-infinite solid. If the optimum n is closer to 1, the material is considered to behave as non-thick. The critical irradiance, $\dot{q}^{"}_{cr}$, is found at the intercept of the best fit line with the abscissa (x–axis). T_{ig} and h_{ig} are calculated from $\dot{q}^{"}_{cr}$ using equation 4.1. Rather than assuming a surface emissivity (ϵ) of one, Janssens recommends that more accurate values for surface emissivity be used in equation 4.1.[1] For non-thick materials Janssens recommends concentrating ignition experiments at high flux levels where the material is more likely to behave as a semi-infinite solid. This will allow a better curve fit with reduced error. If necessary, more data points may be obtained at higher flux levels in order to force this semi-infinite solid behavior.[3]

Once the best fit to the ignition data is determined via equation 4.3, Janssens' method then uses a semi–infinite solid solution, forced through ($\dot{q}^{"}_{cr}$, 0), considering heat losses from the solid surface to be a linear function of surface temperature with a constant total (convective and radiative) heat transfer coefficient, h_{ig}. Janssens uses an approximate curve fit to the exact solution,[3]

$$\dot{q}^{"}_{e} = \dot{q}^{"}_{cr}\left[1 + 0.73\left(\frac{h_{ig}^{2}t}{k\rho c}\right)^{-0.55}\right] \tag{4.5}$$

The ignition data are plotted as $(\frac{1}{t_{ig}})^{0.55}$ versus $\dot{q}^{"}_{e}$ for the semi–infinite case. A best

[1]If surface emissivity is not known for a particular material, Janssens recommends using $\epsilon = 0.9$.[3]

fit straight line is fit to the data and forced through ($\dot{q}^{"}_{cr}$, 0). The effective thermal property, $k\rho c$, is then obtained from the slope of the line, m, as,[3][33]

$$k\rho c = (m0.73\dot{q}^{"}_{cr}h_{ig}^{-1.1})^{-1.818} \tag{4.6}$$

Janssens[3] makes a distinction between observed $\dot{q}^{"}_{o,ig}$ and the calculated $\dot{q}^{"}_{cr}$. The irradiance level below which ignition does not occur during the test period is considered $\dot{q}^{"}_{min}$, an observed parameter (this is synonymous with $\dot{q}^{"}_{o,ig}$ defined by Quintiere and Harkleroad[34]). The derived parameter $\dot{q}^{"}_{cr}$ is obtained via the curve fit described in the previous paragraph. Where $\dot{q}^{"}_{cr}$ is only a parameter derived within the bounds of the ignition model, $\dot{q}^{"}_{min}$ is controlled by physical and chemical phenomena which are not addressed in the model.[3] Janssens proposes that $\dot{q}^{"}_{min}$ be reported as as separate result of the ignition tests. Janssens found that for some materials the observed parameter, $\dot{q}^{"}_{min}$, was much higher than the modeling parameter, $\dot{q}^{"}_{cr}$. In the case of Type X gypsum board heated at a slow rate ($\dot{q}^{"}_{e}$ near $\dot{q}^{"}_{min}$), this is explained by the fact that much of the thin layer of combustible paper on the gypsum board surface is pyrolyzed by the time the surface temperature reaches T_{ig}. At that time, there is not enough fuel left to generate a flammable mixture at the pilot.[3] Janssens found a similar phenomenon occuring for some fire retardant treated materials.

Janssens' method may be particularly applicable to composite materials. The physically thin composite skin of the cored composites may produce results that fit the "non–thick" case. For the purposes of comparison to the standard data reduction method specified in ASTM E 1321[2], Janssens' method is used with the data from this thesis study. Results are presented in Chapters 6 and 7.

Chapter 5

Description of Test Materials

This study includes lab testing of two different types of cored composite (sandwich) materials. The materials were provided by Westport Shipyard, Inc., of Westport, Washington. Westport Shipyard uses these materials in the construction of commercial and passenger boats and large pleasure yachts.[37] Most of the vessels constructed at Westport Shipyard are 80 to 115 feet (24 to 35 m) in length. These vessels are constructed almost entirely of composite materials, including hull, interior, and superstructure. The particular sandwich materials used in this study were built to the specifications used by Westport Shipyard in the recent construction of a 95 foot (29 m) passenger vessel.[37] The laminate schedule is as specified by Jack W. Sarin Naval Architects, Inc., of Bainbridge Island, Washington.[38] The area of the hull where the test materials are used is the topside and transom areas, which extends from the vessel waterline up to the gunwale (upper edge of the ship's side). The hull bottom uses the same sandwich materials, but the laminate facings are thicker.

Figure 5.1: Typical Sandwich Composite Construction

Figure 5.1 shows the typical arrangement of the composite materials in the sandwich. The surface exposed to the external heat flux in the present study is the inner skin, which would be the surface exposed on the interior of the ship's hull. This inner surface is characterized by it's pink resin color and the textured surface due to the topmost layer of woven roving. The outer skin is characterized by it's smooth gelcoat appearance. This exterior gelcoat surface is common on nearly all FRP boats unless the exterior hull is painted.

5.1 GRP/Balsa Core

The laminate schedule, which includes the core materials, is listed below for both test materials. The laminate schedule lists all layers in the composite, from the exterior outer gelcoat surface to the inner skin surface. The GRP/Balsa Core sandwich has a total thickness of approximately 33 mm (1.3 in):

- Outer Skin (thickness = 3.9 mm (0.154 in))
  - Gelcoat
  - 229 g/m^2 (3/4 oz/ft^2) mat (skin-out)
  - 229 g/m^2 (3/4 oz/ft^2) mat
  - 3 x 815 g/m^2 (24 oz/yd^2) woven roving
- Core
  - Mastic
  - 1" 128 kg/m^3 (8 lb/ft^3) Balsa
- Inner Skin (thickness = 2.4 mm (0.095 in))
  - 229 g/m^2 (3/4 oz/ft^2) mat
  - 2 x 815 g/m^2 (24 oz/yd^2) woven roving

Fire retardant polyester resin conforming to MIL-R-21607 is used in all laminates. The balsa core material is described in the manufacturer's literature as end–grain balsa, surface primed for easier installation and reduced resin use. The balsa core sheets are cut for contouring in 0.75 inch x 1.5 inch blocks on a fiberglass scrim backing.

5.2 GRP/Foam Core

The laminate schedule used in the GRP/Foam Core sandwich is as follows, with at total thickness approximately 30 mm (7.6 in):

- Outer Skin (thickness = 3.9 mm (0.154 in))
  - Gelcoat
  - 229 g/m^2 (3/4 oz/ft^2) mat (skin-out)
  - 229 g/m^2 (3/4 oz/ft^2) mat
  - 3 x 815 g/m^2 (24 oz/yd^2) woven roving
- Core
  - Mastic
  - 1” 80 kg/m^3 (5 lb/ft^3) Linear P.V.C. Foam w/ minimum shear strength of 170 PSI. (AIREX R63.80)[1]
- Inner Skin (thickness = 2.4 mm (0.095 in))
  - 229 g/m^2 (3/4 oz/ft^2) mat
  - 2 x 815 g/m^2 (24 oz/yd^2) woven roving

Fire retardant polyester resin conforming to MIL-R-21607 is used in all laminates. Note that the laminate schedules for both the GRP/Balsa and GRP/Foam cored materials are identical with the exception of the core material.

[1] Airex is a Registered Trademark of Airex AG Specialty Foams.

5.3 Preparation for Testing

Samples were cut on a table saw to the dimensions specified in the appropriate test standard. All materials were conditioned at 23 $\pm 3°C$ and a relative humidity of 50 $\pm$ 5%. Prior to inserting into the specimen holder in either the Cone Calorimeter or the LIFT Apparatus, material samples were wrapped with aluminum foil around the back and edges. Unless otherwise noted in subsequent chapters on the sample testing, the samples were backed with a noncombustible refractory insulating material. All sample preparation and mounting procedures were followed as specified in the appropriate test standard [2] [1], unless otherwise noted in the following chapters.

A limited number of tests were performed on the core materials alone and also the GRP skin (without core). The core materials were also provided by Wesport Shipyard. The GRP skins were cut off some of the pre–cut test samples with a band saw in order to remove the core and allow testing of the GRP alone.

Chapter 6

Testing in the Cone Calorimeter

A series of experiments was completed with the test materials in accordance with ASTM E 1354.[1] The goal was to obtain a set of material thermal properties useful for fire modeling and classification of these cored composite materials for use in shipbuilding. The results of this testing will hopefully help create a better understanding of how cored composite materials behave under controlled fire conditions. Parameters such as ignitability, heat release rate, and smoke production are important in the understanding of how materials will behave in a real fire. This chapter presents the results of the cone calorimeter experiments with the test materials. Some problems with the test procedure as applied to cored composites are identified.

6.1 Test Method Description

The Cone Calorimeter test, which is standarized in ASTM E 1354[1] (and also ISO 5660[21]), allows the measurement of the response of materials exposed to an external heat flux ("irradiance") with or without an external ignitor. An electric conical heater is provided to generate radiant heat fluxes ranging from 0 to 100 kW/m^2 at the sample surface. An external spark ignitor is provided if piloted ignition parameters are to be measured. The sample is inserted into a specimen holder and placed on a load cell for measurement of mass loss rate throughout the test. The primary function of the cone calorimeter is to determine heat release rates based on the oxygen consumption principle.[39][40] A general view of the cone calorimeter is shown in Figure 6.1 (from [41]). Specific details of the cone calorimeter equipment and operation are contained in ASTM E 1354.[1]

The cone calorimeter used in the present study is located in the WPI Fire Sciences Laboratory. WPI's cone calorimeter was manufactured in accordance with ASTM E 1354. The software package "CONECALC" calculates the parameters discussed above and produces a detailed printout of each test. Throughout the test, the onboard computer measures and/or calculates mass loss rate, smoke production (specific extinction area), effective heat of combustion, heat release rate, and CO and CO_2 yield. Visible observations are also recorded manually by throughout the tests.

Material samples of 100 mm x 100 mm were prepared in accordance with the test

Figure 6.1: General View of the Cone Calorimeter

standard. In all cone calorimeter tests except for two (as discussed below) the samples were tested with the sample edge frame in place. This was intended to reduce edge effects experienced due to the small sample size. Edge effects can be in the form of flaming or non–flaming combustion at the sample edges. This phenomenon would not be experienced in large scale fires, thus it is important to try to reduce any edge effects in order to more closely approximate large scale burning.

Cone calorimeter experiments provide data on the ignitability (time to ignition), heat release rate, mass loss rate, effective heat of combustion, and visible smoke development. Heat release rate (HRR) is considered by some to be the single most important variable needed to describe a fire hazard.[41] Ignitability parameters are important for relative rankings of materials and also for modeling. Visible smoke development is important for material rankings and classification. The results from the cone calorimeter experiments can also be used to determine the minimum surface flux and temperature necessary for ignition ($\dot{q}''_{o,ig}$, T_{ig}) and the effective thermal property $k\rho c$.

It is not the intent here to provide a complete review of the standard test method, the apparatus, or the theories involved. The ASTM E 1354 Standard Test Method[1] and the literature[41][42] cover these aspects quite well. The reader is referred particularly to the work of Babrauskas[41][42], on which the standard test method is based.

6.2 Experimental Results

6.2.1 General Observations

In the cone calorimeter tests, the materials' top face (GRP skin) usually began producing pyrolysis gases ("outgassing") within a few seconds of exposure. Outgassing was typically followed by a delamination of the GRP skin. This delamination was marked by an audible tearing or ripping sound and an observed bubble forming under the skin. This delamination occurs within the GRP skin between the layers of fiberglass, rather than between the GRP and the core material. This is evident in the fact that delamination occured at approximately the same time (under similar irradiance) when the GRP facing was tested without the core. However, the GRP skin also separates from the core material as the sample burns, as evident from post–test observation. After delamination, most of the samples demonstrated a "deflation" of the gas bubble that had formed under the GRP skin. This "deflation" was usually accompanied by visible escape of gases at the sample edges. In most cases there was usually at least one flash of flame above the sample surface prior to sustained ignition. Once sustained ignition was achieved, the pilot spark was removed.

With the foam–cored samples the core melted and the top sample face receded into the specimen holder. This occured before ignition at lower irradiance levels ($\leq 35kW/m^2$) and throughout the burning phase (after ignition) at all irradiance levels. This was one observed problem with the test method, that the sample's top face was receding farther away from the cone radiant heater. For example, in one test with an irradiance of 35 kW/m^2 the top surface had receded approximately 12 mm by the end of test. Edge ignition sometimes occured as pyrolysis gases from the PVC foam core escaped. Also, when testing the foam–cored materials, the heat release curve often began rising again well into the test (>10 minutes, see Figure 6.8). It is possible that this phenomenon is due to the increased burning of the core material itself, or possibly the back GRP skin begins burning. This phenomenon was not observed in the tests with the balsa–cored material. Perhaps future testing can include the placement of thermocouples within the sample skins and core to help identify the reasons for this increase in heat release rate when it would otherwise be expected to continue falling.

With the balsa–cored samples, the edge effects generally did not appear to be as prevalent, other than the outgassing at the edges as the GRP skin “deflated”. The balsa core material did char at the edges, but the depth of char was not very deep, no more than 2 mm deep at irradiances lower than 50 kW/m^2, and even then the char did not extend all the way down the sides of the sample; much of the balsa core was unaffected near the bottom of the sample away from the exposed face. However, at irradiance levels of 50 and 75 kW/m^2 the balsa core exhibited more edge charring as well as charring of the top face of the core material. The gaps between the balsa wood blocks had widened as the core material burned. This occurred even though the GRP skin was still intact on top of the core. At the higher irradiance levels (50 and 75 kW/m^2), the edge effects were much less prevalent prior to ignition; this was also the case with the foam–cored samples. The extra charring exhibited by the balsa core at the higher irradiance levels was due to the increase heat insult to the sample throughout the test. At lower irradiances, the sample had flamed out before much of the core material was affected.

6.2.2 Ignitability

A total of 30 samples (15 each of the GRP/Balsa core and GRP/Foam core materials) were tested in the Cone Calorimeter. Average time to ignition and standard deviation values for each irradiance are listed in Table 6.1. Ignition data are also plotted in Figures 6.2 and 6.3.

Table 6.1: Cone Calorimeter Test Results - Ignitability

Irrad (kW/m^2)	GRP/Balsa t_{ig} (s)	GRP/Balsa STD DEV	GRP/Balsa # of Tests	GRP/Foam t_{ig} (s)	GRP/Foam STD DEV	GRP/Foam # of Tests
75	24	2	2	24	2	2
50	48	5	3	40	0	3
35	96	9	3	64	13	3
25	238	33	3	151	65	3
20	409	-	1	342	-	1
19	443	-	1	367	-	1
18	no ignition			no ignition		

Table shows average values with standard deviation (STD DEV) at each listed irradiance.
t_{ig} = time to ignition
"# of tests" = number of test runs at the listed irradiance level

The fact that these materials are composites requires particular attention in analyzing the data. Melting core materials (in the case of the PVC cored sandwich), edge effects, and delamination of the GRP skin must be considered in the analysis. Delamination presents an obvious problem with the test method for these materials. The Quintiere and Harkleroad[34] model (described in the LIFT standard, ASTM E 1321[2]), which is commonly used to correlate cone ignition data and derive material

Figure 6.2: Ignition Time (t_{ig}) vs Irradiance ($\dot{q}_e''$) for GRP/Balsa Core (from Cone Calorimeter). Curve is best fit to the data.

Figure 6.3: Ignition Time (t_{ig}) vs Irradiance ($\dot{q}_e''$) for GRP/Foam Core (from Cone Calorimeter). Curve is best fit to the data.

properties, assumes that the material is a semi-infinite solid. When the GRP skin delaminates, it introduces a condition that potentially violates this assumption. These factors, and their influence on data analysis, are discussed below in more detail.

6.2.3 Heat Release Rates

Heat release rate (HRR) data (peak HRR, time to peak HRR, 300 s average HRR, and total heat released) for each material under study are listed in Tables 6.2 and 6.3. The values presented here are the average values of the tests at each irradiance level. Data was also obtained for the GRP skin (no core) and for the core materials alone. One reason for reporting the average HRR over the first five minutes (300 s) is that the HRR has dropped to at least one–half of the peak value by this time, making 300 s an appropriate time frame over which to determine average HRR behavior. This is consistent with the recommendations of Brown *et al*[28] and the test standard[1].

Table 6.2: Cone Calorimeter Test Results - Heat Release Rates (GRP/Balsa Core)

Irrad (kW/m^2)	Peak HRR (kW/m^2)	STD DEV	t_{PHR} (s)	STD DEV	HRR-300 (kW/m^2)	STD DEV	THR (MJ/m^2)	STD DEV	# of Tests
75	207	3	105	0	131	3	50.6	3	2
50	172	2	98	26	116	9	45.9	7	3
35	157	6	220	21	103	6	37.8	3	2
35 no frame	161	-	250	-	111	-	35.1	-	1
25	128	8	343	27	89	3	29.6	2	3
20	131	-	500	-	77	-	23.1	-	1
19	139	-	510	-	76	-	23.4	-	1
GRP (no core)									
35	132	-	105	-	77	-	23.2	-	1
25	119	-	540	-	72	-	22.2	-	1
Balsa (core only)									
35	125	-	20	-	40	-	17.9	-	1
25	126	-	30	-	35	-	10.9	-	1

Table shows average values with standard deviation (STD DEV) at each listed irradiance.

t_{PHR} = time to reach peak HRR

HRR-300 = average HRR over initial 300 seconds after ignition

THR = the total heat released during the entire test

"# of tests" = number of test runs at the listed irradiance level

"no frame" denotes the one test at 35 kW/m^2 irradiance where edge frame was not used

Table 6.3: Cone Calorimeter Test Results - Heat Release Rates (GRP/Foam Core)

Irrad (kW/m^2)	Peak HRR (kW/m^2)	STD DEV	t_{PHR} (s)	STD DEV	HRR-300 (kW/m^2)	STD DEV	THR (MJ/m^2)	STD DEV	# of Tests
75	189	2	135	5	122	7	89.6	3	2
50	177	4	160	7	118	5	82.9	27	3
35	130	18	135	32	80	7	24.7	2	2
35 no frame	150	-	115	-	84	-	25.7	-	1
25	134	2	233	30	87	3	27.3	1	3
20	127	-	385	-	63	-	19.0	-	1
19	141	-	415	-	78	-	24.3	-	1
GRP (no core)									
35	132	-	105	-	77	-	23.2	-	1
25	119	-	540	-	72	-	22.2	-	1
PVC Foam (core only)									
25	151	-	65	-	45	-	13.6	-	1
15	105	-	55	-	30	-	9.2	-	1

Table shows average values with standard deviation (STD DEV) at each listed irradiance.

t_{PHR} = time to reach peak HRR

HRR-300 = average HRR over initial 300 seconds after ignition

THR = the total heat released during the entire test

"# of tests" = number of test runs at the listed irradiance level

"no frame" denotes the one test at 35 kW/m^2 irradiance where edge frame was not used

Figure 6.4 demonstrates the high level of repeatability experienced in the tests. This particular figure is for the GRP/Balsa core at an irradiance of 50 kW/m^2, the results at all other irradiances also displayed the same high level of repeatability.

To address the concern of edge effects experienced with the small scale samples, one sample of each material was tested without the edge frame at an irradiance of 35 kW/m^2. Figures 6.5 and 6.6 show the results of these tests with and without the sample edge frame in place. With regard to heat release rates, the edge effects are more prevalent with the foam–cored material, as can be seen in Figure 6.6. Without the edge frame in place, the foam–cored material showed a more vigorous burning

Figure 6.4: GRP/Balsa Core - HRR Curves at 50 kW/m^2 Irradiance. Curves show high level of repeatability among test data for HRR.

at the edges. The Peak HRR from the foam–cored material was 15% higher without the edge frame in place, although the average HRR and total energy release were not significantly different. With the balsa–cored material, however, the Peak HRR was not significantly different without the edge frame in place. These observations are important when selecting material property data for use in fire modeling. As such it is recommended that any observed edge effects and the implications on the HRR data be reported for any cored composite material study.

Figures 6.7 and 6.8 show a summary of heat release rate curves for both materials over the irradiance test range. For simplicity, only one test at each irradiance is represented. Note that the HRR curves display more than one peak. This phenomenon was also observed for composite materials by Brown *et al*[28]. Brown *et al*

Figure 6.5: GRP/Balsa Core - HRR Curves for 35 kW/m^2 Irradiance. Note the absence of the dip in HRR between the two peaks for the sample tested with no edge frame.

attributed the initial peak in HRR to surface pyrolysis with the subsequent decrease attributed to surface char formation. The second peak was attributed to an increase in gasification rate of the unburned substrate (core), caused by an increase in the bulk temperature of the composite.[28] In the case of the cored composite test materials, the second peak in HRR may be attributed to this increased gasification rate of the lower layers of the GRP skin as well as the unburned core materials, similar to the observation by Brown.[28]

Figure 6.6: GRP/Foam Core - HRR Curves for 35 kW/m^2 Irradiance. Note the higher peak HRR and the absence of a dip between peak HRR for the sample tested with no edge frame.

6.2.4 Smoke Production

The cone calorimeter used in these experiments contains a flow–through optical smoke measurement device, consisting of a helium–neon laser beam and a beam detector for determination of a Specific Extinction Area (SEA) of the smoke being release from the burning sample. It is not the intent of this material study to discuss the smoke production to a great extent. Although, the production of smoke and toxic gases are of great concern to the U.S. Coast Guard and the IMO. GRP materials generally produce greater quantities of smoke than more conventional shipbuilding materials such as wood.[11] The smoke generated from the test materials was very “sooty” and black. It also produced an unpleasant aroma which may be attributed to certain toxic

Figure 6.7: GRP/Balsa Core - RHR Curves Summary. Representative HRR curves for Irradiances of 75, 50, 35, 25, and 20 kW/m^2.

fumes (although toxic gases were not measured in these experiments). As such, it is likely that the smoke production would preclude the use of these materials in large passenger vessels. For comparison purposes, Kim [43] reported a three minute average smoke production for plywood of approximately 30 m^2/kg, and approximately 700 m^2/kg for polystyrene. The test materials in this study produced smoke on the order of 1000 m^2/kg, as shown in Tables 6.4 and 6.5.

A limited number of test runs were performed on the core materials alone, and on the GRP laminate with no core. The smoke data for the GRP laminate were very similar to the data from the sandwich composites. The smoke data for the PVC foam core was approximately 500 m^2/kg for the three minute average SEA. For the balsa core, the SEA was approximately 30 m^2/kg. These results show that a significant

Figure 6.8: GRP/Foam Core - RHR Curves Summary. Representative HRR curves for Irradiances of 75, 50, 35, 25, and 20 kW/m^2.

fraction of the smoke produced is from the GRP skin alone.

6.3 Calculation of Material Properties from Cone Calorimeter Data

This section presents the material properties derived from the cone calorimeter experiments. These include the effective heat of combustion EHC or ΔH_c; effective heat of gasification, L; the critical irradiance for ignition, $\dot{q}^{"}_{cr}$; ignition temperature, T_{ig}; and the effective thermal property $k\rho c$.

The material properties derived from ignitability data are obtained using two different methods: the "standard method" developed by Quintiere and Harkleroad[34]

Table 6.4: Smoke Specific Extinction Area (SEA) - GRP/Balsa Core

Irrad (kW/m^2)	SM-180 (m^2/kg)	STDEV	SM-300 (m^2/kg)	STDEV	# of Tests
75	1215	11	1059	16	2
50	1095	51	946	37	3
35	1076	114	910	121	3
25	1053	19	919	29	3
20	1118	-	998	-	1
19	1059	-	947	-	1

Table shows average values with standard deviation (STD DEV) at each listed irradiance.

SM-180 = average SEA over initial 180 s after ignition

SM-300 = average SEA over initial 300 s after ignition

"# of tests" = number of test runs at the listed irradiance level

and Janssens' "improved" method[3]. The theory and method of Quintiere and Harkleroad [34] is the same method as specified in ASTM E 1321 (for the LIFT Apparatus). Sections 6.3.3 and 6.3.4 discuss these two different data reduction methods and present the results of both.

6.3.1 Effective Heat of Combustion

Heat of combustion, ΔH_c, is defined as the amount of heat released by combustion of a unit quantity of fuel.[44] Generally, ΔH_c is derived by dividing the instantaneous energy release rate by the mass loss rate. The CONECALC software package includes in it's output the effective heat of combustion (EHC) history for the material being tested.

Selection of an EHC value to report to best represent the heat released during the

Table 6.5: Smoke Specific Extinction Area (SEA) - GRP/Foam Core

Irrad (kW/m^2)	SM-180 (m^2/kg)	STDEV	SM-300 (m^2/kg)	STDEV	# of Tests
75	1186	26	1083	59	2
50	1137	55	1028	40	3
35	990	44	904	14	3
25	1072	98	933	76	3
20	1129	-	1035	-	1
19	1122	-	953	-	1

Table shows average values with standard deviation (STD DEV) at each listed irradiance.

SM-180 = average SEA over initial 180 s after ignition

SM-300 = average SEA over initial 300 s after ignition

"# of tests" = number of test runs at the listed irradiance level

burning period was based on the EHC history. Peak values in EHC generally occured after the sample had burned for several minutes and HRR had decreased significantly. Average values for EHC over a time period from ignition to approximately half–way through the HRR decay period were generally very close to the average EHC for the entire burn period. For this reason, the average EHC for the entire burn period was selected for reporting purposes. See Tables 6.6 and 6.7. Because the values were similar regardless of irradiance level, the average EHC values for *all* test runs were then averaged for each material. For the GRP/Balsa Cored material this overall average ΔH_c value is 9.5 MJ/kg (standard deviation 0.6), and for the GRP/Foam Cored material the overall average ΔH_c is 9.4 MJ/kg (standard deviation 1.2).

Table 6.6: Effective Heat of Combustion (EHC) Data - GRP/Balsa Core

Irrad (kW/m^2)	EHC (MJ/kg)	Ave EHC	STDEV
75	9.1	9.3	0.2
	9.4		
50	8.5	9.1	0.6
	10.0		
	8.9		
35	9.0	9.9	0.9
	10.8		
35 no frame	9.5		
25	9.8	9.7	0.3
	10.1		
	9.3		
Overall Average		9.5	0.6

EHC = time averaged over entire test for each listed irrad.

Ave EHC = Average of all test runs at listed irrad.

STDEV = standard deviation of Ave EHC.

"no frame" denotes edge frame not used.

6.3.2 Effective Heat of Gasification, L

An effective heat of gasification, L, for each test material is derived via the method described by Quintiere [4]. Peak HRR values from each cone calorimeter run are plotted against the cone irradiance levels in Figures 6.9 and 6.10. The slope of the lines represent $\Delta H_c/L$. Using the $\Delta H_c/L$ and ΔH_c values for each material, $L$for the GRP/Balsa Core material is 6.2 kJ/g, and for the GRP/Foam Core material is 7.1 kJ/g.

Table 6.7: Effective Heat of Combustion (EHC) Data - GRP/Foam Core

Irrad (kW/m^2)	EHC (MJ/kg)	Ave EHC	STDEV
75	9.9	10.2	0.3
	10.5		
50	11.7	10.4	1.0
	9.2		
	10.4		
35	8.4	8.0	0.5
	7.5		
35 no frame	8.5		
25	8.9	8.8	0.0
	8.8		
	8.8		
Overall Average		9.4	1.2

EHC = time averaged over entire test for each listed irrad.

Ave EHC = Average of all test runs at listed irrad.

STDEV = standard deviation of Ave EHC.

"no frame" denotes edge frame not used.

6.3.3 The ASTM E 1321 Standard Method

As specified in the standard, the ignition data of Table 6.1 are correlated as shown in Figures 6.11 and 6.12. The slope of each plot is the b parameter, used in calculating $k\rho c$. Surface ignition temperature, T_{ig}, is determined from an energy balance equation using the minimum irradiance at which ignition occurred,

$$\epsilon \dot{q}''_{o,ig} = h_c(T_{ig} - T_\infty) + \epsilon\sigma(T_{ig}^4 - T_\infty^4) \equiv h_{ig}(T_{ig} - T_\infty) \tag{6.1}$$

Figure 6.9: GRP/Balsa Core - Peak HRR vs Irradiance. For calculation of Effective Heat of Gasification, L. Line is best fit to the Peak HRR data. Slope ($\Delta H_c/L$) is used to determine effective heat of gasification, L.

where, $\dot{q}^{"}_{o,ig}$ is defined as the lowest irradiance level at which piloted ignition occured in the cone calorimeter. In equation 6.1, a surface emissivity (ϵ) of 1 is assumed, and h_c is assumed to be 0.010 kW/m^2·K (for an upward facing horizontal surface).[45] Equation 6.1 allows h_{ig} to be determined once T_{ig} is known. Using the b parameter and h_{ig}, the effective thermal property, $k\rho c$, is found from,

$$k\rho c = \frac{4}{\pi}\left(\frac{h_{ig}}{b}\right)^2 \tag{6.2}$$

6.3.4 Janssens' "Improved" Method of Data Analysis

Janssens "improved" method[3] provides a means to correlate a material's ignitability data based on the best fit of the data to either a semi–infinite solid (thermally thick)

Figure 6.10: GRP/Foam Core - Peak HRR vs Irradiance. For calculation of Effective Heat of Gasification, L. Line is best fit to the Peak HRR data. Slope $(\Delta H_c/L)$ is used to determine effective heat of gasification, L.

case or a "non–thick" case. Janssens recommends a distinction between the minimum irradiance for ignition, $\dot{q}''_{min}$ (an *observed* parameter), and the critical irradiance for ignition, $\dot{q}''_{cr}$ (a *calculated* parameter). In Quintiere and Harkleroads' method, $\dot{q}''_{o,ig}$ is used to represent both as the same parameter. Janssens describes $\dot{q}''_{min}$ as having specific physical meaning that cannot be predicted by mathematical ignition models because it is controlled by physical and chemical phenomena that are not addressed in the models.[3] $\dot{q}''_{cr}$ is a modeling parameter obtained by a best fit to the ignition data. The spread between $\dot{q}''_{min}$ and $\dot{q}''_{cr}$ depends upon the material involved. Janssens found that this difference is more obvious with a paper-covered gypsum wallboard and some fire retardant treated materials[3]

Using Janssens' method the data reduction procedure is a bit more complicated, but as such may be more applicable to composite materials. Janssens' data reduction

Figure 6.11: GRP/Balsa Core - Correlation of Cone Calorimeter Ignition Data using the standard reduction method.

Figure 6.12: GRP/Foam Core - Correlation of Cone Calorimeter Ignition Data using the standard reduction method.

procedure is as follows:[3]

- Correlate ignition times according to the power law equation

$$(\dot{q}_e^{"} - \dot{q}_{cr}^{"})t_{ig}^n = C \tag{6.3}$$

by plotting $(1/t_{ig})^n$ vs irradiance, $\dot{q}_e^{"}$. Determine the value for n between 0.5 and 1 that results in the best fit. If the optimum n is close to 0.55, the material behaves as a semi-infinite solid. If n is closer to 1, the material behaves as non-thick.

- Find $\dot{q}''_{cr}$ from the intercept of the best fit line to the data with the x–axis.
- Calculate T_{ig} and h_{ig} from the resulting $\dot{q}''_{cr}$ via equation 6.1 (in the equation, use $\dot{q}''_{cr}$ in place of $\dot{q}''_{o,ig}$).
- Determine $\dot{q}''_{min}$ from the experimental data. (note: Janssens arbitrarily sets this at 1 kW/m^2 below the lowest irradiance level at which ignition occured, in this study $\dot{q}''_{min}$ is taken as the actual observed lowest irradiance at which ignition occurred)
- Correlate the data according to the equation

$$\dot{q}''_e = \dot{q}''_{cr}\left[1 + 0.73\left(\frac{h_{ig}^2 t}{k\rho c}\right)^{-0.55}\right] \tag{6.4}$$

by plotting $(1/t_{ig})^{0.55}$ vs irradiance, $\dot{q}''_e$. This is the correlation for the semi–infinite solid case. If the best fit of the data was for the non–thick case as described above, then more data points may be necessary at high irradiance levels, where the material behaves as a semi–infinite solid. Draw the best fit straight line through the data points, force the line through $(\dot{q}''_{cr}, 0)$, and calculate $k\rho c$ from the slope of the line.

To carry out the procedure outlined above, the cone ignition data from Table 6.1 was correlated according the the power law in equation 6.3, varying n from 0.55 to 1. A linear regression analysis was conduction to determine which value of n provided the best linear fit. The criteria for "best fit" was to find the lowest relative error for the estimated slope of the line.[3] This relative error is defined as the ratio of the standard error of the slope to the slope itself (i.e. std err divided by slope). The commercial software package Microsoft Excel was used to conduct the linear regression analysis.

The R^2 values on the Excel–produced graphs are another indicator of fit quality. "R^2" is the coefficient of determination, which measures the strength of association between the curve fit and the test data. The higher the R^2 value, the more reliable the curve fit.[46] Generally, the R^2 values matched the results of the regression analysis. While conducting the regression analysis, it must be kept in mind that the correlations for n values where the calculated $\dot{q}''_{cr}$ was below zero or higher than the observed $\dot{q}''_{min}$ are not valid.

Figure 6.13: GRP/Balsa Core - Ignition Data Correlations using Janssens' "Improved" Method of Analysis. Dashed line is best fit to the power law equation with $n = 0.75$. Solid line is best fit to the data for the semi–infinite case, forced through $(\dot{q}''_{cr}, 0)$. Data points determined to be outside of the semi–infinite solid range were not used in the solid line fit.

For the GRP/Balsa Core material, the best fit was obtained with a n value of 0.75. Figure 6.13 shows the line fit for the $n = 0.75$ case, where $\dot{q}''_{cr}$ is found to be 13.5 kW/m^2. For the GRP/Foam Core material, the best fit was obtained with a n value of 1.0. Figure 6.14 shows the line fit for the $n = 1.0$ case where $\dot{q}''_{cr}$ is found to be 13.3

Figure 6.14: GRP/Foam Core - Ignition Data Correlations using Janssens' "Improved" Method of Analysis. Dashed line is best fit to the power law equation with $n = 1$. Solid line is best fit to the data for the semi–infinite case, forced through ($\dot{q}''_{cr}$, 0). Data points determined to be outside of the semi–infinite solid range were not used in the solid line fit.

kW/m^2. Once the best fit was found, $\dot{q}''_{cr}$ was determined from the x–intercept of the plot. An emissivity of 0.93 (from [3] for a phenolic GRP) and convective heat transfer coefficient (h_c) of 10 W/m^2K[45] were then used to calculate T_{ig} and h_{ig} from equation 6.1. Figures 6.13 and 6.14 also show the plots for the $n = 0.55$ (semi–infinite) case. The reason for forcing the plot for the semi–infinite case through $\dot{q}''_{cr}$ is to create a better fit of that line to the semi–infinite data, and also to meet the $\dot{q}''_{cr}$ value obtained from the best fit line. Semi–infinite behavior is generally expected to occur at the higher irradiance levels, where ignition occurs before the thermal wave reaches the back side of the solid. Since Janssens' recommends obtaining more data at the higher irradiance levels where semi–infinite behavior is more likely, the fit is expected to be better. In this study, where data at higher irradiance levels was limited, it was decided to drop certain data points from the ($n = 0.55$) plot in Figures 6.13 and 6.14 in order to force the line to the data points in the semi–infinite range. This decision is justified by applying some basic fire dynamics and heat transfer analysis, as discussed below.

Finally, taking the slope of the line (m) fit to the data with n equal to 0.55, forced through ($\dot{q}''_{cr}$, 0), $k\rho c$ is calculated from,

$$k\rho c = (m0.73\dot{q}''_{cr}h_{ig}^{-1.1})^{-1.818} \tag{6.5}$$

Backsurface insulation of the GRP skin and thermal penetration time

A fundamental approach was taken to help gain an understanding of what may be happening within the cored GRP composite as it is exposed to radiant heating. If it can be shown that the GRP skin is not behaving as a a semi–infinite solid at the lower irradiance levels, then dropping the data from the semi–infinite plot can be justified.

The first step in this fundamental approach was to try to determine if the air pocket behind the GRP skin (caused by delamination) was acting to insulate the GRP skin. This is evaluated by determining the Biot number (Bi) at the convective boundary at the back surface of the exposed GRP skin. Bi $= h_c\Delta/k$, where Δ is the thickness of the GRP skin (2.4 mm), h is the convective heat transfer coefficient at the boundary, and k is the thermal conductivity of the GRP. The Biot number compares the relative magnitude of surface–convection and internal–conduction resistances to heat transfer. A very low (< 0.1) value of the Biot number means that internal–conduction resistance is negligible in comparison with surface–convection resistance.[47] k is taken as 0.4 $W/m \cdot K$[48] and h is assumed to be 5 W/m^2K[49] for natural convection at the back surface boundary between the GRP skin and the air pocket. With these values, Bi = 0.03, which is less than 0.1 meaning that the air pocket is acting as insulator to the GRP skin.

It is also possible that the PVC foam or balsa wood cores are acting to insulate the GRP skin, also implying that the GRP skin may behave as thermally thin over long durations of heating. Qualitatively speaking, this may indeed be the case, as the thermal conductivities are 0.035 $W/m \cdot K$[50] for the PVC foam and 0.05 $W/m \cdot K$[51] for the balsa wood core material; low values compared to the thermal conductivity of the GRP (approx. 0.4 W/mK[48]). In a boundary condition analysis, this implies an insulating condition at the interface between the GRP and the core materials.

A solid slab of thickness Δ can be treated as a semi–infinite solid if $\Delta = 2\sqrt{\alpha t}$, where α is thermal diffusivity ($\alpha = k/\rho c$) and t is the duration of heating.[49] This criteria was applied to the GRP facing of the test materials with a thickness, Δ, of 2.4 mm. The density (ρ) of the GRP skin was calculated to be 2100 kg/m^3. Specific heat (c) of GRP is 1000 J/kgK.[48]. From the literature[52][48], a range of thermal conductivities (k) for GRP was found to be 0.07 to 0.4. For this range of k, the time for the thermal wave to reach the backsurface of the GRP skin was calculated to be between 7 and 44 seconds. So, for cases where ignition occurred after 44 seconds exposure, semi–infinite solid behavior may not be expected in the exposed GRP skin. This assumes that the air pocket caused by delamination and/or the core materials act as an insulator to the GRP facing, as discussed above. This analysis is consistent with the best fit n values found above: that the GRP skin is behaving as a "non–thick" material.

Since the average time to ignition for the GRP/Balsa core material at irradiance 50 kW/m^2 was 45 seconds, the ignition data for irradiances below 50 kW/m^2 were dropped for the semi–infinite fit ($n = 0.55$ case) in Figure 6.13. Similarly, the data for the GRP/Foam core material taken at irradiances less than 35 kW/m^2, where the average ignition time was 64 seconds, was dropped from the semi–infinite plot in Figure 6.14. For the GRP/Foam core material, it was decided to allow the data for 35 kW/m^2 into the semi–infinite plot since the average t_{ig} was within 50% of the calculated thermal penetration time.

6.3.5 Material Properties

Table 6.8 lists the material properties calculated from the cone calorimeter ignitability data.

As presented in Sections 6.3.1 and 6.3.2, the effective heat of combustion, ΔH_c,

Table 6.8: Material Properties - Calculated From Cone Calorimeter Ignitability Data

Material	n	$\dot{q}''_{min}$ (kW/m^2)	$\dot{q}''_{cr}$ (kW/m^2)	T_{ig} (K)	h_{ig} $(kW/m^2 \cdot K)$	$k\rho c$ $(kW/m^2 \cdot K)^2$s
GRP/Balsa Core	n/a	19	-	720	0.0446	1.03
GRP/Balsa [J]	0.75	19	13.5	650	0.0353	0.75
GRP/Foam Core	n/a	19	-	720	0.0446	0.78
GRP/Foam [J]	1.0	19	13.3	647	0.0350	0.64
GRP, 2.24 mm [34]	-	16	-	663	-	0.32
GRP, 1.14 mm [34]	-	17	-	673	-	0.72

A distinction is made between $\dot{q}''_{min}$ and $\dot{q}''_{cr}$; where data was correlated according to the ASTM E 1321 Standard method, the values for $\dot{q}''_{o,ig}$ are listed in the $\dot{q}''_{min}$ column.

Data correlated by Janssens' method is denoted with a "[J]", otherwise the properties listed were calculated per the ASTM E 1321 Standard method.

The GRP data in the bottom two rows are taken from Ref. [34], and are included here for comparison purposes.

for the GRP/Balsa Core material is 9.5 kJ/g and 9.4 kJ/g for the GRP/Foam Core material. The effective heat of gasification, L, for the GRP/Balsa Core material is 6.2 kJ/g, and 7.1 kJ/g for the GRP/Foam Core material.

6.4 Discussion

The material properties presented above can be used for several purposes such as material classification, relative ranking, and flame spread and fire growth modeling.[41] Modeling full scale fire performance such as the ISO 9705 Room/Corner test is of particular interest to the USCG and the IMO in the qualification of "fire–restricting materials" for High Speed Craft.

According to Janssens' method, the cored composites in this study are not behaving like a semi-infinite solid. The differences in material properties calculated with the standard method from ASTM E 1321 (Quintiere and Harkleroad's method) and with Janssens' method are obvious. This is due to the different boundary conditions used in the two ignition models, to the assumed values for emissivity, and to the values used as the critical irradiance for ignition. Information is not available on how the GRP in Quintiere and Harkleroad's study[34] behaved (i.e. did it delaminate?), so it is difficult to discuss the differences in material properties derived for the test materials and the literature values shown in Table 6.8. The literature values were obtained from the LIFT Apparatus, but material properties should be similar to those obtained from the cone calorimeter. It is interesting to note the relatively low value for $k\rho c$ listed for the 2.24 mm GRP from the literature. The test materials' $\dot{q}''_{min}$ values are similar to the literature values.

For practical purposes, the difference in derived material properties illustrates the importance of knowing where the data came from and how material properties were derived. For example, if a fire modeler was to take material properties from the literature, it would be important to understand how those properties were calculated. The data analysis methods of standard test methods such as ASTM E 1321[2], or the data analysis protocols for common materials that some researchers have proposed cannot be blindly applied to composite materials, especially cored–composites such as the test materials. The fire modeler must consider what may happen in full scale "real world" fires. Will the composite's skin peel away from the core material? Will the core melt away, reducing structural strength? If structural integrity is compromised, will the structure collapse or allow fire spread to adjacent compartments?

A fire modeler that uses published data should also consider the materials' behavior in lab testing and in real world fires. When using small–scale test data, the modeler must consider how edge effects, delamination, core melting, and test sample orientation may affect the results. The experimental results presented in this chapter show that edge effects in the cone calorimeter do not significantly affect ignition times of the cored composites at irradiance levels above 25 kW/m^2. However, at 25 kW/m^2 irradiance, the ignition times do tend to show more scatter, as evidenced by the increase in standard deviation of the ignitability data (see Table 6.1). This may be due to the edge effects. It is also likely that this scatter is caused by the fact that the GRP facing is no longer behaving like a semi–infinite solid; delamination may also be affecting the results. With regard to heat release rates, the edge effects have been shown to affect the peak HRR of the GRP/Foam Core material up to 15%, but the average HRR values, total heat released, and the effective heat of combustion are not significantly affected. On the other hand, the edge effects did not appear to affect the peak HRR of the GRP/Balsa Core material. These are important observations for the fire modeler to note.

It is recommended that any composite material testing program include a written description of observed burning behavior in the report. This description should include a discussion about how edge effects, delamination, or other events tend to affect the results. Photographs are also helpful, but without written documentation to describe what was observed during the experiments, they will be of limited use to the modeler. Video of the tests themselves would also be useful.

6.5 Further Testing in the Cone Calorimeter

Some recommendations for future cone calorimeter experiments with the cored composite materials include:

- More testing at higher irradiance levels. This will allow for better correlation of ignition data using Janssens' method. This way, the materials may be modeled as semi-infinite without having to deal with the analysis as if the materials behave as non-thick.
- A test program on each core material and the GRP skin (no core) would help isolate the burning characteristics of each component and help in understanding how the composite behaves as a whole.
- Vary sample orientation. Experimenting with the materials in the vertical orientation may produce different material properties. Also, LIFT data can be compared without regard to orientation differences.
- Vary sample size. Ohlemiller[26] has done some experiments in the cone calorimeter with larger (6" x 6") samples and a water–cooled frame. Although he did not recommend the procedure for standard tests, a variation on his procedure may be tried to help minimize edge effects.
- Drill holes in the GRP skin. Very small holes in the GRP laminate, drilled at equal intervals over the entire exposed area, may allow an easier route for pyrolysis gases to escape. This may prevent delamination and edge burning.
- Install thermocouples within the composite sandwich. Thermocouples located at the backsurface of the exposed GRP skin, within the core material, and on the backside GRP skin would allow a temperature profile to be taken throughout

the test period. These results may be applied to further analysis of how the GRP facing behaves (i.e. semi–infinite or “non–thick”), as well as providing information about how the core materials are affected throughout the test.

Chapter 7

Testing in the LIFT Apparatus

A series of experiments was completed with the test materials in accordance with ASTM E-1321[2]. The goal was to obtain a set of material thermal properties based on the LIFT Apparatus ignitability data. Although it was originally intended to obtain flame spread data, there was difficulty getting accurate results in the flame spread tests. This chapter summarizes the results of the LIFT Apparatus testing. Some problems with the test procedure as applied to cored composites are identified.

7.1 Test Method Description

The **L**ateral **I**gnition and **F**lame Spread **T**est Apparatus, commonly referred to at the LIFT Apparatus, was developed to determine material properties related to piloted ignition and lateral flame spread. ASTM E1321[2] standardizes the test method.

A general view of the lift apparatus configuration is shown in Figure 7.1[3]. Test

Figure 7.1: General View of the LIFT Apparatus

specimens are exposed to an externally applied radiant heat flux. The results from the test method provide the minimum surface flux and temperature necessary for ignition, $\dot{q}''_{o,ig}$ and T_{ig} and for lateral flame spread, $\dot{q}''_{o,s}$ and $T_{s,min}$. Other material properties derived from the LIFT include the effective thermal property (kρc), a flame heating parameter, ϕ, pertinent to lateral flame spread. The theory behind the derived flame spread properties is applicable to opposed flow (lateral or downward) flame spread. It is not the intent here to provide a complete review of the standard test method, the apparatus, or the theories involved. The ASTM E1321 Standard Test Method[2] and the literature[34] cover these aspects quite well. The reader is referred particularly to the work of Quintiere and Harkleroad[34] on which the standard test method is based.

7.2 LIFT Ignition Tests

A total of 20 samples, 10 each of the GRP/Balsa core and GRP/Foam core materials, were tested in the LIFT Apparatus in the vertical orientation to determine $\dot{q}''_{o,ig}$, T_{ig}, and $k\rho c$. Table 7.1 summarizes results from the LIFT ignition experiments.

7.2.1 Ignition Test Procedure

Ignition samples, 155 mm x 155 mm, were wrapped in aluminum foil and placed into the sample holder. The thickness of material did not allow use of the refractory backing board required by the ASTM standard. In lieu of the backing board a 1/2 inch thick piece of fire retardant plywood was used. Due the thickness of the test materials and the properties of the plywood backing board ($k = 0.12$[34], $\rho =$ approx. 550 kg/m^3) it is believed that that the assumption of no heat loss through the back of the specimen is still valid. In future experiments with these materials it is recommended to use a thinner piece of refractory backing board material. The samples were then inserted into the apparatus in the vertical orientation with the pilot flame lit. The time to ignition was recorded; the test ended after ignition of each sample.

7.2.2 Observations During LIFT Ignition Tests

During ignition tests, phenomenon such as outgassing, delamination, any obvious edge effects, and other such observations were recorded. Outgassing, or the release of pyrolysis gases from the exposed surface, usually occurred within the first minute of exposure, even at the lower incident fluxes. Delamination occurred in all samples of both the balsa-cored material and the foam-cored material.

In the balsa–cored material, delamination did not necessarily cause any unusual behavior, such as flaming at the edges. However, in the foam–cored materials, delamination was usually followed by a visual observation of some melting of the foam core. This was evidenced by intermittent flaming at the top and bottom edges, and primarily at the right edge of the sample. These effects were so severe in the first few test runs that a steel edge frame was fabricated to help minimize these right edge effects in the remaining tests. The edge frame consisted of a piece of steel angle iron approximately 13 cm in length. The flange was cut in order to cover the sample edge and overhang the exposed surface approximately 13 mm. Even with the right edge frame in place, the foam-cored materials usually ignited at the top right edge and flames would then spread downward at the edge. These events were recorded, but the actual time to ignition was not considered to occur until the sample had ignited in the center of the sample.

Delamination was usually followed by a definite “deflation” or outgassing period where gases escaped from behind the GRP skin to the edges of the sample. This "deflation" was not as obvious in the foam-cored samples due to the already–melting core. It was, however, a prominent event in the balsa-cored samples.

Test samples were inspected after each test. In all samples, except those exposed to the lowest fluxes, the foam core was completely charred, and most of the foam core was melted away. The balsa-core fared much better, and in all cases except for the samples exposed to higher heat fluxes the balsa-core was completely intact with very minimal charring. Appendix A contains some photos of these ignition samples. Ignition tests were videotaped in order to keep a visual record of events.

Table 7.1: LIFT Ignition Test Results

GRP/Balsa Core	
Irradiance (kW/m^2)	t_{ig} (s)
12	N.I.
13	885
15	705
20	275
25	140
30	109
30	91
35	75
40	58
45	53

GRP/Foam Core	
Irradiance (kW/m^2)	t_{ig} (s)
12	N.I.
13	N.I.
14	N.I.
15	660
20	210
25	150
30	90
35	64
40	70
45	52

Ignition test results are plotted in Figures 7.2 and 7.3.

Figure 7.2: Ignition Time (t_{ig}) vs Irradiance ($\dot{q}_e''$) for GRP/Balsa Core (from LIFT). Curve is best fit to the data.

Figure 7.3: Ignition Time (t_{ig}) vs Irradiance ($\dot{q}_e''$) for GRP/Foam Core (LIFT). Curve is best fit to the data.

7.3 Calculation of Material Properties from LIFT Data

Material properties are derived here using two different methods: the "standard method" developed by Quintiere and Harkleroad[34] and Janssens' "improved" method[3]. Details of each data analysis method were discussed in Chapter 6.

7.3.1 The ASTM E 1321 Standard Method

The theory and procedure for calculating results of ignition tests in the LIFT apparatus are specified in the ASTM Standard[2] as previously discussed. The plot of test data results $(\dot{q}''_{o,ig})/(\dot{q}''_{e})$ versus $\sqrt{t}$ for each material are shown in Figures 7.4 and 7.5. The b parameter for each material is obtained from the slope of the line in these plots. Surface ignition temperature, T_{ig}, and the total heat transfer coefficient, h_{ig}, are determined using the minimum irradiance at which ignition occurred for each material from equation 6.1. Based on the standard method a surface emmissivity (ϵ) of 1 is assumed, and h_c is assumed as 15 $W/m^2 \cdot K$[2]. Using the b parameter and h_{ig} for each material, the effective thermal property, $k\rho c$, is found from equation 6.2.

Figure 7.4: GRP/Balsa Core - Correlation of LIFT Ignition Data using the standard reduction method.

Figure 7.5: GRP/Foam Core - Correlation of LIFT Ignition Data using the standard reduction method.

7.3.2 Janssens' "Improved" Method of Data Analysis

Janssens' "improved" method was discussed in detail in Chapters 4 and 6. In all calculations with Janssens' method for the LIFT data, emissivity, ϵ, was assumed to be 0.93[3], with a convective heat transfer coefficient, h_c, of 15 $W/m^2 \cdot K$ for the vertical sample orientation.[2] Janssens' method was used to correlate the LIFT ignition data as shown in Figures 7.6 and 7.7. Note that certain data points were dropped when fitting the data to the semi–infinite solid ($n = 0.55$) case. The criteria for justifying this is discussed in Chapter 6.

7.3.3 Material Properties

Table 7.2 lists the material properties calculated from the LIFT ignitability data.

Figure 7.6: GRP/Balsa Core - Ignition Data Correlations using Janssens' "Improved" Method of Analysis (LIFT data). Dashed line is best fit to the power law equation with $n = 0.9$. Solid line is best fit to the data for the semi–infinite case, forced through ($\dot{q}''_{cr}$, 0). Data points determined to be outside of the semi–infinite solid range were not used in solid line fit.

7.4 Comparison of Material Properties Derived from LIFT and Cone Calorimeter Data

To compare the ignitability data from the LIFT Apparatus with that from the Cone Calorimeter, the time to ignition curves were superimposed on each other. See Figures 7.8 and 7.9. The data match well with each other. Table 7.3 presents material ignition properties derived from the LIFT Apparatus along with those from the Cone Calorimeter for purposes of comparison.

In Table 7.3, note that the material ignition properties derived from the LIFT

Figure 7.7: GRP/Foam Core - Ignition Data Correlations using Janssens' "Improved" Method of Analysis (LIFT data). Dashed line is best fit to the power law equation with $n = 1$. Solid line is best fit to the data for the semi–infinite case, forced through ($\dot{q}''_{cr}$, 0). Data points determined to be outside of the semi–infinite solid range were not used in solid line fit.

and Cone Calorimeter data are closer in value for the sets analyzed using Janssens' method. The critical irradiance, $\dot{q}''_{cr}$, values from the LIFT data vary by only 2 kW/m^2 from those of the cone for both materials. With the standard method there is a difference in $\dot{q}''_{min}$ of 4 kW/m^2 for the GRP/Foam Core and 6 kW/m^2 for the GRP/Balsa core. Values for T_{ig} drop in magnitude as the irradiance values $\dot{q}''_{cr}$ and $\dot{q}''_{min}$ drop. This illustrates the fact that Janssens' method produces more conservative values for the ignition temperature.

The effective thermal property, $k\rho c$, for the data sets derived using Janssens' method are more consistent, not only when compared to the properties from each

Table 7.2: Material Properties - Calculated From LIFT Ignitability Data

Material	n	$\dot{q}''_{min}$ (kW/m^2)	$\dot{q}''_{cr}$ (kW/m^2)	T_{ig} (K)	h_{ig} $(kW/m^2 \cdot K)$	$k\rho c$ $(kW/m^2 \cdot K)^2$s
GRP/Balsa Core	n/a	13	-	623	0.0395	1.53
GRP/Balsa [J]	0.9	13	11	586	0.0350	0.77
GRP/Foam Core	n/a	15	-	650	0.0421	1.14
GRP/Foam [J]	1.0	15	11.5	594	0.0357	0.74
GRP, 2.24 mm [34]	-	16	-	663	-	0.32
GRP, 1.14 mm [34]	-	17	-	673	-	0.72

A distinction is made between $\dot{q}''_{min}$ and $\dot{q}''_{cr}$; where data was correlated according to the ASTM E 1321 Standard method, the values for $\dot{q}''_{o,ig}$ are listed in the $\dot{q}''_{min}$ column.

Data correlated by Janssens' method is denoted with a "[J]", otherwise the properties listed were calculated per the ASTM E 1321 Standard method.

The GRP data in the bottom two rows is taken from Ref. [34], and are included here for comparison purposes.

apparatus, but between the different material types as well. This should be expected, as it appears that what is effectively being tested is the GRP facing, as opposed to the composite as a whole. This is consistent with the thermal penetration analysis carried out in Chapter 6 and the fact that all correlations to the data using Janssens' method indicate non–thick behavior. All four $k\rho c$ values derived with Janssens' method vary by only 20%, compared to the four $k\rho c$ values from the ASTM Standard method which vary by 95%!

Figure 7.8: GRP/Balsa Core - Time to Ignition (LIFT and Cone Calorimeter). Curves represent best fit to the respective data sets.

7.4.1 Application of Tewarson's Thermal Response Parameter

Tewarson's Thermal Response Parameter (TRP)[53] was used to compare the differences in material properties derived from the two different analysis methods. TRP combines the effects of the ignition temperature, T_{ig}, and the effective thermal properties, $k\rho c$, into one useful parameter that can be used in engineering calculations to assess resistance to ignition and fire propagation.[53] The TRP is calculated as,

$$\mathrm{TRP} = \Delta T_{ig}\sqrt{k\rho c} \tag{7.1}$$

Figure 7.9: GRP/Foam Core - Time to Ignition (LIFT and Cone Calorimeter). Curves represent best fit to the respective data sets.

where $\Delta T_{ig} = T_{ig} - T_{\infty}$ is the ignition temperature rise above ambient. TRP was calculated from the derived material properties from the standard method and Janssens' method, see Table 7.4. Note that the TRP values are more consistent between the two test materials for the properties derived using Janssens' method.

TRP was then used to predict ignition times from,

$$\sqrt{\frac{1}{t_{ig}}} = \frac{\sqrt{4/\pi}(\dot{q}_e'' - \dot{q}_{cr}'')}{TRP} \tag{7.2}$$

Tewarson states that most materials that behave as thermally thick satisfy equation 7.2.[53] Figures 7.10 and 7.11 show the comparison with experimental data for the GRP/Foam Cored material ignition properties from the cone calorimeter and LIFT

Table 7.3: Comparison of Material Properties Derived From Cone Calorimeter and LIFT Data

Material	n	$\dot{q}''_{min}$ (kW/m^2)	$\dot{q}''_{cr}$ (kW/m^2)	T_{ig} (K)	h_{ig} ($kW/m^2 \cdot K$)	$k\rho c$ ($(kW/m^2 \cdot K)^2 s$)
Cone Cal. Data:						
GRP/Balsa Core	n/a	19	-	720	0.0446	1.03
GRP/Balsa [J]	0.75	19	13.5	650	0.0353	0.75
GRP/Foam Core	n/a	19	-	720	0.0446	0.78
GRP/Foam [J]	1.0	19	13.3	647	0.0350	0.64
LIFT Data:						
GRP/Balsa Core	n/a	13	-	623	0.0395	1.53
GRP/Balsa [J]	0.9	13	11	586	0.0350	0.77
GRP/Foam Core	n/a	15	-	650	0.0421	1.14
GRP/Foam [J]	1.0	15	11.5	594	0.0357	0.74
From Literature						
GRP, 2.24 mm [34]	-	16	-	663	-	0.32
GRP, 1.14 mm [34]	-	17	-	673	-	0.72

A distinction is made between $\dot{q}''_{min}$ and $\dot{q}''_{cr}$; where data was correlated according to the ASTM E 1321 Standard method, the values for $\dot{q}''_{o,ig}$ are listed in the $\dot{q}''_{min}$ column.

Data correlated by Janssens' method is denoted with a "[J]", otherwise the properties listed were calculated per the ASTM E 1321 Standard method.

The GRP data in the bottom two rows is taken from Ref. [34], and are included here for comparison purposes.

apparatus. In Equation 7.2, $\dot{q}''_{min}$ values were used in leiu of $\dot{q}''_{cr}$ for the calculations using the properties derived with the standard method. The experimental data shown in Figure 7.10 represent the average ignition times reported in Table 6.1. The TRP's calculated from material properties derived with Janssens' method appear to predict actual ignition times more accurately than the parameters derived from the standard reduction method. This was also the case with the GRP/Balsa Core materials.

Table 7.4: Thermal Response Parameters Calculated from Derived Material Properties

Material	T_{ig} (K)	$k\rho c$ $(kW/m^2 \cdot K)^2 s$	TRP $(kW - s^{1/2}/m^2)$
Cone Cal. Data:			
GRP/Balsa Core	720	1.03	432
GRP/Balsa [J]	650	0.75	308
GRP/Foam Core	720	0.78	376
GRP/Foam [J]	647	0.64	282
LIFT Data:			
GRP/Balsa Core	623	1.53	407
GRP/Balsa [J]	586	0.77	256
GRP/Foam Core	650	1.14	380
GRP/Foam [J]	594	0.74	258

Data correlated by Janssens' method is denoted with a "[J]"

7.5 LIFT Flame Spread Tests

Two flame spread tests were conducted on each of the test materials. Due to difficulty in obtaining useable data from the flame spread tests, further testing was discontinued. Flame spread tests were conducted at an incident heat flux of 30 kW/m^2 with no preheat period. The reason for removing the preheat time from the test procedure was to prevent charring of the surface. Experience has shown that some charring materials will not support sustained ignition after a certain preheat period, in many cases even if the calculated preheat time t^* is not reached.[54] If sustained ignition is achieved and flame spread is adequately observed and recorded, the ASTM E 1321 method can still be used to correlate data.

In the flame spread tests with the GRP/Foam Core material, the pyrolysis gases

Figure 7.10: GRP/Foam Core - Time to Ignition Data Analyzed Based on Thermal Response Parameter and $\dot{q}''_{cr}$ (Cone Calorimeter).

escaped from the edges as the foam core melted, causing intermittent flaming around the sample edges. In one case, flames had spread across the top edge of the sample and then began burning from the sample bottom edge near the 600 mm mark. At one point, there were three separate flame fronts, all spreading in different directions: one spreading towards the right from the point of initial ignition, one spreading towards the left from the 600 mm mark (opposite direction of expected flame travel), and a third front spreading toward the right from the 600 mm mark.

Generally, the test materials showed resistance to flame spread. Although ignition occured near the expected time, flame spread was very slow. Figure 7.12 shows the flame front position as a function of time for the GRP/Balsa Core material. The flame front extinguished itself before it could reach a point on the sample where the

Figure 7.11: GRP/Foam Core - Time to Ignition Data Analyzed Based on Thermal Response Parameter and $\dot{q}''_{cr}$ (LIFT).

incident heat flux was less than the minimum observed in the ignition tests. For example, from the ignition tests, $\dot{q}''_{o,ig}$ was 15 kW/m^2 for the GRP/Foam material. The flame spread tests were run with a heat flux of 30 kW/m^2 at the 50 mm position. Based on the flux profile obtained from the radiant panel, the panel produced a heat flux of 15 kW/m^2 just beyond the 350 mm position. At the very least, one would expect flame spread to continue beyond the point of $\dot{q}''_{o,ig}$, in fact the minimum flux for flame spread, $\dot{q}''_{o,s}$, is usually much lower than that for ignition. At no time during the flame spread tests of either material did the flame front propagate beyond the point of $\dot{q}''_{o,ig}$, except for the case mentioned above where the flame front jumped forward to the 600 mm position at the edge.

Janssens' has proposed an improved method for conducting flame spread tests

Figure 7.12: GRP/Balsa Core - Flame position as a function of time

and for correlating flame spread data.[33]. This improved method does not require a preheat period, but the data analysis is much more involved. A computer program has been developed by Janssens' for this purpose.

7.6 Further Testing in the LIFT Apparatus

Some recommendations for further experiments with the test materials in the LIFT Apparatus include:

- Vary sample size in the ignition tests. A larger sample size (for example, 155 mm x 300 mm) would help to minimize the edge effects experienced at the samples' right edge.
- Vary orientation. Testing the materials in the horizontal position would make comparison to cone calorimeter data perhaps more relevant.

- Vary ignition source. A spark ignitor in the LIFT Apparatus would remove the interaction between the pilot flame and the plume above the flame front. The author has observed incident heat fluxes at the 50 mm position of 0.5 to 1 kW/m^2 higher with the pilot flame on. A spark ignitor would alleviate this problem.

- Conduct experiments with the GRP skin alone (no core), to help minimize edge effects.

- Conduct experiments with the core materials alone to help isolate and identify burning behavior that is observed when tested as a composite sandwich.

It is recommended that additional experiments be conducted in order to try to effectively get flame spread parameters for the test materials. This may be accomplished by one or more of the following:

- Conduct the flame spread experiments differently, either by changing the radiant panel heat flux up or down, introducing a short preheat period, introducing a moving pilot, or a combination of the above;

- Introduce a short preheat period, less than t^*. This would be accounted for when correlating flame spread data ($v^{-1/2}$ vs $\dot{q}_e''$·F(t), where F(t) = b$\sqrt{t}$ for $t \leq t^*$);

- Establish a procedure to keep a pilot flame above the flame front. In the flame spread experiments discussed in this chapter, the pilot was relit a few times in order to maintain a flame front. If a moving pilot flame could be developed, it may be possible to maintain the flame front longer and more adequate data may be obtained.

- Research Janssens' proposed method for testing and analyzing flame spread data. Perhaps there is something in his method that would better apply to the test materials.

- Modify the apparatus to allow flame spread testing of a sample with a larger vertical dimension, for example 300 mm vertical x 800 mm long. This may help to minimize edge effects, especially at the top edge. The exposure on this larger sample should be held to the standard 155 mm x 800 mm size, centered vertically on the sample. A modified sample frame which covers all but 155 mm x 800 mm of the sample would be required.

Chapter 8

Modeling Full–Scale Fire Performance

This chapter presents the results of eight computer model runs using the fire growth model developed by Quintiere.[4] Emphasis is placed on how the different material properties derived in the previous chapters affect the model output. As discussed in Chapter 3, the IMO recommends certain criteria for classifying fire–restricting materials based on ISO 9705 Room/Corner test performance. Full scale testing can be quite expensive, thus an effort to predict full scale performance from bench–scale tests such as the cone calorimeter and the LIFT Apparatus has been made in recent years, although the USCG and IMO have not yet approved the use of predictive models for qualifying materials. Results are presented and a discussion includes the affect of different material properties on the model predictions. The chapter concludes with a discussion about application of predictive models for classifying fire–restricting materials.

8.1 The ISO 9705 Full Scale Room Fire Test

ISO 9705 "Fire Tests – Full Scale Room Fire Test for Surface Products"[5] standardizes what is commonly called the "Room/Corner" fire test. The corner fire scenario takes place in a room 2.4 m x 3.6 m x 2.4 m high with a doorway opening 0.8 m x 2.0 m high. The test material lines three walls and ceiling of the room. A 0.17 m square burner is placed at floor level in contact with the wall lining material in the corner opposite the doorway. The burner output is 100 kW for 10 minutes, followed by a 300 kW output for another 10 minutes until test completion.[5] Flashover is considered to have occured in the test compartment when a 1 MW energy release rate is obtained.[4][55]

8.2 Predictive Models

Some models have been shown to accurately predict time to flashover in the ISO 9705 test compartment. Several different researchers have developed models for this purpose. Among them are Karlsson[56], Magnusson[57][58], Quintiere[4][55], and Janssens[59]. These models typically operate by modeling flame spread, both upward (concurrent) and downward (opposed–flow), on the wall and ceiling lining materials and calculating the resulting heat release rate from the burning lining materials. This section includes a brief introduction to the model developed by Quintiere, which has been coded for use on a personal computer.

8.2.1 Quintiere's Fire Growth Model

Quintiere[4] developed a mathematical model to simulate fire growth on wall and ceiling materials. The model predicts the burning area, the upper layer gas temperature, and the total heat release rate in the room among other things. It uses material property data derived from cone calorimeter and LIFT tests. The input routine is very flexible with regard to room dimensions, ignition source strength and location, and material properties. This flexibility gives the model the potential for application to other room fire scenarios besides ISO 9705 Room/Corner test prediction. It will be useful for future incorporation into a more comprehensive compartment fire model that can handle several different room and wall/ceiling lining configurations.

In addition to upward flame spread (concurrent flow), Quintiere's model incorporates a calculation of upper layer gas temperature and associated thermal feedback to the wall lining materials. It also incorporates a lateral or downward flame spread routine and a calculation of the burnout front location based on the total available energy of the test material, $Q^{"}$.[4]

The results presented by Quintiere for the 13 Swedish fire test materials show good agreement to the experimental results.[4] Quintiere conducted a sensitivity analysis with his model, changing the material property data (within acceptable limits) for energy release per unit area, Q", and the material's effective heat of gasification, L, to achieve an even better fit to the experimental results.[4]

In a more recent paper, Quintiere *et al*[55] presented model results compared to the EUREFIC fire test materials and eight other materials used as cabin interior finish materials in commerical aircraft (FAA Materials). The model results compared well with experimental results for time to flashover for the EUREFIC materials. In some cases, making small changes within the range of uncertainty for material property data yielded better agreement with experimental results. For the FAA Materials, Quintiere *et al* did not have experimental results from the room/corner test, but rather compared results to post–crash fire tests conducted by the FAA. The application of the model to the FAA Materials was viewed as successful in terms of consistency with the limited results of the post–crash fire tests.[55]

8.3 Application of Quintiere's Model

Quintiere's model[4][55] was used with the material properties derived for the two test materials. The values for burner flame height, heat flux from the burner flame, flame heat flux in the spread region, and room dimensions were set to the same values used by Quintiere.[4] The burner flame heights corresponding to 100 kW and 300 kW are set to 1.3 m and 3.6 m respectively. The burner heat flux in the initial pyrolysis area is set to 60 kW/m^2.[4] The material property input parameters used for the various model runs are tabulated in Table 8.1. Eight model runs were completed; one for each of the two test materials based on cone calorimeter data reduced with the ASTM 1321 standard method, one for each of the two test materials based on cone calorimeter data reduced with Janssens' method, one for each of the two test materials based on LIFT data reduced with the standard method, and one for each of the two test materials based on LIFT data reduced with Janssens' method.

Table 8.1: MODEL INPUT– Material Property Data (Quintiere's Model)

Material	T_{ig} (K)	$k\rho c$ $(kW/m^2K)^2s$	Φ $^{(a)}$ (kW^2/m^3)	$T_{s,min}$ $^{(a)}$ (K)	ΔH_c (kJ/g)	L (kJ/g)	$Q"$ $^{(b)}$ (kJ/m^2)
From Cone Calorimeter Data, Standard Reduction Method:							
GRP/Balsa Core	720	1.03	9.97	353	9.5	6.2	45,900
GRP/Foam Core	720	0.78	9.97	353	9.4	7.1	82,900
From Cone Calorimeter Data, Janssens' Method:							
GRP/Balsa Core	650	0.75	9.97	353	9.5	6.2	45,900
GRP/Foam Core	647	0.64	9.97	353	9.4	7.1	82,900
From LIFT Data, Standard Reduction Method:							
GRP/Balsa Core	623	1.53	9.97	353	9.5	6.2	45,900
GRP/Foam Core	650	1.14	9.97	353	9.4	7.1	82,900
From LIFT Data, Janssens' Method:							
GRP/Balsa Core	586	0.77	9.97	353	9.5	6.2	45,900
GRP/Foam Core	594	0.74	9.97	353	9.4	7.1	82,900

[a]Flame spread data is taken from Ref [34] for 2.24 mm GRP
[b]Based on Cone data at 50 kW/m^2 irradiance

The input values for the total available energy per unit area, $Q"$, are taken from the cone calorimeter data at 50 kW/m^2, and is assumed constant for the model test period. The parameter $Q^{"}$ is used by the model to calculate upward burn–out front.[4]

Material properties derived from flame spread experiments – the surface temperature for flame spread, $T_{s,min}$, and the flame heating parameter, Φ – are used by the model's lateral (opposed–flow) flame spread component. The upward (concurrent) components usually prevail during the model run during the pre–flashover stage. The lateral flame spread component of the model starts when the global surface temperature of the surface lining reaches $T_{s,min}$.[4] Since flame spread properties for the test materials were not obtained, values from the literature[34] for a 2.24 mm GRP were used.

Table 8.2: Model Output (Quintiere's Model)

Material	Time to reach 1 MW (s)
Cone Data, Std Method:	
GRP/Balsa Core	614
GRP/Foam Core	624
Cone Data, Janssens' Method:	
GRP/Balsa Core	284
GRP/Foam Core	370
LIFT Data, Std Method:	
GRP/Balsa Core	470
GRP/Foam Core	609
LIFT Data, Janssens' Method:	
GRP/Balsa Core	178
GRP/Foam Core	274

8.3.1 Discussion of Model Results

The results, shown in Table 8.2, demonstrate how the different material properties affect the prediction model results. The model results for time to flashover (1 MW) have a very large range. Figures 8.1 and 8.2 show graphs of the heat release rate history given by the model output for the room/corner test configuration. For the GRP/Balsa Core material, the times range from 178 seconds to 614 seconds depending on the material properties. For the GRP/Foam Core material, the range is from 274 to 624 seconds. In three of the eight model runs, the burner strength had increased from 100 kW to 300 kW at 10 minutes before the compartment went to flashover. All of the model runs with the material properties derived with Janssens' method reached flashover before the 10 minute point, indicating a more conservative approach. This is a strong illustration of the importance of having accurate material properties input to the model. It shows that a fire modeler cannot blindly take material properties as input to a computer model and expect the results to be "correct." Indeed the range of model results for the test materials can make a major impact on decisions made based on engineering methods. The response of fire personnel and the available safe egress time are two examples of important information that use time to flashover data.

In order to evaluate the validity of Quintiere's model for the test materials, full scale tests must be carried out. Only then can a determination be made as to which

Figure 8.1: Net HRR Curves from Quintiere's Model for GRP/Balsa Core. Net HRR is total HRR from the model output minus the burner strength. Burner is increased from 100 kW to 300 kW at 600 seconds.

data analysis methods derive the most accurate material properties for the purposes of modeling.

8.3.2 Use of Predictive Models for Qualifying Fire Restricting Materials

This section discusses how predictive models such as Quintiere's[4] may be useful in qualifying fire–restricting materials, or for screening candidate products. As of present, neither the USCG or the IMO has approved the use of a predictive model such

Figure 8.2: Net HRR Curves from Quintiere's Model for GRP/Foam Core. Net HRR is total HRR from the model output minus the burner strength. Burner is increased from 100 kW to 300 kW at 600 seconds.

as Quintiere's for qualifying fire–restricting materials. In the meantime, predictive models continue to improve in scope and accuracy, as bench–scale test methods and data analysis methods also improve. The results presented in this chapter should in no way be interpreted to mean the test materials are not safe in their present–use condition. Without full scale validation, the model output is useful only to discuss the affect of material property variations and to qualitatively discuss how predictive models may be used.

As presented in Chapter 3, the IMO's recommended criteria for qualifying a fire–restricting material for use in a High Speed Craft are:[6]

- the time average of the heat release rate (HRR) excluding the ignition source HRR does not exceed 100 kW;
- the maximum HRR (excluding the ignition source HRR) does not exceed 500 kW averaged over any 30 second period of time during the test;
- the time average of the smoke production rate does not exceed 1.4 m^2/s;
- the maximum value of the smoke production rate does not exceed 8.3 m^2/s averaged over any 60 second period of time during the test;
- flame spread must not reach any further down the walls of the test room than 0.5 m from the floor excluding the area which is within 1.2 m from the corner where the ignition source is located; and
- no flaming drops or debris of the test sample may reach the floor of the test room outside the area which is within 1.2 m from the corner where the ignition source is located.

All six of the requirements listed above must be fulfilled in order to qualify as a fire–restricting material.[6] Quintiere's model is helpful for screening products to meet the HRR criteria. Since the model output also includes the location of the pyrolysis and burnout fronts throughout the "test", the model can also be useful for screening products based on the requirement of flame spread not reaching any further down the wall of the test room than 0.5 m from the floor. Quintiere's model does not predict smoke generation, thus the criteria for smoke production cannot be evaluated. Likewise, the criteria for flaming drops or debris cannot be evaluated with the present model.

The model results indicate that the test materials would probably not pass the HRR criteria listed above, although they would pass the downward flame spread requirement. These model runs were completed for the purposes of determining the impact that different material properties would have on the model results, and to qualitative discuss the application of the model to prediction of full scale test results. *These model results should not be interpreted as an indication that the test materials are "not safe" for use in their present application until such time as the materials can be tested in the full scale.*

Appendix C contains a complete listing of the model input parameters used in this chapter.

Chapter 9

Conclusions

9.1 General Summary

A material study was conducted in order to gain an understanding of how cored composites perform under controlled fire conditions. Test data and material properties such as ignitability, heat release rates, and smoke production were obtained. The results of this study can be used as a starting point for further research in this area, as this study has only scratched the surface in a new era of shipbuilding and maritime regulation of composite materials. It is realized that the use of composites in ship structures is here to stay, and that it is important to develop suitable test standards and qualifying procedures for composite materials.

The International Maritime Organization has taken the first step in allowing the marine industry to take initiative in this area. With the development of the High

Speed Craft Code[15] and the qualifying procedures for fire–restricting materials[6], the IMO has opened the door to further composite materials research and improved shipbuilding methods.

The theory of piloted ignition of solids was reviewed, with emphasis on justifying the use of *solid* material properties to represent a phenomenon – flaming ignition – that actually occurs in the gas phase adjacent to the solid surface. It was shown that a relationship between surface temperature and the mass flow rate of pyrolysis products justifies the assumption of a solid ignition temperature. Mathematical models of the ignition process were reviewed in the context of their application to ignition of semi–infinite and thermally–thin solid materials.

The results of bench–scale testing in the cone calorimeter and the LIFT apparatus were presented. Material properties were derived from ignitability data from both the test apparatuses using two different analysis methods: the "standard method" developed by Quintiere and Harkleroad[34] and specified in ASTM E 1321[2], and Janssens' "improved" method[3]. The effects of delamination, core melting, and edge effects were discussed in the context of how they affect experimental results and material properties.

The derived material properties were used as input to Quintiere's fire growth model[4] to predict full–scale fire behavior in the ISO 9705 Room/Corner test. The effects of different material properties on the model output were discussed, along with a discussion of how predictive fire models such as Quintiere's may apply to qualification of fire–restricting materials.

9.2 Standard Test Methods Applied to Cored Composite Materials

Perhaps the most important finding of this thesis is that the two bench–scale test methods used in the study – the Cone Calorimeter[1] and the LIFT Apparatus[2] – must be used with an understanding that the cored composites may not react as a solid homogeneous material would be expected to. The non–homogeneous nature of the cored composite materials creates problems that are not normally encountered with "common" building materials. Delamination of the GRP skin, melting of the foam core, and edge effects are factors that must be taken into consideration when evaluating the test data.

Delamination was observed in every test, at every irradiance level, with both the GRP/Balsa Core and the GRP/Foam Core materials. Delamination was always followed by an observed "deflation" and often rapid expulsion of pyrolysis gases from the sample edges and top face. It was common to see intermittent flaming prior to ignition as these gases ignited briefly and then burned out.

In Chapter 6, edge effects were shown to affect the peak HRR of the GRP/Foam Cored material, causing a peak 15% higher than the average peak with the sample edge frame in place. However, average HRR values and the effective heat of combustion were not significantly affected. At irradiance levels $\leq 25kW/m^2$ the ignition times began to show more scatter. This may be attributed to edge effects, delamination of the GRP facing, or a combination of both. Edge effects were more severe in the LIFT apparatus, where samples were tested in the vertical position. In the LIFT apparatus, ignition often occured first at the top right edge of the sample, especially with the GRP/Foam Core material. This is attributed to the escape of pyrolysis gases from the sample edges, and the acetylene pilot flame also seemed to have an effect.

In both test apparatuses, the melting of the foam core caused problems. In the cone calorimeter, the exposed face receded into the test frame as the sample heated and burned. This causes the incident irradiance to decrease throughout the test as the face gets further away from the cone radiant heater. In the LIFT apparatus, the melting of the foam core was evident in the large amount of pyrolysis gases seen escaping at the edges and traveling through the sample frame. Sometimes these gases would ignite at a distance away from the pilot flame.

The problems discussed above do not mean that the test methods are not applicable to cored composites, but rather that factors such as delamination, edge effects, and melting core materials must be taken into consideration when evaluating the data. Every effort should be made to minimize these effects. The sample edge frame used in the cone calorimeter was shown to be effective in reducing the edge effects. Likewise, the right edge frame fabricated for use in the LIFT ignition tests was effective in minimizing the edge effects, although not as effectively as the cone sample frame was. Melting of the core material is difficult to avoid, as heat is surely going to transfer through the GRP skin and eventually the melting temperature of the foam core will be reached. Delamination may be avoided in future experiments by drilling small holes in the GRP skin, although this has not yet been verified with actual testing. Drilling holes in the GRP skin would also create a new problem of the material not being representative of the end use configuration.

9.3 Ignition Data Analysis Methods

The thermal penetration depth analysis in Chapter 6 showed that the GRP skin was behaving as a thermally–thin material at ignition times greater than around 45 seconds. What this means is that, in effect, the material that was really being tested was the GRP skin, rather than the sandwich composite as a whole. This statement is supported by the backsurface insulation analysis, which determined that the core materials and/or the air pocket that was formed after delamination were acting to insulate the GRP skin. With this in mind, it would be expected that the derived properties of T_{ig} and $k\rho c$ would be consistent for both the test materials, and also among the different test apparatus. However, when the ignition data was analyzed with the "standard method"[2][34] this was not the case. The $k\rho c$ values derived using the standard method varied by as much as 95%. On the other hand, the same properties derived using Janssens' "improved" method[3] produced results much more consistent between the two materials and between the two test apparatuses. The $k\rho c$ values derived using Janssens' method varied by only 20%. Derived values for $\dot{q}''_{cr}$ were also much more consistent using Janssens' method. $\dot{q}''_{cr}$ ranged from 11 kW/m^2 from the LIFT data to 13.5 kW/m^2 from the cone calorimeter data.

Tewarson's Thermal Response Parameter (TRP)[53] was used to predict ignition times and compared to the experimental data. The results of this analysis showed that the properties derived using Janssens' method more accurately predicted the experimental results, as shown in Figures 7.10 and 7.11.

When the material properties were input into Quintiere's fire growth model, the properties derived using Janssens' method were more conservative. In fire modeling, it is better to err on the conservative side. This, coupled with the fact that the material properties derived with Janssens' method were more consistent, would indicate that Janssens' method is better suited to analyzing the data for cored composite materials. The fact that the data itself is used to determine how the material behaves – as a semi–infinite solid or as "non–thick" – help to give credence to Janssens' method, especially as applied the cored GRP materials.

Chapter 10

Future Work

This chapter makes recommendations for future work with the materials used in this study and with composite materials in general.

10.1 Further Testing with the GRP Sandwich Composites

Of immediate interest with the test materials is how the GRP laminate behaves without the core materials. Likewise, more testing should be completed on the core materials alone in both the cone calorimeter and the LIFT Apparatus. Varying test sample size, orientation, and edge protection are also areas of further study. Material sample modification such as drilling holes in the GRP skin may help in understanding how delamination affect materials properties. Drilled holes may allow pyrolysis gases to escape out of the sample face rather than through the edges. Also, thermal measurements within the sample laminate, core, and back surface via thermocouples would allow a temperature profile to be obtained. A temperature profile within the composite itself would allow further deductions to be made with regard to how the melting core affect performance, and can also be applied to further develop mathematical models such as Tucker's heat and mass transfer model for composites.

10.2 Test Methods and Data Analysis

Varying the pilot ignition source in the LIFT from an acetylene flame to a spark ignitor would be an interesting pursuit, particularly how it may help improve the standard test method. This would be relatively easy to do.

More study should be put into evaluation of the newer data analysis methods for ignitability. First, data for common building materials should be reevaluated using analysis methods such as the ones proposed by Janssens[3] and Silcock and Shields[36]. Then further testing of the materials used in this study and other composite materials should continue. Analysis of ignition data by standard methods and the newly proposed methods should be compared. Eventually a conclusion as the best method for data reduction for all materials may be achieved.

10.3 Intermediate and Full Scale Testing

It would be interesting to test the materials in an intermediate scale apparatus. This may be particularly valuable in years to come as an alternative to full scale testing.

In order to validate the flame spread models for prediction of the ISO 9705 Room/Corner test with the test materials, a series of full scale experiments must be completed. This is now possible in the WPI Fire Lab as the room fire test apparatus is completed.

10.4 Structural Strength Testing

Structural strength testing of composites exposed to heat is important from a design and regulatory standpoint. Of particular importance is residual strength after being exposed to fire or radiant heat. A practical example is the compartment boundaries for an engineroom that have local exposure to high heats for extended periods of time. To understand how exposure to hot environments over the lifetime of the vessel is to be a step closer to a safer ship design. Likewise, post–fire structural integrity is important to allow a vessel to return to port in the event of a fire at sea.

10.5 Smoke and Toxic Gas Production

Although smoke data was taken in this study, not much emphasis was placed on the evaluation of the data. An area of immediate study would be an analysis of the data obtained in this study, as well as further testing to obtain toxic gas production as the test materials burn. The cone calorimeter can be modified to allow collection of toxic gas data. From a life safety standpoint, this is an area of immediate concern to regulatory agencies and vessel owners concerned with prevention of injury or death from toxic smoke products.

10.6 Development of Full–Scale Prediction Models

The existing fire models allow prediction of heat release rates and flame spread in the Room/Corner configuration. These models, especially Quintiere's [4] [55], have potential application in more comprehensive room fire models as well. It is possible to combine the flame spread models like those used in ISO 9705 prediction with existing zone models to acheive a more accurate prediction of room fire performance with certain wall linings.

In order to achieve a method of qualifying fire restricting materials based on bench–scale data, these models will have to be modified to include prediction of smoke production. Further analysis of bench–scale smoke data and development of models to predict full–scale smoke production will have to be incorporated.

10.7 Continued Industry Involvement

Continued testing with other types of composite materials is imperative if the marine industry is to continue improving its technology base. (The MARITECH program is helping in this task immensely.) Varying the resin type, reinforcing fiber type, core material, and construction methods of composites in fire testing is also important. Shipyards involved in the construction of large composite vessels should be contacted in order to obtain test samples of what they are presently building with. This not only ensures that research keeps up with industry, but it keeps the industry informed about what fire research is being done, and what kinds of fire testing is available to them. Without industry and fire science working together, it will take much longer to accomplish growth in both sectors.

Finally, the U.S. Coast Guard should maintain involvement in fire protection. This ensures that regulations are kept in step with current fire test standards, and that the needs of the maritime industry are met to their fullest extent. The safety of life at sea depends on it.

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