

Heat release of polymer composites in fire

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Abstract

The relationship between heat release rate and other fire reaction properties of fibre reinforced polymer composite materials is investigated. The heat release rate and fire reaction properties of thermoset matrix composites reinforced with combustible fibres (aramid, extended-chain polyethylene) or non-combustible fibres (glass, carbon) were determined over a range of heat flux levels using the oxygen consumption cone calorimeter technique. The fire reaction properties that were measured were time-to-ignition, smoke density, carbon monoxide yield, carbon dioxide yield, mass loss rate and total mass loss. It is discovered that these reaction properties (apart from ignition time) are linearly related to the heat release rate for composites containing non-combustible fibres. When the reinforcement is combustible, however, the heat release rate only appears to be related to the carbon monoxide yield, mass loss rate and (in some cases) smoke density. This study clearly shows the importance of the relationship between heat release rate with smoke density and carbon monoxide yield, the two reaction properties that influence the survival of humans in fire.

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1. Introduction

One of the main safety concerns with using fibre reinforced polymer (FRP) composites is their combustibility. Many polymer composites ignite when exposed to high heat flux, releasing heat that can, in some circumstances, contribute to the growth of the fire. Significant quantities of smoke and toxic fumes may also be released, respectively limiting visibility and posing a health hazard. For these reasons, stringent fire regulations govern the use of composites in aircraft, ships, buildings, land transport, oil and gas facilities, and other applications. These regulations require that the fire reaction properties meet specified levels. The reaction properties that are often used to define the fire hazard include the heat release rate, time-to-ignition and flame spread rate. These properties are important because they influence the temperature and spread of a fire. Other

important properties include smoke density and yield of carbon monoxide gas because these determine survivability.

Of the many fire reaction properties, it is generally recognised that heat release rate is the single most important in controlling fire hazard [1,2]. Heat release rate is defined as the mass loss rate of the material times its heat of combustion. The amount of heat released from a polymer composite is controlled by the combustion of flammable gas products resulting from the decomposition of the organic components. Although the resin matrix is generally the main source of flammable volatiles, the decomposition of organic fibres (such as aramid or polyethylene) can also produce volatiles. The decomposition reactions of the organic components may themselves reduce the heat release rate. The reactions of the polymers and organic fibres generally used in composites are endothermic, i.e. absorb heat. Therefore, the net heat release rate is a complex property determined by the heat generated by the decomposition reactions of the volatiles released by the decomposing composite less the heat absorbed by the endothermic decomposition reactions of the polymer matrix and organic fibres. Other thermal processes may also affect the heat release rate, including changes to the surface

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emissivity of the composite as it decomposes, the specific heat of the reaction gases that can have a convective cooling effect, and variations in the heat flux and the oxygen content of the fire.

As mentioned, heat release rate is the critical fire reaction property because it is the driving force for fire spread. It also controls other reaction properties [1,2]. For example, Babrauskas [3] has shown that the heat release rate has a large influence on the yield ratio of CO/CO₂ gases generated by burning polymethyl methacrylate (PMMA). The fire behaviour of a range of thermoset and thermoplastic matrix composites has been determined, although the influence of heat release rate on other reaction properties has not been widely investigated [4–19]. Sorathia and colleagues [20] were the first to examine the effect of heat release rate on the flame spread rate of composites. The dependence of other fire reaction properties, such as time-to-ignition, gas emission levels and smoke production, on the heat release rate has not yet been investigated.

The aim of the present study is to investigate the relationship between the peak and average heat release rates and the other fire reaction properties of polymer composites. Specifically, the paper will determine the relationships between the heat release rate and the smoke production, carbon monoxide yield, carbon dioxide yield, time-to-ignition, mass loss rate and total mass loss. These relationships are investigated for composites with different thermoset polymer matrices (ie. polyester, vinyl ester, epoxy, phenolic), reinforced with non-combustible fibres (E-glass or carbon) as well as combustible fibres (aramid or polyethylene). In addition, the relationship between heat release rate and the fire reaction properties of the resins and organic fibres is investigated.

2. Materials and experimental techniques

2.1. Composite materials

The fire reaction properties were determined for the materials listed in Table 1. The table provides information on the composition, polymer content and thickness of the specimens. The composites are divided into two groups: (i) non-combustible fibre (woven E-glass, chopped E-glass or unidirectional carbon) and (ii) combustible fibre (woven aramid (Kevlar™) or woven extended-chain polyethylene (Spectra™)). The polymers used for the matrix were isophthalic polyester, epoxy and three types of vinyl ester, which are all highly combustible. That is, these polymers yield a substantial quantity of flammable volatiles when they thermally decompose. In addition, two types of phenolic resin were used, possessing much better flammability resistance due to their lower yield of volatiles. None of the polymers contained flame retardant additives.

The composites were fabricated into flat panel specimens using an autoclave under the conditions given in Table 2.

In addition, specimens were prepared of the aramid or polyethylene fibres without a polymer matrix. Specimens were also made from the different matrices without fibre reinforcement. These were cast in an open mould and cured under the same conditions as the composites.

2.2. Fire testing

The fire reaction properties were measured using a Stanton Redcroft cone calorimeter according to the standard method prescribed in ASTM E1354. The operating principles of the oxygen consumption cone calorimeter technique are described by Babrauskas [21]. Fig. 1 shows the test chamber to the cone calorimeter containing a burning composite specimen. The composite samples were 100 mm × 100 mm in size, and were held in a retaining frame that protected the specimen edges during testing. This minimised accelerated burning and egress of volatiles at the specimen edges. The following incident heat flux values were employed in the fire tests: 25, 35, 50, 75 and 100 kW/m². Measurements of hot face temperature showed that these heat fluxes produced maximum laminate surface temperatures, respectively, of about 525, 580, 650, 750 and 850 °C. The carbon/epoxy system was subjected to the same range of heat fluxes omitting 35 kW/m². The other samples were tested only at 35, 50 and 75 kW/m². Fire tests were performed at different heat flux levels to determine whether any correlations found between the heat release rate and the other fire reaction properties were dependent on or not influenced by the external heat flux.

The following quantities were measured using the cone calorimeter:

- *Peak heat release rate.* This was the maximum heat release rate measured at any point over the test period.
- *Average heat release rate.* This was calculated from the integral of the heat release rate over the entire period that heat was released by the specimen.
- *Time-to-ignition.* This was defined as the minimum exposure time required for the specimen to ignite and sustain flaming combustion. The spark igniter to the cone calorimeter was used to induce ignition.
- *Average smoke density.* This was measured by the decrease in transmitted light intensity of a helium-neon laser beam located within the fume extraction duct. The smoke density is expressed in terms of average specific extinction area (SEA) with units of m²kg⁻¹, which is a measure of the instantaneous amount of smoke being produced per unit mass of specimen burnt [21].
- *Yields of carbon monoxide and carbon dioxide.* These were measured using a CO/CO₂ gas analyser located in the exhaust duct. Both the peak and average yields of these gases were determined.
- *Mass loss.* The peak and average mass loss rates together with the total mass loss was measured using the load cell located beneath the specimen holder. The total mass loss

Table 1
Details of the composites, reinforcements and resin matrix

Specimens	Reinforcement	Matrix	Matrix content (wt%)	Thickness (mm)
Woven glass/polyester	600 g/m ² plain woven E-glass fabric (Colan)	Polyester—Crystic 3-491PS (Huntsman Chemical Company)	28.5	4.0
Woven glass/vinyl ester (type I)		Vinyl ester—Derakane 411 (Dow Chemicals)	31.4	4.6
Woven glass/vinyl ester (type II)		Vinyl ester—Derakane 8084 (Dow Chemicals)	30.1	4.4
Woven glass/phenolic (type I)		Phenolic—Resinox CL1723 (Huntsman Chemical Company)	32.0	4.5
Chopped glass/polyester	450 g/m ² chopped	Polyester—Crystic 3-491PS	29.8	4.1
Chopped glass/vinyl ester (type I)	E-glass mat (Colan)	Vinyl ester—Derakane 411 (Dow Chemicals)	34.6	4.5
Chopped glass/vinyl ester (type II)		Vinyl ester—Derakane 8084 (Dow Chemicals)	32.5	4.4
Chopped glass/phenolic (type I)		Phenolic—Resinox CL1723 (Huntsman Chemical Company)	32.3	4.7
Carbon/epoxy	Unidirectional carbon/ epoxy prepreg (Cytec)	Epoxy	36.0	8.0
Aramid/epoxy	173 g/m ² style 352, 1150	Epoxy—Epon 828 (Shell)	35.2	4.0
Aramid/vinyl ester (type II)	Kevlar-49 (Du Pont)	Vinyl ester—Derakane 8084 (Dow Chemicals)	32.1	4.0
Aramid/phenolic		Phenolic—Resinox CL1759 (Huntsman Chemical Company)	35.2	4.1
Extended chain polyethylene/ epoxy	94 g/m ² 650 denier Spectra 1000 (Allied Signal)	Epoxy—Epon 828 (Shell)	35.0	4.0
Extended chain polyethylene/vinyl ester (type II)		Vinyl ester—Derakane 8084 (Dow Chemicals)	36.8	4.2
Extended chain polyethylene/ phenolic (type II)		Phenolic—Resinox CL1759 (Huntsman Chemical Company)	39.9	5.3
Polyester		Polyester—Crystic 3-491PS (XXX)	100	4.2
Vinyl ester (type I)		Vinyl ester—Derakane 411 (Dow Chemicals)	100	4.2
Vinyl ester (type II)		Vinyl ester—Derakane 8084 (Dow Chemicals)	100	4.2
Phenolic (type I)		Phenolic—Resinox CL1723 (Huntsman Chemical Company)	100	4.2
Phenolic (type II)		Phenolic—Resinox CL1579 (Huntsman Chemical Company)	100	4.2
Epoxy		Epoxy—Epon 828 (Shell)	100	4.2
Aramid	173 g/m ² style 352, 1150 Kevlar-49 (Du Pont)		0	4.2
Extended chain polyethylene	94 g/m ² 650 denier Spectra 1000 (Allied Signal)		0	4.2

was calculated as a percentage of the initial specimen mass.

3. Results and discussion

3.1. Heat release rate

Fig. 2 shows the typical variation in heat release rate (HRR) with time for a composite material reinforced with non-combustible fibres. This heat release rate curve is for the woven glass/vinyl ester tested at a heat flux of 50 kW/m². There is an initial delay period before the composite releases heat, and this is because the temperature

of the material is below the pyrolysis temperature of the organic matrix. Following this induction period, there is a rapid rise in the heat release rate due to the combustion of volatiles, in this case mainly low molecular weight hydrocarbons, near to the composite/fire interface. Following the peak heat release rate (PHRR), the HRR decreases progressively with time due to the formation and thickening of a surface char layer that slows the decomposition reaction rate in the underlying material. The HRR also declines as a result of the declining resin content in the sample. Eventually the heat release rate becomes negligible, as the last of the resin matrix is decomposed.

The heat release rate curves for the composite materials reinforced with glass and carbon fibres were similar in

Table 2
Fabrication conditions of the composite specimens

Composite Material	Fabrication condition	
	Max. autoclave overpressure (kPa)	Cure temperature
Woven glass/polyester	350	40 °C for 1 h + 80 °C for 1 h
Woven glass/vinyl ester (type I)	350	40 °C for 1 h + 80 °C for 1 h
Woven glass/vinyl ester (type II)	350	40 °C for 1 h + 80 °C for 1 h
Woven glass/phenolic (type I)	350	60 °C for 1 h + 80 °C for 2 h
Chopped glass/polyester	350	40 °C for 1 h + 80 °C for 1 h
Chopped glass/vinyl ester (type I)	350	40 °C for 1 h + 80 °C for 1 h
Chopped glass/vinyl ester (type II)	350	40 °C for 1 h + 80 °C for 1 h
Chopped glass/phenolic (type I)	350	60 °C for 1 h + 80 °C for 2 h
Carbon/epoxy	500 kPa for 1 h + 750 kPa for 2 h	115 °C for 1 h + 180 °C for 2 h
Polyethylene/epoxy	350	80 °C for 2 h + 120 °C for 2 h
Polyethylene/vinyl ester (type III)	350	40 °C for 1 h + 80 °C for 1 h
Polyethylene/phenolic (type II)	350	60 °C for 1 h + 80 °C for 2 h
Aramid/epoxy	350	80 °C for 2 h + 120 °C for 2 h
Aramid/vinyl ester (type III)	350	40 °C for 1 h + 80 °C for 1 h
Aramid/phenolic (type II)	350	60 °C for 1 h + 80 °C for 2 h

profile to that presented in Fig. 2. The heat release rate was substantially higher for composites with a polyester, vinyl ester or epoxy matrix, compared to those with a phenolic matrix. The HRR results for the composites reinforced with glass fibres are presented in Brown and Mathys [13].

Fig. 3 presents typical HRR curves at 50 kW/m² for vinyl ester composites reinforced with polyethylene and aramid fibres. These curves are very similar in profile to those with other polymer matrices (ie. epoxy, phenolic). The curves for the polyethylene and aramid composites are substantially different from each other and from the profile shown in Fig. 2 for the non-combustible fibre composite. The curve of the composites reinforced with polyethylene shows an initial peak in heat release rate, and this is attributed to the decomposition of fibres close to the surface. The second

larger peak is caused by the combined heat release from the fibres and matrix. The polyethylene fibres at the surface release heat before the polymer matrix because of their lower pyrolysis temperature. UHMW polyethylene begins to decompose in an inert atmosphere at about 290 °C whereas the decomposition temperature of the vinyl ester matrix is about 350 °C [22,23]. The aramid curve in Fig. 3b shows an initial peak due to decomposition of the polymer matrix near the hot surface, followed by a small second peak also due to the polymer matrix near the surface. As opposed to the polyethylene fibres, the aramid reinforcement has a higher pyrolysis temperature ($T \approx 500$ °C) than the vinyl ester, and therefore the matrix releases heat before the fibres [24]. A third broad peak is observed in the heat release-time profile, and this is due to decomposition of both the polymer matrix and aramid fibres. It is also seen that the heat release rates for the composite containing aramid fibres is, on average, much lower. This is because the decomposition of aramid yields a much lower amount of flammable volatiles than polyethylene fibres. Based on the mass loss data

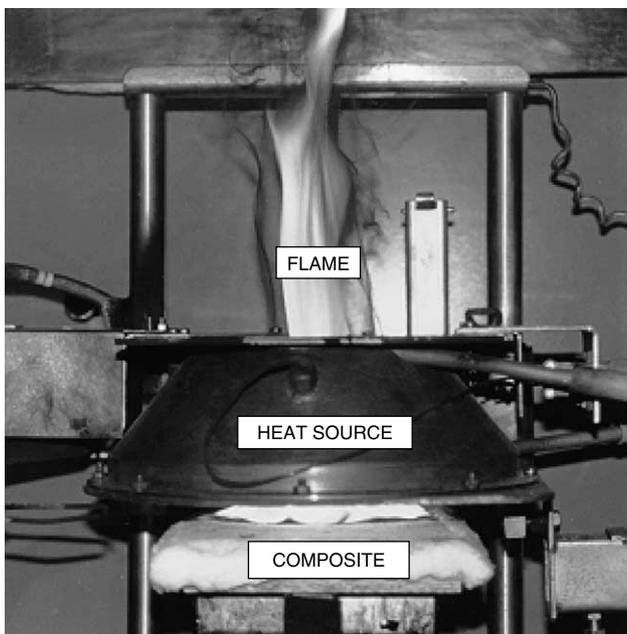


Fig. 1. The cone calorimeter used to measure the fire reaction properties.

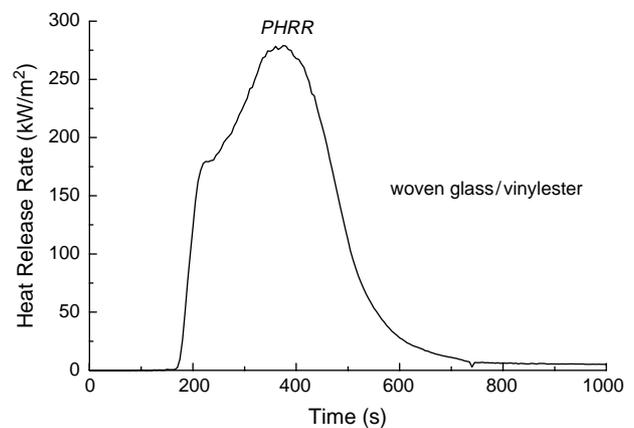


Fig. 2. Typical heat release rate curve for a non-combustible fibre composite. The curve is for a woven glass/vinyl ester composite tested at the heat flux of 50 kW/m².

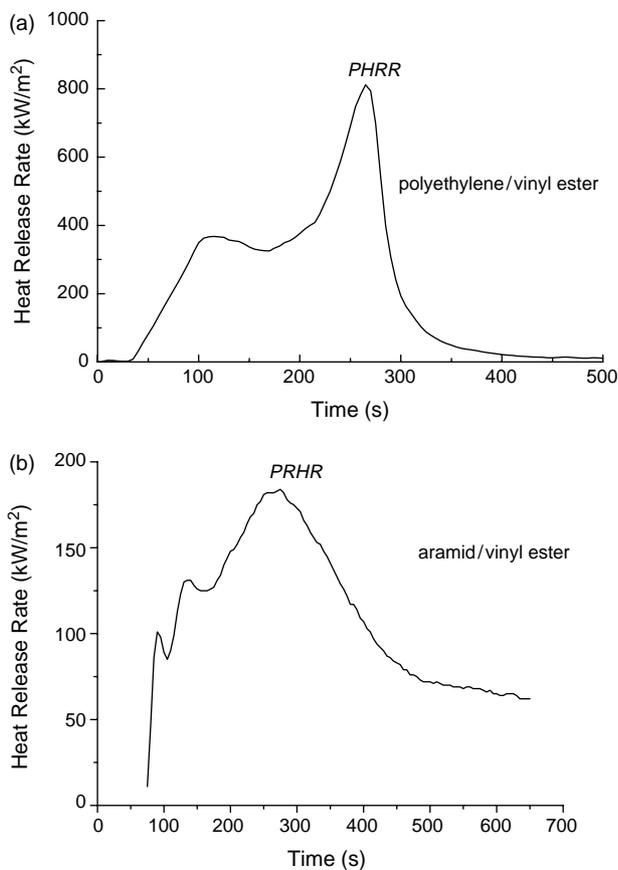


Fig. 3. Typical heat release rate curves for the (a) polyethylene fibre and (b) aramid fibre composites. The curves are for the polyethylene/vinyl ester and aramid/vinyl ester composites tested at the heat flux of 50 kW/m².

measured during the cone calorimetry tests on the fibre only specimens, it is estimated that the aramid and polyethylene fibres yield, respectively, about 55% and 80–85% of their original mass as gas products. The HRR curves for all the composite specimens reinforced with aramid or polyethylene fibres evaluated in this study can be seen in Brown et al. [9].

The thermal decomposition of the resins and organic fibres was investigated further by thermogravimetric analysis (TGA) in an inert (nitrogen) atmosphere. Nitrogen was used as the atmospheric gas in the TGA rather than air or oxygen because (except for the near surface region) the endothermic decomposition reactions of the organic constituents occur with little or no oxygen present. The TGA of the pure resins was performed at a heating rate of 25 °C/min. The TGA curves for the polyethylene and aramid were measured at heating rates of 25 and 10 °C/min by Coneas et al. [22] and Bourbigot et al. [24], respectively. The TGA measurements were performed on the fibre alone in the absence of a polymer matrix.

The remaining mass fraction against temperature curves for the fibres and polymers are presented in Fig. 4. Three types of vinyl ester were used in the composites, but the TGA curve for only one vinyl ester is given because the curves

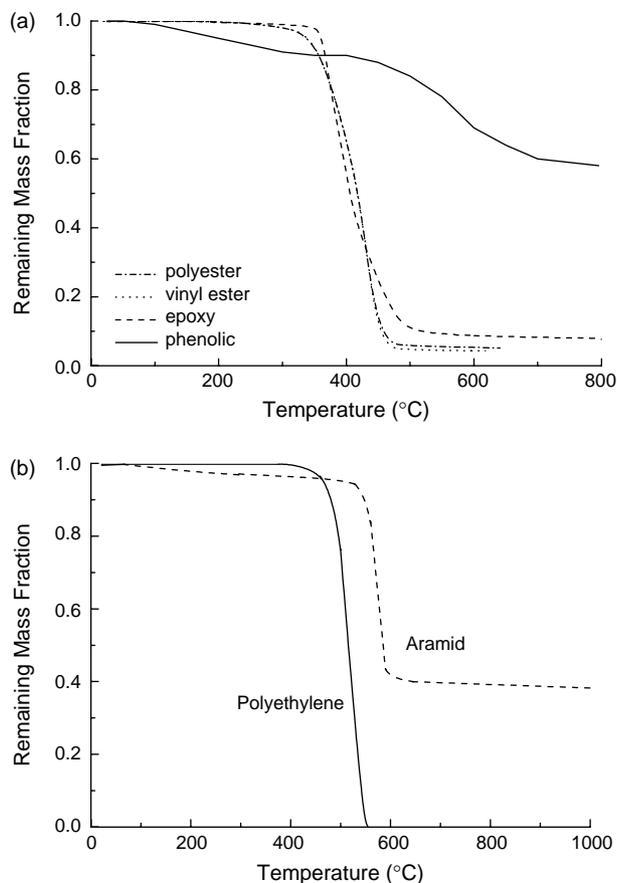


Fig. 4. TGA curves for the (a) polymers and (b) organic fibres.

were virtually identical for the three polymers. Likewise, two types of phenolic resin were used, but only one TGA curve is presented because both polymers had similar curves. Fig. 4 shows that decomposition of the polyester, vinyl ester and epoxy commences at about the same temperature of 350 °C. Above this temperature the resins are rapidly decomposed in an endothermic process that is dominated by random-chain scission of the main polymer chain [23,25–28]. The decomposition reactions are largely complete by 480 °C, with the polyester and vinyl ester leaving less than 5% of their initial mass as char while the epoxy yielded about 10% char. This demonstrates that these resins undergo substantial volatilization, with most of the gases being low molecular weight combustible hydrocarbons [26,28]. The decomposition of the phenolic resin is characterised by multiple-stage reactions. A small loss in mass occurs in the first stage when the phenolic is heated to 100–120 °C, and this is due to the loss of moisture absorbed from the atmosphere together with water formed as a by-product of the cure reaction. The TGA curve remains relatively flat until the main decomposition reaction occurs over a temperature range of 400–500 °C, which yields a large amount of char residual (about 60% of the original mass).

The decomposition of polyethylene occurs as a single-stage process over a similar temperature range as the

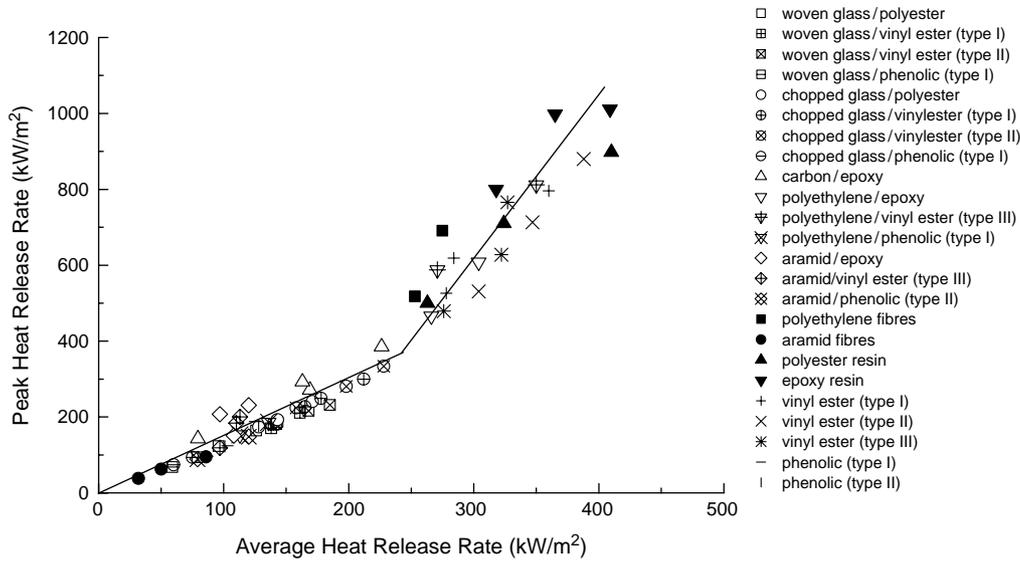


Fig. 5. Plot of AHRR against PHRR for the composites and their combustible fibres and resins.

polyester, vinyl ester and epoxy resin, although this material is completely volatilized and does not produce any char. The decomposition of the aramid fibre, on the other hand, occurs by a series of multiple-stage reactions. A very small loss in mass occurs at about 100–120 °C, and this is due to the loss of moisture absorbed from the air by the fibre. The TGA curve remains flat at higher temperature until the main pyrolysis reaction between 500 and 575 °C [24]. Due to the high aromatic content of aramid, the fibres yield a relatively high amount of char.

Fig. 5 shows the PHRR values for the composites plotted against average heat release rate (AHRR). Included in the figure is heat release rate data for the polyethylene and aramid fibres and resins alone. It is seen that there is a bi-linear relationship between PHRR and AHRR, with a kink in the curve occurring when the AHRR and PHRR reached about 250 and 300 kW/m², respectively. The heat release rate data for the various composite materials, with the exception of the polyethylene laminates, form the initial linear region that is characterised by a gradual rise in AHRR with PHRR. The AHRR and PHRR relationship for the polyethylene composites and the different resins rises more rapidly. Presumably this is because the release rate of

flammable volatiles from the polyester, vinyl ester, epoxy and polyethylene is substantially higher than the glass, carbon and aramid reinforced composites, which increases both PHRR and AHRR at a more rapid rate.

Table 3 gives the linear correlation coefficients between the PHRR and AHRR for the different classes of fibre composites. The number of samples used in the calculation of the correlation coefficients are given in the table, and with the exception of the glass reinforced composites, the sample sizes are small. Despite this, it is apparent that a strong correlation exists for the composites reinforced with glass, carbon or polyethylene fibres ($R > 0.98$). However, the correlation coefficient is relatively low ($R = 0.66$) for the aramid fibre composites. The amount of heat release data for these composites is small (sample size = 8), and significant scatter occurred that significantly reduced the average correlation coefficient. Fig. 6 is a plot of the heat release data for the aramid composites tested at the different heat

Table 3
Correlation coefficient between the peak heat release rate (PHRR) and the average heat release rate (AHRR) for the different types of fibre composite materials

Composite	Linear correlation coefficient (PHRR-AHRR)	Sample size
Glass fibre composites	0.992	22
Carbon fibre composites	0.992	4
Polyethylene fibre composites	0.984	6
Aramid fibre composites	0.659	8

This table corresponds to the data plotted in Fig. 5.

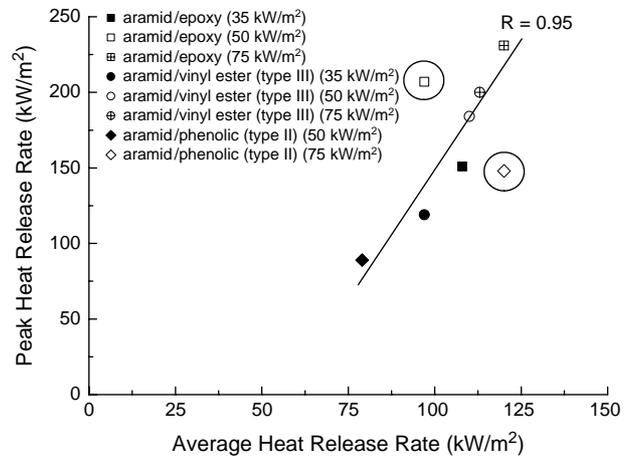


Fig. 6. Plot of AHRR against PHRR for the aramid composites tested at different incident heat fluxes.

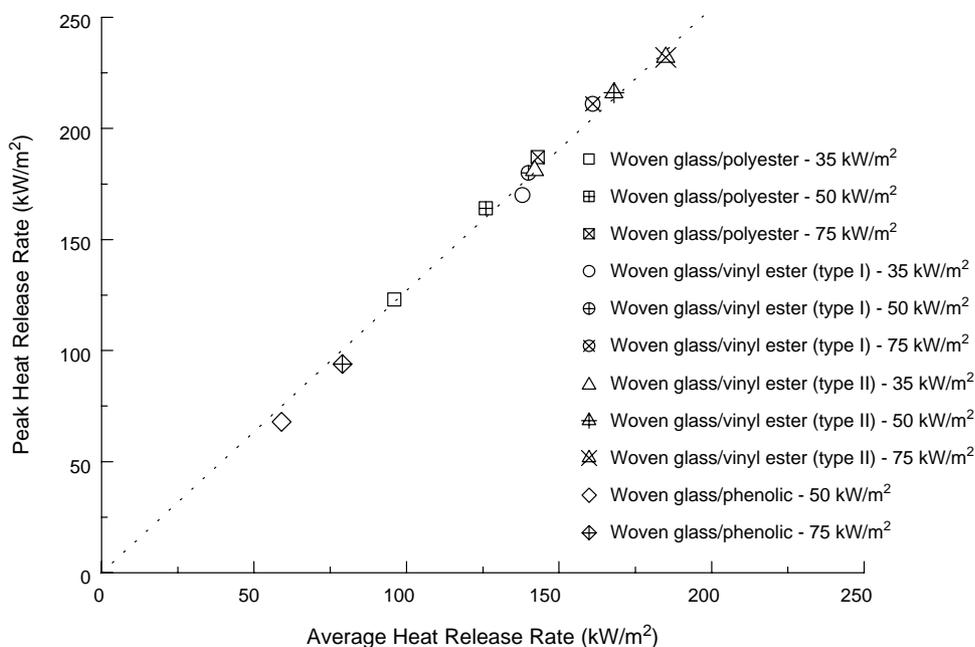


Fig. 7. Plot of AHRR against PHRR for the composites reinforced with woven glass fibres tested at different incident heat fluxes.

fluxes, and it is seen that most of the data shows a linear relationship between PHRR and AHRR. However, there are two out-lying data points (which are circled in the figure) that reduce significantly the linear correlation coefficient due to the small sample size. When these two data points are removed from the analysis the linear correlation coefficient for the aramid composites increases to 0.95.

The linear relationship between PHRR and AHRR for the composites was found to hold over the range of external heat flux levels used. For example, Fig. 7 shows a plot of PHRR against AHRR for the different woven glass composites tested at 35, 50 and 75 kW/m², and the strong linear relationship exists for all heat flux levels. As expected, this figure also shows that both the PHRR and AHRR increase with heat flux due to the increased yield rate of flammable volatiles as a result of the higher decomposition reaction rate of the polymer matrix. However, the figure also shows that the correlation between PHRR and AHRR is not dependent on the external heat flux, at least over the range studied here.

The correlation between PHRR and AHRR was investigated further by examining published heat release data for other types of composites reinforced with non-combustible fibres. Fig. 8 shows a plot of PHRR against AHRR data for the glass and carbon fibre composites studied here, together with data from Sorathia [6] and Koo et al. [19] for a large number of composite systems. This includes data for composites with high temperature thermoset resins (eg. BMI, phthalonitrile) and high temperature thermoplastics (eg. PPS, PEEK, PAS). With the exception of a few data points, it is seen that a strong linear relationship exists between PHRR and AHRR for this diverse range of composite materials. The correlation

coefficient for all the data, including the out-lying points, is 0.94. Therefore, the linear relationship found between PHRR and AHRR for the materials studied here appears to be universally true for all types of thermoset and thermoplastic composites.

3.2. Relationship between smoke formation and heat release rate

Many types of polymer composite release dense smoke that limits visibility and can cause disorientation for people attempting to escape from a fire. The smoke consists of fine soot particles (typically less than 2 μm) produced by the thermal decomposition of the polymer matrix and (if present) organic fibres. Smoke can also contain microscopic fragments of non-combustible fibres, although these usually account for a small percentage of the total smoke content. The importance of smoke in human survival in a fire has prompted the characterisation of the smoke properties for a wide variety of thermoset and thermoplastic matrix composites [5–7,10,13–17,29–31]. However, the relationship between smoke density and heat release rate has not been fully investigated.

Fig. 9 presents a plot of the average specific extinction area (SEA) values against AHRR. As expected, the phenolic composites have a significantly lower smoke yield than the polyester, vinyl ester and epoxy composites due to their higher char yield. Furthermore, the composites containing aramid fibre produce less smoke than the glass composites with epoxy and vinyl ester polymer matrices. It appears that the charring process that occurs in composites with aramid fibre and/or a phenolic matrix causes a reduction in the smoke yield. The SEA values for all the composites show

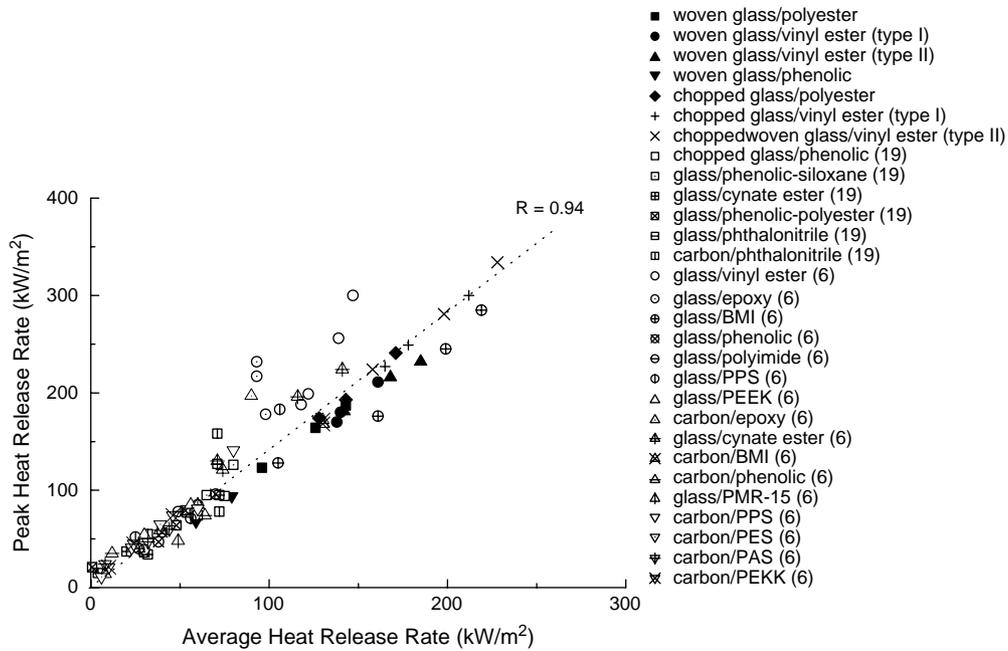


Fig. 8. Plot of AHRR against PHRR for a wide variety of glass and carbon reinforced composites containing thermoset or thermoplastic resins.

a general linear increase with heat release rate in Fig. 9, although the rate of increase is much lower for the composites containing polyethylene fibres. Presumably this is because of the higher heat release rate due to the increased yield of flammable volatiles from both the polyethylene fibres and polymer matrix. Table 4 shows the linear correlation coefficient values between SEA and the peak and average heat release rates. The linear correlation coefficient values for the glass, carbon and polyethylene fibre composites are above 0.88, indicating that the heat release rate of these materials has a strong relationship to smoke density. It is believed that this relationship exists because the endothermic decomposition

of the polymer matrix and organic fibres determines both the heat release rate and the amount of smoke released. The correlation coefficient is not as high for the aramid fibre composites.

The dependence of smoke density on HRR for composites with non-combustible fibres was investigated further by analysing published smoke data for other types of composite reinforced with glass or carbon fibres. Fig. 10 presents a compilation of our smoke data with data by Sorathia [6] for various types of thermoset and thermoplastic matrix composites. Despite some scatter (particularly for the glass/BMI), there is a general increase in SEA with AHRR, with a correlation coefficient of 0.78.

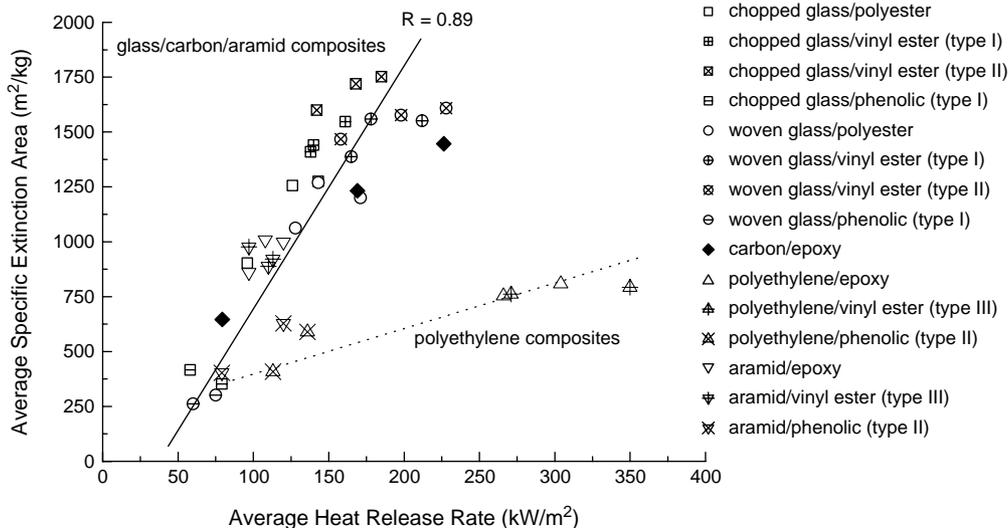


Fig. 9. Plot of average SEA against AHRR for the composites.

Table 4

Linear correlation coefficients for smoke specific extinction area (SEA) against the heat release properties for the different types of fibre composite materials

Composite	Linear correlation coefficient (Av. SEA-PHRR)	Linear correlation coefficient (Av. SEA-AHRR)	Sample size
<i>Average Smoke Extinction Area (SEA)</i>			
Glass fibre composites	0.992	0.888	22
Carbon fibre composites	0.974	0.991	4
Polyethylene fibre composites	0.879	0.929	6
Aramid fibre composites	0.606	0.518	8

This table corresponds to the data plotted in Fig. 9.

This further supports the observation that the smoke produced is (in almost all cases) strongly related to the heat release rate.

3.3. Relationship between CO and CO₂ yields and heat release rate

The gas products released by a decomposing composite depend on the chemical nature of the organic constituents, oxygen availability, and the temperature of the fire. Tewerson and Macaione [32], for example, have shown that polyester matrix composites can release a mixture of gases that include CO, CO₂, low molecular weight organics such as propylene, benzene, toluene and styrene, and organic ring compounds including aromatic C–H and aromatic C–H–O. As another example, phenolic laminates yield, in addition to water, CO, CO₂, toluene, benzene and various aromatic compounds. While the types and amounts of the gas products can vary between materials, all polymer composites release CO and CO₂ [5,6,15,19,29,32]. CO is a major safety concern because it is lethal at a relatively low concentration, with human death occurring within one hour at a concentration of about 1500 ppm. Babrauskas [3] suggests that the yield of CO

and CO₂ from combustible materials is related to the heat release rate properties, but as yet this dependence has not been investigated for composites.

Plots of the average yields of CO and CO₂ gases against AHRR for the composites are shown in Figs. 11 and 12. It is apparent that an increase in HRR is almost always associated with an increase in the CO yield. The linear correlation coefficients for the individual classes of composites are given in Table 5 which shows there is a good correlation between the CO yield and both peak and average heat release rate, except the aramid fibre laminates. Carbon monoxide is a reaction product of the incomplete combustion of volatiles at the fire/composite boundary. It can also be a by-product of the decomposition of certain polymers. An increase in the heat release rate, which is a measure of the decomposition rate of the volatiles, should therefore be accompanied with an increase in the yield of CO gas.

Fig. 12 shows that the average yield of CO₂ gas is not as strongly related as the CO yield on the heat release rate. The CO₂ yields for all the composites fall within the limits of ~1–2 kg/kg, and appear to be independent or only weakly related to the heat release rate. This seems to indicate that the mechanisms controlling the CO₂ yield are complex

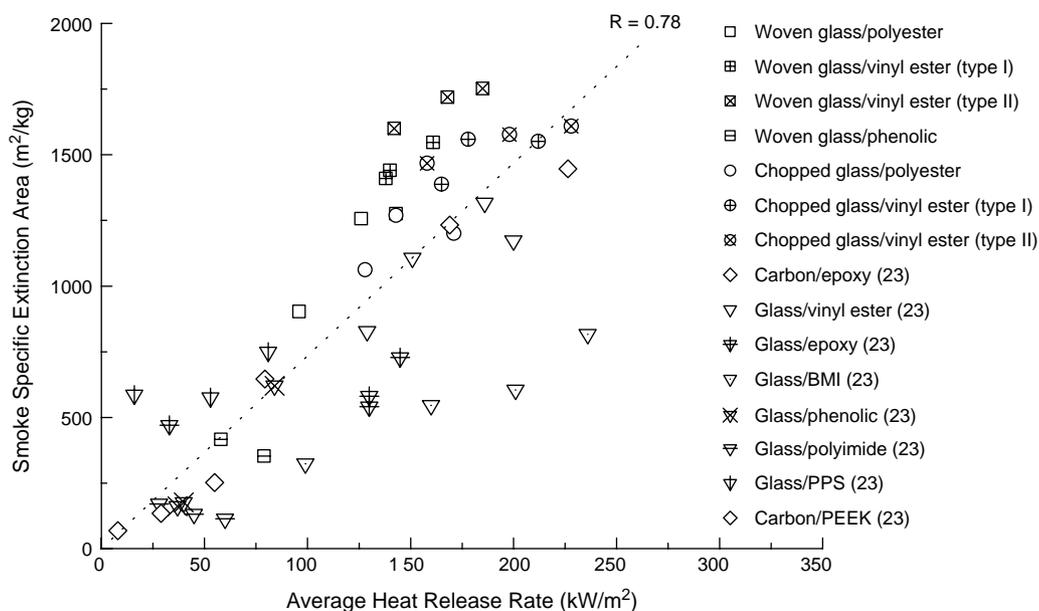


Fig. 10. Compilation of data showing relationship between average smoke specific extinction area and average heat release rate for various thermoset and thermoplastic matrix composites reinforced with non-combustible fibres.

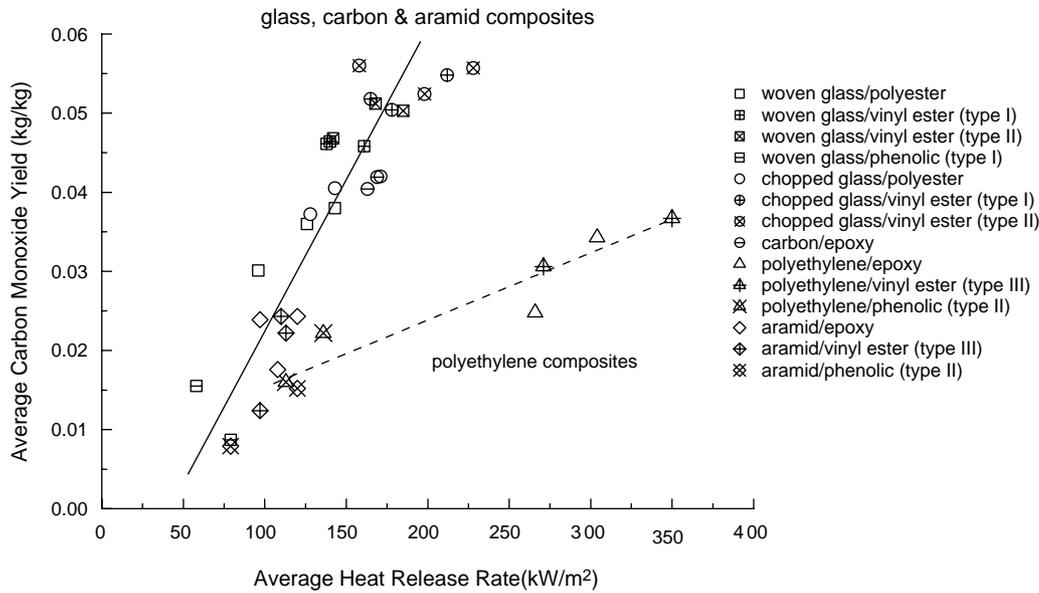


Fig. 11. Plots of AHRR against the average CO yield for the composites.

and are dependent on factors other than just the heat release rate. It is likely that CO₂ shows a weaker relationship than CO on heat release rate because the CO₂ yield is determined not only by the decomposition reaction rate but also by oxygen availability in the fire. The strong influence of oxygen availability on the production of CO₂ may mask any dependence of CO₂ yield on heat release rate. The cone calorimeter technique has a high flow rate of air passing through the fire test chamber, and this should ensure sufficient oxygen is available to produce CO₂.

It is interesting to note, however, that the linear correlation coefficient values in Table 5 for the composites with non-combustible fibres are positive whereas the values for the composites with combustible fibres are negative, suggesting that for these materials a reduction in the CO₂

yield will occur with increasing heat release rate. An analysis of data from other fire studies performed on high temperature polymer composites report data that also shows the CO₂ yield is slightly related to or independent of heat release rate [6,19].

The relationship between the peak heat release rate and the peak yield rates of CO and CO₂ gases from the composites was also investigated. A strong correlation between the PHRR and peak gas yields for CO and CO₂ was observed for both the woven glass and chopped glass fibre composites. For example, Fig. 13 shows that the peak yields of CO and CO₂ increased at a linear rate with the PHRR for the woven glass composites. In this material, the PHRR is a measure of the maximum rate of thermal decomposition of the polymer matrix. It is to be expected that the maximum

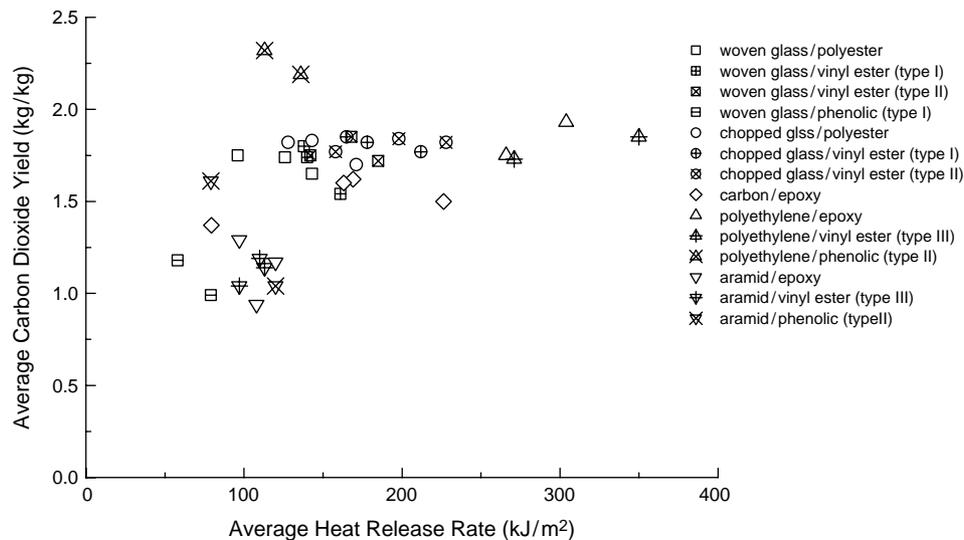


Fig. 12. Plot of AHRR against the average CO₂ yield for the composites.

Table 5

Linear correlation coefficients for (a) CO and (b) CO₂ yields against the heat release properties for the different types of fibre composite materials

Composite	Linear correlation coefficient (Av. CO-PHRR)	Linear correlation coefficient (Av. CO-AHRR)	Sample size
<i>Average CO yield</i>			
Glass fibre composites	0.891	0.918	22
Carbon fibre composites	0.924	0.992	3
Polyethylene fibre composites	0.952	0.938	6
Aramid fibre composites	0.960	0.619	8
Composite	Linear correlation coefficient (Av. CO ₂ -PHRR)	Linear correlation coefficient (Av. CO ₂ -AHRR)	Sample size
<i>Average CO₂ yield</i>			
Glass fibre composites	0.756	0.736	22
Carbon fibre composites	0.573	0.544	3
Polyethylene fibre composites	-0.795	-0.841	6
Aramid fibre composites	-0.257	-0.709	8

This table corresponds to the data plotted in Figs. 11 and 12.

yield of combustion gases, including CO and CO₂, will be dependent on the maximum decomposition reaction rate and thereby the PHRR. Table 6 shows the linear correlation coefficients between PHRR and maximum CO and CO₂ yields, and the correlation is strong for the fibreglass composites. However, the correlation is poor for the combustible fibre laminates.

3.4. Ignition time

Time-to-ignition is an important fire reaction property because it defines the time that a composite material can withstand the heat flux radiated by a fire before it experiences sustained flaming combustion. A plot of ignition time against AHRR for the composites is presented in Fig. 14. Included in the plots are the ignition times for the different resins and the combustible fibres. No clear correlation is seen between the heat release rate and ignition times for any of the material systems.

Table 7 gives the linear correlation coefficients between the ignition time and the PHRR and AHRR values, and for

the glass and polyethylene fibre composites the values are low. However, the correlation is reasonably good for the carbon and aramid fibre laminates. Based on this analysis, it is difficult to conclude that heat release rate is related to the ignition time. Although, it would be expected that no correlation exists between time-to-ignition and heat release rate. This is because ignition of the composite specimens (with the exception of the phenolic matrix laminates) occurred before any appreciable amount of heat had been released. Ignition usually occurs at a time well before the composite reaches its PHRR, and therefore no relationship is expected. The AHRR is a measure of the average amount of heat released by a composite over the entire combustion process, whereas ignition is an instantaneous event that occurs very early in the combustion process when the temperature is sufficiently high and the rate of decomposition produces sufficient volatiles to commence flaming combustion. For this reason, no correlation should be expected between ignition time and heat release rate properties. Instead, other studies have shown that the ignition time is dependent on the decomposition reaction temperature and mass loss rate of a composite [4,33].

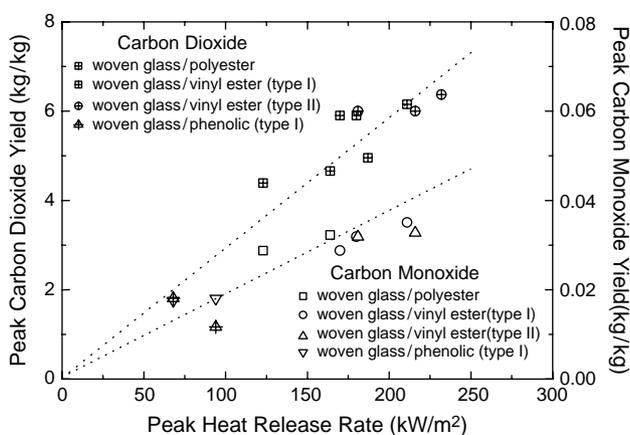


Fig. 13. Plot of PHRR against the peak yields of CO and CO₂ gases from the woven glass composites.

3.5. Relationship between mass loss and heat release rate

Fig. 15 shows the relationship between total mass loss and AHRR for the composites reinforced with combustible and non-combustible fibres. The total mass loss is a measure of the extent of thermal decomposition and subsequent volatilisation of a combustible material in fire. As expected, the total mass loss values for the composites containing combustible fibres are generally much higher than the non-combustible fibre laminates because the organic fibre reinforcement and polymer matrix are both degraded. Table 8 shows the linear correlation coefficients between the mass loss and heat release rate properties, and a good correlation exists for the glass and carbon composites. This is because an increase in the heat release rate generally

Table 6

Linear correlation coefficients for the peak yields of CO and CO₂ gases with the peak heat release rates for the different types of fibre composite materials

Composite	Linear correlation coefficient (Peak CO-PHRR)	Linear correlation coefficient (Peak CO ₂ -PHRR)	Sample size
Woven glass composites	0.913	0.928	9
Chopped glass composites	0.916	0.871	11
Polyethylene fibre composites	0.817	−0.438	4
Aramid fibre composites	0.558	0.214	7

This table corresponds to the data plotted in Fig. 13.

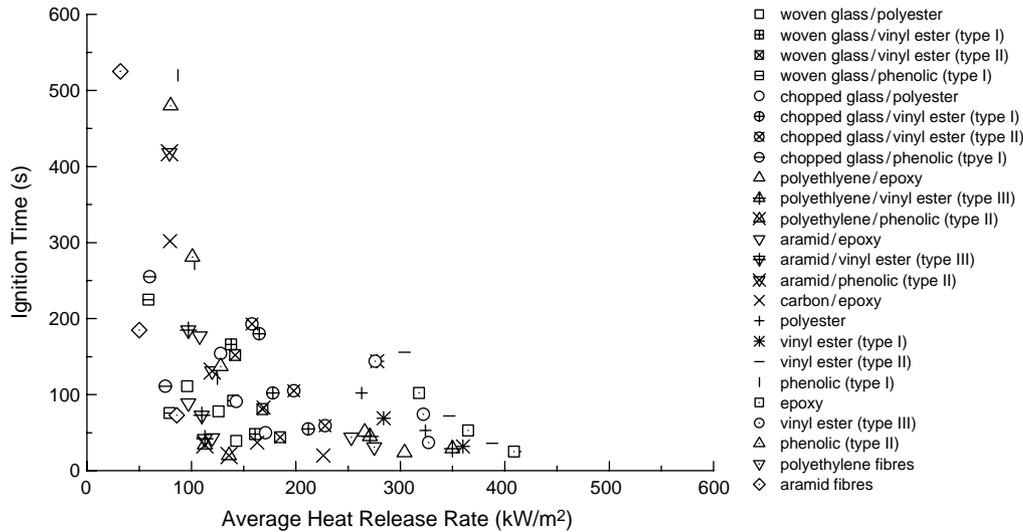


Fig. 14. Plot of AHRR against ignition time.

indicates more complete pyrolysis and volatilisation of the polymer matrix, resulting in a greater loss in mass. Although it is interesting to note that the correlation coefficient values for mass loss are higher for PHRR than AHRR. With both the aramid and polyethylene fibre composites, on the other hand, the mass loss does not show a strong relationship with their HRR properties.

The relationship between the heat release rate and the peak and average mass loss was also studied. Fig. 16 shows plots of PHRR against peak mass loss rate and AHRR against average mass loss rate for the composites, resins and combustible fibres. Both plots show a strong linear correlation, which is to be expected because both the heat release rate and mass loss rate are dependent on the decomposition reaction rate. The linear dependence between heat release rate and mass loss rate is indicative

that the materials have similar values for heat of combustion. Brown et al. [9] and Brown and Mathys [12] measured the effective heat of combustion for the combustible and non-combustible fibre composites, respectively. The materials were indeed similar, with almost all the composites having effective heat of combustions values within the range of 19–23 MJ/kg except for the polyethylene composites that had higher values of between 30 and 33 MJ/kg.

4. Conclusions

Heat release rate is recognised as the single most important fire reaction property of combustible materials. This study has shown that heat release rate is strongly

Table 7

Linear correlation coefficients for ignition time against the heat release properties for the different types of fibre composite materials

Composite	Linear correlation coefficient (Ignition time-PHRR)	Linear correlation coefficient (Ignition time-AHRR)	Sample size
Glass fibre composites	−0.500	−0.535	22
Carbon fibre composites	−0.933	−0.925	4
Polyethylene fibre composites	0.136	0.183	6
Aramid fibre composites	−0.890	−0.816	8

This table corresponds to the data plotted in Fig. 14.

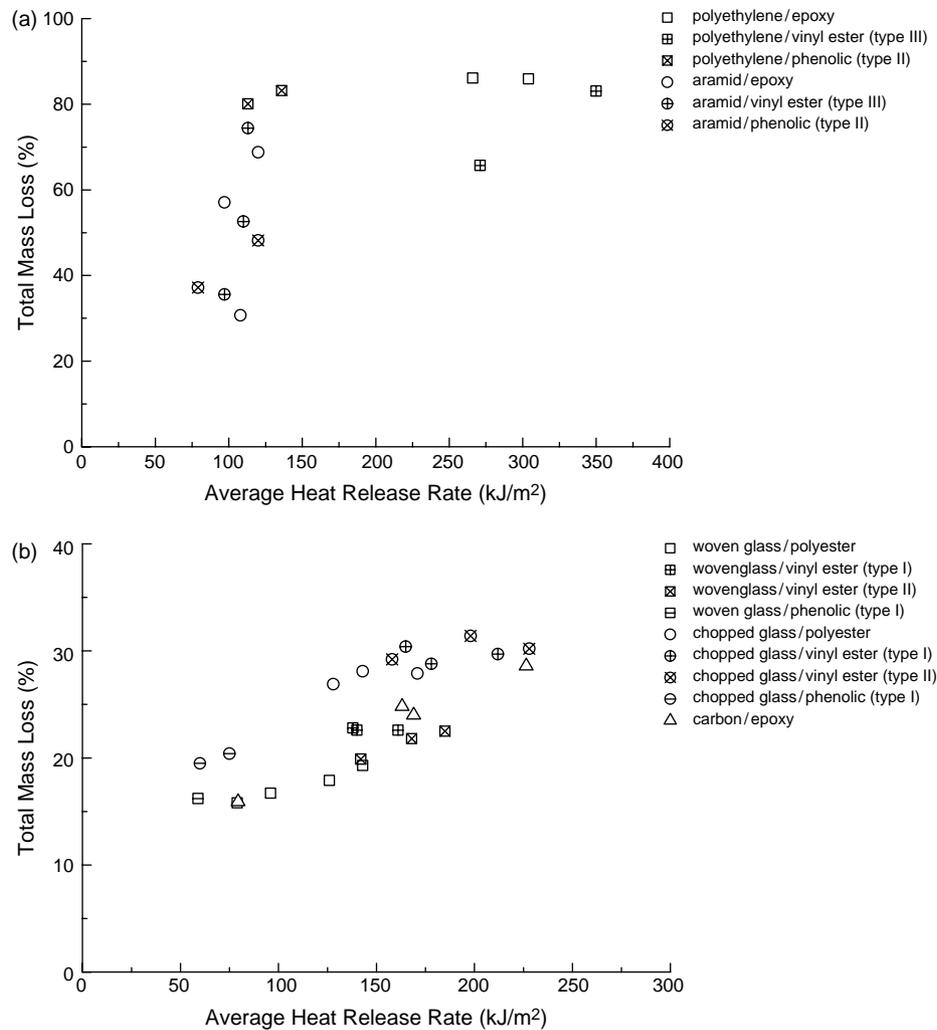


Fig. 15. Plots of AHRR against total mass loss for the (a) combustible fibre composites and (b) non-combustible fibre composites.

related to several fire reaction properties of composites reinforced with combustible or non-combustible fibres when measured using an oxygen consumption cone calorimeter. It is important to note that the relationships observed here between heat release rate and other reaction properties are for well-ventilated fire conditions (as experienced in the cone calorimeter), and these relationships may be altered under different fire conditions, such as a fire environment with a low oxygen content.

Smoke extinction area, yield of carbon monoxide gas, mass loss rate and total mass loss all increase linearly with

HRR for composites with non-combustible fibres. This is because the endothermic decomposition reaction rate of the polymer matrix and heat release rate are related. The HRR and mass loss rate, as is expected, are also similarly related. The PHRR and AHRR for composites with non-combustible fibre are linearly related, and therefore the smoke, carbon monoxide yield and mass loss properties show a strong correlation with both of these heat release rate parameters. While the magnitude of the external heat flux affected the magnitude of the fire reaction properties, the correlations observed between heat release rate and the other

Table 8

Linear correlation coefficients for total mass loss against the heat release properties for the different types of fibre composite materials

Composite	Linear correlation coefficient (Mass loss-PHRR)	Linear correlation coefficient (Mass loss-AHRR)	Sample size
Glass fibre composites	0.817	0.771	22
Carbon fibre composites	0.991	0.989	4
Polyethylene fibre composites	-0.078	0.024	6
Aramid fibre composites	0.825	0.517	8

This table corresponds to the data plotted in Fig. 15.

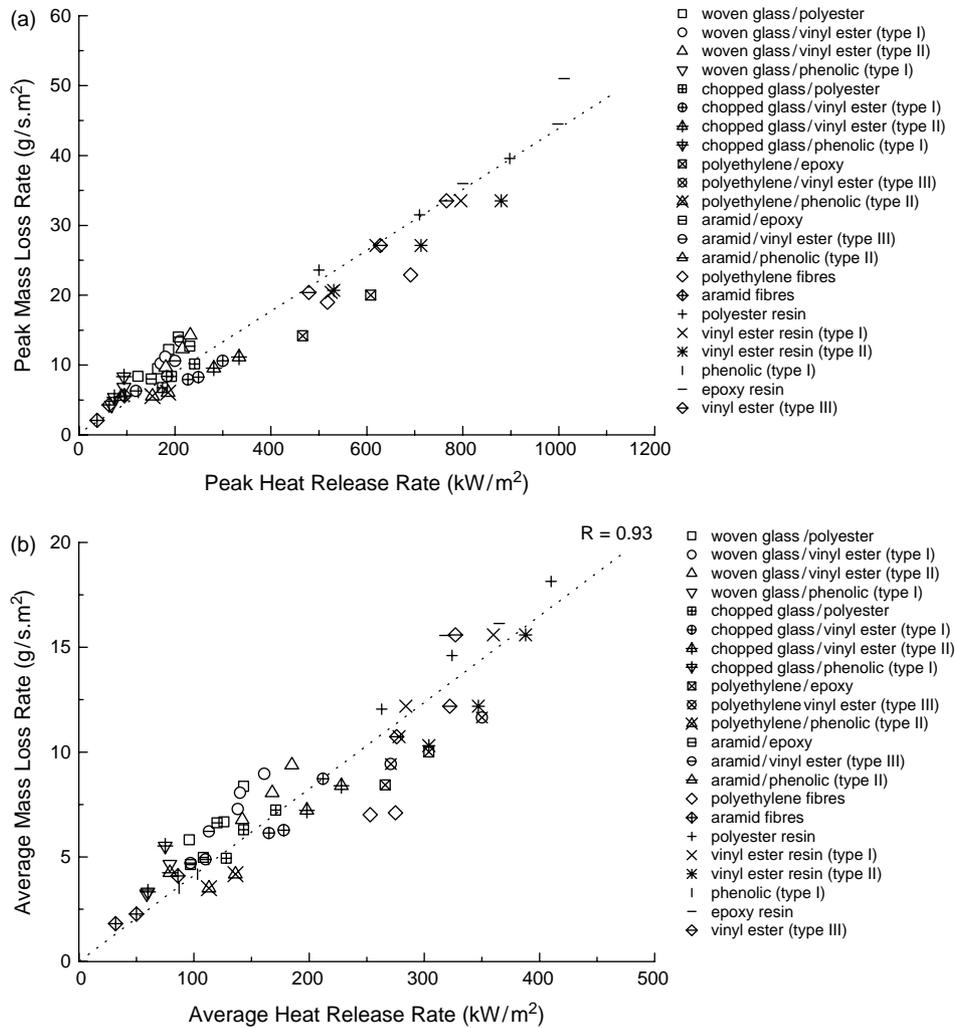


Fig. 16. Plots of (a) PHRR against peak mass loss rate and (b) AHRR against average mass loss rate for the composites.

properties occurred for all heat flux levels. The only reaction property measured in this study for the non-combustible fibre composites that is not clearly related to heat release rate is the time-to-ignition. This is because the ignition time is controlled by other factors, most notably the decomposition reaction temperature of the organic constituents.

Compared with the composites containing non-combustible fibres, the heat release rate of the laminates with combustible fibres does not appear to be as strongly related to as many fire reaction properties. The only properties that show a strong correlation with HRR are the yield of carbon monoxide gas and the mass loss rate. Smoke density, carbon dioxide yield and total mass loss are only slightly related to or independent of the heat release rate.

The incident heat flux appears to have no significant influence on the relationships observed between HRR and the other fire reaction properties. When a strong correlation exists between the HRR and another reaction property, this correlation occurs regardless of the magnitude of the incident heat flux over the range studied here (25–100 kW/m²). As expected, however, many of the

reaction properties, including HRR, increased with the heat flux.

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