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Cone Calorimeter Evaluation of the Flammability of Composite Materials

James E. Brown Emil Braun William H. Twilley

U.S. DEPARTMENT OF COMMERCE National Bureau of Standards National Engineering Laboratory Center for Fire Research Gaithersburg, MD 20899

March 1988



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NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director



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Cone Calorimeter Evaluation of the Flammability of Composite Materials

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James E. Brown Emil Braun William H. Twilley

Abstract

A study was undertaken to evaluate the fire performance of composite materials using the cone calorimeter as the bench-scale method of test simulating the thermal irradiance from fires of various magnitudes. Five parameters were derived from the calorimetry measurements to characterize the ignitability and flammability of the composite materials.

Three of the parameters are, to a large extent, empirical since radiative heat losses from the samples were unknown. These parameters are: 1) minimum external radiant flux (MERF) required to produce pilot ignition in a predetermined exposure time; 2) thermal sensitivity index (TSI) which indicates the burning intensity dependence on external heat flux; and 3) extinction sensitivity index (ESI) which indicates the propensity for continued flaming combustion without an external heat flux. MERF values at 300 s for 3 mm composites panels of a FR epoxy resin and a poly(phenylene sulfide) (PPS) resin composites were about 18 and 28 kW/m², respectively. The TSI of the PPS resin composite had the greatest dependency on external flux. Additionally, the ESI of the PPS composites was the only one to indicate an external flux requirement to sustain combustion during the first 60 s after ignition. The other two parameters determined were yields of gaseous products of combustion and average extinction area, σ , normalized to the CO, yields.

The values were found to be essentially constant at external fluxes ranging from 35 to 75 kW/m 2 , with few exceptions.

1. Introduction

The purpose of this project is to assist the Navy with selection criteria for ship components made of synthetic resins or composites of fiber-reinforced resins by systematically assembling data on the flammability properties of these materials. The ultimate use of such a data base assembly is input for a method for accurately predicting the real fire performance and flammability characteristics of composites and resins from bench-scale tests. This is an interim report.

There are numerous naval ship components where the use of composites would provide substantial advantages over metals with respect to weight reduction, corrosion resistance, and design simplification. Furthermore, for some applications, the non-magnetic character of composites is uniquely advantageous. On the other hand, the resin matrix of a composite, being an organic component, presents an increased potential for fire hazard. Hence, in order to make wise engineering decisions assessing trade-offs, such as weight savings versus flammability, information must be available on the fire performance of candidate materials in various fire scenarios. A recent review [1]* found no report of bench-scale test methods by which the fire performance of materials could be predicted.

^{*}Number in brackets refer to references given at the end of this report.

The primary objective of this phase of the study is to determine the rate of heat release (RHR) of selected composites and resins burned under various levels of radiative heating. These levels simulate fire scenarios in which the composite material is itself burning or in which it may be near another burning material. The rate of heat release, q, of fires, especially the peak q, is the primary characteristic determining the size, growth, and suppression requirement of a fire environment [2]. This flammability characteristic can be measured using a bench-scale instrument. These values approximate the RHR of a surface element of a full-scale object in a real fire environment. Combined with other measurements, such as flame spread rate (the rate of growth of the surface element) and ease of ignition, the fire hazard contribution of the object can then in principle be calculated. Some such computational methods are already under development for other applications [3].

The calculations of Huggett [2] demonstrated that the average heat of combustion for a broad range of materials is a constant 13.1 kJ/g oxygen consumed, with an accuracy of ± 5% or better. Thus the RHR can be determined with good accuracy from two simple measurements, the flow rate of air through the combustion system and the oxygen depletion in this flow [4]. A bench-scale apparatus, the Cone Calorimeter, developed and described by Babrauskas [5], utilizes this oxygen consumption principle to determine the RHR per unit area q". The name "Cone Calorimeter" was adopted from the geometric configuration of its radiant heater. Data from this instrument can be used in research to predict the full-scale fire behavior of certain furnishings and wall lining materials [6]. The predictive method defines an environment as

having n objects with surface areas divided conceptually into m small uniform areas, A, during combustion, so that q at any time is given by

$$\dot{\mathbf{q}} = \sum_{\mathbf{n},\mathbf{m}} (\dot{\mathbf{q}}_{\mathbf{n},\mathbf{m}}) (\mathbf{A}_{\mathbf{n},\mathbf{m}}) \tag{1}$$

The Cone Calorimeter has a well characterized and controlled irradiance source. Babrauskas and Parker [7] deduced that the spectral distribution of this source approximates the irradiance in compartment fires, where radiation is the primary process for energy transfer. Thus it was concluded that the instrument suitably determines the ignitability of upholstery and wood in fire-like environments.

We report the results of Cone Calorimetry measurements on a variety of composites and materials typical of those which may be used in ship components. The primary measurement using the Cone Calorimeter is RHR as a function of time under pre-selected, constant levels of irradiance simulating radiant fluxes from real fires of various magnitudes. Simultaneously-determined time-to-ignition, mass loss, combustion product yields, and smoke obscuration are also reported.

2.0 Materials

The materials used in this study are listed in Table 1. For the most part, only the generic classification of the resin and a general classification of the fiber reinforcement are known. Where greater detail of the materials is available, it will be indicated when the test results are presented. The generic classification of the resin and fiber identification were provided by the indicated sources. In general, the resin reinforcement was a glass fiber

fabric except for a sample set of Ryton** panels in which carbon fibers were used. Several tests were performed on composite materials for which neither the identity of the fiber nor the resin was known. These latter tests were performed at the specific request of the Navy.

Test specimens were cut into 10 cm by 10 cm squares at the full thickness of the supplied product. The specimens were maintained at laboratory conditions (approximately 40-45% RH and 25°C) prior to testing.

3.0 Measurement Technique

The data reported here were obtained using the NBS Cone Calorimeter which is shown schematically in figure 1. The Cone Calorimeter and its function have been previously described by Babrauskas [5] and Babrauskas and Parker [7]. Briefly, it is a bench-scale rate of heat release calorimeter based on the principle of oxygen consumption [2]. The energy release rate is computed from the measurements of mass flow rate and oxygen depletion in the gas flow through the exhaust stack. An external radiant energy flux of up to 110 kW/m² may be applied to the surface of a sample by a temperature-controlled radiant cone heater. An electric spark igniter mounted above the specimen was used to ignite the pyrolysis products generated by a specimen exposed to a preset irradiance. The ignition delay time for each composite material usually was

^{**}Certain commercial materials are identified in this report in order to adequately specify the experimental procedure. In no case does such identification imply recommendation by the National Bureau of Standards nor does it imply that the material identified is necessarily the best available for the purpose.

measured at three different radiant flux levels. In general, specimens are exposed to flux levels of 35, 50, and 75 kW/m². Ignition delay time measurements were made by an operator with a stop watch as part of the standard test procedure used to determine the rate of heat release. Samples were placed under the cone heater and the amount of time necessary to ignite the evolving decomposition products by the spark of an electric arc was recorded.

A load cell was used to continuously measure changes in sample mass, while products of decomposition, (i.e., CO, CO₂, and total unburned hydrocarbons) were monitored by appropriate gas analyzers. By combining the mass loss data and the gas concentration data, specific gas species yields were computed (mass of product/unit mass of material gasified). Smoke obscuration was characterized by the attenuation of a laser beam and reported as the extinction area per unit mass of material consumed. Data from all the measurement devices were collected every five seconds by a digital data acquisition system and stored for later data reduction.

4.0 Results and Discussion

4.1 Ignition

The objective here is to obtain a measure of the resistance of materials to pilot ignition under radiative heating. The number of different radiant flux levels and the replication number were limited by material availability.

Therefore, for example, the Koppers Dion sample was tested in duplicate at four flux levels (the three cited above plus $25~\mathrm{kW/m^2}$), while ignition of the Corflex assembly was measured at only three flux levels.

The times to pilot ignition are reported in Table 2. Where duplicate measurements were made, the average values are reported (one half of the difference between the two measurements is shown in parentheses). As expected, the data show that as the incident flux increases the ignition delay time decreases. It should also be noted that the <u>range</u> of ignition delay time for all materials tested at a given radiant flux increased with decreasing radiant flux (figure 2), with ranges of 21 s to 55 s at 75 kW/m² and 92 s to 390 s at 35 kW/m². Therefore, in very large fires, one might expect similar ignition-delay times for all composites, whereas in incipient fires one would expect ignition-delay times to depend on the chemical composition of the resin and configuration of the material.

There are two possible modes of radiative ignition: one is auto-ignition and the other is pilot ignition. Auto-ignition results solely from the external heating of the material substrate, without the presence of a high temperature source near the material surface. Pilot ignition refers to forced ignition of the fuel vapors by a high temperature pilot source such as a hot wire, spark, or small flame. For auto-ignition to occur, the fuel/air ratio above the material substrate must be within the flammability limits and the gas phase temperature must be above an ignition temperature. Because of the existence of an intentionally supplied hot spot, pilot ignition only requires that the

fuel/air ratio above the material substrate in the vicinity of the pilot source be within the flammability limit.

The gasification (pyrolysis) rate of the resin controls the speed at which the vapor concentration at the composite surface approaches its lower flammability limit. The gasification rate is temperature dependent. Therefore, it appears reasonable to suppose that ignition occurs only after the surface temperature of the resin has reached a critical level, the ignition temperature. This ignition temperature could vary somewhat with ignition conditions, such as heat flux level, on char-forming materials due to the insulating effect of the char.

Kashiwagi [8,9] investigated the effect of external radiant flux on the surface temperature at ignition and the ignition delay time of red oak and poly(methyl methacrylate) (PMMA) in auto- and pilot-ignition modes. He used a high powered CO₂ laser to irradiate (60-160 kW/m²) the sample surface, while simultaneously measuring sample surface temperature with a small diameter chromel-alumel thermocouple. An electrically heated wire was placed near the sample surface for pilot-ignition tests. These tests showed that for PMMA the surface temperature of the substrate at ignition was relatively constant, approximately 400°C, for both auto- and pilot-ignition modes. The surface temperature of red oak, a char former, at ignition increased as the external flux decreased.

Atreya [10] reported results of tests on different types of wood and found that, for the pilot-ignition mode below an external flux of 25 kW/m 2 , the wood

surface temperature at ignition increased with decreasing external radiant flux. Above 25 kW/m 2 the surface temperature at ignition was constant at approximately 350°C.

Rasbash et al. [11] used an electrically heated radiant panel to irradiate samples of PMMA at 11 kW/m² and above. Using a small hydrogen flame as a pilot, they found that surface temperatures decreased slightly with decreasing external radiant flux. At 24 kW/m², the reported surface temperature was about 275°C and decreased to 250°C at 11 kW/m². This is about 150°C below the value reported by Kashiwagi [9]. Instrument-dependent conditions for surface temperature measurement may account for the differences in pilot-ignition results between Kashiwagi and Rasbash.

Thomson and Drysdale [12] measured the surface temperature at ignition in the presence of a pilot flame of six common thermoplastics using two different instruments over an irradiance range of 10 kW/m² to 40 kW/m². Table 3 summarizes their results. Within experimental error, they found that the surface temperature at ignition was not significantly affected by changes in the level of external radiant flux, above some minimum value. This is indicative of a unique ignition temperature for a range of irradiance levels. These thermoplastic materials are known to undergo gasification by pyrolysis without significant secondary reactions such as char formation reactions. Simple bond scission of aliphatic carbon chains will lead to volatile and combustible products.

Brown [13] recorded the surface temperature of a series of composite panels exposed to different radiant flux levels in the cone calorimeter. Table 4 summarizes those results for the surface temperature at pilot ignition using an electric spark. While the data show some scatter, in general, the surface temperature at ignition is relatively constant for each material and is greater than the thermoplastics above (Table 3) due to enhanced stability from cross links and aromatic components.

All of the materials listed in Tables 3 and 4 behave qualitatively the same as those shown in figure 2 with respect to ignition and radiant flux. The presence of inorganic fibers does not appear to alter the ignition behavior. If it is then assumed that this trend is applicable in general to all composites (i.e. that the pilot ignition occurs at a fixed surface temperature, dependent only on the thermal gasification characteristics of the substrate), one can use the simple thermal heat-up model derived by Carslaw and Jaeger [14] to suggest a form or trial function that ignition-delay time might have with respect to the heat absorbed from the constant external radiant flux. Heat losses are ignored in this simple model. Furthermore, this model assumes that the substrate can be treated as an inert, thermally thick, and opaque solid. Then the delay time to reach the ignition temperature is given by:

$$t_{ig} = \frac{\pi k \rho c}{4} \left(\frac{T_{ig} - T_{o}}{\dot{q}} \right)^{2} \qquad (2)$$

where

 t_{ig} = ignition delay time (s) k = thermal conductivity (kW/m/K) ρ = density kg/m³) c = heat capacity (kJ/kg/K) T_{ig} = ignition temperature (K) T_{o} = initial temperature (K)

 \dot{q} = external radiant flux absorbed at the surface of the solid (kW/m²)

Equation (2) shows that the ignition delay time, t_{ig} , is proportional to $1/\dot{q}^2$ provided, however, that the temperature wave does not reach the back surface of the sample before ignition. If, however, the material is thermally thin, that is, if the thermal wave hits the back surface before ignition occurs, the solid material will have an ignition delay proportional to about 1/q. Additionally, equation 2 provides an approximate basis for determining the influence of k, ρ , and c on ignition behavior. Therefore, a log-log plot of ignition time versus flux should give a straight line with a slope of minus 2 for an inert, thermally thick, and opaque material. Figure 3 shows the results for the Koppers Dion 6692T panel 25 mm thick and a Corflex panel, 3 mm thick. A linear regression line drawn through these data results in negative slopes for the two lines of 2.3 and 1.7, respectively, for the Koppers and Corflex panels. Table 5 is a listing of the slope of the regression line for each composite. It is recognized that derived values are essentially empirically based since heat losses are not known. However, plots of the data appear to be linear as was shown by typical examples in figure 5. Moreover, ignition apparently occurs before the thermal wave penetrates the back surface.

Plotting ignition-delay data for all Cone Calorimeter experiments (Table 2) as illustrated in figure 3 allows one to extrapolate the regression line to some chosen location. Extrapolation to 600 s, the recommended time limit for ignition in this apparatus, represents the minimum external flux (MERF)

necessary to produce pilot ignition after a protracted exposure of 600 s to irradiative heating. The MERF values (at 600 s) are listed in table 5, although these values may not be completely realistic because of the extensive extrapolation (for some materials) from a limited data range. Moreover, a real fire on a ship, whose radiant flux requires at least 600 s for pilot ignition of a composite material, is expected to be detected and suppressed before the composite becomes involved in the fire growth. A more practical application of the ignition times would involve determining the required irradiance to cause ignition at some other time, such as 300 s, for example. This represents an estimate of the maximum external flux from a fire in the environment where composites are used that the composite could withstand before the material would begin to contribute to the fire growth. The values obtained at 300 s are also listed in Table 5 and are called MERF300. Although the data for ignition are very limited, the maximum deviation of the regression slope from the theoretical value of minus 2 towards a value of minus 1, was 0.5 (25%) for the 3 mm Derakane panel. This difference, in part, may be due to heat loss from the back surface of the thin sample. Similar effects may be attributed to the thin Corflex panel even though the regression slope, minus 1.9, closely approximates the idealized value, minus 2. These materials indicate the lowest MERF values for ignition 12 and 18 kW/m², respectively, for $MERF_{600}$ and $MERF_{300}$.

4.2 Rate of Heat Release

We present in this section the Cone Calorimeter results on the heat released as measured by the oxygen consumption during the combustion of several

materials under radiative heating in a fully ventilated atmosphere (21% oxygen). It has been established [2] that the carbon in organic materials need not be fully oxidized to carbon dioxide for the relationship of 13.1 kJ of heat released per gram of oxygen consumed to hold true. Thus, typical reaction products of combustion in fire environments, consisting of partially oxidized pyrolysis products, such as, hydroxy and carbonyl compounds and soot, do not significantly affect the accuracy of the Cone Calorimeter results.

Results of heat release rates were obtained here for a broad range of resins, including epoxy, polyester and poly(aryl thio-ether) resins, whose structures and chemical compositions are very different, suggesting individual degrees of susceptibility to oxidation and gasification under radiative heating.

Profiles of the rates of heat release with respect to time, under constant external irradiance, were found to have features which are unique to the composite studied. The profiles appear to depend primarily on the chemical composition of the resin and the thickness of the composites. Figures 4, 5, and 6 demonstrate typical variations observed in the RHR-time profiles of, respectively, a 25 mm (1 inch) thick polyester/glass fiber (Koppers Dion 6692T), a 3 mm (1/8 inch) thick epoxy/glass fiber panel (Corflex), and a 3 mm thick poly(phenylene sulfide)/glass fiber (Ryton) composite panel, each of which was radiatively heated at 35, 50, and 75 kW/m². The polyester composite also was radiated at 25 kW/m². In each of the figures, the curves for the composite generally show an initial sharp rise in the RHR which occurs at about the time of ignition and increases to a maximum or peak RHR for each irradiance level. The peak RHR duration is short. The subsequent decrease in

irradiance level. The peak RHR duration is short. The subsequent decrease in initial RHR is attributed to increase in thickness of the char layer. The char layer reduces the transfer of heat to the substrate (resin) below the surface thereby reducing the rate of gasification of the resin.

In general, all of the curves exhibit at least two maxima for RHR. The initial peak is due to surface volatilization and char formation, as discussed above. The second peak is a result of an increase in the gasification rate of the unburned substrate (mass loss rate data will be discussed below) caused by an increase in the bulk temperature of the substrate. The bulk temperature increases because the unburned substrate is no longer thermally thick, i.e., the thermal wave has reached the back surface. Back surface temperatures should increase as the second peak of RHR is approached. While these measurements were not made in this investigation, Parker [15] has shown the same phenomenon with wood, a char forming material. He observed two maxima in RHR; the second peak increased as the back surface temperature increased.

The separation with respect to time of the RHR maxima is dependent on the sample thickness, irradiance level and chemical composition of resin. For example, the 3 mm thick Corflex and Ryton panels tested at 35 kW/m² have peak separation times of about 150 s and 350 s, respectively. This difference is attributed to the chemical composition of the resins, the difference in thermal properties, and difference in flame heat feedback rates.

It may be seen that the intensity of the RHR follows the race at which volatiles are pyrolyzed from the specimens, and, to a large extent, is

indicative of the thermal stability of the resin and its propensity to gasify. The mass loss rates with respect to time of the polyester, epoxy, and PPS composites are shown, respectively, in figures 7, 8, and 9. The purpose of presenting the mass loss curves at this time is to show that the dq"/dt versus time curves follow the time profile of mass loss rate, dm"/dt, versus time curves. The ratio of these two quantities (\dot{q} "/ \dot{m} ") at any given time is the effective heat of combustion ($\Delta h_{c,eff}$) of the gases evolved at that time. The mass loss rates and heat of combustion will be discussed further in a later section.

Since the RHR, in most cases, changes quite significantly with time, it appears that more meaningful information may be gained about the fire behavior of the composites under radiative heating if the rates of heat release are averaged over periods of time during the burning process. Not only are the advantages of curve smoothing brought forward to clarify trends in the heat release data, but Babrauskas and Krasny [16] demonstrated that the rate of heat release averaged over 180 s could best be used to predict the fire performance of upholstered furnishings in large-scale experiments. Kanury and Martin [17] also have used average values for deducing physicochemical properties of essentially homogeneous materials in fire environments. The proposed ASTM Method P 190 [18] specifies that average q" values for the first 60, 180, and 300 s after ignition, or for other appropriate periods, be included in the report of the cone calorimeter results. In addition to the recommended practice in ASTM P 190, the average RHR over 60 s intervals from ignition are reported.

Figure 10a shows a plot of the RHR averaged as recommended in P 190 from ignition up to 360 seconds for the Koppers composite under the four irradiance levels previously mentioned. A similar plot, figure 10b, shows the 60 s interval averages for the RHR. As expected, the recommended procedure shows a rather smooth change in the average RHR up to 360 s after ignition. In every case this includes the initial peak RHR's but may not include the second The effect of irregular volatilization of fuel from the surface is reduced. Figure 11b shows a more irregular pattern. However, the first 60 s intervals are identical. Figures 11a/11b are similar plots for the Corflex composite which shows more distinction between the irradiance levels for the first two minutes. Thereafter, the curves tend to coalesce or merge around 180 seconds after ignition as the effect of the back surface is felt. Figures 12a/12b demonstrate the behavior of the average RHR of Ryton composite over the post-ignition period. This composite shows, as previously suggested, the greatest sensitivity to irradiance level. The lowest irradiance level, 35 kW/m², as was seen in the ignition data, provides barely enough energy to promote combustion. On the other hand, the average RHR at irradiances of 50 and 75 kW/m² provides for an increasing average until 300 and 240 s, respectively, when the panels are burned out.

The cone calorimeter results obtained in this study on the rates of heat release averaged at the various times, as previously indicated, are presented in tables 6 through 13. Table 6 presents all of the results obtained for the 25 mm thick Koppers polyester composite. This table includes the data illustrated in figure 10. The q" value averaged at 60 s for one of the

specimens tested at 35 kW/m^2 appears to be larger than expected. An explanation for this behavior is not known at this time.

Table 7 summarizes average RHR, $\overline{\dot{q}}$ "(t), values for a 13 mm (1/2 in) thick Koppers polyester composite consisting of various configurations of glass fiber reinforcements in composites containing 42% and 54% of brominated (fire retardant) polyester resin and in composites containing 42, 43, and 51% of the non-brominated polyester matrices. The glass fiber reinforcements in the composites include (1) fibers woven into a mat from continuous strands and then stitched along with other chopped fibers (stitched woven roving and chopped strand); (2) reinforcements from woven roving and woven mat; and (3) non-woven spirally interlocked fiber mat. The effect of bromine as a flame retardant can be seen readily by comparing the average q" values at 60 s of the untreated samples (first three samples listed) with the two bromine containing samples. It appears that the presence of bromine in the polyester results in a reduction of average q" on the order of 35 to 40% overall. On the other hand, we note that the average q" values of the brominated specimens in this table (which were 13 mm thick) are generally a factor of two greater than the average \dot{q} " of the 25 mm specimens radiatively heated at 50 kW/m² shown in table 6. The difference in any rate of heat release may be attributed, in part, to the difference in sample thicknesses, i.e., 25 mm versus 13 mm, but other unknown factors are also responsible for the early differences. The thicker samples provide a greater heat sink resulting in a smaller volume of resin being raised to the decomposition temperature per area of surface irradiated. This trend is also seen in T_{ig} at about 40 s for the 13 mm sample and T_{ig} of about 60 s for the 25 mm sample (Table 2).

Next, the average q" values are summarized for three types of epoxy resin composites. The average q" values of a fire retardant epoxy are listed in Table 8. Tests were performed on the assembly as received and on the individual outer panels. These results show that there are only small differences between the average RHR values of the thermally thin (3 mm) and thick assemblies (about 37 mm) and suggest that the heat loss from the back surfaces of the thin samples is relatively small as a result of effective insulation in the sample holder. The results for the composite with a vinyl ester type of epoxy resin are listed in Table 9. The average q" results for the third resin type, high performance epoxy resin composite prepared at DTRC laboratory [13], are shown in Table 10. Although the composition of the resin is not known beyond it being an amine-cured epoxy resin, it appears that the fire performance of this latter resin closely resembles that of the FR epoxy composite shown in Table 8.

Table 11 summarizes the average RHR of the four Ryton (PPS) panels. We note that ignition did not occur when specimens reinforced with woven carbon fibers were heated at a flux of 35 kW/m². The same result was found for one specimen reinforced by a swirl mat of glass fibers. Overall, the RHR at this flux level is low. Where results are not reported at the various post-ignition times, sustained flaming combustion did not occur. The average q" results of another composite prepared at DTRC from a bismaleimide (BMI) and graphite fibers and tested at NBS are listed in Table 12 [13]. The results from an experimental composite, prepared from vinyl styryl pyridine and BMI, and reinforced with glass fibers are shown in Table 13. This experimental

composite which is designed as a heat shield, is composed of only two plies of fibers (≈ 1 mm). Having such a low mass per unit surface area contributes to low rates of heat release and fairly short periods of flaming combustion. It may be seen in reviewing the average \dot{q} data in Tables 6 through 13 that the composites with polyester and epoxy resins generally show maximum \dot{q} (t) values in the first 60 s post ignition. The \dot{q} (t) values generally decrease with time after the first 60 s which suggest that the peak RHR is associated with initial surface burning of the composite rather than subsequent combustion of the pyrolyzate from the interior of the composite. For irradiances of 50 kW/m² or more, the composites with PPS, BMI, and vinyl poly(styryl pyridine)BMI resins show maxima at times greater than 60 s. For these samples, the maximum \dot{q} "(t) is not the initial peak.

4.3 Fire Sensitivity Indices

Kanury and Martin [17] and Kanury [19] reported simplified models by which heat release rates (peak, instantaneous, and average values) may be related to basic properties of materials in fire environments using the Spalding B number concept. These authors and Tewarson and Pion [19] deduced from energy conservation at the sample surface that the heat release rate q' may be expressed by the following equation

$$\dot{\mathbf{q}}^{"} = (\Delta \mathbf{H}_{c.eff}/\mathbf{L}) [\dot{\mathbf{q}}_{T}^{"} + \dot{\mathbf{q}}_{e}^{"} - \dot{\mathbf{q}}_{\ell}^{"}]$$
(3)

where

 $\Delta H_{c.aff}$ = effective heat of combustion

L = heat of gasification (pyrolysis)

 $q_T^{"}$ = heat transferred from flame to material surface

q" = imposed external flux

 $q_{\ell}^{"}$ = heat flux loss by the surface to ambient

The slope $(\Delta H_{c,ff}/L)$ of a plot of the measured RHR against the external radiant flux provides one measure of the flammability of materials; it is a key determinant of the B number value. This parameter, the thermal sensitivity index (TSI) [17], provides a basis by which the fire performance of the materials may be indexed and compared over a broad range of external irradiances, simulating different fire environments. The intercept of such a plot in principle indicates whether the flame is self-sustaining in the absence of an external irradiant flux for the time period under consideration. We will call this parameter the extinction sensitivity index (ESI); Kanury and Martin [17] called this parameter the limiting thermal index. Equation 3 can be expressed as

$$\dot{q}'' = (TSI) \cdot \dot{q}_{e}'' + (ESI). \tag{4}$$

We illustrate the dependence that the average RHR has with respect to imposed heat flux levels by plotting the average \dot{q} " at 60 s versus external flux, \dot{q} ". Using 60 s average \dot{q} " minimizes the effect of sample thickness and conductive heat losses. Figure 13 show the results for composites whose resins are polyester, FR epoxy, poly(phenylene sulfide), and BMI. This plot illustrates the TSI and ESI at 60 s interval on resin composition.

Table 14 summarizes the slopes, intercept, average effective heat of combustion, and minimum external radiant flux (MERF $_{\rm 3\,0\,0})$ necessary for ignition within 300 s. The ESI values (slopes) are estimates of the sensitivity of the combustion intensity to variations in external irradiance and show that the Koppers composite, Corflex Panel Assembly, and BMI Panel had about the same sensitivity to variations in \dot{q}_a ". Because of differences in sample thickness these samples should not be compared to each other without caution. However, the TSI values indicate that the rate of heat release of these samples, although not the same in magnitude, would be fairly insensitive to small changes in external irradiance. This suggests that in a real fire the decay in an external fire imposing energy on a target material made from one of these composites would not be reflected as rapidly in a reduced heat release rate of the target material as compared to the materials with higher TSI values. For example, the Ryton Panels, which ranged in value from 1.3 to 1.8, would be expected to respond most strongly to variations in source irradiance.

The Ryton Panels also exhibited a negative intercept, ESI. This suggests that the heat loss from the flame is greater than its flux to the surface. With the removal of an external heat source these materials can be expected to self-extinguish, while the other materials with a positive ESI would be expected to continue burning at least for the first 60 s. The intercepts indicate that the epoxy matrix composites exhibit the most potential for sustained combustion with an external radiant flux following ignition.

In Table 14, the effective heat of combustion values are averages taken from each exposure over the entire measurement; they are computed from the ratio of \dot{q} " to mass loss rate, \dot{m} ". These values fall into two groups, the lower one (about 12 kJ/g) where the resin is flame retarded and the upper values (20-25 kJ/g) where it is unretarded.

The minimum external radiant flux (MERF $_{300}$) values necessary for ignition within 300 s are repeated here for comparative purposes; ignitability is another important flammability parameter that does not depend on the same fuel characteristics as rate of heat release.

4.4 Product Generation

Table 15 summarizes the combustion product yields and mass loss at the various radiant flux levels. Average values obtained from entire experimental periods are reported since the quantities generated remained fairly constant with time (see figures 18 and 19 for CO and CO_2 , respectively). The values for hydrocarbons (HC), CO, and CO_2 yields have been normalized to the sample weight loss. While all of these tests were conducted under well-ventilated conditions, combustion efficiency can still be determined by the $\mathrm{CO/CO}_2$ ratio and the $\mathrm{HC/CO}_2$ ratio, Table 16. The data indicates that, in general, the $\mathrm{CO/CO}_2$ ratio is independent of external irradiance, with the exception of Ryton Swirl Mat Panel. For this panel the $\mathrm{CO/CO}_2$ ratio decreases with increasing irradiance. The Koppers composites show a flux dependence on the $\mathrm{HC/CO}_2$ ratio such that it decreases with increasing flux, while the other materials are constant with flux variations.

Smoke obscuration reported here is the average specific extinction area, $\sigma({
m avg})$, given by

$$\sigma(\text{avg}) = \left[\left(\sum_{i} \dot{V}_{i} \Delta t \right) / \left(m_{i} - m_{f} \right) \right] \left[\left(1/L \right) \ln \left(I_{o} / I \right) \right]$$
 (5)

where

 \dot{V} = flow rate in exhaust duct (m³/s)

 Δt = time interval of measurement(s)

 $m_i - m_f = mass loss (kg)$

L = distance through which light is measured (m)

 I_0 = initial light intensity

I = final light intensity

In Table 16 are listed the σ/CO_2 ratios for the materials tabulated in Table 15. In general, the σ/CO_2 ratio is constant for a material over the range of irradiances investigated. However, as with the HC/CO_2 ratio, the σ/CO_2 ratio for the Koppers composite show a similar apparent dependence on external irradiance. Also the σ/CO_2 ratio for the lab epoxy, BMI, and Ryton Swirl Mat are an order of magnitude less than the Corflex Panel and nearly two orders of magnitude less than Koppers. This indicates that one of these three materials would be best suited for applications where smoke obscuration is a primary concern.

5.0 Summary of Results

The cone calorimeter was used to evaluate the fire characteristics of a series of composite materials. Ignition delay time, heat release rate, yield of gaseous products and smoke were measured.

The results of an analysis of the ignition delay time data showed that:

- $T_{ig} \propto 1/\dot{q}^2$ was a usable, but simplified approximation of the data; one must be cautious in extrapolating the data with it.
- This relationship applied to all of the composite materials including the sandwich assembly (i.e. Corflex).
- There is some indication that the slope of the regression line, for a given material composition is a function of the thickness of the material (e.g. Derakane Panels and Corflex Assembly versus Corflex Panel).
- Given the limited data set, glass fiber configuration appear to have no effect on ignition delay time.

The results of an analysis of heat release rate data show that:

- Thermal sensitivity index (TSI) and extinction sensitivity index (ESI) can be inferred from the external heat flux dependence of the average rate of heat release during the first 60 s after ignition.
- The TSI and ESI values were inferred from averaged RHR data related to the external flux by regression analysis as defined to show:

$$\dot{q}$$
" = TSI $\cdot\dot{q}$ " + ESI

- TSI values indicate a dependence of fire growth rate on external flux during combustion.
- ESI values indicate whether a composite is expected to selfextinguish during the first 60 s of combustion if the external heat flux is removed.
- Comparison of the TSI or the ESI values to MERF values show no correlation.

Product generation data show that the $\mathrm{HC/CO_2}$, $\mathrm{CO/CO_2}$, and $\sigma/\mathrm{CO_2}$ ratios were essentially constant with external irradiance (from 35 kW/m² to 75 kW/m²) for the various composites tested. However, three exceptions were found:

• a FR polyester and a FR epoxy resin composites showed a decreasing HC/CO_2 ratio with increasing external irradiance;

- the PPS composite showed a decrease in ${\rm CO/CO_2}$ ratio with increasing external irradiance; and
- the PPS and BMI resin composites $\sigma/{\rm CO}_2$ values were an order of magnitude less than the epoxy and polyester resin composites.

6.0 Conclusions and Recommendations

The Cone Calorimeter can measure an array of flammability parameters for composite materials. These include the external radiant flux requirements for pilot ignition and sustained flaming combustion, the flux dependency of the rate of heat release, and the relationship of flux level to combustion efficiency as reflected in the yields of combustion and pyrolysis products. Since these measurements are based in the fundamentals of fire science, we expect they will correlate well with the larger-scale compartment fire behavior.

Thus, this development represents the first step towards predicting the performance of composite materials in various fire environments. Therefore, we recommend investigating the use of these parameters from the Cone Calorimeter and, additionally, a radiant-flux-based flame spread index to provide the basic data from bench-scale measurements for correlation with larger-scale (quarter scale and full scale, for example) compartment fire measurements. The bench-scale parameters will then serve as input for hazard prediction models of the type already under development at the NBS Center for Fire Research.

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References

- [1] Brown, J.E., Loftus, J.J., and Dipert, R.A., "Fire Characteristics of Composite Materials: A Review of the Literature", NBSIR 85-3226, U.S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, MD 20899.
- [2] Huggett, C., "Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements", Fire and Materials, 4, 61 (1980).
- [3] Bukowski, R.W., Jones, W.W., Levin, B.M. Forney, C.L., Stiefel, S.W., Babrauskas, V., Braun, E., and Fowell, A.J., "Hazard I. Volume 1: Fire Hazard Assessment Method", NBSIR 87-3602, U.S. Dept. of Commerce, National Bureau of Standards (1987).
- [4] Parker, W.J., "Calculation of Heat Release by Oxygen Consumption for Various Applications", J. Fire Sci. 2, 380 (1984).
- [5] Babrauskas, V., "Development of the Cone Calorimeter A Bench-Scale Heat Release Apparatus Based on Oxygen Consumption", Ibid <u>8</u>, 81 (1984).
- [6] Babrauskas, V., "Bench-Scale Methods for Prediction of Full-Scale Fire Behavior of Furnishings and Wall Linings", Technology Report 84-10, Society of Fire Protection Engineers, Boston, MA.
- [7] Babrauskas, V. and Parker, W.J., "Ignitability Measurements with the Cone Calorimeter", NBSIR 86-3445, U.S. Dept. of Commerce, National Bureau of Standards (1986).
- [8] Kashiwagi, T., "Experimental Observation of Radiative Ignition Mechanisms", Combustion and Flame, 34, 231-244 (1979).
- [9] Kashiwagi, T., "Effects of Sample Orientation on Radiative Ignition", Combustion and Flame, <u>44</u>, 223-245 (1982).
- [10] Atreya, A., "Pyrolysis, Ignition and Fire Spread on Horizontal Surfaces of Wood", NBS-GCR-83-449, U.S. Dept of Commerce, National Bureau of Standards (1984).
- [11] Rasbash, D.J., Drysdale, D.D., and Deepak, D., "Critical Heat and Mass Transfer at Pilot Ignition and Extinction of a Material", Fire Safety Journal, 10, 1-10 (1986).
- [12] Thomson, H.E. and Drysdale, D.D., "Piloted Ignition of Plastics", Proceedings of Fundamental Aspects of Polymer Flammability, Eds: Cox, G. and Stevens, G., Institute of Physics Short Meetings Series #4, London, England (1987).
- [13] Brown, J.E., "Report of Test on Combustion Characteristics of Fiber Reinforced Resin Panels", FR-3970, U.S. Dept. of Commerce, National Bureau of Standards (1987).

- [14] Carslaw, H.S. and Jaeger, J.C., Conduction of Heat in Solids, 2nd Ed., Oxford University Press (1959).
- [15] Parker, W.J., "Development of a Model for the Heat Release Rate of Wood A Status Report", NBSIR 85-3163, U.S. Dept. of Commerce, National Bureau of Standards (1985).
- [16] Babraskas, V. and Krasny, J., "Predictions of Upholstered Chair Heat Release Rates from Bench-Scale Measurements", Fire Safety Sci. Eng. ASTM SP-882, Harmathy, T.Z., Ed., American Society for Testing and Materials, Philadelphia, 1985, pp.268-284.
- [17] Kanury, A.M. and Martin, B.M., "A Profile of the Heat-Release Rate Calorimeter", International Symposium on Fire Safety of Combustible Materials, University of Edinburgh, UK (1975).
- [18] Proposed Test Method for "Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter", P 190, American Society for Testing and Materials, Philadelphia, Pa.
- [19] Kanury, A.M., "Modeling of Pool Fires with a Variety of Polymers", Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA (1975).
- [20] Tewarson, A. and Pion, R.F., "Flammability of Plastics I. Burning Intensity", Combustion and Flame, <u>26</u>, 85-103 (1976).

Composite Materials

o l	Koppers Co., Inc.	Dow Chemical Co.	Corflex Corp. per DTRC	Phillips Petro- leum Co.	Dow Chemical Co.		
Source	Корре	Dow (Corflex per DTRC	Phillips leum Go.	Dow (DTRC	DTRC
Potential Applications	Boat Hull	Pump Body, Duct Material, Bulkhead	Ventilation Ducts	Undefined	Barrier material	Experimental	Experimental
Fiber Reinforcement	Glass Woven Roving	Glass	Glass	Glass: 1.Chopped Mat 2.Swirl Mat Pre- preg 3.Woven Mat Prepreg Carbon(Graphite)	Glass	Graphite	Graphite
Resin Classification	Polyester, Brominated	Vinyl Ester type Epoxy	Epoxy filled with aluminum silicate	Poly(phenylene sulfide)	Vinyl Poly(styryl pyridine)/Bismaleimide	Ероху	BMI
Material	. Koppers Dion Panels	. Derakane	. Corflex Panel Assembly	. Ryton Panels	. Experimental 2-Ply Composite	. Lab. Epoxy Panels	. Lab. BMI Panels
	1.	2.	ب	4	5.	. 9	7.

TABLE 2

Ignition Delay Times for Composite Materials
Exposed to Various External Flux Levels

Ignition Delay Time (s)

·	Incide	nt Flux (kW/	<u>m²)</u>	
Material (thickness)	<u>25</u>	<u>35</u>	<u>50</u>	<u>75</u>
Koppers 6692T (25 mm)	263	120(10)*	60(2)	21
Dow Derakane (3 mm)	* * *	129	55	45(2)
Dow Derakane (25 mm)	• • •	390	187	55(2)
Corflex Panel (3 mm)		92(5)	54(2)	25
Corflex Assembly (37 mm)	• • •	122	70(0)	30(2)
Ryton Panels (3 mm):				
Glass Mat (Chopped)		183+	66	27(2)
Glass Mat Swirl		191(7)	97	28(5)
Glass Woven Mat Prepreg	•••	154(7)	75	29(1)
Carbon Fiber: Wöven Prepreg		N.I.	88	38(3)
Lab. Epoxy Panel (3 mm) ^(a)		116	76	40
Lab. BMI Panels (3 mm) ^(a)		211	126	54

^{*}Numbers in parentheses indicate range about a mean where duplicate measurements were made.

^{*}Duplicate tests performed; only one specimen ignited.

N.I. = No ignition during a 600 s exposure.

⁽a) Values taken from reference [13].

Ignition Temperature of Six Polymers as Measured by Thomason and Drysdale*

TABLE 3

<u>Material</u>	Temperature(°C)
Polyoxymethylene	277 - 300
Poly(methyl methacrylate)-la	298 - 328
Poly(methyl methacrylate)-2ª	276 - 317
Polypropylene	331 - 345
Polystyrene	337 - 369
Polyethylene	360 - 367

a: Poly(methyl methacrylate)s from two different sources were used.

^{*}Taken from Reference [12].

TABLE 4

Surface Temperature of Coated and Uncoated Graphite Fiber Reinforced Composites 3 mm Thick at Pilot Ignition*

Resin/Coating	Incident Flux(kW/m²)	Surface Temperature (°C)
Ероху	35 50 75	390 425 375
Epoxy/Nextel Prepreg.	35 50 75	390 400 400
Bismaleimide	35 50 75	515 500 455
Bismaleimide/Nextel Prepreg.	35 50 75	455 475 440
Bismaleimide/Nextel Dry .	35 50 75	455 470 490

^{*}Taken from Reference [12]

TABLE 5

Minimum External Flux for Long Exposure Time and for 300 s

Exposure To Cause Ignition Computed from the Regression of Ignition

Delay Time and External Flux

Material	Regression	MERF ₆₀₀ a	MERF ₃₀₀ b
	Slope	(kW/m^2)	(kW/m^2)
Vonnera (600T (25 mm)	2 2	18	24
Koppers 6692T (25 mm)	-2.3	10	24
Derakane Panel (3 mm)	-1.5	13	20
Derakane Panel (25 mm)	-2.7	31 .	40
Corflex Panel (3 mm)	-1.7	12	18
Corflex Assembly	-1.9	15	22
Ryton Panels (3.2 mm):		·	
Glass Mat (Chopped)	-2.5	21	28
Glass Mat (Swirl)	-2.6	23	31
Glass Woven Mat Prepreg	-2.1	18	25
Carbon Woven Prepreg	-2.1	20	28

a: Minimum External Radiant Flux necessary to cause ignition after 600 second exposure.

b: Minimum External Radiant Flux necessary to cause ignition after a 300 second exposure.

TABLE 6

Results of Averaging the Rate of Heat Release of 25 mm (l in) Koppers Dion 6692T Panels (FR Polyester/Glass Fiber Composite)

Experiment	Flux	Av	Average Rate of Heat Release (kW/m²)	of Heat R	elease (k	W/m^2	
Number	(kW/m^2)	s 09	120 s	180 s	240 s	300 s	360 s
1094		50	40(35)*	35(25)	30(5)	25(5)	20(<5)
1095 1096	35 35	55 70	65(60) 55	55(40) 45	70(35) 40	65(25) 40	60(20) 35(25)
1086 1087	50	09	.50(40) 45(35)	45(35) 40(25)	45(35) 35(25)	40(35) 35(25)	40(35) 30(25)
1097	75	80	80(75)	70(55)	(07)59	(07)09	55(40)

"Values in parentheses are averaged over the previous 60 sec interval.

TABLE 7

and Average Rates of Heat Release of Koppers Dion Polyester Composites Irradiated Influence of Glass Fiber Configuration on the Ignition Delay at 50 kw/m^2

	Resin	Fiber			.0	q"(t), kW/m ²	01		
		Reinforcement	$\frac{t}{t_i}$ (s)	s 09	120 s	180 s	240 s	300 s	360 s
1.	Iso-orthophthalic Polyester, 42%	Glass Combo		215	180 (145)*	165 (135)	155 (125)	150 (118)	145 (125)
2.	Isophthalic (unsaturated), 43%	BI PLY	20	210	75 (145)	65 (135)	155 (130)	145 (120)	145 (120)
	Polyester, 51%								
3.	Isophthalic (unsaturated) Polyester, 43%	Glass Combo	57	235	190 (150)	175 (140)	165 (135)	160 (130)	155 (130)
. 4	Brominated Iso- phthalic Polyester, 54%	Glass Woro Mat	35	135	115 (95)	105 (85)	100 (85)	100 (85)	95 (85)
5.	Brominated Iso- phthalic Polyester, 42%	Woro S2		130	110 (90)	100 (80)	95 (80)	0 (80)	0 (80)

Fiber Reinforcement:

Glass Combo = stitched woven roving and chopped strand

BI PLY = woven roving and woven mat Glass Woro Mat = non woven spirally interlocked fibers

Glass Woro S2 = same as woro mat of S2 glass

* Values in parentheses are interval (60 s) arranged

Interval Averaged Rate of Heat Release of 3 mm Corflex Panels and Panel Assembly (FR Epoxy-Fiberglass Composites)

360 s	;	90 (10)	:	105	;	95	105 (40)	105 (35)	:	100
300 s	!	105 (15)	100 (10)	120 (20)	i t	105 (50)	120 (60)	120 (55)	125 (50)	115 (40)
240 s	140 (7)	130 (30)	120 (20)	145 (45)	130 (25)	120 (80)	135 (100)	135 (95)	145 (75)	135 (65)
180 s	160 (175)	160 (145)	(90)	180 (180)	165 (75)	135 (115)	145 (145)	150 (140)	170 (140)	160 (115)
120 s	155 (140)*	170 (170)	190 (205)	180 (185)	215 (215)	145 (120)	145 (135)	155 (140)	185 (180)	185 (175)
<u>s 09</u>	170	170	175	175	215	170	160	170	190	190
Flux, kW/m ²	35	35	50	50	75	35	50	20	75	75
Sample	Corflex Panel	Corflex Assembly								
Experiment Number	1137	1170	1534	1535	1161	1140	1536	1537	1155	1154

interval. *Values in parentheses are averaged over the previous 60 s

TABLE 9

Interval Averaged Rates of Heat Release of 25 mm Thick Dow Derakane Pump Housing (Vinyl Ester Epoxy-Fiber Glass Composite)

Rvnarimant			Average Rate of Heat Release (kW/m²)	te of Hea	it Release	e (kW/m²)	
	Flux, kW/m²	<u>s 09</u>	120 s	180 s	240 s	300 s	360 s
	35	295	255 (110)*	220 (130)	200 (111)	180 (111)	165 (100)
	50	225	195 (160)	170 (130)	155 (115)	145 (105)	140 (100)
	50	190	170 (150)	160 (145)	160 (150)	160 (160)	160 (155)
	75	240	225 (205)	210 (175)	195 (160)	185 (140)	175 (125)
	75	217	205 (190)	190 (160)	175 (140)	165 (130)	160 (140)
	75	240	225 (205)	215 (190)	200 (150)	185 (135)	175 (125)

*Values in parentheses are averaged from the previous 60 s interval.

TABLE 10

Interval Averaged Rates of Heat Release of 3 mm
Thick Laboratory Samples of Epoxy-Graphite Fiber
Composite Panels^a

		Ave	erage Rate	of Heat R	elease (kW	<u>/m²)</u>	
Experiment Number	Flux (kW/m²)	(60 s)	(120 s)	(180 s)	<u>(240 s)</u>	(300 s)	(360 s)
	35	150	155 (160)*	120 (50)	95 (20)	75 (≃0)	
2302	50	185	170 (155)	135 (60)	105 (15)	85 (10)	75 (10)
2311	75	210	190 (165)	145 (60)	150 (25)	100 (≃0)	

⁽a) Taken from Ref. [12]

^{*} Values in parentheses are averaged over the previous 60 s interval.

TABLE 11

Results of Post-Ignition Averaging of the Rate of Heat Release of 3 mm Thick Ryton Panels (Reinforced Poly(phenylene sulfide))

360 s	20 (25)	80 (30)	100	100 (45)	10 (15)	0 (0)	55 (55)	120 (40)	105 (30)
e (kW/m²) 300 s	20 (20)	90 (105)	115	110 (75)	10 (10)	0	55 (60)	135 (150)	120 (100)
eat Releas 240 s	20 (10)	85 (135)	130	120 (155)	10 (5)	0	95)	135 (180)	130 (180)
Average Rate of Heat Release 120 s 180 s 240 s	20 (5)	70 (75)	130	105 (125)	10 (5)	(0) 0≈	50)	115 (135)	110 (115)
<u>Average</u> 120 s	30 (10)*	65 (60	115	95	10 (5)	(0)	45 (55)	110 (140)	110 (130)
s 09	50 N.I.	75	110	100	20	<>	35	75	06
Flux (kW/m ²)	35	20	75	75	35	35	50	75	75
Fiber Reinforcement	Chopped Mat				Swirl Mat				
Experiment Number	1385 1386	1545	1374	1381	1387	1388	1543	1375	1382

360 s	\$	\$	55 (45)	80	80 (25)	: :	70 (25)	80 (35)	80
300 s	\$	<5	55 (110)	95	06)	: :	80 (20)	90 (35)	06
eat Releas 240 s	<5	\$	55 (95)	100	95 (110)	: :	95 (35)	100 (40)	105
Average Rate of Heat Release (kW/m^2) 120 s 180 s 240 s 300 s	<5	< <u>\$</u>	50 (64)	95	90 (110)	: :	115 (60)	120 (130)	125
Average 120 s	5	2	45 (60)	06	85 (85)	: :	90 (115)	120 (150)	130
s 09	10	2	35	85	. 08	N . I .	09	85	100
$F1ux (kW/m^2)$	35	35	20	75	7.5	35 35	20	75	7.5
Fiber <u>Reinforcement</u>	Woven Mat					Woven Mat Graphite Fibers			
Experiment Number	1389	1390	1544	1379	1383	1391 1392	1546	1380	1384

 $N.I. = \mbox{No Ignition} \ \ \, \mbox{\starValues in parentheses are averaged over the previous 60 s interval} \ \ \, \mbox{\starValues in parentheses} \ \ \, \mbox{\starValues} \ \ \ \, \mbox{\starValues} \ \ \ \, \mbox{\starValues} \ \ \, \mbo$

TABLE 12

Results of Post-Ignition Averaging of the Rate of Heat Release of a 3 mm Thick Laboratory Sample of BMI-Graphite Fibers Composite^a

			A	Average q" (kW/m²	(kW/m^2)		
Experiment <u>Number</u>	$F1ux$ (kW/m^2)	(s 09)	(120 s)	(180 s)	(240_s)	(300 s)	(360 s)
2296	35	105	130 (130)*	135 (140)	120 (90)	105 (40)	90 (10)
2308	50	120	145	145	130	110	96
2313	75	140	(170) 170 (200)	(150) 165 (155)	(90) 145 (75)	(33) 125 (30)	(12) 105 (25)

Values in parentheses are averaged from the previous 60 s interval. (a) Taken from Reference [12]

TABLE 13

Results of Post-Ignition Averaging of the Rate of Heat Release of a 2-Ply-Reinforced Vinyl Poly(styryl pyridine) - BMI Resin Experimental Composite

Experiment			Ave	Average q", kW/m²	.W/m ²		
	Flux, kW/m ²	s 09	120 s	180 s	240 s	300 8	300 s 360 s
	35	10	5(<5)*	(≈0)	5(=0) <5(=0) <5(=0)	<5(≈0)	1
	35	7	5(<5)	5 (<5)	;	;	;
	50	25	19(15)	16(10)	15(10)	15(15)	15(15)

* Values in parentheses are averaged from the previous 60 s interval.

TABLE 14

Comparison of Inferred Flammability Indices of Composite Materials

$^{\mathrm{MERF_{309}}}_{\mathrm{CkW/m}^2}$)	24	18	22	18	28		28	31	25		28	28 ± 2.4
$\overline{\text{ESI}}^{+}(k\text{W/m}^{2})$	30	125	100	100	75		5	-55	-40		;	
$\overline{\text{TSI}}^*$	9.0	1.1	9.0	1.4	6.0		1.3	1.6	1.8		1.6	1.6 ± .20
$\Delta H_{\rm c}$, eff $({ m kW/m}^2)$	12 ± 2	12 ± 0.9	12 ± 0.4	20			+1		23 ± 2.2			23 ± 1.3
	Koppers Dion 6692T (25 mm)	Corflex Panel (3 mm)	Corflex Panel Assembly (37 mm)	Lab. Epoxy Panel (3 mm)	Lab. BMI Panel (3 mm)	Ryton Panels (3 mm)	Chopped Mat	Swirl Mat	Woven Mat	Graphite Woven	Mat	Average

[&]quot; TSI = Thermal sensitivity index.
+ ESI = Extinction sensitivity index.

TABLE 15
Average Yields of Combustion Products for Various
Types of Composite Materials

<u>CO</u> 2 ^a	0.09 0.11 0.16 0.11	0.77 0.87 2.63 0.78 0.77	1.9 0.9 1.4	1.6 1.5	0.93 1.42 1.50
<u>CO</u> ^a	0.008 0.010 0.011 0.011	0.011 0.015 0.132 0.014 0.013	0.04 0.10 0.06	0.04 0.04 0.02	0.38 0.15 0.14
<u>Hydrocarbons</u> ^a	0.10 0.10 0.07 0.06 0.03	0.09 0.08 0.08 0.01 ≈0	0.02 0.02 0.01	0.02 0.02 0.01	0.05 0.009 0.004
Extinction <u>Areas (m²/kg)</u>	1630 1500 970 1205 1570	2600 2600 1835 1790 2805	740 790 800	530 600 760	270 630 490
Total Wt Loss, &	6 9 111 17 20	56 52 54 56 . 56	17 20 19	24 24 26	23 24 32
Initial Mass.g.	465 471 471 467 466	60 54 54 63 55	69 74 73	74 76 76	54 54 56
Flux (kW/m²)	25 35 35 50 75	Panel 35 35 50 50 75	35 50 75	35 50 75	:1s 35 50 75
	6692T 1095 1096 1086 1097	Corflex Pa 1137 1170 1534 1535 1161	Lab. Epoxy Panels	Lab. BMI Panels	Ryton Panels (Swirl Mat) 1385 , 1545 1381

(a) Ratio average of mass generation rate to the mass loss rate

Table 16

and $\sigma/{\rm CO}_2$ Different	$\sigma/CO_2 (m^2/kg) = \frac{(x10^{-4})}{(x10^{-4})}$	1.8 1.3 0.6 1.1 0.9	0.3 0.3 0.2 0.4	0.04 0.09 0.06	0.03 0.04 0.05		0.03
	0/C0 ₂ (0000	0 0 0	0 0 0		000
Ratio of Average Yields for ${\rm CO/CO_2}$, ${\rm HC/CO_2}$, for Various Types of Composite Materials at External Irradiances	HC/CO ²	1.11 0.91 0.44 0.55 0.18	0.12 0.09 0.03 0.01	<0.01 0.02 <0.01	0.01 0.01 0.01		0.05
Ratio of Avera for Various Ty	<u>c0/co</u>	0.09 0.09 0.07 0.10	0.01 0.02 0.05 0.05 0.02	0.02 0.11 0.04	0.03 0.03 0.01		0.33
	Flux (KW/m²)	25 35 35 50 75	1s 35 35 50 50 50 75	35 50 75	35 50 75	Mat	35 50 75
	Materials	Koppers 6692T 1095 1096 1086	Corflex Panels 1137 1170 1534 1535 1161	Lab. Epoxy/ Graphite	Lab. BMI/ Graphite	PPS/Chopped	1385 1545 1381

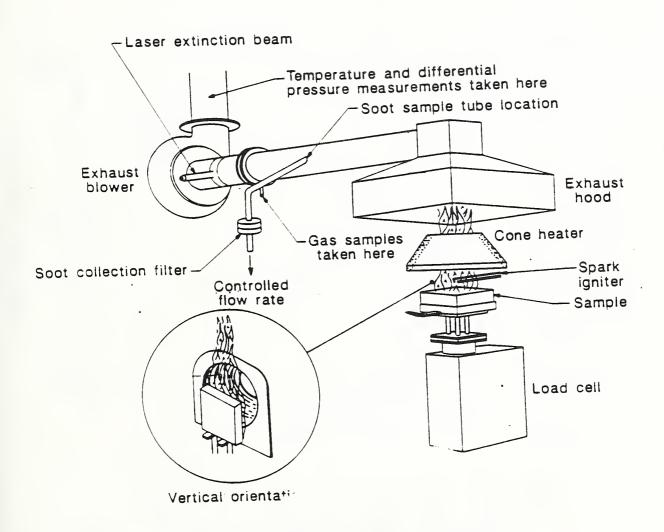


Figure 1. Schematic Representation of Cone Calorimeter

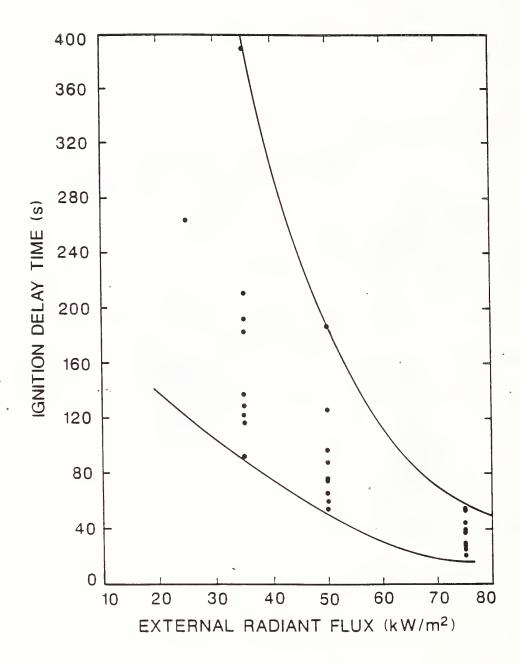


Figure 2. Range of Ignition Delay Times as a Function of External Radiant Flux for All Composites

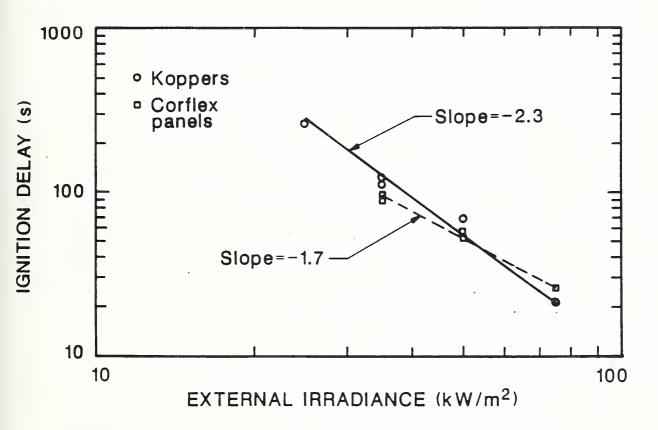


Figure 3. Ignition-Delay Time for Two Composites as a Function of External Radiant Flux

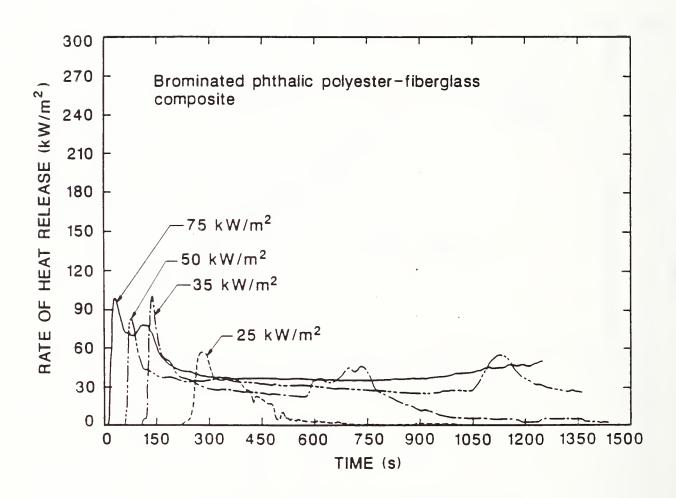


Figure 4. Effect of Irradiance on the Rate of Heat Release from a 25 mm FR Polyester/Glass Composite

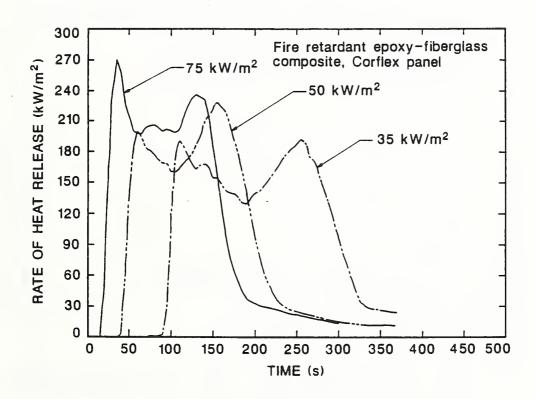


Figure 5. Effect of Irradiance on the Rate of Heat Release from a 3 mm FR Epoxy/Fiber Glass Composite

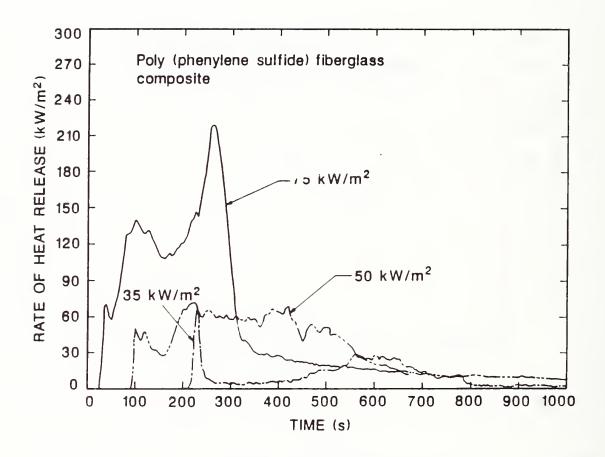


Figure 6. Effect of Irradiance of the Rate of Heat Release from from 3 mm Poly(phenylene Sulfide)/Fiber Glass Composite

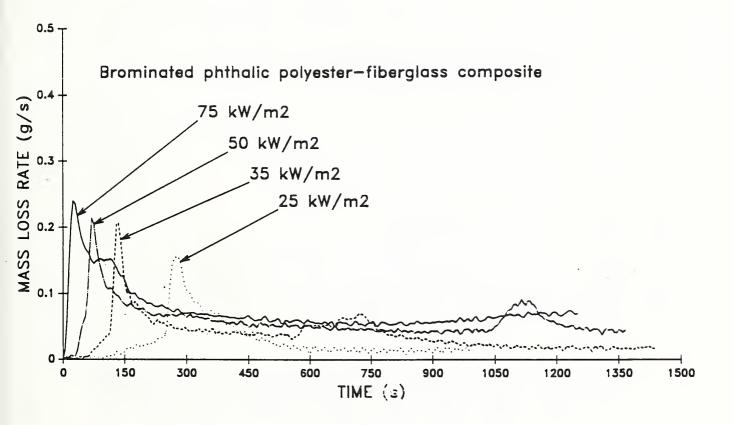


Figure 7. Effect of Irradiance on the Mass Loss Rate from a FR Polyester/Fiber Glass Composite

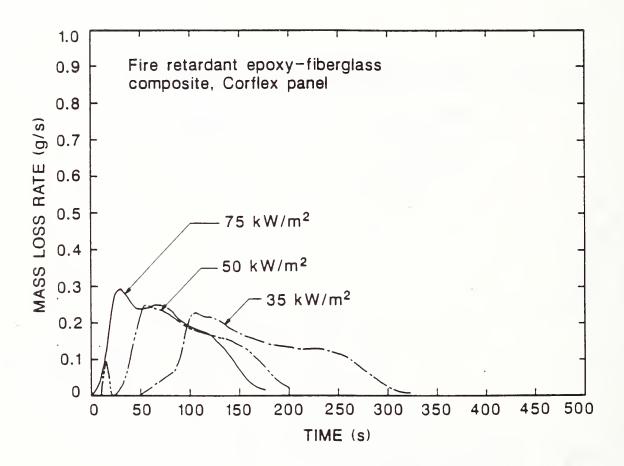


Figure 8. Effect of Irradiance on the Mass Loss Rate from a 3 mm Thick FR Epoxy/Fiber Glass Composite

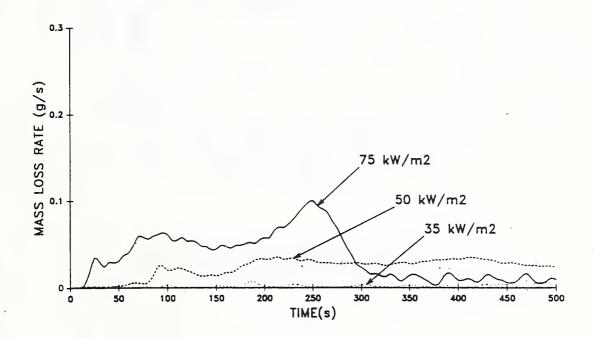
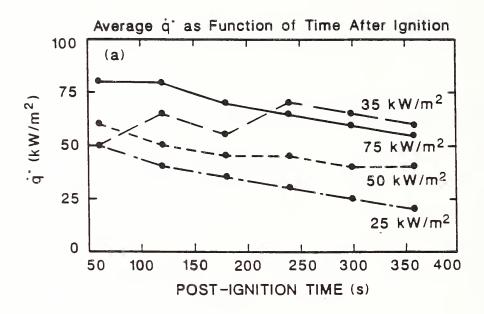


Figure 9. Effect of Irradiance on the Mass Loss Rate from a 3 mm Thick Poly(phenylene Sulfide)/Fiber Glass Composite



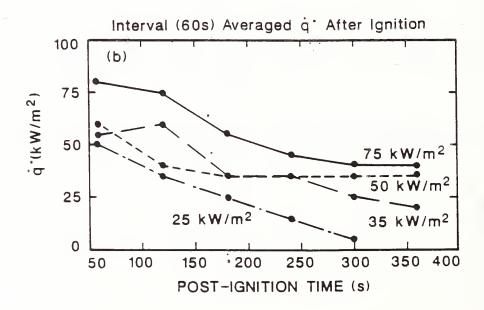
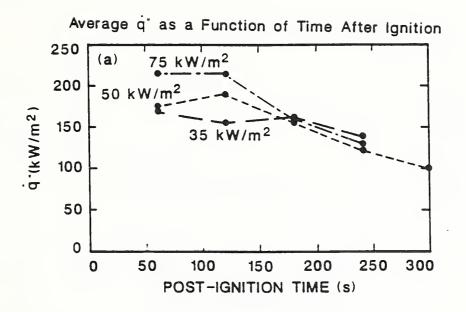


Figure 10. Average q as a Function Time After Ignition of Irradiatively Heated Koppers Dion 6692T Composite (FR Polyester/Glass)
Panels



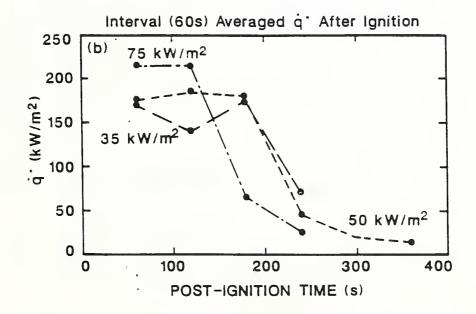
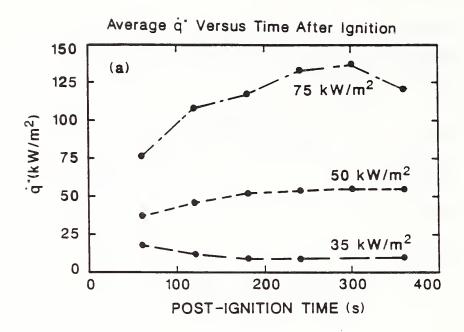


Figure 11. Average q as a Function of Time After Ignition of Irradiativel Heated 3 mm Corflex (FR Epoxy/Glass) Panels



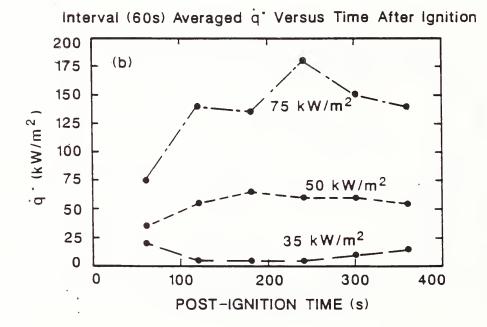


Figure 12. Average q as Function of Time After Ignition for Irradiatively Heated 3 mm Ryton Panels (Poly(phenylene sulfide)/Fiber Glass)

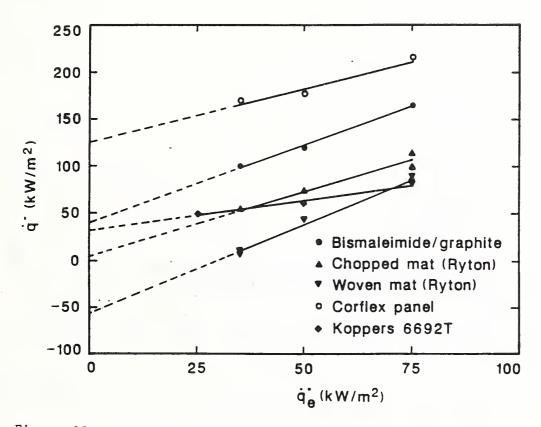


Figure 13. Average Rate of Heat Release Up to 60 s Post Ignition of Several Composites as a Function of External Flux

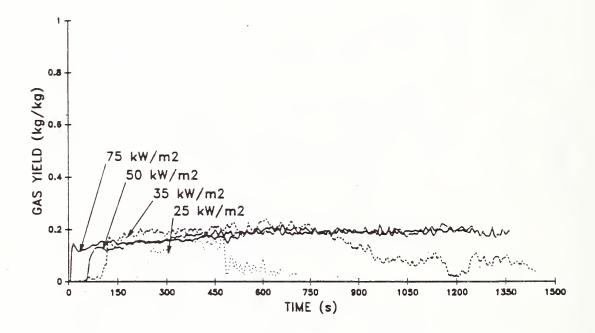


Figure 14. The Effect of Irradiance on the Production of ${\rm CO_2}$ from 25 mm FR Polyester-Fiber Glass Composite

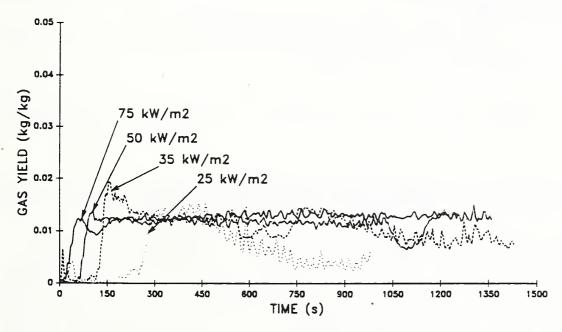


Figure 15. The Effect of Irradiance on the Production of CO from a FR Polyester/Fiber Glass Composite

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A study was unde	ertaken to evaluate	the fire performance of	composite had of test
materials using	the cone calorimet	er as the bench-scale met from fires of various mag	nitudes. Five
simulating the c	derived from the	calorimetery measurements	to characterize
the ignitability	v amd flammability	of the composite materia	ls. Three of the
parameters are,	to a large extent,	empirical since radiativ	e heat losses from
the samples were	e unknown. These pa	rameters are: 1) minimum	external radiant
flux (MERF) requ	uired to produce pi	lot ignition in a predete	rmined exposure
time; 2) therma	l sensitivity index	(TSI) which indicates th	e burning intensity
dependence on ex	xternal heat flux;	and 3) extinction sensiti	stion without an
which indicates	the propensity for	continued flamming combu 300 s for 3 mm composite	s panels of a FR
external heat 1.	a poly(phenylene s	ulfide) (PPS) resin compo	sites were about 18
and 28 kW/ m^2 , re	espectively. The T	SI of the PPS resin compo	site had the
greatest depende	ency on external fl	ux. Additionally, the ESP	of the PPS
composites was	the only one to ind	icate an external flux re	quirement to
sustain combust:	ion during the firs	t 60 s after ignition. T	mbustion and
parameters dete	rmined were yields	of gaseous products of co ized to the CO ₂ yields.	mbuscion and
		; capitalize only proper names; and se	
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