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Towards the Development of a Test and Design Framework for Fire Engineering with Fibre Reinforced Thermoplastics

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Abstract

Thermoplastic composites are under intensive development and are rapidly gaining traction in the aerospace, automotive, marine, and building and construction industry. Their light-weighting potential, low cost, capacity for recycling and the high degree of freedom in their manufacturing makes thermoplastics composites desirable in many industries. Nevertheless, in order to be able to use thermoplastic composites in high temperature applications, it is important to understand their fire performance. Parameters such as the effect of fibre architecture, fibre length, fibre type, and matrix type are all critical for fire engineering considerations in thermoplastic composite materials.

A literature review was conducted on the fire performance of composite materials, revealing that most studies related to the fire performance of composite materials focused on continuous fibre reinforced thermosetting composites and was predominately geared towards applications in the aerospace sector. In cases where fibre reinforced thermoplastics were investigated, the research was primarily concerned with establishing the effectiveness of various additives and nanofillers. The effect of matrix nature, fibre length, and fibre type on the fire performance of such materials has not yet received sufficient attention.

The research for thesis aims to address some of these identified gaps through an in-depth investigation. The principle aim of the study is to establish a nexus between key fire parameters, composite constituent properties, and manufacturing parameters. Understanding this nexus is an important step towards the development of a design framework for the fire engineering of thermoplastic matrix composites.

Prior to studying gaps found in literature, the fire performance of continuous glass fibre reinforced polypropylene (PP) was investigated in order to explore the fire performance of a commercially available composite. The transition from thermally thin to thermally thick was found to occur right in the range of part thickness relevant to practical composite applications (i.e., 3-10mm). It was found that the effective heat of combustion of the polypropylene matrix was different to that found in other studies, suggesting the possibility of different additives modifying the chemical structure of polypropylene.

Next, the gaps identified in the literature were examined. First, the effect of fibre architecture was addressed through studying the fire performance of a polycarbonate resin and the role of glass fibre reinforcement in altering its fire performance. Results showed that glass fibre reinforcement improves PC performance by delaying its ignition, decreasing its heat release rate, and lowering the mass loss rate. Three fibre weave types were tested and exhibited similar times to ignition. However, unidirectional fibre had a 35% lower peak heat release rate when compared to plain and twill weave fibres.

Second, the effect of fibre length on the fire performance of fibre reinforced non-charring polymer composites was studied. Polypropylene composite was investigated with respect to the fibre length and modification of the matrix. Three different fibre lengths, 3 mm, 12 mm, and continuous fibres, were used as reinforcements. Results showed that continuous glass fibre reinforcement exhibited the best fire performance at 20 kW/m^2; while 3mm fibre had the best performance at 35kW/m^2. 12mm fibre reinforced polypropylene exhibited the lowest performance in comparison to 3mm and continuous glass fibre reinforcement. Melic-anhydride (MA) modified PP was found to increase the heat release rate by up to 44% and the time to ignition by up to 10%. The glass fibre reinforced composite made with MA modified PP had a 5 to 12% lower mean heat release rate and a similar time to ignition in comparison to the glass fibre composite made by unmodified PP. This suggests improved fibre adhesion plays a role in the fire performance of glass fibre reinforced polypropylene.

Third, the effect of fibre type and fibre length on the fire performance of fibre reinforced charring matrix composites was studied. Glass, basalt and carbon fibre reinforced PC with 6 mm, 12 mm, and 20 mm long fibre reinforcement composites were tested. Transient plane thermal conductivity measurements were taken from 30°C to 160°C to determine the in-plane and out-of-plane thermal conductivity. A flame spread test was conducted to the measure flame spread rate and critical heat flux for flame spread.

This complementary information, which is rarely found, provides a more complete picture of factors driving the various fire performance aspects. For example, the results clearly show that for low conductive fibres, fibre length is not a relevant factor. As the thermal conductivity of the fibre increases, the contribution of the fibre length becomes a significant factor. The results show that composites with high thermal conductivity take a longer time to ignite. On the other hand, a higher thermal conductivity also results in a higher heat release rate, more rapid flame spread, and higher mass loss rate.

After studying different aspects of the fire performance of thermoplastic composites, a comparison was made with a thermoset composite in terms of fire and post-fire properties. The fire performance of a continuous glass fibre reinforced polycarbonate thermoplastic composite was evaluated against the fire performance of a continuous glass fibre reinforced epoxy thermoset composite. Both composites had a fibre volume fraction of 47% and nominal thickness of 3.9 mm. Plain weave fabric was used with both composite. The two composites were compared at incident heat fluxes of 25 kW/m^2, 35 kW/m^2, and 50 kW/m^2. A post-fire four bending test was used to investigate the post-fire residual mechanical properties.

Finally, the way the choice of fibre and matrix can affect fire properties of composite materials was investigated through a number of tests that took into account the fibre type, fibre form, and matrix type. This research ultimately proposes a qualitative decision framework to select constituents for cases where fire performance of the composite is of concern.

Declaration by author

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Publications included in the thesis

Journal papers

1- Y. M. Ghazzawi, A.F. Osorio, and M.T. Heitzmann, *The effect of fibre length and fibre type on the fire performance of thermoplastic composites: The behaviour of PC as an example of charring matrix*. Journal of Constructions and Building Materials 2020, Vol. 234, 117889 (Chapter 7)

2- Y. M. Ghazzawi, A.F. Osorio, D. Martin ,A. P. Basnayake, and M.T. Heitzmann, *The effect of fibre length on the fire performance of thermoplastic composites: The behaviour of PP as an example of non-charring matrix.* Submitted to: Journal of Thermoplastic Composite Materials 2020 (Chapter 6)

3- Y. M. Ghazzawi, A.F. Osorio, and M.T. Heitzmann, *Fire performance of continuous glass fibre reinforced polycarbonate composites: The effect of fibre architecture on the fire properties of polycarbonate composites.* Journal of Composite Materials 2018, Vol. 53(12), pp.1705-1715 (Chapter 5)

Peer-reviewed Conference papers

1- Y. M. Ghazzawi, A. P. Basnayake, A.F. Osorio, J. H. Medina, and M.T. Heitzmann, *Fire and post fire properties of glass fibre reinforced epoxy and polycarbonate composite: A comparative study.* 22nd International Conference of Composite Materials (ICCM22), Melbourne-Australia, 2019 (Chapter 8)

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Contributions by others to the thesis

Contributor	Statement of contribution
M. T. Heitzmann	Paper editing and supervision
A. F. Osorio	Paper editing and supervision
D. Martin	Paper editing and supervision

Chapter 4

A. S. Castaneda helped (PhD student, University of Queensland) in performing the Icone test for glass fibre reinforced polypropylene samples.

Chapter 5

Dr. Toseef Ahmed (Scientist, SABIC) performed the scanning electron microscopy for the burned glass fibre reinforced polycarbonate sample.

C. Kudisonga (PhD student, University of Queensland) performed the thermogravemetric analysis for the glass fibre reinforced polycarbonate samples.

Chapter 6

A.P. Basnayake (PhD student, University of Queensland) performed the 3D C-scan and the thermogravemetric analysis for the glass fibre reinforced polypropylene samples.

Dr. M. Murphy (postdoctoral research follow, University of Queensland) organized differential scanning calorimetry for glass, basalt, and carbon fibre reinforced polycarbonate samples.

Statement of parts of the thesis submitted to qualify for the award of another degree

No works submitted towards another degree have been included in this thesis

Research involving human or animal subjects

No animal or human subjects were involved in this research

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Composite materials, fire performance, fibre length, fibre type, thermal conductivity, polycarbonate, polypropylene, cone calorimetry, LIFT apparatus

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DSC	Differential Scanning Calorimetry
EHC	Effective Heat of Combustion
FTIR	Fourier Transform Infrared
FST	Fire, Smoke, and Toxicity
HRR	Heat Release Rate (per unit area)
PP	Polypropylene
PC	Polycarbonate
PPO	Polyphenylene Oxide
PEI	Polyether Imide
PEEK	Polyether Ether Ketone
SABIC	Saudi Basic Industries Corporation
STA	Simultaneous Thermal Analysis
SEM	Scanning Electron Microscope
Ti	Time to ignition
Tg	Glass Transition Temperature
TGA	Thermal Gravimetric Analysis
Tm	Melting Temperature

1. Introduction

1.1 Motivation

Stringent emission reduction directives and an increased consumer awareness drive demand for lightweight materials with high mechanical and physical properties. These are properties that composite materials are predestined to satisfy. A particularly promising class of composite materials are thermoplastic matrix composites. In addition to great light weighting potential, thermoplastic composites are advantageous compared to their thermosetting cousins, when it comes to short-cycle-time potential, recyclability, and low cost. They can be moulded into complex shapes and welded together, enabling functional integration and the reduction of parts and assembly operations. These are compelling reasons for the use of thermoplastic matrix composites in many applications and strong drivers for the continued growth of the composite sector (see Figure 1.1).

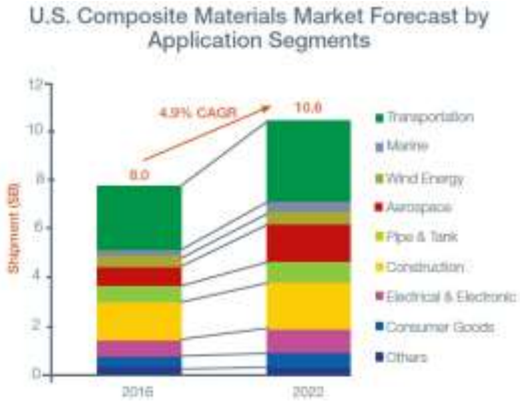

Figure 1.1: US composite market forecast. Taken from [1]

Fibre reinforced thermoplastic composites are rapidly gaining popularity in a large number of industries, foremost the mass transport industry (see Figure 1.1). Technological advances such as organo sheet forming in combination with injection over-moulding has enabled the mass production of highly reinforced thermoplastic composite materials. Applications which warrant the use of the structural materials often also have fire performance requirements [2-4].

It is well understood that both the fibre and matrix contribute to composite properties. While the prediction of the mechanical properties of composites from their constituent properties has been researched for the past 60 years and methods such as rule of mixture, classical laminate theory or the use of failure models are well accepted, the prediction of fire performance is not well established and fire-related accidents are still occurring [2-11].

Not unlike their mechanical properties, the fire performances of matrices and fibres differ greatly. The matrix is typically an organic material with low thermal stability. On the other hand, the majority of technical fibres are thermally stable, which gives them a favourable fire performance. One major difficulty associated with the fire engineering of composite materials is that one cannot just look at the constituent properties individually to determine the fire performance of the resultant composite. There is a complex interaction between the fibre, matrix and additives, which greatly affects the behaviour of the material during a fire. For example, a change in the matrix type changes the charring behaviour and, in return, significantly alters the fire performance of a composite.

The work done to predict and compare the fire properties of composites in the literature remains patchy. There is a large variety of thermoplastic polymers to choose from, and even polymers of the same type can vary greatly depending on the specific commercial grade. Very often, differences between grades and the specifics of the polymer chemistry of a given grade are closely guarded trade secrets. Furthermore, the presence of additives such as fire retardants, compatibilizers, and fillers makes determining the fire properties of composites even more challenging since these additives have their own fire properties, not to mention that in many cases, the formulation and ingredients are not disclosed. These factors make it extremely challenging to compare research results even if the same polymer type and fibre was used.

On top of the already complex matrix composition, there are further parameters to be taken into account once fibres are added. Parameters such as fibre type, fibre form or fibre length all have the potential to change the behaviour of the composite during a fire event. In addition, popular test methods such as the UL94 method or other Bunsen burner tests, while simple to conduct, present a complex boundary condition. This makes it challenging to extract the fundamental mechanisms from these tests that are necessary to study fire behaviour with a more holistic approach.

This thesis aims to establish a better understanding of the complex constituent interactions of some sample composite materials during a fire event and ultimately leads to the development of a test and design framework. This work systematically explores the contribution of the matrices and fibres to fire behaviour based on a carefully selected test matrix. Two polymer matrices are considered in this study. One is a commodity low char matrix (polypropylene) and one is an intermediate char yield engineering matrix (polycarbonate). Fibres ranging from 3 mm long to 20 mm long were used to explore the effect of fibre length. While glass fibre was the main fibre used in the study, carbon and basalt fibre were also investigated in order to explore the role of fibre type. Plain, twill, and unidirectional (UD) fabrics were used in order to study the role of fibre architecture on the fire performance of composites. All composites tested in this study were specifically produced for the purpose of this research and have been produced with constituents where the type, grade and additives were known.

1.2 Aims and objectives

The aim of the research for this thesis is to study the fire performance of fibre reinforced thermoplastic composites. Fibres included in the study are glass, basalt, and carbon fibre; using polypropylene and polycarbonate as fibre matrices. The heat release rate, time to ignition, heat of combustion, flame spread rate, mass loss rate, critical heat flux, and basic char formation behaviour are the fire properties included in the examination. A heat flux range from 25 to 70 kW/m^2 is considered in the study. The research has the following objectives:

I. Develop a fundamental understanding of the evolution of key fire performance properties when transitioning from an unreinforced to a fibre reinforced thermoplastic composite structure.
II. Investigate the role of the matrix type on fire performance.
III. Investigate the effect of different fibre architecture, fibre lengths, and fibre types on the key fire performance properties of the composites.
IV. Suggest a qualitative design/decision framework to guide the selection of composites based on fire performance considerations.

1.3 Thesis outline

The researcher considered two types of thermoplastic matrices, and three types of fibres. Different combinations of thermoplastic matrices (polypropylene and polycarbonate) and fibres (glass fibre, basalt fibre, and carbon fibre) were used to study and address the proposed research objectives. Studies with the two matrices were used to understand the effect of matrix in relation to effective heat of combustion and char yield. Parametrization of variables such as fibre length, fibre architecture, and fibre type were also used to investigate the fire performance of reinforced thermoplastic composites. Details on the research plan are shown in Figure 1.2. Chapter 1 is the introduction to the thesis. Chapter 2 is the literature review. In Chapter 3, the characterization methods are described. In Chapter 4, the fire performance of a fibre reinforced composite manufactured from a commercially available glass fibre reinforced polypropylene commingled fabric examined and reviewed. In Chapter 5, the fire performance of a polycarbonate matrix and the role of fibre architecture on the fire performance of composite materials are investigated and presented. In Chapter 6, the effect of a fibre/matrix compatibilizer and the effect of fibre length on the fire performance of non-charring matrix are studied and described. In Chapter 7, the effect of fibre type and fibre length on the fire performance of a charring matrix are explored and discussed. In Chapter 8, the fire performance of thermoplastic matrix (polycarbonate) composite is compared to the fire and post-fire performance of a common thermoset (epoxy) composite. In Chapter 9, a design framework is suggested for the optimized fire performance of thermoplastic composites and critical concluding remarks are provided. References for Chapters 1, 2, 3 are placed at the end of the thesis while for other chapters, the references are placed at the end of the respective chapters.

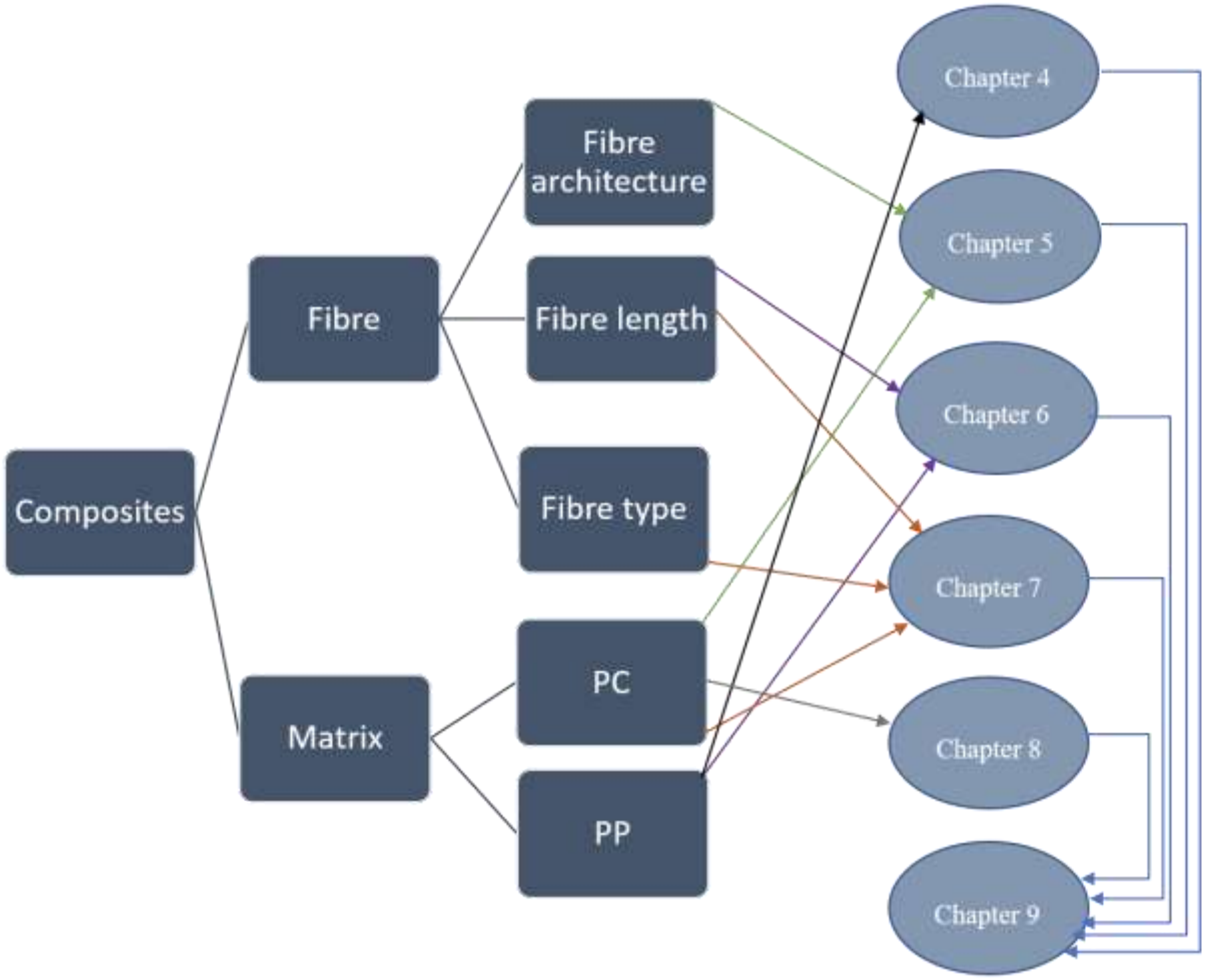

Figure 1.2: Thesis structure

2. Literature review

Due to their multi-material nature, the fire performance of composites is a very complex subject. A literature review was conducted covering different aspects of composites' fire performance to identify any gaps in research, to uncover some relevant aspects worthy of investigation and potential parameters of interest and to inform the researcher about possible methods to do so.

2.1 Ignition of solids

Solids burn in two steps. In the first step, the material generates fuel as a result of thermal decomposition. In the second, the fuel vapour generated from the burned fuel mixes with oxygen and undergoes combustion. In this work, the second stage is not considered as a limiting factor. Hence, the burning of solids is addressed by mainly considering the heat transfer and thermal decomposition processes happening within the solid. Figure 2.1 shows the typical behaviour of ignition in solids.

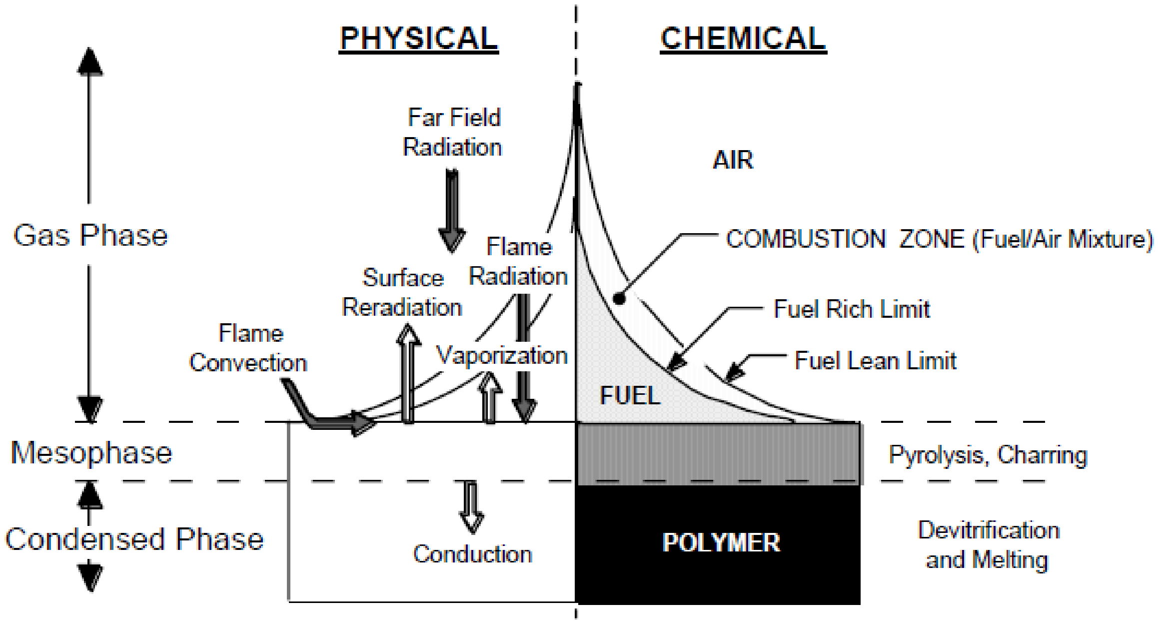

Figure 2.1: Schematic showing solid ignition behaviour. Taken from [12]

2.1.1 Solid-phase processes

2.1.1.1 Heat Transfer

When a solid is exposed to a heat source, its temperature will start to increase. The rate at which the temperature of the solid increases depends on the amount of energy provided, the thermal properties of the solid, and the boundary conditions. Therefore, material thermal properties are important when considering the burning of solids.

There are two types of heat transfer regimes in solids, those for materials which are thermally thin and those for thermally thick materials. Thermal thickness is determined using the Biot number (Bi), which is a ratio of the heat transfer on the surface of the solid to the heat transfer within the solid. Thermally thin behaviour occurs when $Bi<0.1$ and it implies that the solid heats evenly, resulting in negligible temperature gradients. Thermally thick behaviour occurs when $Bi>0.1$ and it results in the development of temperature gradients in the solid. Most materials behave as thermally thick solids [13].

Given the relative importance of heat transfer in solid combustion, the fire performance of composites has typically been categorized based on their thermal thickness [13].

2.1.1.2 Thermal decomposition and pyrolysis

When a polymer is exposed to a heat source, its temperature keeps increasing and simultaneously it undergoes a chemical structure change until the polymer reaches the temperature where pyrolysis occurs. Pyrolysis is the breaking of the polymer chain into smaller molecules. At this stage, ignition can happen. If the melting temperature is below the ignition temperature such as in the case of polypropylene, matrices can drip both before and after ignition. However, if the ignition temperature is just below and close to the melting temperature, such in the case of polymethylmethacrylate, dripping will not occur.

Thus, the ignition temperature of a solid is traditionally assumed to be equal to its pyrolysis temperature, and the time to ignition can be obtained by calculating the time required to heat the solid to its ignition temperature Table 2.1 shows the ignition temperature of certain polymers (measured at critical heat flux) where the sample weight was 0.2 g [14].

Table 2.1: Ignition temperature and time to ignition for polymers [14]

Polymer	Ignition temperature ºC	Time to ignition (s)
Polyethylene	430	130
Polypropylene	440	120
Nylon	488	83
Polyurethene	552	16
Polycarbonate	580	65
Phenol resin	614	69
Polystyrene	518	51

2.1.1.3 Charring

Some materials, after being burned, have a residue that did not fully burn after going through pyrolysis. This residue is called char. Char has a major effect on thermal decomposition behaviour. While the amount of energy released from ignition is equivalent to the product of the mass loss and effective heat of combustion, in case of non-charring polymers, the burnt polymer will be completely transformed into heat energy. However, for a charring polymer, only a fraction of the polymer will be transformed into heat energy. Char acts as a heat sink, preventing the material from being fully burnt. Char also slows down the burning rate (also called heat release rate) because of its poor heat conductivity. The amount of char generated by a material depends on its chemical structure. Waxy polymers generate little to no char. Polymers with an aromatic structure generate a reasonable amount of char. The amount of char generated also depends on the temperature of the heat source. When the temperature is higher, less char is generated and vice versa [15].

2.1.2 Gas phase processes

2.1.2.1 Combustion reaction

Gas phase reactions release energy as a result of combustion reactions. These reactions are several orders of magnitude faster than thermal decomposition. Therefore, away from extinction conditions, the gas phase reaction is not a limiting factor in the burning of solids [13].

2.2 Stages of fire

2.2.1 Initiation and fire growth

2.2.1.1 Ignition

When a material is heated to its critical ignition temperature, if a strong pilot is present, a flame will generate over the solid. This is achieved by exposing the solid to an external amount of heat which may be the result of nearby fire or the pilot source. Materials require a minimum level of heat energy in order to reach the temperature required for ignition. This is called the critical heat flux (CHF). By definition, a material will never ignite below its CHF. Table 2.2 shows CHF values for different polymers [16].

Table 2.2: Critical heat flux for different polymers [4]

Polymer	Critical heat flux (kW/m^2)
Polyethylene	15
Polypropylene	15
Polycarbonate	20
Nylon	20
Polyethylene terephthalate	10
Polymethylmethacrolate	10
Polyvinyl chloride	10

The CHF and ignition delay time can be obtained using standardized testing equipment such as the cone calorimeter and testing protocols such as ISO 5660-1. The ignition delay time is inversely proportional to the amount of external heating provided. That is, for values around the CHF, the time to ignition tends to infinity; as the externally applied heat flux increases the time to ignition is reduced. In the extreme that the external heat flux is very large, the time to ignition tends to zero. If the applied heat is higher than the critical heat flux, the time to ignition (t_{ig}) can be obtained from the following expressions depending on the material's thermal thickness [13].

For thermally thick material $$t_{ig} = \frac{\pi}{4} k\rho c \,.\left(\frac{T_{ig} - T_0}{q_{in}}\right)^2 \qquad (2.1)$$

For thermally thin material $$t_{ig} = \rho c \tau \,.\frac{T_{ig} - T_o}{\text{q"}} \qquad (2.2)$$

Where t_{ig} is the time to ignition, k is the thermal conductivity of the material, T_{ig} is the ignition temperature, T_o is the ambient temperature, q'' is the applied heat flux, ρ is the material density, c is the specific heat capacity of the solid, and τ is the slab thickness.

3.2.1.2 Flame spread

Fire growth is related to the ability of an already existing fire to ignite its surroundings, and thus flame spread is an important metric when addressing fire growth. In its simple form, flame spread is a series of piloted ignition processes in which the flame acts as both the heat source and the pilot.

Given its relationship to the ignition process, flame spread is controlled by the amount of heating provided to the solid, the thermal behaviour of the solid and the orientation. Similarly, to ignition, there is a minimum heat flux below which the flame spread rate is zero. As the amount of external heat flux applied increases, so does the flame spread rate, to the point where it approaches infinity for values around the CHF.

Flame spread behaviour can be characterised using standardised testing methodologies such as ASTM E1231. This test measures the lateral flame spread rate as a function of the externally applied heat flux. This test can be used to derive the flame spread parameter (FSP) which is used to rank flame spread behaviour in solid fuels. A large FSP means that the fire will have more tendency to spread over the surface of the material.

2.2.2 Steady burning

Steady burning is associated with the burning behaviour once the solid ignites. It is typically characterised in terms of the mass of fuel consumed and the amount of energy released.

2.2.2.1 Heat release rate (HRR)

The heat release rate is defined as an amount of heat energy generated per unit area as a result of the continuous burning of the material. The HRR is calculated as the product of the mass loss rate and the heat of combustion. The mass loss rate (MLR) of a solid depends on the amount of energy into the solid (q''), the energy required to reach pyrolysis the fuel (q''_{ext}), and the heat loss of the solid material (q''_{loss}) as per the expression below [13].

$$ML = \left(\frac{\text{q}'' + \text{q}''\text{ext} - \text{q}''\text{loss}}{L_v}\right)^2 \qquad (2.3)$$

The steady state burning process is dependent on the material and the thermal thickness as per Figure 2.2.

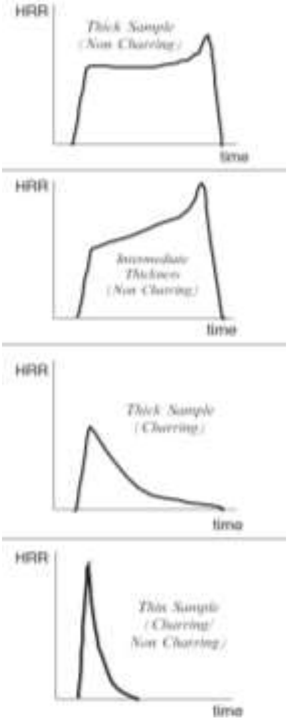

Figure 2.2: Types of heat release curves from cone calorimetry [13]

The HRR can be obtained in the lab by using cone calorimetry according to ISO 5660-1, either by using the mass loss rate or oxygen consumption (see Section 3.2.1 for more details).

2.2.3 Extinction

Extinction happens when the fuel is fully consumed or the pyrolysis rate is no longer sufficient to maintain a sustained flame. There are multiple factors that can reduce the pyrolysis rate such as melting or dripping. If the CHF is higher than the material’s melting temperature, part of the material will melt before ignition takes place and thus will not undergo pyrolysis. Another limiting factor is the formation of char. When the char layer is thick enough, it can lower the heat transfer to the solid and hence can cause the flame to extinguish before the fuel from the solid is completely consumed.

2.3 Key fire parameters

Fire performance within the context of ignition and fire growth deals with the ability to increase the time to ignition, the thermal inertia and the CHF. The mass loss rate and heat release rate are used to evaluate fire performance during steady burning. Reduction in both values is desirable since it will limit the contribution to the fire [15, 17-20].

2.3.1 Thermal inertia (I_{th})

The time to ignition in thermally thick solids is proportional to the thermal inertia. Materials with a high thermal inertia have a higher time to ignition. The thermal inertia may be increased either through changes in density, thermal conductivity, or the specific heat capacity. Modification of the thermal properties is one possible way to increase the thermal inertia. This parameter is experimentally obtained by measuring each individual property or performing piloted ignition experiments at different external heat flux levels according to ISO 5660-1 [13].

2.3.2 Critical heat flux (CHF)

As previously stated, the CHF is a key parameter for ignition. The greater the value of the CHF, the more difficult a material is to ignite. The CHF provides a direct method to characterise the ease of ignition of a material. The CHF is experimentally determined using a cone calorimeter, utilizing ISO 5660-1 standard.

2.3.3 Time to ignition (t_{ig})

The time to ignition can be estimated using mathematical expressions. In some particular applications there are specific requirements for t_{ig} at specific heat exposure levels. Longer t_{ig} values are indicative of better fire performance. This value may be predicted using mathematical formulas or derived from experiments following ISO 5660-1.

2.3.4 Flame spread rate

The flame spread rate is difficult to predict using mathematical expressions and thus it is typically measured in experiments. Lower flame spread rates are indicative of reduced fire growth. Materials may be classified on their measured spread rates and/or parameters derived following standardised flame spread tests such as ASTM E1321.

2.3.5 Mass loss rate (MLR)

This is typically expressed as the rate of mass loss per unit time. Materials with low MLR values provide a smaller contribution to the fire than those with larger values. The MLR captures the combined effects of heat transfer within the solid, charring, and thermal decomposition. The MLR is typically obtained from cone calorimeter experiments following the procedures outlined in ISO 5660-1.

2.3.6 Heat release rate (HRR)

This parameter is very similar to the MLR, except that it also accounts for the energy released during combustion. Lower HRR values indicate better fire performance since this implies a reduced contribution to the fire. The HRR is typically obtained from cone calorimeter experiments following the procedures outlined in ISO 5660-1.

2.3.7 Char yield

Char yield values are important during the steady burning and extinction stages of a fire. High char yields reduce the actual amount of energy released, reducing heat transfer into the virgin portions of the solid, which can subsequently increase the likelihood of extinction. The char yield is typically expressed as the percentage of mass remaining after cone calorimeter testing. Behaviour such as melting and/or dripping can affect char yield measurements.

2.4 Fire performance of common thermoplastics

2.4.1 Matrix contribution

Polymer matrices are generally classified into thermosets and thermoplastics. Since thermoset composites are still the more popular composites in various industries, the fire performance of thermoset composites has been well considered in literature; particularly thermoset matrices such as epoxy and phenolic resins. This includes investigating nano material modified resins, additives for improved fire performance, and different fibres such as glass fibre, carbon fibre, and basalt fibre. The research interest in thermoset composites is driven by the use of thermoset composites in applications such as aerospace that require certain fire properties to meet FAA regulations [15, 21-33].

Thermoplastic composites have not received the same attention as thermosets, with insufficient work currently on the fire performance of thermoplastic composites. In fact, most of the studies on thermoplastic composites relate to short fibre reinforced polymer composites, focusing mostly on glass fibre [15, 34-42]. Thermoplastic composites are replacing thermosets in many applications. Therefore, certain fire performance requirements in industries such as aerospace, construction, railway, automotive manufacture, and oil and gas are necessary.

2.4.1.1 Classification

The fire performance of matrices is generally more critical than the fire performance of the fibre. While fibres such as glass, carbon, and basalt have a melting temperature higher than 1000 ºC as seen in Table 2.3, polymers usually ignite at a temperature lower than 600ºC as seen in Table 2.1.

Based on their chemical and physical properties, in addition to the polymer’s price, thermoplastic polymers are typically classified into three categories: general purpose, engineering, and high performance polymers. General purpose polymers such as polyethylene, polypropylene, and polystyrene have poor fire properties. This is due to their aliphatic backbone. Engineering polymers such as polycarbonate, nylon, and polyacetal have some resistance to fire due to their aromatic chemical backbone, resulting in the ability to char during fire. High performance polymers such as polyphenylene oxide, polyether amide and polyether ether ketone exhibit the highest fire performance among other thermoplastics [15, 43, 44] . One general purpose thermoplastic polymer (polypropylene) and another engineering thermoplastic polymer (polycarbonate) are considered in this research.

2.4.1.2 Charring characterization

Polymer matrices can be classified based on their chemical decomposition. There are polymers that produce no char and polymers that do [15]. The char yields of common thermoplastic matrices are shown in Figure 2.3.

Polymers producing no char

Aliphatic polymers such as polyethylene (PE) and polypropylene (PP) are generally susceptible to fire. They have poor thermal resistance in addition to random chain scission when exposed to high temperature. Polyolefins also tend to completely decompose; leaving no char. Because of their waxy nature, they can act as a fuel, resulting in more severe fires.

Polymers producing char

Generally aromatics such as polycarbonate (PC), polyether ether ketone (PEEK), poly ether imide (PEI), also known as ULTEM®, and polyphenylene ether (PPE), also known as polyphenylene oxide (PPO®), tend to produce char when they are exposed to fire. Figure 2.4 shows the structure of aromatic polymers.

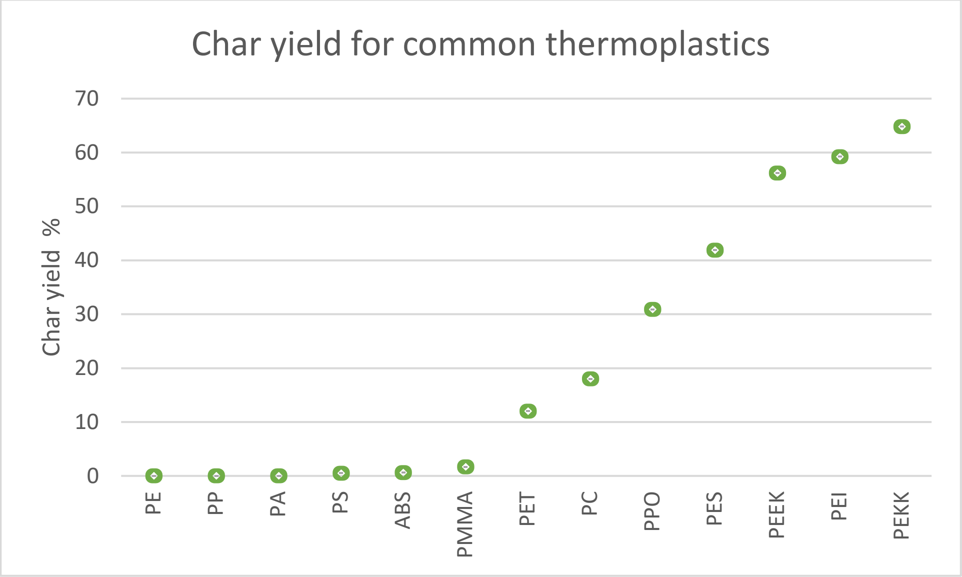

Figure 2.3: Char yield for common thermoplastic matrices. Adapted from [45]

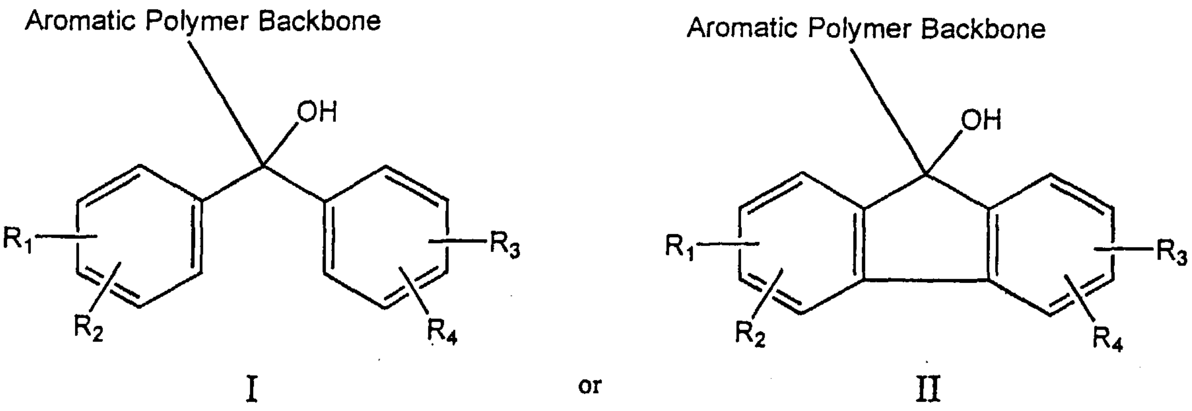

Figure 2.4: Structure of aromatic polymers. Taken from [46]

2.4.1.3 Common thermoplastic matrices

Two thermoplastic matrices were considered in the literature review. Polypropylene and polycarbonate are selected because they generate no char and reasonable amount of char respectfully. In addition, all three matrices are common in industry.

<u>Polypropylene</u>

A polymerization of propylene monomer, polypropylene is one of the most commonly used polymers on the market. Its low price and reasonable mechanical and physical properties make it (along with polyethylene) the polymer of choice in many applications.

In addition to being a very popular polymer, polypropylene is also the first choice for fibre matrices [47-50]. The reason why polypropylene is preferred over polyethylene as a composite matrix is that polypropylene binds better to fibres in addition to having a lower melt viscosity than polyethylene. Figure 2.5 shows the structure of polypropylene.

Polypropylene has poor fire performance because of its organic and waxy nature. Ongoing research in this area aims at improving the fire performance of polypropylene by using additives and fillers [41]. The addition of these fillers can cause the viscosity of the polymer to increase leading to a manufacturing problem. Nevertheless, this has its disadvantages. They can lower the mechanical and physical properties of the polymer [51-53]. Possible impregnation methods for the polypropylene matrix include melt impregnation, film stacking, and comingled yarn [54].

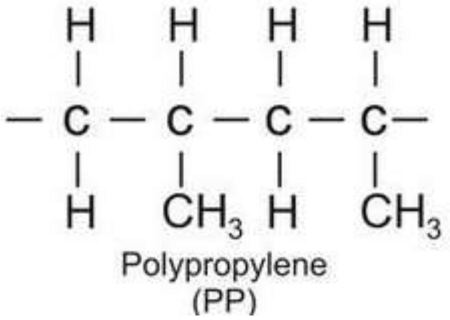

Figure 2.5: Structure of Polypropylene. Taken from [55]

Polycarbonate

Polycarbonate referred to in the research can be made by polymerizing of biphenyl A or polymerizing bisphenol A with different monomers such as diphenyl carbonate, tetramethylbisphenol A, or tetrabromobisphenol A. The name polycarbonate is derived from the carbonate group in its structure [56]. Figure 2.6 shows the structure of polycarbonate.

Polycarbonate is an engineering thermoplastic polymer with preferable thermal, optical and mechanical properties. Polycarbonate is used in a wide range of applications such as car head lamps, lenses, large water bottles, and bullet proof windows.

Polycarbonate is of research interest for use as a thermoplastic matrix for fibres [57-59]. The glass transition temperature of polycarbonate is around 150˚C. In addition, polycarbonate produces char during a fire, making it a good choice for low cost thermoplastic matrices with reasonable fire performances.

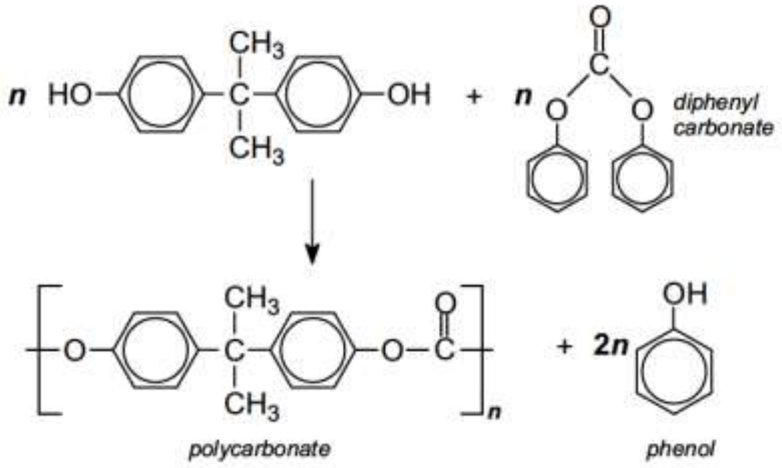

Figure 2.6: Polymerization of Polycarbonate. Taken from [56]

2.4.2 Contribution of fibres

Although the fibres considered in the study do not commonly ignite due to their ignition temperatures higher than 1000ºC [60], they still contribute to the fire performance of composites. Since they usually do not ignite and hence their heat of combustion is considered to be 0 kJ/kg, they have a diluting effect. In addition, due to their relatively high thermal conductivity to the matrix, they will contribute to improve the fire performance of composites by delaying ignition and conducting the heat away from the material.

High ignition temperature

Due to their very high ignition temperatures, basalt, glass and carbon fibres will not ignite in an ordinary fire, especially if no petrol fuel is involved [60]. Hence, a lot of heat energy generating from the fire will be dissipated in the fibre mass. As a result, fibres, especially if the fibre volume fraction is high, can minimize the energy released by the burning material and slow down fire growth by acting as a heat sink. In addition, since these fibres do not usually ignite, with the presence of char, they can maintain the structural rigidity of the solid.

Thermal conductivity

Fibres such as carbon, glass, and basalt have relatively high thermal conductivity when compared to polymer matrices. This property can cause the spread of the heat all over the material’s surface, minimizing the heat concentration on the material and thus causing a delayed ignition.

2.4.2.1 Classification and characterization

The fibre length, shape, and orientation are well known parameters that affect the mechanical properties of composites. Short fibre composites are the most commonly used fibres in industry. This is due to their low cost and ease of manufacture. However, short fibre composites have significantly lower mechanical properties when compared with long and continuous fibre composites. The selection of short, long, or continuous fibre depends on the required mechanical properties and the application for which the composite material will be used [61].

Although some research has been done on short fibre, long fibre, and continuous fibre composites, there is no enough evidence that directly compares the effect of fibres on the fire performance of composites [15]. However, fibres are known to affect the mechanical properties. Figure 2.7 shows the effect of fibre length on the mechanical properties.

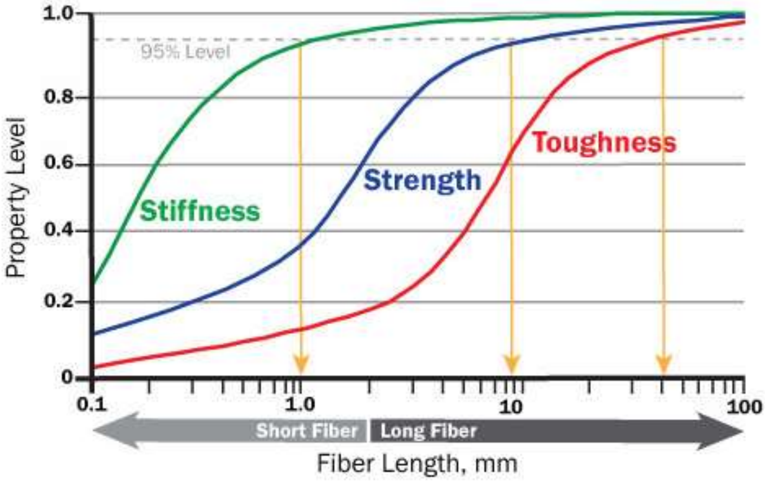

Figure 2.7: A comparison between long and short fibres [51]

2.4.2.3 Performance of common fibres

There are many different fibre types on the market. However, the most common for thermoplastic composites are: glass fibre, carbon fibre, and basalt fibre. A comparison of the common properties of the first three is presented in Table 2.3.

Table 2.3: Thermal properties of common fibres. Adapted from [62]

Fibre	Glass Fibre	Basalt Fibre	Carbon Fibre
Softening temperature °C	850	950	-
Max service temperature °C	300	600	400
Melting temperature °C	1200	1450	3000
Thermal expansion µm/m °C	5.4	8	2
Thermal conductivity W/m K	0.031 – 0.038	0.034 – 0.04	>1

Glass fibre

Glass fibre (previously called glass wool) was invented by Games Slayter in 1933 [63]. Currently, three are different glass fibre types on the market: E-glass, S-glass, and C-glass, the most common of which on the market are E-glass. E-glass is the spin of alumino-lime silicate with less than 1% alkali oxide. It is used in applications that require electrical, corrosion, and acid resistance. The mechanical and thermal properties of E-glass are in the mid-range among other glass fibres. Conversely, the price of S-glass is the highest among all glass fibres. S-glass is used in high end applications [64].

Glass fibre has a melting temperature of around 1200˚C and a continuous use temperature above 300˚C. Due to its inorganic nature, glass fibre has a good resistance to fire. It is recommended to increase the use of glass fibre when fire resistance is required [65]. Being the most commonly used fibre reinforcement, glass fibre is also the most well covered reinforcement in literature. The key properties of glass fibre are shown above in Table 2.3.

Carbon fibre

The first carbon fibre material was invented by Joseph Swan in 1860 [66] for use in light bulbs. In 1958, Roger Bacon invented high performance carbon fibre by spinning rayon [67]. Rayon is a semi-synthetic material made from cellulose and was one of the early carbon fibres with decent properties. Nevertheless, the carbon yield of rayon based carbon fibre is below 20%; making rayon based carbon fibre economically unfeasible.

In the 1960's, the first successful production of polyacrylonitrile (PAN) based carbon fibre was achieved. PAN carbon fibre is the most commonly used carbon fibre today. Its carbon yield of more than 50%, its relatively low cost, and its ability to crosslink effectively have all made PAN the most widely used of today's carbon fibres although there are some ongoing research efforts to find an alternative to PAN [68].

Carbon fibre (CF) reinforced composites offer a higher stiffness to weight ratio and a higher strength to weight ratio than metals. However, due to their cost, the highest performance CF composites have been restricted to military aircraft and space programs; the lower performance varieties of CF are found in sports goods. More recently, carbon fibre composites have entered civilian aeroplanes such as the Airbus A380 and the Boeing 787 Dreamliner [69]. A middle ground of carbon fibre reinforced composites for consumers is still missing. Current research on carbon fibres is directed at cost-cutting technologies so that they can be integrated into the mass automotive sector. Efforts are equally being made in increasing the manufacturing rate of composite articles. In the transport sector, the driving force for fibre composites is weight reduction for fuel efficiency [70].

Carbon fibre has a service temperature of around 400˚C (due to oxidation). It also has an exceptional heat conduction capability (most common other fibres being insulators to heat). Nonetheless, due to its organic nature, carbon fibre has a poor resistance to fire. Wherever fire resistance is concerned, carbon fibre fails in comparison with glass fibre and basalt fibre [71].

Basalt fibre

The first attempt to make basalt fibre was made by Paul Dhe in 1923 [72]. However, basalt did not receive much attention in the USA where glass fibre was the main industry focus. Basalt was only used by the Soviet Union military until 1996. The late commercial start of basalt has made it less common today compared to glass fibre. Basalt fibre is still in its early development; its production cost is relatively high and its mechanical properties have not reached their maximum potential.

Basalt fibre is spun from volcanic basalt rock which is a result of the cooling down of volcanic lava. Basalt is considered the strongest natural fibre, with mechanical and physical properties almost similar to those of E-glass [73]. Being spun of a natural material makes basalt fully recyclable unlike carbon and glass fibres.

Basalt has a glass transition temperature of around 1000˚C, a service temperature of 600˚C, and a melting temperature of around 1500˚C, giving it superior thermal resistance to glass and carbon fibres. It is also inorganic. Thus, basalt is highly recommended when the fire properties of the material are critical.

2.5 Research gaps

2.5.1 Comparison of similar compounds

When comparing two composites or trying to study a composite material in terms of its fire performance, one of the most important aspects to be aware of is the compounding formulation of the composite. There are several studies on the effect of the matrix or the fibre on fire performance, or this effect after modification of the fibre and the matrix [34-39, 47, 74]. However, the effect of the compounding formulation has not been taken into account. It is essential to make sure that the compounding formulation is controlled in terms of the molecular weight of the matrix and the presence of additives, especially if those additives can potentially affect the fire performance.

2.5.2 Fibre architecture

Fibre architecture or fabric weaving has a major role in composite design. There are several studies concerning the effect of fibre architecture on the fire performance of composites [75-79]. It can be concluded from the literature that five different fabric types (plain, twill, quasi-isotropic, matt, and unidirectional (UD)) have been considered. The results are as yet inconclusive and some even contradict others. This is in part due to the fact that in some research the fibre volume fractions and manufacturing methods were not controlled. In addition, different fibres have different properties. Hence, it cannot be generalized that a specific fibre architecture is the best for all fibre types.

2.5.3 Fibre length

Fibre reinforcement is used in different lengths. The choice of fibre length is driven by structural requirements as well as manufacturing and economic considerations. It is well understood that the higher aspect ratio fibres offer better mechanical properties in fibre reinforced composites [80-83]. However, it is not well understood how fibre length affects their fire properties.

Previous work has considered the fire performance of continuous and chopped fibre reinforced composites [25, 47, 84-88]. Although longer fibres result in higher thermal conductivity [89], there is not enough evidence to suggest a relationship between the fibre length and the fire performance of fibre reinforced composites.

2.5.4 Fibre type

There are not many studies concerning the effect of fibre type on the fire performance of composite materials. In some of these, the comparison between fibres is not adequate [78, 87, 90]. In order to properly study the effect of the fibre type, the two fibres must have the same geometry and identical matrices.

2.5.5 Measurement of critical fire performance aspects

There are important factors in determining the fire performance of composites. One of the most important is thermal conductivity which can vary with the change of the fibre geometry, fibre type, and compounding formulation. An alteration in the thermal conductivity leads to a major difference in the thermal inertia which, in turn, is a major factor in determining the fire performance of any material (Section 2.3). Although thermal conductivity does not vary much with the change of the matrix, the thermal conductivity of fibres ranges from 1 W/m K to 15 W/m K for glass fibre and carbon fibre, respectfully. It is important when trying to study the effect of the matrix type, fibre type, and fibre geometry to know the thermal conductivity, so as to understand how the fire performance is modified with adjustments to the fibre or matrix formulation.

2.6 Engineering aspects

When assessing the fire performance of a material, one always faces the challenge that the term “fire performance” is somewhat subjective and is used as a catchphrase to summarise a number of performance parameters. The criteria for what is deemed “good fire performance” largely depends on the desired application and the fire engineering strategy/philosophy followed. It is therefore beneficial to review the key criteria that are used across different industries to assess fire performance. Applications where composites are heavily featured and where fire is a major concern include aerospace and air transportation, building and construction, railways, and the automotive industry. Fire safety requirements for each sector are briefly discussed in the sections below. Since the rest of the study is agnostic with respect to application, the reader is referred to this section to determine which properties are desirable for a given application. Table 2.4 lists the key standards of the industries considered into his section.

Table 2.4: Standard fire safety standards for different applications

Application	Fire safety standards
Aircrafts	FAR 23, 25, 29, 29, 33; ASTM E648-19
Building and construction	BS 476; BS 9999; NFPA 251; ISO 834, 3008, 3009
Railways	EN 45545; NF F16-101, F16-201, X70-100; DIN 5510; BS 6853; ASTM E162-98, E662, E1537-98
Automotive	FMVSS 302;NFPA 556; ISO 3795; DIN 75200; BS AU 169

2.6.1 Aerospace

While most countries have their own aviation administration and regulations, the majority of national regulations follow the Federal Aviation Administration (FAA) or the European Union Aviation Safety Agency (EASA). Both regulations have a similar structure and intent. The discussion presented here focuses on the FAA guidelines and regulations. The FAA establishes fire safety requirements related to aircraft manufacturing, operation, and maintenance. Thanks to very cautious aviation rules and regulations in relation to aircraft fire safety criteria, accidents related to inflight fires did not exceed 3.5% of total aircraft accidents in the period between 1987 and 1996 while the total contribution of fire to the fatality rate was only 4.9% between 1992 and 2001 [2]. Such a low rate of fire related accidents would not have been achieved without stringent fire safety measures and a design philosophy that avoids fires at all costs.

2.6.1.1 Design philosophy

There are a number of points that drive the underlying fire engineering philosophy for aircraft which are specific to aviation and distinct from the other industries discussed in this section:

- Due to the high weight penalty in aviation, the means to fight fires on board is restricted.
- Active firefighting systems are reserved for critical areas that are difficult to access.
- During an inflight fire event, evacuation is rarely possible (the evacuation time required by FAA = 90s as per FAR part 121 if the plane is on the ground).
- Aircrafts are enclosed and pressurized.

Due to these constraints, the following design philosophy has been adopted [2] [3]:

- High fire resistance in areas that cannot be accessed during flight (cargo, engines)
- Active fire suppression in areas that cannot be accessed
- Low flame spread materials (materials with low heat conductivity for slow fire spread)

- Long ignition delay time (materials that take a long time to ignite when exposed to heat source)

2.6.1.2 Standards and fundamental parameters

The FAA has developed Federal Aviation Regulations (FAR) standards that must be followed for testing materials used in aircraft. The aircraft cabin and cargo compartments (other parts of the aircraft requires high performance materials which are not covered in this research) are covered by such regulations in relation to the fire behaviour of materials and other properties not investigated in this research. According to this standard for these locations within the aircraft (FAR 25.853), the time to ignition, peak heat release, and total heat release are acceptable fire performance parameters [3].

Cabin materials are tested for their heat release and heat release rate. The heat release is defined as the amount of heat energy released by burned material during combustion; while the heat release rate is defined as the rate at which the material releases heat energy. These are both tested under an external heat flux of 35 kW/m^2 which simulates heating due a nearby fire, equipment failure, or other reasons. Compliance to FAR 25.853 (a-1) requires an average maximum heat release rate below 65 kW/m^2 during the first five minutes of burning and an average total heat release of less than 65 kW min/m^2 during the first two minutes of the test.

Horizontal spread tests using a Bunsen burner according to FAR 25.853 may be used to examine the fire properties of aircraft cabins and cargo compartments. The same standard provides acceptance criteria for maximum burn rates for aircraft cabins (0.06 m/min) and cargo compartments (0.1 m/min).

Vertical spread tests can also be done utilizing a Bunsen burner in compliance with FAR 25.853 and FAR 25.855 for the cabins and cargo compartments. The flame drip time in the test cannot exceed 3 s (for a cabin) or 5 s (for a cargo compartment). The maximum flame time cannot exceed 15 s while the maximum burn length cannot exceed 0.15 m (for a cabin) or 0.2 m (for a cargo compartment).

Aircraft cabin materials are also tested for smoke generation. In this test, the amount of smoke generated by the material (specific optical density) is measured in a per unit basis over a period of four minutes from the point of ignition. FAR 25.853 (c-1) requires that the specific optical density during this four minute period does not exceed 200 if the material is to be qualified for use in aircraft cabins.

2.6.2 Building and construction

Despite the awareness and efforts of governments, fire is still a major issue in the built environment. Between 2013 and 2014, in Australia, according to the Australian Fire and Emergency Service Authorities Council (AFAC), 98 people died as a result of building fires [4]. During the same period, 322 people died in Britain [5] and 3275 people died in the USA [6].

2.6.2.1 Design philosophy

The following design considerations are important:

- The life and safety of building occupants and responders must be preserved. Fatalities are not acceptable.
- Building content and activities in a building are difficult to control.
- A large proportion of the fuel load comes from the interior of the building (furniture etc.)
- Most buildings are relatively easy and quick to evacuate when compared to aerospace. Some exceptions apply for critical infrastructure (hospitals, airports, etc.)
- Structural integrity must be maintained during the evacuation.
- The cost to the building owner in a fire should be minimized.

Independent of the nature of a building, the above considerations result in the formulation of a fire safety strategy. The correct implementation of such a strategy ensures the life and safety of building occupants as well as emergency response personnel, and structural integrity while also minimizing property loss. The formulation, implementation and verification of a fire safety strategy is achieved through the use of prescriptive designs such as approved building codes, or through an explicit quantification of the level of safety using a performance-based design.

2.6.2.2 Standards and fundamental parameters

In general, building materials must not contribute to the growth of a fire, by limiting the internal or external spread of fires and retaining a minimum level of structural performance during and after a fire. These requirements are stated in building codes and implemented through a combination of standardized testing and performance testing. One of the most common fire safety standards is the British standard BS 476 which highlights building material fire resistance requirements.

A combustion chamber is utilized to determine the flame propagation index of the material in compliance with BS 476-6. The test takes into account the ignition characteristics, heat release rate, and thermal properties of the material in order to obtain the index. Although there is no specified limit, the higher the number on the index, the more the material contributes to the acceleration of flame growth.

A radiation panel can be used with a pilot burner to measure the flame spread of building materials in compliance with BS 476-7. The same standard specifies that a flame shall not continue to spread for more than 1.5 min and the maximum spread distance specified is 0.165 m for Class 1 materials and 0.710 m for Class 3 materials

A radiator cone accompanied by a pilot flame application mechanism is used to determine the ignitability of a material in compliance with BS 476-15. The test is done by subjecting the material to a heat source for a maximum of 15 min using a specific heat flux, depending on the application and the total flame time is recorded from the point when a sustained flame occurs.

2.6.3 Railways

Railways fire accidents can result in multiple casualties. Recently, on 31 October 2019, a Tezgam passenger train in Pakistan caught fire due to the illegal use of a stove by a passenger inside the train. 74 people died and 43 people were injured as a result [8]. In March 2010, a Comeng train in Australia caught fire because of train motor failure. The train driver noticed it early and acted in time by stopping the train and evacuating the passengers. No casualties were reported [9].

2.6.3.1 Design philosophy

When designing railways, the following must be considered:

- When trains are stopped during a fire event, firefighting resources might not always be available or the train can be more difficult to access (if it is in a bridge or tunnel).
- If in a tunnel, there may be a suffocation risk in the case of a fire.
- Local evacuations from one carriage to another are possible in most cases.
- If the train is in an area that can be easily accessed, the evacuation of passengers is generally relatively easy compared to an aeroplane or high rise building.

Due to design considerations, the following design philosophy has been adopted:

- High flame resistance materials
- Easy escape in case of emergency

2.6.3.2 Standards and fundamental parameters

One of the most common standards for railway fire requirements is the European EN 45545. In lab tests, an external radiant heat flux between 25 and 50 kW/m^2 is used to test samples, the heat flux depends on the location and function of the sample. Fire requirements in passenger areas are different to those applicable to cargo areas [10]. For instance, to represent fire due to newspaper or rubbish, a flame source is used for the duration of three min with a heat flux ranging from 25 to 30 kW/m^2. To represent the horizontal surface of floor and seats, a 25 kW/m^2 heat flux is used with a sample area of 0.1 m^2. Surfaces such as walls and ceilings can be represented in a lab test using a heat flux of 50 kW/m^2 and a sample area of 0.1 m^2. In general, the material used in trains must have a low flame spread rate and limited smoke production.

2.6.4 Automotive

According to the National Fire Protection Association (NFPA), fire represents the cause of 20% of vehicle accidents. In addition, according to the Swedish Civil Contingencies Association statistics, fire related automotive accidents has increased from only 400 reported fire related accidents in 1998, to 1600 reported accidents in 2016 [11]. Hence, fire is a critical issue in the automotive industry.

2.6.4.1 Design philosophy

When designing cars, the following must be considered:

- Automotive vehicles are relatively small hence the fire will always be close to fuel.
- Compared to the above mentioned industries, the number of people affected by the fire is small (e.g., a passenger car may carry 1-5 people).
- The asset value is low compared to the other applications.
- Fire can start for many reasons such as smoking, flammable goods, overheating, and battery malfunction.

Due to design considerations, the following design philosophy is adopted:

- Difficult to ignite materials, particularly in areas with high temperatures, e.g., engine bay
- Materials with a low flame spread

2.6.4.2 Standards and fundamental parameters

In general, the motor vehicle material must not be easy to ignite and should have a low flame spread rate due to the presence of multiple potential ignition sources in the vehicle's interior (e.g., cigarettes) and exterior (e.g., engines). The federal Motor Vehicle Safety Standard (FMVSS) has included a flammability test for motor vehicle interiors (FMVSS 302).

A vertical Bunsen burner can be used to measure the time to ignition and flame spread rate for automotive materials in compliance with FMVSS 302. The material is exposed to flame for 15 s and, if it ignites, the flame spread rate shall not exceed 0.102 m/min for the material to be acceptable for use by most automotive manufacturers (some manufacturers apply stricter criteria).

2.6.5 Summary

It is vitally important to understand the fire performance criteria for applications and certain industries have set precise minimum standards to be reached for materials used in the production of their machinery. For homogeneous materials, fire performance can be linked to their fundamental properties which are well understood. However, the same cannot be said for composites; particularly thermoplastic composites. Table 2.5 outlines a summary of the fire performance requirement standards for the aerospace, construction, railways and automotive applications.

In general, each industry has its own test methods but that there are a number of general tests that can be undertaken. Cone calorimetry can be used to obtain time to ignition, heat release rate, total energy release, and mass loss rate utilizing ISO 5660-1. The flame spread rate can be obtained using a LIFT apparatus utilizing standard ASTM E-1321. It is important to understand the fire performance requirements of composite applications in order to realize the key fire performance parameters for composite materials. It is important to mention that the selection of heat flux in fire testing is done using fire testing standards recommendations, the heat flux used in applications related to materials, and literature values as guidelines.

Table 2.5: Materials design requirements based on application

Application	Design approach	Critical performance criteria
Aerospace	Limit likelihood of ignition Minimize flame spread Minimize smoke production	Time to ignition Heat release rate Flame spread rate
Buildings and construction	Eliminate/limit contribution to the fire Provide structural integrity during and after a fire Provide compartmentation to fires	Flame spread rate Heat release rate Residual strength
Railways	Minimize flame spread Minimize smoke production	Flame spread rate Heat release rate
Automotive	Limit likehood of ignition	Time to ignition Heat release rate

3. Materials and experimental techniques

In order to deal with this complex and multi-faceted problem, key design aspects were isolated and are investigated in a self-contained experimental study. Each individual study will contribute to the development of the design framework which is the ultimate goal of the project.

3.1 Materials

Two matrices (PP and PC) and three fibres (glass, basalt, carbon) were used throughout the study. Due to the importance of controlling the compound ingredients, materials were specifically compounded to fit the purpose of the research in each chapter. These are shown in Table 3.1

Table 3.1: Materials list

Material	Manufacturer	Grade	Specification	Comments	Use
Comingled glass fibre reinforced PP	Owens Corning	Twintex	60% fibre volume fraction	Benchmark material	Chapter 4
Polycarbonate	SABIC	PC2200	Melt index = 22 g/10 min	-	Chapters 5 and 8
Glass fibre	Swiss Composite	Eglass	Plain weave 280 g/m^2	-	Chapters 5, 6, and 8
Glass fibre	Swiss Composite	Eglass	Twill weave 280 g/m2	-	Chapter 5
Glass fibre	Swiss Composite	Eglass	UD weave 287 g/m^2	-	Chapter 5
Polypropylene	Lyonell Basell	HP568S	Melt index = 38 g/10 min	-	Chapter 6
Glass fibre reinforced PP	Lyonell Basell	HP568S	Fibre lengths = 3 and 12 mm Fibre weight fraction = 30%	Specially compounded by Duromer, Australia	Chapter 6
Polycarbonate	Lotte Advanced Materials	Infino SC-1220R	Melt index= 22 g/10 min	-	Chapter 7
Glass fibre reinforced PC	Lotte Advanced Materials	Infino SC-1220R	Fibre lengths = 6, 12, and 20 mm	Special compound by Plasticomp	Chapter 7
Basalt fibre reinforced PC	Lotte Advanced Materials	Infino SC-1220R	Fibre lengths = 6, 12, and 20 mm	Special compound by Plasticomp	Chapter 7
Carbon fibre reinforced PC	Lotte Advanced Materials	Infino SC-1220R	Fibre lengths = 6, 12, and 20 mm	Special compound by Plasticomp	Chapter 7
Epoxy	Gurit	Ampreg 22	Fast hardener		Chapter 8

3.2 Manufacturing process

Samples in each chapter of the thesis were manufactured in a unique way to fit the purpose of the chapter. Typically, all samples were made into a 250 x 250 mm plates via compression moulding and then cut into 100 x 100 mm. However, different impregnation methods were employed. Throughout the thesis, three impregnation methods were used which are prepregs, solution impregnation, and film stacking

In Chapter 4**,** commingled fabrics (prepregs) were used. The fabric was cut and laid up, then placed in a compression moulding machine at 230˚C under 1.5 MPa for 25min to make the composite used in the fire testing. The nominal ply thickness of the fabric was 1.524 mm with an areal weight of 1492 g/m^2.

In Chapter 5, solution impregnation was used to impregnate the fabric. Fabrics were then laid up and compression moulded at 260ºC under a constant pressure of 1.25 MPa for 20min. Nominal sample thickness was 4 mm.

In Chapters 6**,** the continuous fibre reinforced composites were manufactured using film stacking. The fabrics were laid up with the films interleaved and compression moulded at 240ºC under a constant pressure of 1MPa for 10min. Nominal sample thickness was 6 mm.

In Chapter 7, the continuous fibre reinforced composites were manufactured using film stacking. The films were dried for 4h at 100ºC . The chopped fibre reinforced PC samples were dried for 4 h at 100ºC and compression moulded at 270ºC under a constant pressure of 1.5 MPa for 10 min. Nominal sample thickness was 6 mm

In Chapter 8, the manufacture of the glass fibre reinforced polycarbonate composites using film stacking is highlighted. The films were dried for 4h at 100ºC. After drying, the fabrics were laid up with the films interleaved and compression moulded at 270ºC under a constant pressure of 2 MPa for 10 min. The manufacturing of glass fibre reinforced epoxy was done using vacuum assist resin transfer moulding. The process was done in room temperature under a constant pressure of 0.1 MPa. Nominal thickness for all samples was 4 mm

3.3 Test methods

In order to fulfil the purpose of the work, a series of optical, thermal, and fire tests needed to be done. The procedures for these are briefly outlined below.

3.3.1 Cone calorimetry

Fire Testing Technology, iCone Calorimeter is a type of equipment dedicated to measuring key fire performance parameters such as the time to ignition, heat release rate, mass loss rate, critical heat flux, and effective heat of combustion following standard procedures set out in ISO 5660-1. The time ignition is measured by visual monitoring of the sample from the point the sample is placed under the heat source until ignition happens. The heat release rate is determined by monitoring the oxygen consumption where every oxygen atom is assumed to generate 13.1 MJ of energy when consumed. The mass loss rate is established by constantly measuring the weight of the sample while it is burning. The critical heat flux is calculated by exposing the sample to a range of heat fluxes where ignition of the sample is expected to happen and recording the minimum heat flux needed for ignition. The effective heat of combustion is the product of the heat release rate and the inverse of the mass loss rate. The heat release rate can be obtained from either the oxygen consumption or mass loss rate. Figure 3.1 shows a schematic of an Icone calorimeter which is the equipment used in the research.

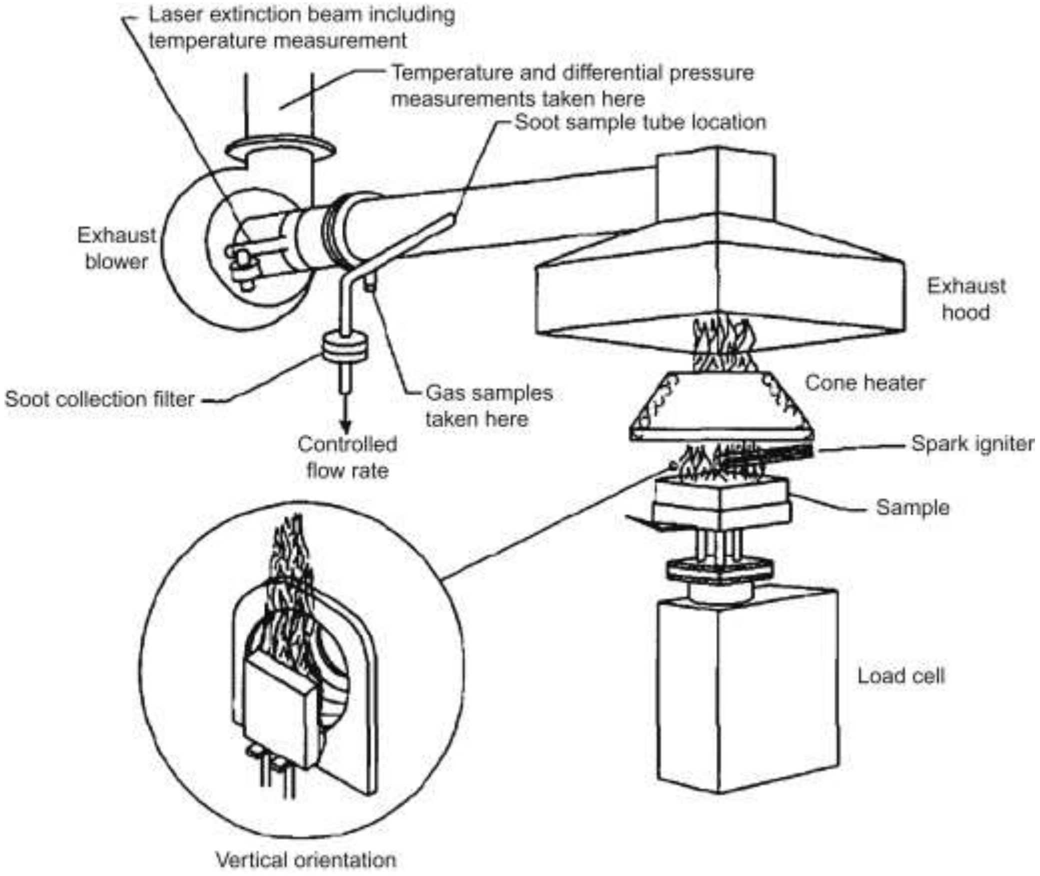

Figure 3.1: Schematic of Icone calorimeter [91]

3.3.2 Transient plane thermal conductivity

The Hot Disk® TPS 1500 is a piece of equipment used for measuring both the in-plane and out-of-plane thermal conductivity, thermal diffusivity, and specific heat capacity for an isotropic material as per ISO 22007-2 standard. The equipment is capable of dealing with solid, liquid, and powder materials. The TPS 1500 is operated by heating the sample via a sensor and measuring the heat resistance and total temperature increase as a means to derive the thermal properties of the sample. Figure 3.2 shows a schematic drawing of the entire TPS 1500 operation which was used in the research.

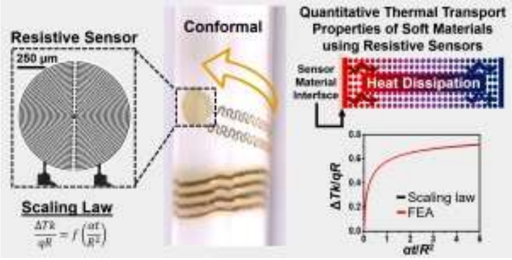

Figure 3.2: A schematic of transient plane thermal conductivity test [92]

3.3.3 Flame spread test

The flame spread properties are measured using a horizontal LIFT apparatus as per ASTM E1321. The setup consists of a heating panel and a sample located at a certain distance and angle from the heating source as per test requirements. The test is video recorded and image processing of the video is used to measure the flame spread velocity and flame spread rate. An external heat flux is applied to the sample and, in this way, the flame spread rate as a function of the external heat flux is obtained. Figure 3.3 shows the LIFT apparatus setup which was used in the research.

Figure 3.3: LIFT apparatus setup

3.3.4 Thermogravemetric analysis (TGA)

Perkin Elmer STA 6000 was used for TGA as per standard test method E 1131-08 in order to to study the material's performance at a temperature range from 30ºC to 800ºC in both air and nitrogen. Knowing the temperature performance of the material can provide a general understanding of the material's temperature sensitivity and char yield. Figure 3.4 shows a TGA curve for PC in both air and nitrogen.

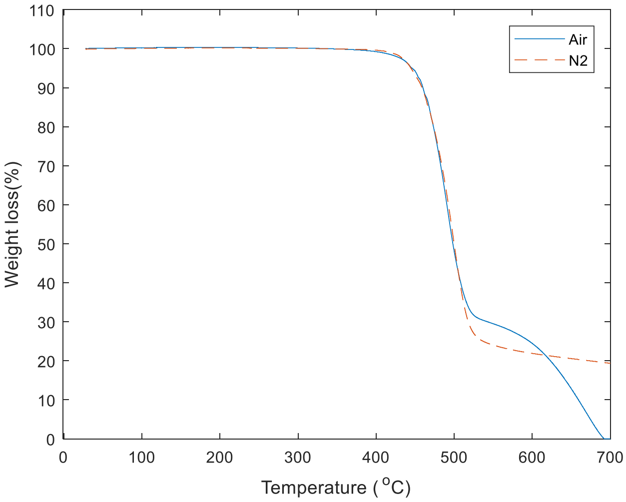

Figure 3.4: TGA for PC in air and nitrogen

Chapter 4

Fire properties of commingled glass fibre reinforced polypropylene: An initial investigation

Motivation

Before getting into studying the fire performance of the selected matrices (PP and PC) and the selected fibres (glass, basalt and carbon), the fire performance of a commercially available glass fibre reinforced PP is studied in this chapter in order to use it as a benchmark for following studies.

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Fire properties of commingled glass fiber reinforced Polypropylene: an initial investigation

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Abstract

The ability to predict the fire performance of composite materials is essential to enable new applications in aerospace, automotive manufacturing, and the built environment. The research presented herein represents an initial step towards the development of tools and techniques required to reliably predict the fire performance of fibre reinforced thermoplastic composites. Glass fibre reinforced polypropylene composite laminates were produced from comingled fabrics via compression moulding. Cone calorimetry test was used to determine the heat release rate, time to ignition, and mass loss of the glass fibre reinforced polypropylene.

Author contribution percentages (Chapter 4)

Author	Sample manufacturing	Testing	Data Analysis	Paper writing	Paper editing
Yousof Ghazzawi	80%	70%	60%	70%	-
Michael Heitzmann	20%	-	20%	20%	70%
Andres Osorio	-	-	10%	10%	20%
Angela Castaneda	-	30%	-	-	-
Juan Hidalgo	-	-	10%	-	10%

4. Fire properties of commingled glass fibre reinforced polypropylene

4.1 Introduction

The aim of the investigation was to study the effects of sample thickness on the fire behaviour. The results show that, for typical composite wall thicknesses (2-10 mm), the time to ignition, peak heat release rate and mass loss rate are sensitive to changes in the sample thickness and heat flux. On the other hand, the mean effective heat of combustion and the total mass loss were found to be unaffected by the change in thickness. For predominantly thin composite structures, it is therefore critical to consider these thickness sensitivities during fire performance characterization and fire engineering design.

Stringent emission reduction regulations and an increased consumer awareness drive demand for lightweight materials with high level mechanical and physical properties. Composites present an interesting family of materials with enhanced properties and are poised to play a major role across different industries. Fibre reinforced thermoplastic composites are rapidly gaining popularity in a large number of industries, the foremost being the mass transport industry. Technological advances such as organo sheet forming in combination with injection over-moulding have enabled the mass production of highly reinforced thermoplastic composite materials.

Most of the commonly used matrices are organic and have a relatively poor fire performance. On the other hand, the majority of technical fibres are thermally stable, which gives them a favourable fire performance. One major difficulty associated with the fire engineering of composite materials is that the reaction to fire of the resultant composite cannot be easily determined by its individual constituent properties. There is a complex interaction between the fibre, matrix and additives, which greatly affects the behaviour of the material when exposed to fire conditions.

The reaction to fire of thermoset composites has been well covered in the literature, particularly thermoset matrices such as epoxy and phenolic resins.

Thermoplastic composites have not received the same attention as thermosets. In fact, to date most of the work on thermoplastic composites is related to short fibre reinforced polymer composites, focusing mostly on glass fibre [1-5]. In general, thermosets have a superior fire performance than thermoplastics since the latter usually exhibit melting behaviour at temperatures below pyrolysis. In contrast, thermosets generally show better thermal stability and do not melt. They usually also have a higher char yield, which slows the transfer of heat to the pyrolysis reaction zone, thus having a positive effect on the burning behaviour [6].

The fire behaviour of solids is often categorized into thermally thin, or thermally thick materials. This categorization refers to the temperature distribution within the solid. Thermal thickness is not necessarily indicative of the physical thickness of the material. Instead, it is a result of the solid thermal properties, and the boundary conditions. Whether a material can be classified as a thermally thin or thick element is normally expressed as a function of the Biot number (Bi), defined as $Bi=hL/k$ where h is the heat transfer coefficient, L is the characteristic length, and k is the thermal conductivity. The Biot number is a non-dimensional parameter that correlates to the exchange of convective heat between a solid and a fluid with respect to the heat conducted within the solid [7].

In materials with a large Biot number ($Bi>>1$), heat transfer into the solid is larger than conduction within the solid and thus, in this case, the heat transfer leads to the development of thermal gradients within the solid. Materials exhibiting thermal gradients are referred to as thermally thick solids. Conversely, in materials with a small Biot number ($Bi<<1$), conduction within the solid is much larger than the heat transfer into the solid, resulting in an approximately uniform temperature distribution. Materials with a uniform temperature distribution are referred as thermally thin.

Composite materials exhibit complex thermo-physical properties, making the categorization of their thermal thickness, and ultimately their fire behaviour, a challenge. This research investigates the influence of thickness on the fire behaviour of a glass fibre reinforced polypropylene. Experiments were conducted using two external heat flux values and three different sample thicknesses. The characterization of the fundamental flammability parameters, including the ignition delay time for piloted ignition, heat release rate, and mass burning rate, is accomplished using cone calorimetry testing following ISO 5660-1

4.2 Experimentation

4.2.1 Materials

Twintex® comingled plain glass fibre reinforced polypropylene with a glass fibre weight fraction of 60% was used in this work. The nominal ply thickness of the fabric is 1.524 mm with a weight per unit area of 1492 $g.m^{-2}$ .10 x 10 cm test specimen were manufactured via compression moulding at 230 ˚C under 1.5 MPa for 25 min.

4.2.2 Test method

Flammability behaviour of the samples was studied using a series of piloted ignition tests. All tests were performed using the iCone Calorimeter following the recommendations outlined in ISO 5660-1. Data collected during the experiments was used to examine the effect of the sample thickness and external radiant flux in the piloted ignition delay time, heat release rate, and mass loss rate of the samples.

The piloted ignition delay time (t_{ig}) is defined as the time required by the sample to ignite after the initiation of the heat exposure. The time to ignition depends on the external heat flux used and the material thermo-physical properties of the material. The sample thickness tends to play a significant role when subjected to low heat fluxes. The Heat Release Rate (HRR) is defined as the energy released by the combustion process. The heat release rate can be obtained by means of calorimetry techniques [14] such as mass loss calorimetry (the rate of mass loss times the heat of combustion) or oxygen consumption calorimetry (the rate of consumption of oxygen proportional to the energy released). Measuring the HRR over time allows assessment of the burning rate and of the contribution of the material to the fire. By analysing the HRR curves, we can understand whether the specimen is behaving as thermally thick or thin [15]. Finally, the mass loss rate (MLR) is defined as the rate of mass change in the sample. Once the material ignites, this corresponds to the mass burning rate. Estimates of the MLR are important in order to calculate the effective heat of combustion (EHC) of the sample if the HRR is known.

Measurements of the piloted ignition delay time, heat release rate, mass loss rate, and heat of combustion can be used to characterize the fire behaviour of materials. Parameterization of the sample thickness, composition, and external radiant flux can be used to characterize the material flammability and its sensitivity to different parameters. This particular study focuses on the effect of the sample thickness and external radiant flux. Three sample thicknesses and two external radiant fluxes were investigated. A repeat of each sample was performed. Table 4.1 summarizes the experimental test matrix.

Table 4.1 Test samples configuration

Sample #	Measured thickness/mm	No. plies	Heat flux kW.m^{-2}
S1	3.45	4	20
S2	4.54	6	
S3	6.94	8	
S4	3.34	4	35
S5	4.57	6	
S6	7.05	8	

4.2.3 Sample preparation

The sample was prepared as per the standard ISO 5660-1. A 10 cm gap was maintained between the sample and the heat source. A rectangular sample holder, with a 2 cm wide frame, was used to hold the sample. A 10 x 10 cm sample was used with total exposed area of 88.4 cm^2 were 11.6 cm^2 of the sample was covered by the sample holder. After taring and calibration, the sample was placed under the heat source prior to the start of the test as shown in Figure 4.1.

Aluminium foil was used to cover the sample edge and back surface (surfaces that are not exposed to the fire). Insulation was placed at the back face of the sample to minimize heat losses. No grid was used on the front surface.

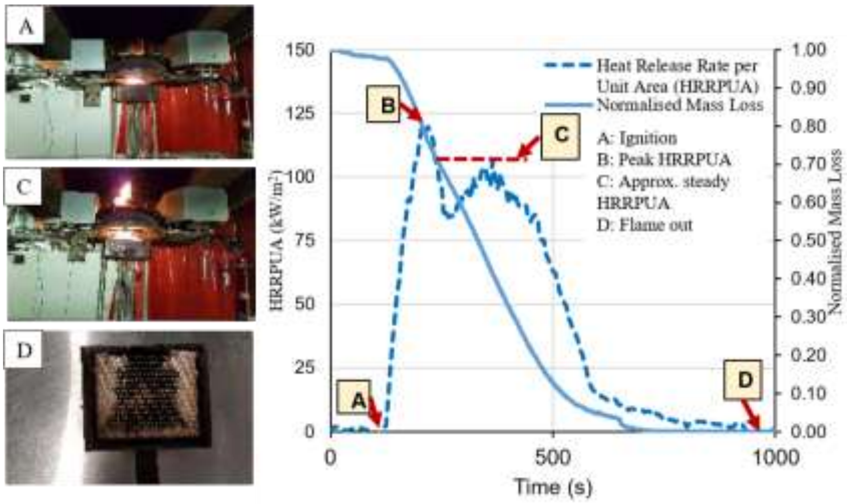

Figure 4.1: Graphical representation of the test

4.3 Results

Figure 4.1 shows the general behaviour of the sample during the test. Before ignition, the sample releases no heat with only a minor decrease in mass. Starting at ignition Point A, the heat release rate and loss in mass increase very rapidly. After reaching the peak HRR value

(Point B, Figure 4.1), the heat release reaches a steady state (Point C, Figure 4.1). After flame out (Point D, Figure 4.1), the PP is fully consumed and only glass fibre remains.

Table 4.1 shows the test results for samples with three different thicknesses and two different heat fluxes used. Total mass loss is comparable for all heat fluxes and sample thicknesses covered in this study. Visual inspection of the residues suggests that all PP was consumed during the test and that only the glass fibre remained. This was to be expected, as glass fibre needs a much higher heat flux to be consumed. The average EHC (amount of energy released per unit area) was found to be 17.33 MJ/m^2.

Table 4.2 Test results for different sample thicknesses and heat flux

Heat flux kW.m^{-2}	Thickness /mm	Peak HRR kW.m^{-2}	Mass loss %	Mean EHC MJ.kg^{-1}	Total heat release MJ.m^{-2}	Time to ignition s
20	3.45	119	36.9	17.8	39	128
	4.54	115	35.3	17.2	46.1	159
	6.94	95	35.4	17.00	66.4	183
35	3.34	169	38.3	17.9	38.8	52
	4.57	129	37.0	17.1	50.8	56
	7.05	122	37.9	17	71.5	55
			36.8 ± 3.18	17.33 ± 1.05		

As shown in Table 4.1, the time to ignition is clearly influenced by the change in sample thickness. For a heat flux of 20 kW/m^2, it changes from 128 seconds for the thinnest sample (3.45 mm thick) to 183 seconds (an increase of 43%) for the thickest sample (6.94 mm thick). Figure 4.2A shows the heat release rate profile for the three different thicknesses. The peak HRR value is comparable for the sample thicknesses of 3.45 and 4.54 mm (at 119 and 115 kW/m^2, respectively) but is significantly lower for the higher thickness of 6.94 mm (96 kW.m^2). Although the total mass loss is almost the same in the three different samples, the mass loss rate is different. This can be seen in Figure 4.2B, which shows the normalized mass over the duration of the test.

For a heat flux of 35 kW/m^2, time to ignition values are comparable for all thicknesses. This indicates that time to ignition is less sensitive to sample thickness for high heat flux values (see Table 4.1). Figure 4.3A shows the peak values for heat release rate for the different thicknesses. The peak heat release rate for the thin sample (3.34 mm) is significantly higher (170 kW.m^2) compared to the other two samples, where comparable peak heat release rates were observed (129 and 122 kW.m^2). The rate of mass loss for the three samples can be seen in Figure 4.3B.

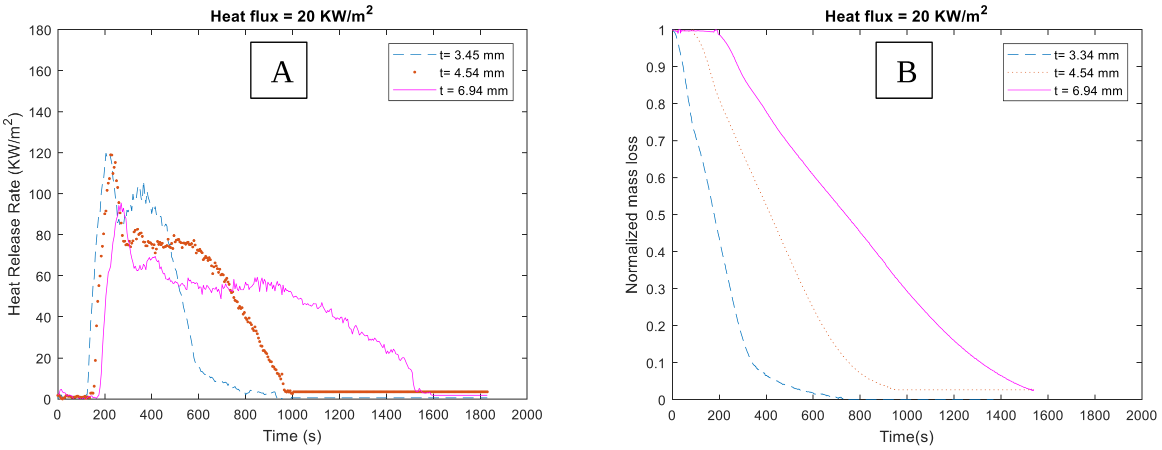

Figure 4.2 HRR values for different sample thicknesses. Heat flux = 20 KW/m^2

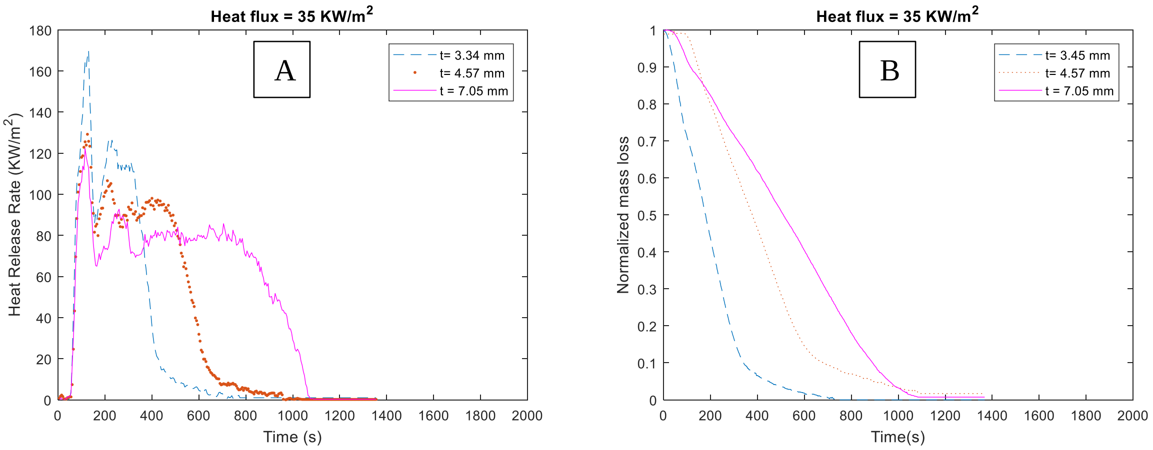

Figure 4.3: HRR and normalized mass loss for different sample thicknesses. Heat flux = 35 kW.m^2

4.4 Conclusions

As expected, the visual inspection of the residues suggests that the glass fibres do not directly take part in the combustion. This is evident when comparing the nominal matrix mass fraction (40%) with the average mass loss (36.8%). The small difference between these can likely be explained by the matrix material being squeezed out during the manufacturing process. The effective heat of combustion measured was 17.3 MJ.kg-1. This is substantially lower than the effective heat of combustion typically reported for polypropylene (44 MJ.kg-1) [16]. The reason for this is not entirely clear. It could be a result of either a fire retardant additive used in the Twintex polypropylene fibres or it could be an indication that the fibre reinforcement significantly changes the specific energy evolved during the combustion of this type of polypropylene. This highlights the importance of a control virgin polymer sample where the composition is known.

The prediction of fire behaviour from polypropylene's constituent properties is not always this trivial, which can be shown by comparing the peak heat release rate for polypropylene (1,525 KW/m^2 @ 35 KW/m^2 heat flux) [13] and the one measured in the experiments presented here (170 KW/m^2). Clearly the relationship is not linear. When comparing the peak heat release rates for different thicknesses, we further note a clear influence of the sample thickness on the peak heat release rate. In our case, the peak heat release rate dropped by 28% when the thickness was increased from 3.34 mm to 7.05mm for heat flux of 35 KW/m^2 and by 20% for heat flux of 20 KW/m^2. This suggests that the peak heat release rate follows a much more complex behaviour and is a function of the fibre loading, heat flux and sample thickness.

Another example of a fire parameter which is not trivial for prediction of fire behaviour is the time to ignition. Not only do the results show a strong influence of the sample thickness, but also a strong sensitivity to heat flux. Across the thickness range tested, a difference of 39% was observed for a heat flux of 20 KW/m^2 and 9.5% for a heat flux of 35KW/m^2. This behaviour can be explained by the thermal gradient in the test specimen. For thick samples and a low heat flux, a more pronounced thermal gradient exists in the through thickness direction of the sample and hence the sample behaves as thermally thick ($B\rightarrow\infty$). With a decreasing sample thickness and in a higher heat flux, the ratio between the internal and external heat transfer resistance becomes smaller ($Bi\rightarrow 0$).

The results for the peak heat release rate and time to ignition highlight that the sample thickness can have a significant influence on certain fire parameters.

With real industrial applications in mind, the results presented here show that even for relatively simple parameter variations such as the sample thickness, key fire performance parameters such as the peak heat release rate and time to ignition, are difficult to predict from a sample's constituent parameter values. It is also evident that a much more comprehensive investigation is required to derive these complex relationships. This will be the focus of our future work.

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Chapter 5

Fire performance of continuous glass fibre reinforced polycarbonate composites: The effect of fibre architecture on the fire properties of PC composites

Motivation

After the benchmark study presented in Chapter 4, it was concluded that in order to well understand the contribution of the matrix and fibre to the fire performance of polycarbonate composite materials, a virgin, non-modified matrix has to be included in the research. It was also found that all fibres included in an investigation into the fire performance of such materials have to have similar key properties in terms of aerial density and fibre diameter and they must also source from the same manufacturer to avoid manufacturer differences.

Review

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Fire performance of continuous glass fibre reinforced polycarbonate composites: The effect of fibre architecture on the fire properties of polycarbonate composites

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and Michael T Heitzmann[1,2]

Abstract

The fire performance of polycarbonate (PC) resin and the role of glass fibre reinforcement in altering its fire performance were examined. Three different fibre weaves with a comparable surface density (plain, twill, and unidirectional glass fabrics) were used as reinforcements. E-glass fabrics were solution impregnated with PC/dichloromethyl, laid up, and compression moulded to consolidate the glass fibre reinforced PC composite. Cone calorimetry tests with an incident radiant flux of 35 kW/m^2 were used to investigate the fire properties of PC resin and its composites. Results showed that glass fibre reinforcement improves PC performance by delaying its ignition, decreasing its heat release rate, and lowering the mass loss rate. The three fibre weave types exhibited similar times to ignition. However, the unidirectional fibre had a 35% lower peak heat release rate when compared to the plain and twill weave fibres.

Author contribution percentages (Chapter 5)

Author	Sample manufacturing	Testing	Data Analysis	Paper writing	Paper editing
Yousof Ghazzawi	100%	100%	70%	100%	-
Michael Heitzmann	-	-	20%	-	70%
Andres Osorio	-	-	10%	-	30

5. Fire performance of continuous glass fibre reinforced polycarbonate composites: The effect of fibre architecture on the fire properties of PC composites

5.1 Introduction

Thermoplastic composites are trending in several applications in the aerospace, automotive, and construction industries, just to name a few. This is due to their ease of manufacture, short cycle times, and the low cost of the matrix. In composites, the choice of materials used is predominantly driven by structural design considerations. Understanding how these decisions affect fire performance is important so that safety implications are clear from the onset. Although the thermal and combustion properties of many thermoplastic matrices are to some extent known [1, 2], the fire performance of thermoplastic composites is still an active area of research [3-12]. In addition to improving mechanical properties, fibre reinforcement can be used to affect the behaviour of a polymer matrix during a fire [13].

Previous work on thermoplastic composites has focused on improving the fire performance using fire retardant additives. More recently, research has centred on improving the fire performance of thermoplastics by changing the reinforcement type, fibre length, quantity of fibre, fibre orientation, and fabric architecture [14-18].

The reaction to fire of a composite involves a complex interplay of factors: the matrix composition and thermal properties, fibre properties, fibre loading and fabric architecture. For instance, in PP and PET matrices with basalt fibres, a twill weave composite has the minimum burning rate followed by a matt weave and a plain weave [19]. In a self-reinforced PP composite, a plain weave fabric has the minimum peak heat release rate followed by a unidirectional weave fabric [20]. In glass fibre, a unidirectional fabric has the minimum peak heat release rate followed by plain and twill; while in flax fibre, unidirectional and twill fabrics have a similar peak heat release rate [21]. This is clear evidence that the fabric architecture influences thermoplastic composites' performance in fire. It also indicates that this relationship is also driven by the matrix and fibre type.

The majority of prior work on the fire performance of thermoplastics has focused on commodity thermoplastics such as polypropylene [22-25] or high performance thermoplastic matrices such as PPS and PEEK [26-29]. Engineering thermoplastics such as PC have received minimal attention. PC is a relatively high temperature thermoplastic matrix with a glass transition temperature of around 150^{o} C and a char yield of approximately 22% [30]. Good thermal stability, toughness and a relatively high char yield combined with a relatively low cost and availability make PC an attractive choice in applications in which fire performance may be a concern.

The aim of this study is to evaluate the fire performance of a PC matrix and a continuous glass fibre reinforced PC. Plain, twill, and unidirectional glass fibre fabrics are compared in order to determine the influence of fabric architecture on the fire performance of continuous glass fibre reinforced PC composites. Cone calorimeter tests are used to analyse and compare the fire performance of these composites in terms of their time to ignition, heat release rate, mass loss, and residual mass. The choice of fire performance parameters included in the study is based on their importance as key parameters [31, 32]. Other important parameters such as flame spread rate and limiting oxygen index are not included in the study since they require different test setups. Thermogravimetric test results and scanning electron microscope pictures are used to complement the analysis and further explain the findings. Details of the samples are given in Table 5.1.

5.2 Material

SABIC PC (PC2200) grade with a melt index of 22 g/10 min was used as the matrix material for all samples. E-glass fibre fabrics were sourced from Swiss Composite, a plastic fabrication company. Three types of fibre architectures, plain weave, twill weave, and unidirectional weave, with comparable weight to area ratios (areal weights) were used. The specific fabrics were: plain weave, 280 g/m^2, twill weave, 280 g/m^2, and unidirectional weave, 288 g/m^2. The nominal fibre volume fraction was 50%. In this investigation, fabric architecture refers to the weave type whereas fibre orientation refers to the fibre angle. The role of fibre orientation in the fire performance of PC composites is not a parameter in this study and thus it remained constant in all samples. Samples were manufactured using a solution impregnation method. The solution (12% wt. PC, 88% wt. dichloromethyl) was impregnated individually into each fibre layer. Samples were dried for two hours at 40^{o}C in a vacuum oven fitted with a cold trap in order to recover the solvent.

After drying, the fabrics were laid up and compression moulded at 260^{o}C under a constant pressure of 1.25 MPa for 20 min. Samples were cooled to 60^{o}C while maintaining pressure prior to releasing the press. Twenty layers of fabric were used to make 250 x 250 mm plates with a thickness of 4.2±0.15 mm. Finally, plates were cut into 100 x 100 mm samples for the cone calorimeter tests.

Two sets of virgin (unreinforced) PC matrices were manufactured. One had the same PC mass as the glass fibre reinforced composites (Set 1) and another had a comparable thickness to the glass fibre reinforced composite (Set 2). The two sets were used as benchmarks for comparing the fire behaviour of the glass reinforced samples against that of the unreinforced PC samples. Set 1 had an average thickness of 2.3±0.22 mm and Set 2 had an average thickness of 4.5±0.12 mm.

5.3 Experimental

Samples were tested for heat release rate (HRR), time to ignition (t_{ig}), mass loss rate (MLR) using a cone calorimeter (Fire Testing Technologies, Icone Calorimeter) according to ISO 5660-1. The backs of the 100 x 100 mm specimens were wrapped with aluminium foil in order to minimise radiation heat losses and prevent spurious mass loss readings due to melting and dripping. The back faces of the samples were insulated using an inorganic insulation in order to minimise heat losses. A retaining frame, as suggested in ISO 5660-1, was used to restrain the exposed surface of the sample and prevent contact with the heating element.

All the tests were performed with an incident radiant flux of 35kW/m^2. Piloted ignition of the samples was accomplished using an electric spark located 10 mm above the sample. A sampling rate of 1 Hz was used to record the mass and heat release data. All PC composite specimens had comparable thicknesses with the exception of the first set of PC control samples. Thermogravimetric analyses (TGA) with a PerkinElmer STA 6000 in air and nitrogen at a rate of 10^{o}C/min from room temperature to 700^{o}C was used to analyse the thermal decomposition of samples. Sample weights between 10 mg and 12 mg were used. PC pellets were used for the virgin PC. For the PC composite, samples were taken from different parts of the composite plate and three repetitions were done. The most representative sample based on prior knowledge of the fibre weight fraction was selected. Scanning electron microscope (SEM) images of samples after fire exposure were used to investigate the interaction between the fibre architecture and the matrix, which contributed to the analysis of the observed fire behaviour.

5.4 Results and Discussion

Three samples of each configuration were tested to find the residual mass, time to ignition, flameout time, time to peak HRR and peak HRR. Results reported for three repeats as an average with a 90% confidence interval are shown in Table 5.1.

Table 5.1: Cone calorimeter test results for virgin PC and PC composite with three different weaving types

		Set 1	Set 2	CP	CT	CUD
Initial mass	(g)	25.7±2.3	53.6±2.3	81.0±1.4	82.8±1.0	81±1.2
Thickness	(mm)	2.3±0.2	4.5±0.1	4.2±0.1	4.4±0.2	4.2±0.1
Fibre volume fraction	%	-	-	51.0±1.0	49.5±0.5	50.5±0.5
Residual mass	(g)	5.4±0.8	11.7±5.5*	61.1±0.9	60.8±0.5	62.4±0.7
Residual mass	(%)	21.2±1.5	21.7±9.5*	75.5±1.1	73.4±0.6	77.4±1.7
Time to ignition	(s)	129±59	167±38	252±7	270±11	265±11
Flameout time	(s)	436±47	774±30	667±16	684±13	717±40
Burning time	(s)	304±72	511±42	416±23	415±13	446±32
Time to peak HRR	(s)	213±49	370±60	387±27	437±19	430±21
Peak HRR	(kW/m^2)	422±59	331±55	227±24	224±39	164±20
MARHE	(kW/m^2)	128±7	148±10	74±2	77±2	63±1
Total heat release	(MJ/m^2)	48±2	105±21	46±4	52±7	44±6
Effective heat of combustion	(MJ/kg)	22.6±0.7	21.5±1.2	23±1.4	24±2.2	23.6±2.6
Avg specific MLR	(g/s.m^2)	5.7±0.9	6.2±1.0	5.5±0.2	6.2±1.4	5.5±0.4

*High error margin due to char blown by air during testing. PC$_m$: PC mass similar to the matrix mass in composite. PC$_t$: PC thickness similar to composite thickness. CP: plain weave fibre composite. CT: twill weave fibre composite. CUD: unidirectional fibre composite. MLR: mass loss rate. -: not measured

5.4.1 Effect of fibre reinforcement

Based on the TGA results shown in Figure 5.1, PC starts losing weight around 450°C. Approximately 75% of the mass is lost between 450°C and 500°C. At temperatures above 500°C, the rate of thermal decomposition is reduced. Above 500°C, PC behaviour in air is different to its behaviour at the same temperature in nitrogen. In air, PC loses mass at a slower rate between 500°C and 600°C but this increases again above 600°C until PC loses all its weight at 700°C. In nitrogen, PC starts stabilizing at 500°C with 20% remaining weight at 700°C. Glass fibre reinforced PC composites also start decomposing at around 450°C, as shown in Figure 5.2. It can be noted that the PC in the glass fibre composite decomposes at the same rate as virgin PC (see Figure 5.1). This indicates that the glass reinforcement has no effect on the mass loss of PC.

According to the TGA results, the mass residue of pure PC in air is zero and about 20% in nitrogen. Reinforced PC showed a mass residue of 70% in air and 75% in nitrogen. The fibre mass fraction in reinforced PC is about 70%, which equates to the percentage residue observed in TGA tests done in air, showing that all the PC is consumed. In this study, reinforced PC has approximately 30% PC by mass. The higher mass residue observed in nitrogen is because of the charring nature of PC. Based on these TGA results, the expected amount of char from pure PC would be about 6% of the total weight of the sample. Therefore, the mass residue observed for reinforced PC burned in nitrogen is the sum of the fibre residue (about 70% by mass) and the PC char residue (about 5% by mass)

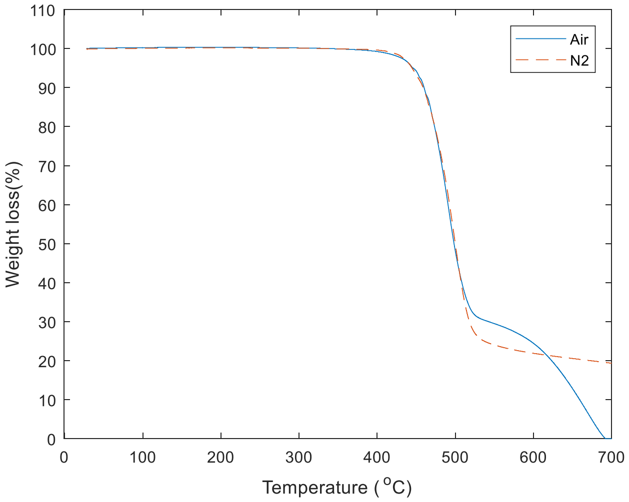


Figure 5.1: TGA results for pure PC samples

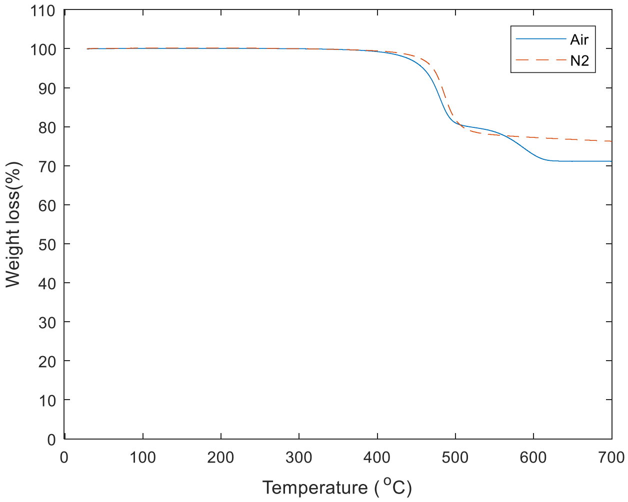


Figure 5.2: TGA for glass fibre reinforced PC composite

There is not much difference in the mass residues, which suggests that fibre reinforcement does not significantly affect the thermal decomposition of the matrix. The enhanced fire performance of the glass fibre reinforced PC composite can be observed in the times to ignition presented in Table 5.1. For an incident radiant flux of 35 kW/m^2, Set 1 samples ignited in 129 ± 59 seconds and Set 2 samples ignited in 167±38 seconds (+29%). The longer time to ignition observed in

Set 2 samples is associated with the larger mass of the sample and the associated thermal mass. Larger thermal masses will require larger amounts of energy to reach the same temperature.

Times to ignition of glass fibre reinforced PC samples were 252±7, 270±11, and 265±11 seconds for plain, twill, and unidirectional fibre architecture, respectively. The increased ignition delay times suggest a change in the temperature evolution of the solid and its thermal decomposition. Thermal decomposition is linked to the evolution of the temperature within the solid. The observed changes in the ignition delay time suggest that the addition of fibre modifies the thermal properties of the material and the heat transfer process.

Figure 5.3 presents the mass loss history of Set 1, Set 2, and the plain weave glass fibre composite. In this figure, it can be observed that Set 1 (equal matrix mass) has the largest mass loss rate, followed by the plain weave glass fibre composite, and finally Set 2 (equal thickness). As expected, the mass loss in Set 1 is the fastest due to this set’s smaller thermal mass. Set 2 samples had the lowest mass loss rate, which could be attributed to the longer time to reach the pyrolysis temperature and intumescence. The addition of glass fibre to the PC matrix reduced the mass loss rate of the sample when compared to Set 1 samples.

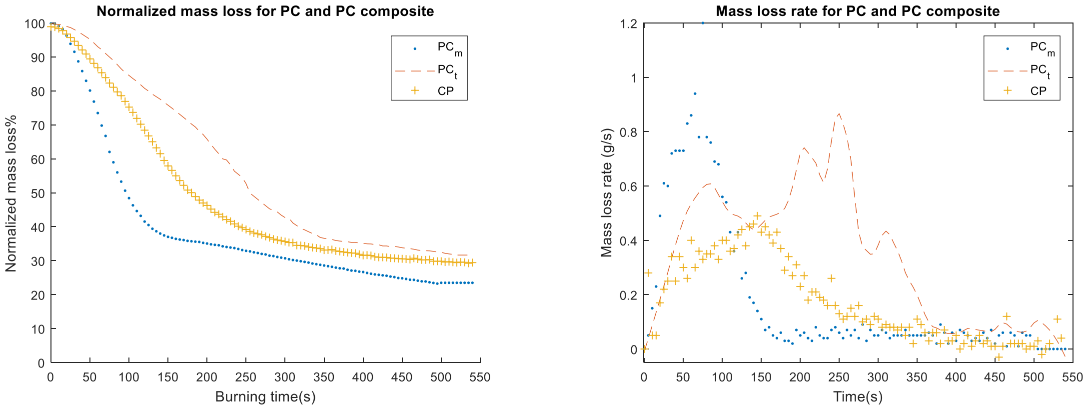


Figure 5.3: Mass loss and mass loss rate history for PC and PC composite specimens

The differences in the mass loss rate of the samples can be explained in terms of the heat transfer within the sample. Set 1 samples will be expected to have the fastest mass loss rates since they have the smallest initial mass and their thermal properties are those of pure PC. The addition of glass fibre does not change the PC mass in the composite, however it is likely that it affects its thermal properties, i.e. density, thermal conductivity, and specific heat capacity. Modification of the thermal properties will affect the heat transfer within the solid, and, with that, the rate at which the solid undergoes thermal decomposition.

The effect of the glass fibre on the thermal properties of glass fibre reinforced PC composites can be observed in the differences in the time to ignition. For a thermally thick solid, the ignition delay time may be estimated according to Equation 5.1 [32].

$$t_{ign} = \frac{\pi}{4} k\rho c_p \left(\frac{T_{ig} - T_0}{\dot{q}"_{ext} - \dot{q}"_{loss}} \right)^2 \tag{5.1}$$

where $k\rho c_p$ is the thermal inertia, T_{ig} is the ignition temperature, $\dot{q}"_{ext}$ is the externally applied radiant heat flux and $\dot{q}"_{loss}$ is the heat surface loss by radiation and convection. Both Set 1 and Set 2 samples have similar ignition delay values, however all three glass fibre reinforced composites have significantly longer ignition delay times. Given that all samples have the same matrix, it could be argued that all of them would have a similar ignition temperature (T_{ig}). Under this assumption, differences in the ignition delay time may be attributed to changes in the thermal inertia ($I_{th} = k\rho c_p$) of the samples arising from the addition of glass fibre. Changes to the thermal properties will affect heat transfer within the samples and the rate at which they undergo thermal decomposition.

The fact that the Set 2 sample in Figure 5.3 had a smaller mass loss rate has to do with the increased thermal mass of the sample in comparison to Set 1 and plain weave samples. In the first instance, the larger thermal mass requires a greater heat input in order to undergo thermal decomposition. Additional factors such as charring and intumescence will also affect the thermal decomposition rate and the residual mass. A thicker char layer will result in a lower heat transfer to the solid and, with it, a reduced thermal decomposition rate that will ultimately result in a higher residual mass. Figure 5.4 shows a top and back view of a burned glass fibre reinforced PC sample. The pictures show that the PC composite still maintains some structural integrity due to the PC residue. From the TGA presented in Figure 5.1, it can be seen that PC has a mass residue of 22%. This is further investigated using SEM.

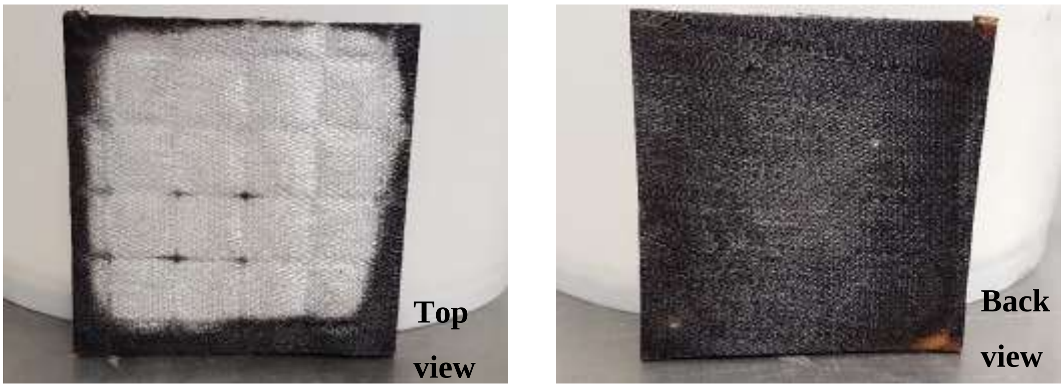


Figure 5.4: Glass fibre reinforced PC after fire testing

The heat release rate data for a representative sample of Set 1, Set 2, and plain weave composites is shown in Figure 5.5. In this figure, the Set 1 sample exhibited behaviour typically associated with thermally thin samples, a short burning time with a sharp peak heat release rate value of about 422±59 kW/m^2. In comparison, the Set 2 sample exhibited behaviour associated with thermally thick materials. The peak heat release rate of this sample was about 331±55 kW/m^2, making it lower than that of Set 1. This is expected, given the lower mass loss rate of the Set 2 samples as shown in Figure 5.3. Set 2 samples also had a longer burning time, 511±42 seconds versus 304±72 seconds for Set 1. The plain weave glass fibre reinforced composites had a peak heat release rate value of 227±24 kW/m^2, resulting in a noticeable reduction of glass fibre reinforced composites when compared to a pure PC matrix. The improved heat release rate and peak heat release rate performance of PC composites when compared to the virgin PC are correlated to PC composites having 50% lower total heat release, as shown in Table 5.1.

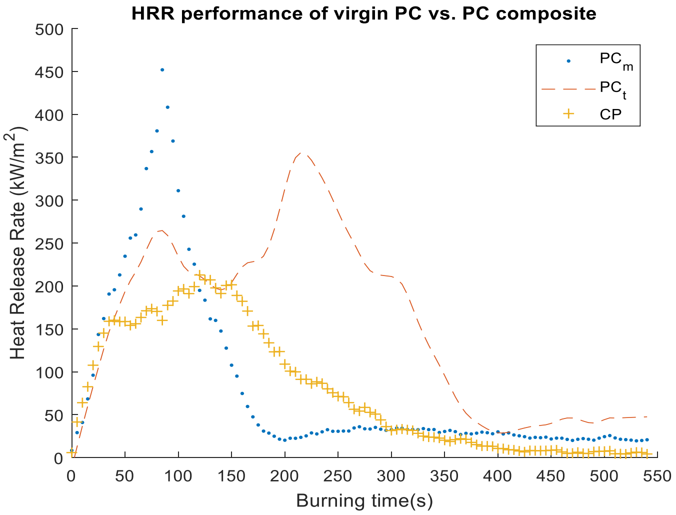


Figure 5.5: HRR curves for PC and PC composite

5.4.2 Effect of fibre architecture

The addition of glass fibres showed a reduction of the peak heat release rate and the maximum average heat radiation emission (MAHRE). The reduction in both these values is attributed to the reduced mass loss rate of glass fibre reinforced composites in addition to the reduction in the heat of combustion (ΔH_c). The heat release rate is calculated using Equation 5.2.

$$HRR = \dot{m}''_b \Delta \mathrm{H}_{\mathrm{C}}^{eff} \tag{5.2}$$

Reductions in both the specific mass burning rate ($\dot{m}''_b$) and/or the heat of combustion will result in reductions in the heat release rate. $\Delta \mathrm{H}_{\mathrm{C}}^{eff}$ is the effective heat of combustion in the pyrolysis product in flame.

As shown in Table 5.1, the three fabric weaves used in this study exhibited a comparable time to ignition, 252±7, 270±11, and 265±11 seconds for plain, twill, and unidirectional fibre architecture, respectively. Differences between the three fabric architectures are within the acceptable margins for error, and therefore it is not possible to conclude that the fibre architecture has an effect on the ignition delay time of glass fibre reinforced PC composites. Figure 5.6 shows the mass loss rate curve for the three fibre architectures. Once again, there is not enough evidence to suggest that the fibre architecture has a significant effect in the mass loss rate nor the percentage of mass residue; all fibre architectures had similar percentages of mass residue. Interestingly enough, the percentage of mass residue observed by using the cone calorimeter closely matched the value obtained from the TGA testing done in nitrogen.

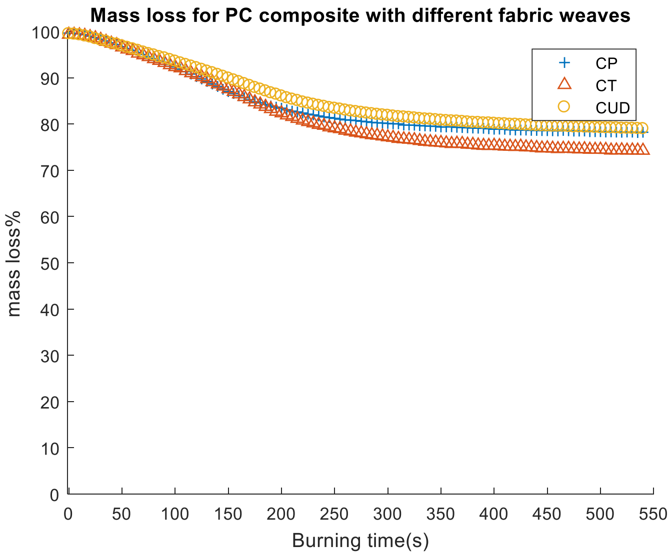


Figure 5.6: Mass loss rate for PC composite with different weaves

In terms of the heat release rate, the plain and twill weave composites behaved similarly. Both the peak heat release rate and the MAHRE were comparable for plain and twill weave samples. In this respect, unidirectional fibres were noticeably less when compared to plain and twill weaves composites. For example, plain weave composites had a peak heat release rate value of 227±24 kW/m^2, whereas unidirectional fibre composites had a value of 164±20 kW/m^2, approximately 25% less. Examples of heat release rate data for representative plain, twill and unidirectional weave samples are displayed in Figure 5.7.

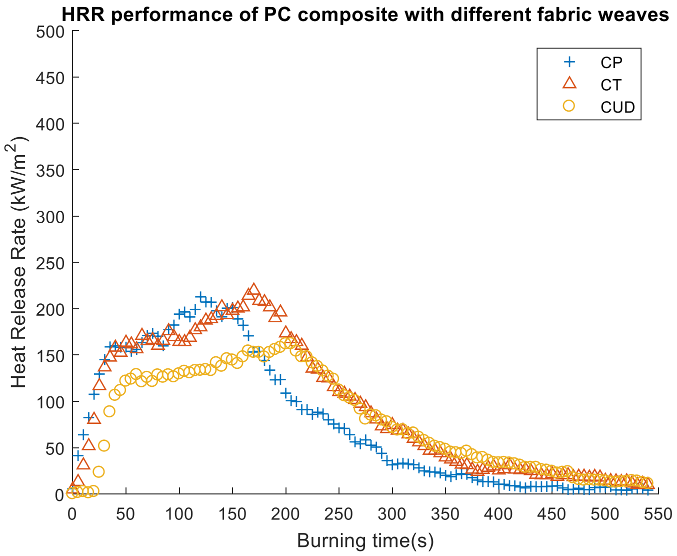


Figure 5.7: HRR curves for PC composites with different weaves

Scanning electron microscopy was carried out to investigate the structure of the composite samples after their exposure to fire. Due to the difficulty in preparing the samples for SEM (as layers were fracturing), the sheets were secured with scotch tape and cross-sectioned using a single edged stainless steel blade. The cross-sectioned sheets were attached to 12.5 mm diameter Al SEM stubs and Au-Pd sputter coated for 1-2 mins at a deposition current of 25 mA under 0.1 mbar pressure. Figures 5.9-5.11 show the SEM images for each kind of composite sample after cone calorimeter testing. Cross-sectioned layers with thicknesses ranging from 85 to 200 μm of glass fibre were used for this observation. SEM images show that there is a remaining PC matrix after testing (the light coloured material observed in some regions of the specimen). It is interesting to note that the char residue from the matrix is mainly situated within the fibre tows (see Figures 5.9-5.11 b & c) and that the gaps between the weft and warp do not contain char residues (see Figures 5.9-5.11 a).

Most of the char residue appears to be disconnected from the fibre. Only in a few cases, the char residue appears firmly connected to the fibre. It was found that the PC composite exhibited some structural rigidity after the fire testing. Based on the SEM images we can conclude that the residual strength is likely achieved through an interlocking structure formed between the PC matrix char and the fibre weave. Due to the lack of char adhering to the fibre surface, we can further conclude that char/fibre adhesion is likely not the driving mechanism in the post fire strength retention. This ultimately suggests that the large surface area and mechanical interlocking are primarily responsible for the post fire retention of some structural integrity. No evidence of fibre breakage, oxidisation or degradation was observed.

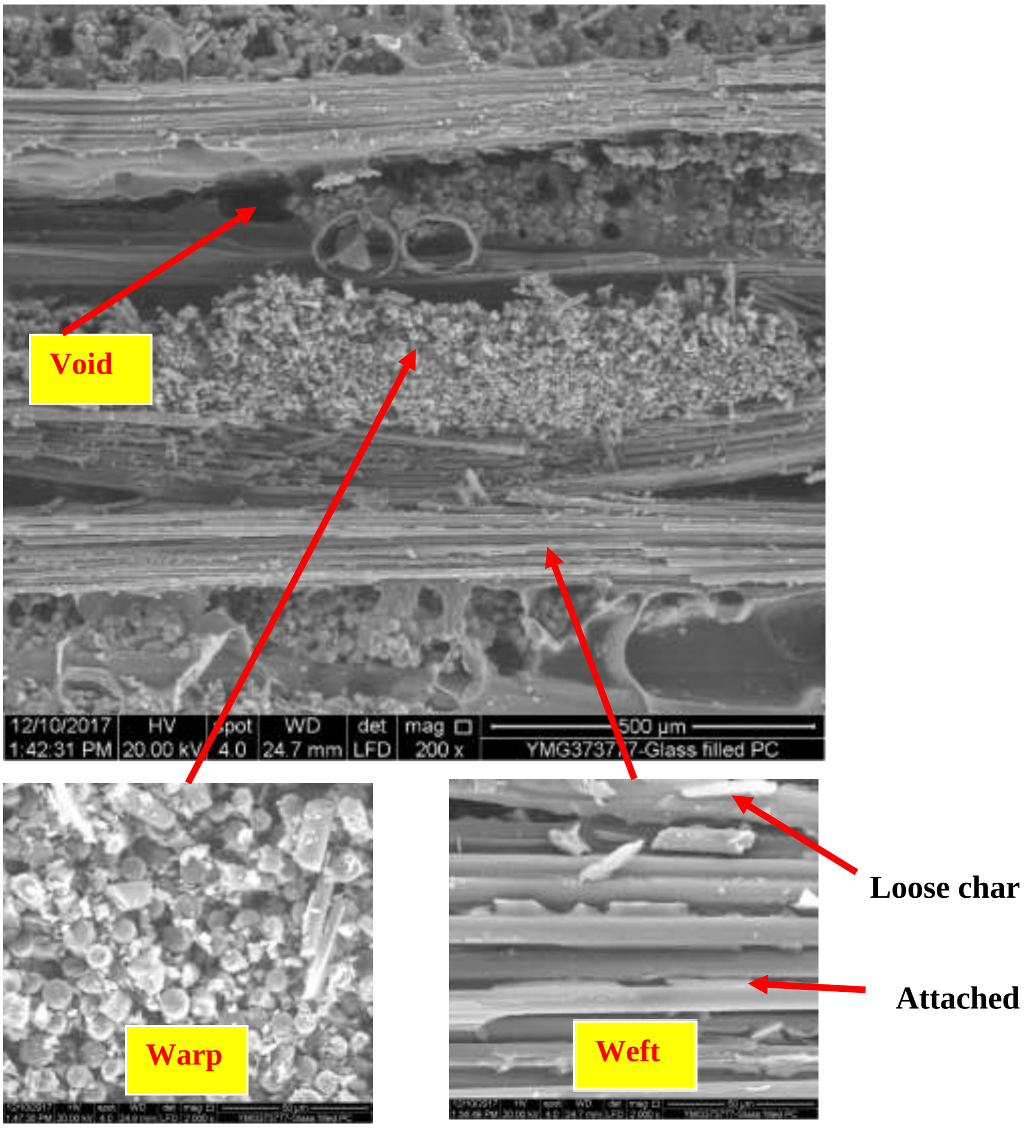
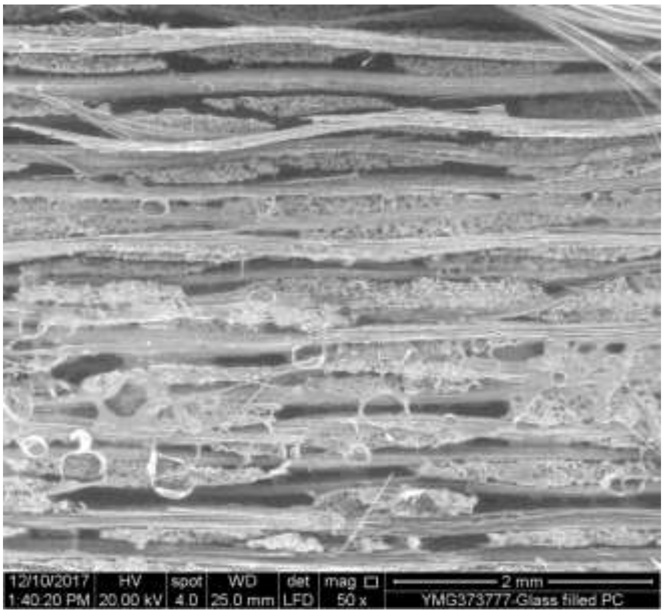
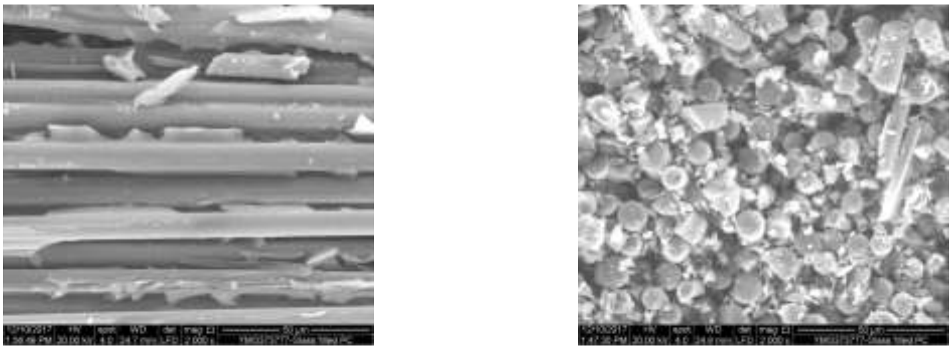


Figure 5.8. SEM images for PC reinforced samples after cone calorimeter testing

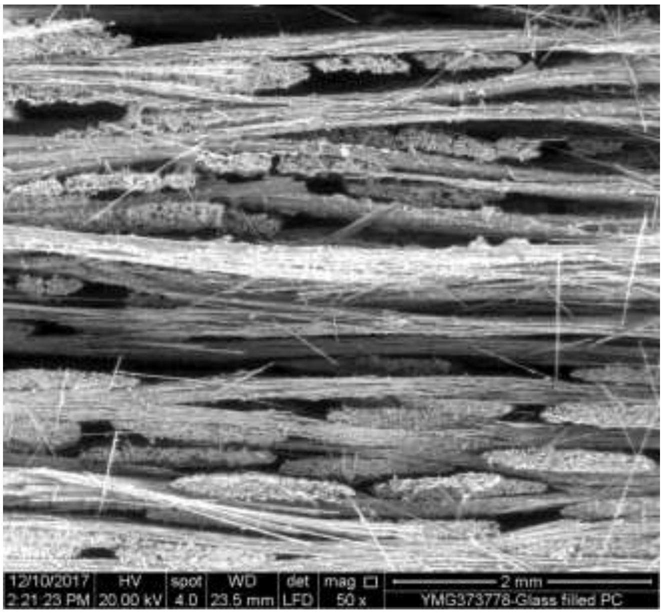


a) General SEM image of cross-section

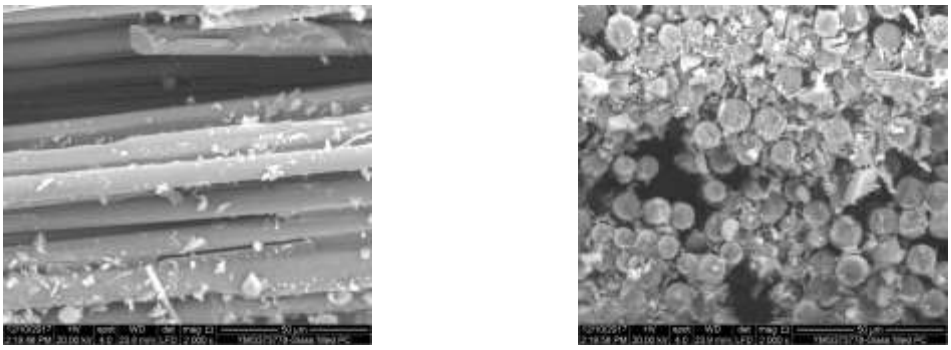


b) 2000x magnified side view SEM image c) 2000x magnified top view SEM image

Figure 5.9: SEM images for plain weave PC composite after fire testing

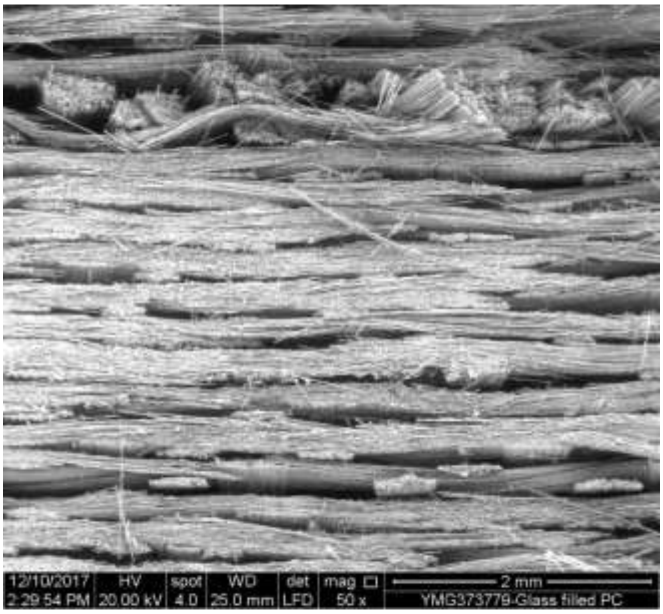


a) General SEM image of cross-section

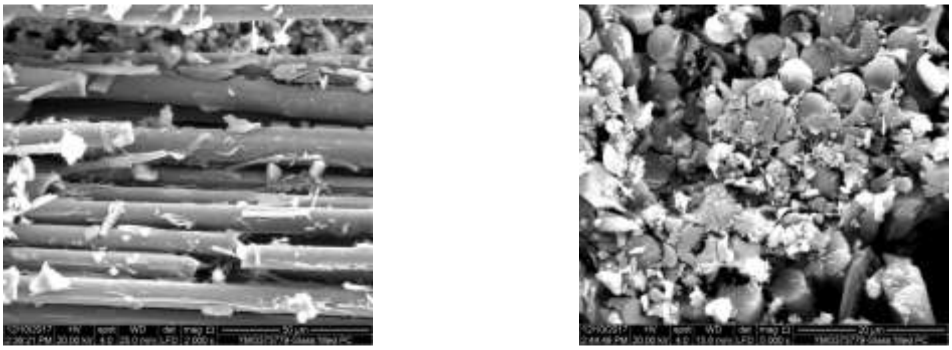


b) 2000x magnified side view SEM image c) 2000x magnified top view SEM image

Figure 5.10: SEM images for twill weave PC composite after fire testing



a) General SEM image of cross-section



b) 2000x magnified side view SEM image c) 5000x magnified top view SEM image

Figure 5.11: SEM images for unidirectional weave PC composite after fire testing

5.5 Conclusion

Virgin PC was found to have good fire properties in terms of it being thermally thick with a thickness as low as 4.5 mm and a relatively high char yield of 22%. Glass fibre reinforcement provides a significant improvement to the fire performance of PC. It causes delayed ignition and a lower heat release rate, with an effective heat of combustion nearly equal to that of PC. This could be due to the thermal properties of glass fibres and a resulting change in combustion/pyrolysis conditions at a micro level. Another contributing factor is that PC composites have 50% less consumable mass when compared to virgin PC. In addition, the glass fibre is not consumed by fire.

The different fibre architectures investigated did not seem to have a major effect on time to ignition and mass loss rate. However, the peak heat release rate value was significantly lower in unidirectional fibres. SEM images of composite samples show that the residual char is primarily located within the fibre tows and is mostly detached from the fibre surface. Therefore it is concluded that the post fire residual integrity of the composite is a function of the relatively high char yield and mechanical interlocking between fibre and char particles.

In order to further explain the reason behind different fibre architectures having different fire properties for a comparable fibre volume fraction and the same aerial density, more emphasis needs to be put on examining the thermal characteristics of glass reinforced PC and how these change as a function of the fibre architecture. Fire performance encompasses characteristics such as ease of ignition, contribution to the fire and even residual capacity. Fibre reinforced composites provide an opportunity to optimize the fire performance of thermoplastics for specific fire performance requirements. Manipulation of the thermal properties can lead to significant changes in the fire performance of materials. Additional work is necessary to analyse the effect of the fibre architecture and fibre type on the thermal properties of solids and to tailor the fire performance of composites for particular applications.

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Chapter 6

The effect of fibre length on fire performance of thermoplastic composites: The behaviour of PP as an example of a non-charring matrix

Motivation

After studying the fire performance of a PC matrix, the corresponding performance for a PP matrix must also be examined. Fibre architecture was found to have a limited effect on the fire performance of composites. Therefore, it was decided to move on to studying the effect of fibre length in this chapter. As seen in Chapter 4, matrix formulations affect the overall fire performance. Hence, the formulations in this study are controlled and fibre length is the only variable. A PP matrix is normally mixed with a compatibilizer in order to enhance its binding to fibre. The effect of the compatibilizer on fire performance of the composite is also considered in this chapter

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The effect of fibre length and matrix modification on the fire performance of thermoplastic composites: The behaviour of PP as an example of non-charring matrix

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Abstract

The fire performance of fibre reinforced polypropylene was investigated with respect to fibre length and modification of the matrix. Three different fibre lengths, 3mm, 12mm, and continuous fibres were used as reinforcements. E-glass continuous fabrics were melt impregnated with polypropylene and consolidated via compression moulding. 3mm and 12mm E-glass fibre reinforced polypropylene pellets were compression moulded. Cone calorimetry tests with incident radiant fluxes of 20kW/m^2, 30kW/m^2, and 35kW/m^2 were used to investigate the fire properties of polypropylene glass fibre composites. Results showed that continuous glass fibre reinforcement exhibits the best fire performance at 20 kW/m^2; while 3mm fibre has the best performance at 35kW/m^2. 12mm fibre reinforced polypropylene exhibited the lowest performance in comparison to 3mm and continuous glass fibre reinforcement. In comparison to unmodified PP, melic-anhydride (MA) modified PP was found to increase the heat release rate by up to 44% and the time to ignition by up to 10% depending on the heat flux applied. The glass fibre reinforced composite made with MA modified PP has a 5 to 12% lower mean heat release rate and a similar time to ignition as the glass fibre reinforced composite with unmodified PP. This suggests improved fibre adhesion plays a role in the fire performance of glass fibre reinforced polypropylene.

Author contribution percentages (Chapter 6)

Author	Sample manufacturing	Testing	Data Analysis	Paper writing	Paper editing
Yousof Ghazzawi	100%	90%	80%	100%	-
Michael Heitzmann	-	-	10%	-	70%
Andres Osorio	-	-	10%	-	25%
Asanka Basnyake	-	10%	-	-	-
Darren Martin	-	-	-	-	5%

6. The effect of fibre length on the fire performance of thermoplastic composites: The behaviour of PP as an example of a non-charring matrix

6.1 Introduction

Thermoplastic composites are becoming more widely used in the aerospace, automotive, marine, and construction industries. Polypropylene (PP) is one of the most common matrices used in glass fibre reinforced composites for automotive and consumer goods applications. In addition to the short cycle time and high toughness that thermoplastics generally provide, PP offers a low cost and low density compared with other thermoplastics. With the increased demand for thermoplastic composites comes an increasing demand for fibre performance.

The choice of fibre length for reinforcement is driven by structural requirements as well as manufacturing and economic considerations. It is well understood that the higher aspect ratio fibres offer better mechanical properties for fibre reinforced composites [1-4]. However, it is not well understood how fibre length affects the fire properties.

Previous work has considered the fire performance of continuous and chopped fibre reinforced composites [5-11]. Although longer fibres result in higher thermal conductivity [12], there is not enough evidence in the literature to suggest a relationship between the fibre length and fire performance of a fibre reinforced PP composite.

In most work on composites to date, investigations were made into composites which have a fire retardant modified matrix [13-23]. The presence of fire retardant overwhelms other effects associated with fibre length, orientation or aspect ratio. In a recent work, the increase in fibre length was found to improve the fire performance of a carbon fibre reinforced thermoplastic composite in terms of the heat release rate [24].

Glass fibres are inert and only oxidise at temperature above 800ºC. In contrast, PP undergoes thermal degradation at around 300ºC. When added as reinforcement, fibres can have a diluting effect and may also enhance the composites’ thermal properties (heat capacity and conductivity). This typically improves their fire performance. In Table 6.1, different glass fibre reinforced composites are compared in terms of the time to ignition (Ti), effective heat of combustion (EHOC), and peak heat release rate (PHRR). In all cases, glass fibre improved both the heat release rate and peak heat release rate. Factors such as the time to ignition and effective heat of combustion are not always influenced by the presence of the fibre. The fibre volume percentage has a major influence on what fire performance parameters are improved by fibre addition [25].

Table 6.1: A comparison between matrices and its glass fibre reinforced composite tested at 35 kW/m^2 heat flux

		PP	PC[26]	PEEK[10]	GFRPP	GFRPC[26]	GFRPEEK[10]
Ti	(s)	208	167	110	238	252	115
EHOC	(kW/m^2)	29	21.5	19.9	44	23	19.8
PHRR	(kW/m^2)	418	331	415	325	227	120

Organic materials such as polyethylene (PE) and PP do not adhere well to inorganic fibres such as glass fibre due to its low polarity. Matrix adhesion to fibre is critical to mechanical and thermal properties of the fibre [27-30]. PP is commonly modified with MA (MH), an organic acid with the formula [C_2H_2 (CO) 2O] in an attempt to improve the adhesion to glass fibres. The addition of MH to PP leads to a drop in the mechanical and physical properties of the PP matrix. However, because of the improved adhesion between the glass fibre and PP and the fact that mechanical properties are fibre dominated, the overall mechanical properties of the glass fibre reinforced PP improve significantly.

A large number of studies have shown that MH modification improves mechanical properties such as compression, shear, and transverse properties as a result of improved adhesion between the PP and glass fibre [28, 31-35]. The effect which MH modification has on the fire performance has not received much attention.

This study aims to investigate the role which fibre length and matrix modification have on the fire performance of PP. Samples made from unmodified PP, MH modified PP and the glass fibre reinforced PP composites, made with a modified and unmodified matrix, are compared to explore the influence of chemical modification and physical adhesion on the fire performance of a PP composite. The PP composite is made with chopped 3 mm and 12 mm long glass fibres as well as continuous fibre to study the effect of fibre length on the fire performance of PP composite.

Cone calorimetry tests are conducted to investigate the fire performance of the PP composite in terms of the key fire parameters: time to ignition, heat release rate, and mass loss rate. Thermogravimetric analysis is used to compare the degradation behaviour of the unmodified PP, MH modified PP, and glass fibre reinforced PP.

6.2 Material

Lyonell Basell HP568S PP homopolymer with a melt index of 38g/10 min was used as a matrix. The 280g/m^2 E-glass plain weave fabrics were sourced from Swiss Composite. The 3mm and 12mm chopped fibre reinforced PP were produced with long fibre technology by Duromer Australia. All PP composites had a nominal fibre weight fraction of 30% wt.

The continuous fibre reinforced composites were manufactured using film stacking. The films were dried for 4h at 100ºC. After drying, the fabrics were laid up with the films interleaved and compression moulded at 240ºC under a constant pressure of 1MPa for 10min. Samples were cooled to 50ºC while maintaining pressure prior to releasing the press. 7 layers of fabric were used to make a 250 x 250mm plate.

The chopped fibre reinforced PP samples were dried for 4h at 100ºC and compression moulded at 220ºC under a constant pressure of 1 MPa for 10min. Samples were cooled to 50ºC while maintaining pressure prior to releasing the press. 415 g of pellets were used to make a 250 x 250 mm plate.

Samples were manufactured according to the combinations shown in Table 6.2. The purpose of the test matrix was to study the effect of fibre length and, secondly, to investigate the effect of MH addition on the fire performance of the composite. All compression moulded plates had a nominal thickness of 6mm and were cut to 100 x 100 mm samples for the cone calorimeter test using waterjet cutting.

Table 6.2: Testing sample combinations

Sample	PPN	PPM	S	L	N	M
Matrix	HP568S	ZH27-PL1010	ZH27-PL1010	ZH27-PL1010	HP568S	ZH27-PL1010
MA (% matrix)	0%	2%	2%	2%	0%	2%
Fibre loading (%)	0%	0%	30%	30%	30%	30%
Fibre length (mm)	N/A	N/A	3	12	100	100

CT images were obtained with a Bruker micro resolution Skyscan to verify sample quality, fibre orientation and distribution. We noticed a large difference in the fibre architecture and distribution. As Figure 6.1-A shows, the 3 mm fibre reinforced PP fibres are nested together, distributed randomly in the plane (X-Y plane). In the 12 mm glass fibre reinforced PP (Figure 6.1-B), fibres are also randomly distributed along the X and Y axes but individual bundles are not well separated. This phenomenon is regularly observed in long fibre compression moulded components. Continuous glass fibre reinforced PP (Figure 6.1-C) appeared to be maintaining the original plain weave alignment with no sign of fibre breakage or tilting.

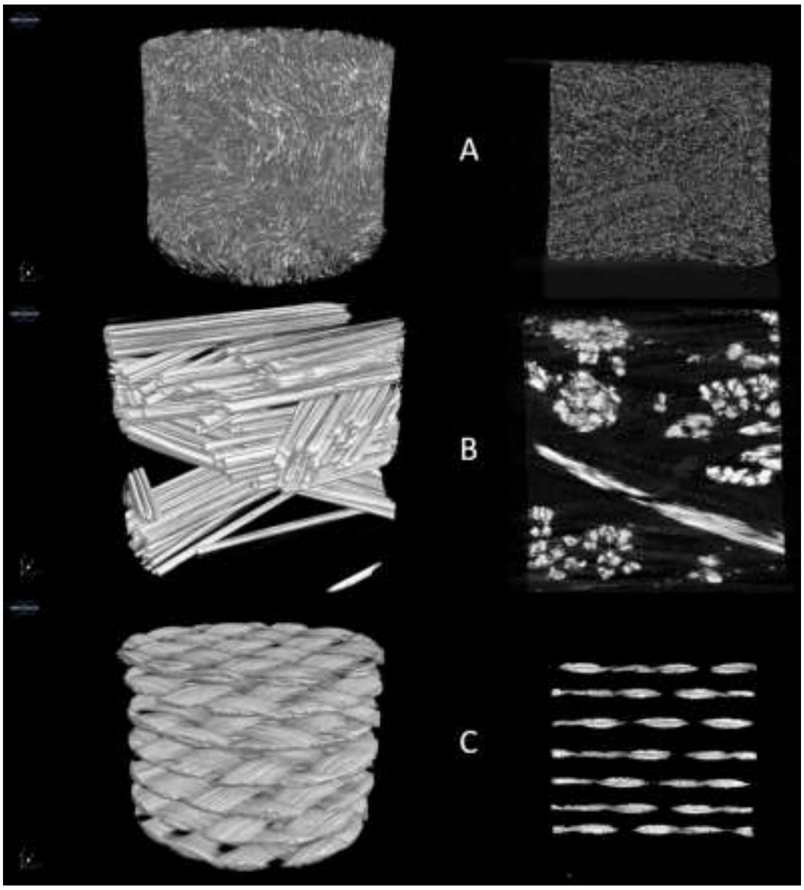

Figure 6.1: CT scan image for A) 3 mm fibre, B) 12 mm fibre, and C) continuous fibre

6.3 Experimental

Samples were tested for the heat release rate (HRR), time to ignition (t_{ig}), and mass loss rate (MLR) using a cone calorimeter (Fire Testing Technologies, Icone Calorimeter) according to ISO 5660-1 . The time to ignition is defined as the time the material takes to ignite when exposed to a given heat flux. The heat release rate is the amount of energy released per unit of area; it is one of the key fire performance parameters as it provides information about the fire growth and rate of fire spreading. The mass loss rate is the mass loss per unit of time; it provides information regarding how quickly the material is losing mass in the case of fire [36, 37]. The backs of the 100 x 100 mm specimens were wrapped with aluminium foil in order to minimise radiation heat losses and prevent spurious mass loss readings due to melting and dripping. The back face of the sample was insulated using an inorganic insulation so as to minimise heat losses. A retaining frame as suggested in ISO 5660-1 was used to restrain the exposed surface of the sample and prevent contact with the heating element.

Incident heat fluxes of 20, 30, and 35kW/m^2 were used. Testing below 20kW/m^2 was not considered since 20kW/m^2 is close to the critical heat flux of polypropylene. Testing beyond 35kW/m^2 was not considered since polypropylene was nearly behaving as thermally thin at 35kW/m^2. Piloted ignition of the samples was accomplished using an electric spark located 10mm above the sample. A sampling rate of 1 Hz was used to record the mass and heat release data. All virgin PP and PP composite specimens had comparable thicknesses. Thermogravimetric analyses (TGA) was performed with a PerkinElmer STA 6000 in air and nitrogen at a rate of 10ºC/min from room temperature to 700ºC. Sample weights between 10mg and 11mg were used. PP and chopped fibre reinforced PP TGA samples were obtained directly from the pellets.

6.4 Results

Three repetitions per sample were performed to obtain the time to ignition, heat release rate, mass loss behaviour, burning time, peak heat release rate, total heat release, and effective heat of combustion. The naming conventions are as shown in Table 6.2. Result averages are reported with 90% confidence interval as shown in Table 6.3. TGA results are shown in Figure 6.2. Figure 6.3, Figure 6.4 and Figure 6.5 show the effect of heat flux on the fire performance of PPM, S, L, and CM in terms of mass loss, mass loss rate, and heat release rate, respectively. Polynomial fitting of order 15 was used to smoothen the plots.

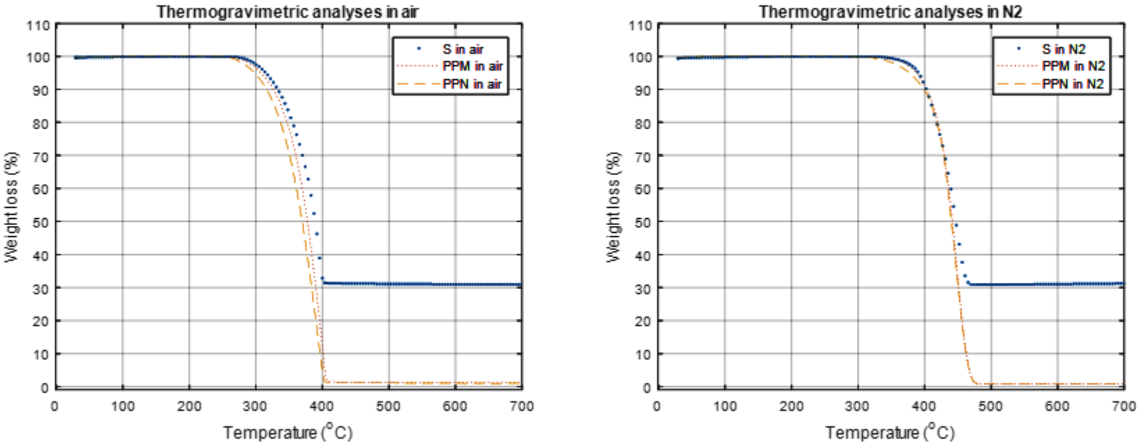

Figure 6.2: TGA for S, PPM and PPN done in air and N_2

Table 6.3: Cone calorimetry test results for PP and PP composites

@20 kW/m^2		PPM	S	L	CM
Initial mass	(g)	54.9±1.4	67.6±1.7	66.4±0.7	63.4±3.4
Thickness	(mm)	6.1±0.0	6.0±0.1	6.0±0.1	5.9±0.0
Residual mass	(g)	10.3±7.0	22.9±2.1	26.7±1.7	22.9±3.1
Time to ignition	(s)	208.7±35.5	233.0±19.9	209.0±27.6	238.7±19.5
Flameout time	(s)	948.0±43.9	1166.0±150.6	1025.0±126.5	1073.7±114.7
Mean HRR	(kW/m^2)	139.0±2.9	189.3±30.8	194.0±11.1	189.0±29.8
Time to peak HRR	(S)	468.3±12.9	625.0±30.4	553.3±21.2	620.0±91.2
Peak HRR	(kW/m^2)	418.1±57.3	390.0±83.7	473.4±13.4	325.3±3.8
MARHE	(kW/m^2)	146.7±23.7	214.7±17.3	209.0±3.4	178.0±16.6
Total heat release	(MJ/m^2)	126.3±31.2	209.7±16.2	191.7±14.7	178.3±29.7
Avg. specific MLR	(g/s.m^2)	8.6±2.5	7.2±1.4	6.8±0.8	6.8±0.6
Heat of combustion	(MJ/kg)	28.8±11.2*	46.8±1.8	48.2±2.66	43.9±1.6
@30 kW/m^2		PPM	S	L	CM
Initial mass	(g)	55.2±1.6	66.7±0.7	68.3±1.7	65.9±0.9
Thickness	(mm)	6.0±0.0	6.1±0.0	6.0±0.1	6.0±0.2
Residual mass	(g)	10.0±4.8	21.5±3.6	23.5±0.7	23.4±4.8
Time to ignition	(s)	111.0±4.5	119.0±12.7	119.7±13.1	119.7±10.2
Flameout time	(s)	662.7±42.2	814.7±48.8	737.0±59.9	798.0±22.8
Mean HRR	(kW/m^2)	230.0±42.5	253.3±9.7	243.7±51.2	233.0±43.8
Time to peak HRR	(s)	381.7±46.4	485.0±43.8	460.0±22.3	523.3±76.5
Peak HRR	(kW/m^2)	715.8±165.1	503.1±43.6	673.5±82.1	503.9±115.2
MARHE	(kW/m^2)	262.7±40.0	293.0±10.3	312.0±31.6	274.7±15.7
Total heat release	(MJ/m^2)	155.0±29.4	211.7±9.9	203.3±19.5	192.0±8.8
Avg. specific MLR	(g/s.m^2)	13.8±.4	9.6±0.5	11.9±2.0	9.5±1.3
Heat of combustion	(MJ/kg)	34.7±9.6*	46.9±2.6	45.4±3.6	45.3±3.8
@ 35 kW/m^2		PPM	S	L	CM
Initial mass	(g)	53.6±0.6	66.6±1.3	65.7±1.5	66.6±0.5
Thickness	(mm)	5.9±0.1	5.9±0.0	5.9±0.0	5.9±0.0
Residual mass	(g)	9.0±5.9	17.4±3.7	23.3±2.5	21.2±1.1
Time to ignition	(s)	76.7±7.8	71.3±14.1	80.0±10.5	76.3±3.7
Flameout time	(s)	605.0±72.0	834.3±100.3	558.3±71.4	683.3±37.2
Mean HRR	(kW/m^2)	190±42	250.3±27.4	265.7±25.4	263.0±4.5
Time to peak HRR	(s)	290.0±22.3	403.3±25.8	338.3±12.9	386.7±7.4
Peak HRR	(kW/m^2)	854.4±79.1	540.4±15.9	773.4±45.6	636.9±91.3
MARHE	(kW/m^2)	279.3±36.4	338.0±30.5	353.3±20.1	333.3±10.4
Total heat release	(MJ/m^2)	120.6±46.5	215.7±30.0	186.0±17.8	185.3±1.5
Avg. specific MLR	(g/s.m^2)	12.3±3.2	9.6±0.6	12.5±1.0	12.1±0.8
Heat of combustion	(MJ/kg)	35.0±4.7*	43.8±1.8	43.9±3.8	42.3±1.9

PPM: MH modified PP. S: 3mm fibre reinforced PP. L: 12mm fibre reinforced PP. CM: Continuous fibre reinforced MH modified PP.

*As a result of dripping especially at lower heat fluxes, the value of the total heat of combustion was lower than expected. Bomb calorimetry tests were performed to obtain the proper value of the heat of combustion for the PP matrix and it was found to be 47.23±0.05MJ/kg

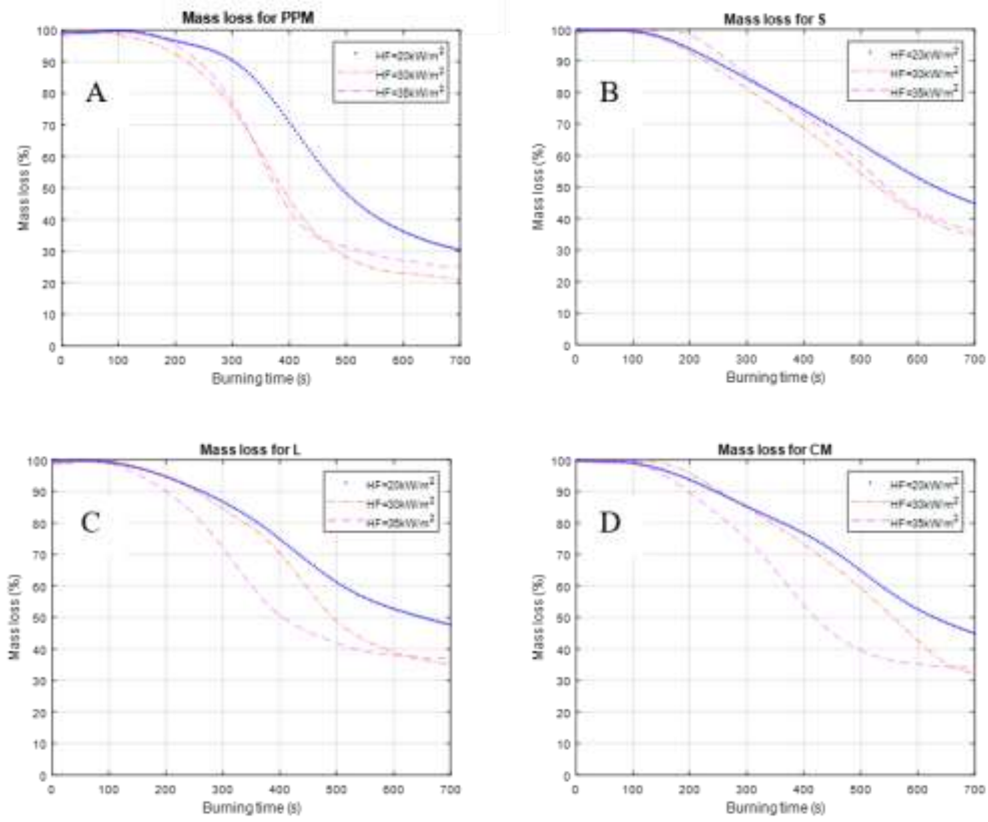

Figure 6.3: Mass loss of different samples at three different heat fluxes

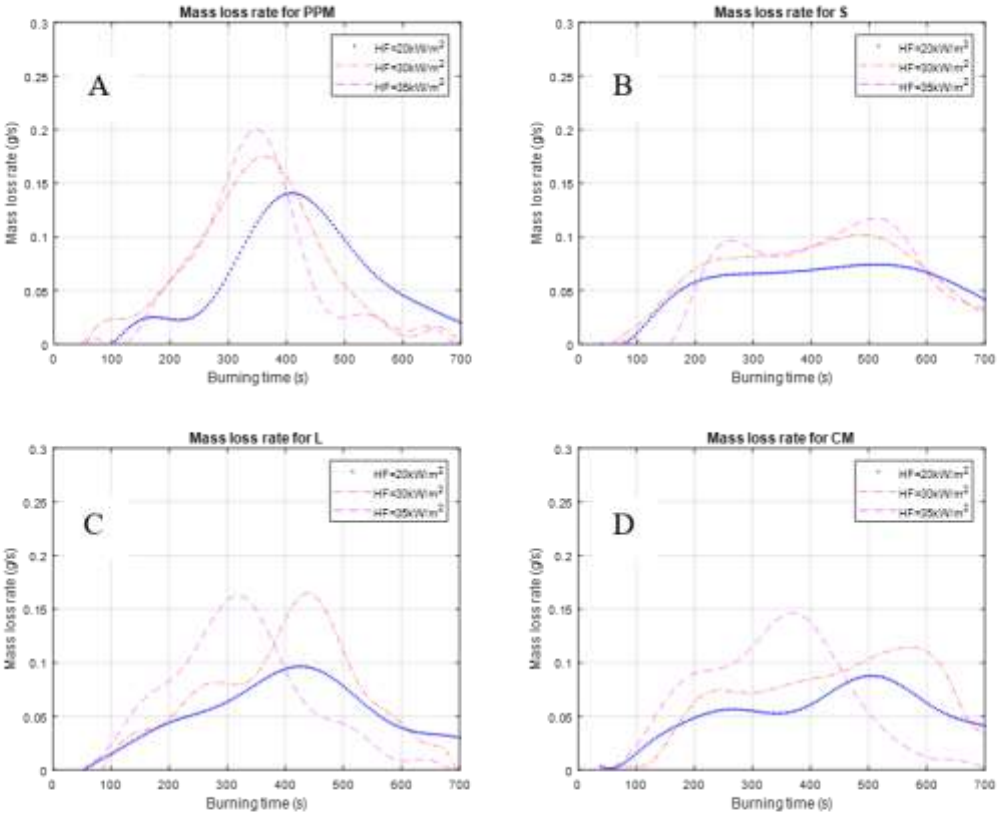

Figure 6.4: Mass loss rate of different samples at three different heat fluxes

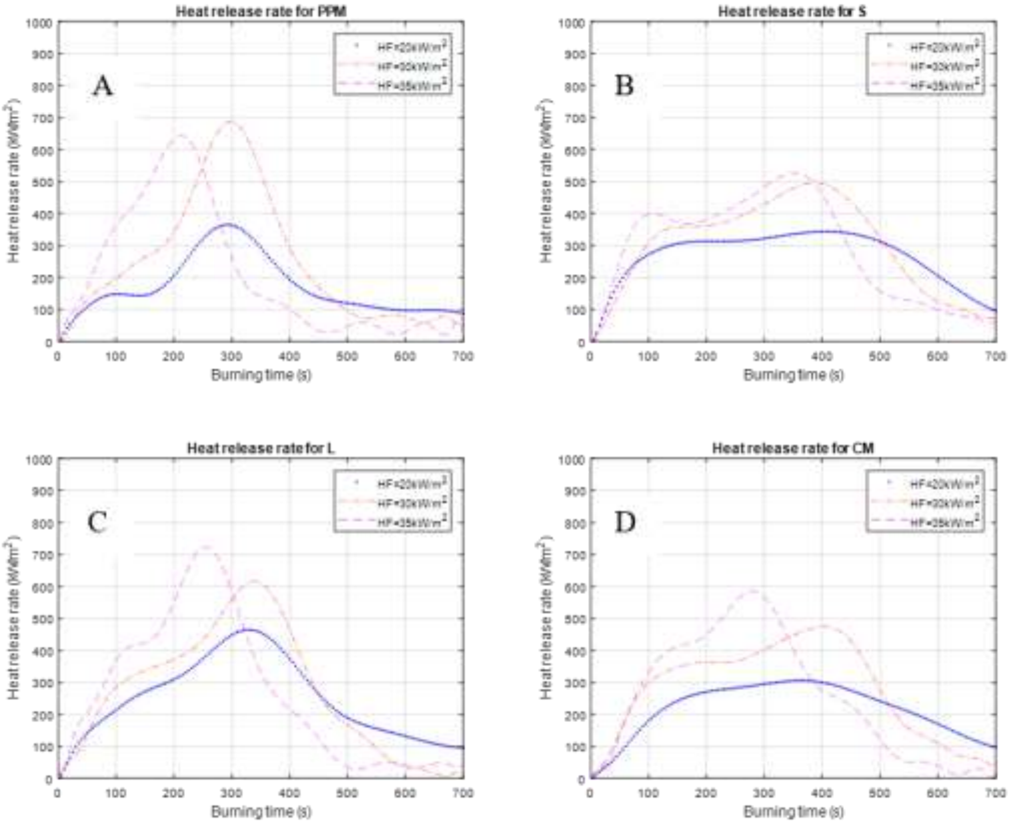

Figure 6.5: Heat release rate of different samples at three different heat fluxes

6.4.1 Effect of heat flux on all samples

The time to ignition is very sensitive to heat flux change. It decreased by 41% to 50% when the heat flux was increased from 20kW/m^2 to 30kW/m^2; and further decreased by 33% to 40 % when the heat flux changed from 30kW/m^2 to 35kW/m^2. The difference between samples with respect to the time to ignition was marginal. The effect of the heat flux on the time to ignition is shown in Figure 6.6-A.

The peak heat release rate increased by 29 % to 71% when the heat flux increased from 20 kW/m^2 to 30 kW/m^2; it further increased by 7% to 26% when the heat flux increased from 30 kW/m^2 to 35 kW/m^2. The 3mm glass fibre reinforced PP was the least sensitive to the heat flux change. It increased by 29% and 7% when the heat flux increased from 20 kW/m^2 to 30 kW/m^2 and from 30 kW/m^2 to 35 kW/m^2, respectively. The effect of the heat flux on the peak heat release rate is presented in Figure 6.6-B.

The mean heat release rate increased by 21% to 64% when the heat flux increased from 20 kW/m^2 to 30kW/m^2. However, when the heat flux increased from 30 kW/m^2 to 35 kW/m^2, the mean heat flux values either did not increase, or rose by up to 13%. It was noticed that the mean heat release rate for the 3mm long fibre reinforced PP remained unchanged when the heat flux increased from 30 kW/m^2 to 35 kW/m^2. The effect of the heat flux on the mean heat release rate is illustrated in Figure 6.6-C

Not unexpectedly, samples were observed to have a much higher mass loss rate at 30 kW/m^2 heat flux in comparison to 20 kW/m^2 heat flux. However, the difference in the mass loss rate between 30 kW/m^2 and 35 kW/m^2 was marginal.

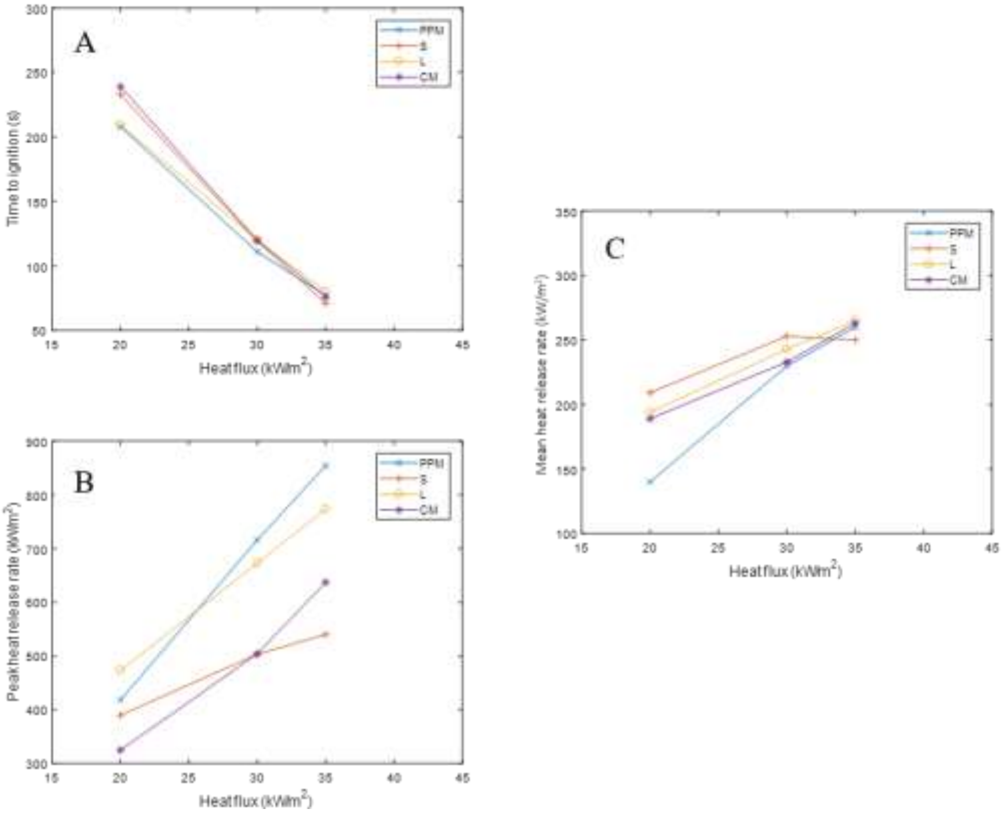

Figure 6.6: Effect of heat flux on fire performance parameters

6.4.2 Effect of fibre length

Fibre reinforced samples were compared to PPM in terms of the time to ignition, peak heat release rate, mean heat release rate, and mass loss rate.

In terms of the time to ignition, the fibre length does not appear to have a significant effect; changes are within ±5%. This could be due to the low fibre volume fraction (14%). In this work, the fibre weight fraction is 30%. The effect of the fibre length on the time to ignition is shown in Figure 6.7-A

Fibre length shows a significant effect on the peak heat release rate. At 20 kW/m^2 heat flux, the continuous fibre reinforcement reduced the peak heat release rate of PP by 32%. This was followed by the 3mm fibre reinforcement which caused a 7% reduction in the peak heat release rate. 12 mm long fibre reinforcement behaved unexpectedly, causing an increase of 13% in the peak heat release rate of PP. At a heat flux of 30 kW/m^2, both continuous fibre and 3mm fibre reinforcements caused a 30% drop in the peak heat release rate of PP. Long fibre reinforcement caused a 7% reduction in the peak heat release rate of PP. At 35 kW/m^2, short fibre reinforcement caused the most significant reduction among all fibre lengths. It reduced the peak heat release rate of PP by 37%. Continuous fibre reinforcement caused a 24% reduction while long fibre reinforcement caused a 10% reduction in the peak heat release rate. The effect of the fibre length on the peak heat release rate is demonstrated in Figure 6.7-B.

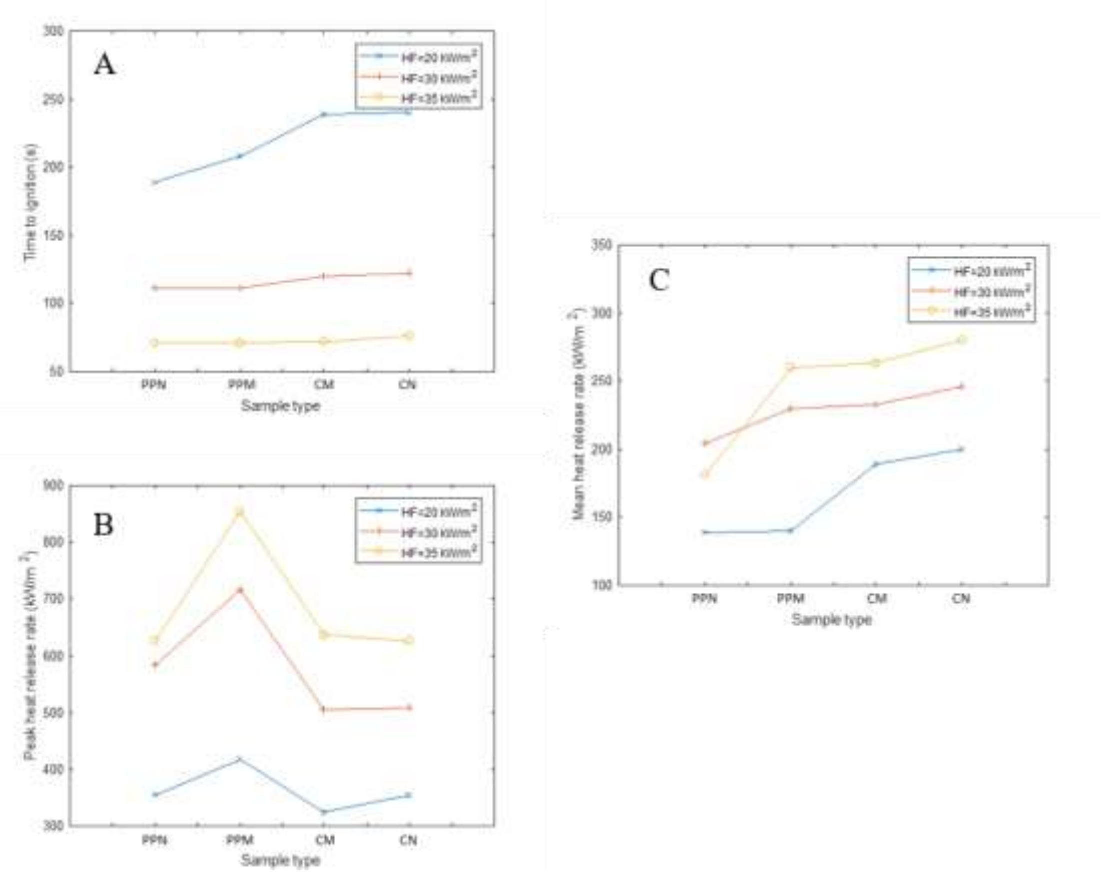

Figure 6.7: Effect of fibre length on fire performance parameters

All fibre reinforcements affect PP negatively in terms of the mean heat release rate. At 20 kW/m^2 heat flux, continuous fibre reinforcement caused the least significant increment to the mean heat release rate at 33%, followed by long fibre reinforcement which increased the mean heat release rate of PP by 39%. Short fibre reinforcement caused the most significant increment among all fibre reinforcements, increasing the mean heat release rate by 49%. At 30 kW/m^2 heat flux, continuous fibre reinforcement had no effect on the mean heat release of PP. 12 mm and 3mm fibre reinforcements caused a 6% and 10% increment, respectively, in the mean heat release rate of PP. At 35 kW/m^2 heat flux, fibre reinforcements appear to have no effect on the mean heat release rate of PP. The effect of the fibre length on the mean heat release rate is presented in Figure 6.7-C.

Fibre reinforcements did not seem to have a noticeable effect on the mass loss behaviour of PP. This is seen in Figure 6.3. However, fibre reinforcement considerably reduced dripping of PP, especially at lower heat fluxes. While virgin PP loses up to 40% of its weight via dripping at 20 kW/m^2 and 30 kW/m^2 incident heat fluxes, with the presence of fibre reinforcement, the dripping reduced to around 5% for S, L, and CM samples.

6.4.3 Effect of PP modification

Table 6.4 shows the average values of the fire performance of modified PP (PPM), unmodified PP (PPN) and continuous fibre reinforced PP made by both modified PP (CM) and unmodified PP (CN). PPN is used as a reference value and all other changes in values are referred to as a percentage change of PPN.

Table 6.4: The effect of PP modification on fire performance of PP and glass fibre reinforced PP

Effect of PP modification	Heat flux in kW/m^2	PPN	PPM	CM	CN
Time to ignition (s)	20	189	208 (+10%)	239 (+26%)	240 (+26%)
	30	111	111 (0%)	120 (+8%)	122 (+10)
	35	71	71 (0%)	72 (+1%)	76 (+7%)
Peak HRR (kW/m^2)	20	355	418 (+18%)	325 (-8%)	354 (0%)
	30	584	716 (+23%)	504 (-14%)	508 (-13%)
	35	626	854 (+36%)	637 (+2%)	626 (0%)
Mean HRR (kW/m^2)	20	139	140 (+1%)	189 (+36%)	200 (+44%)
	30	204	230 (+13%)	233 (+14%)	246 (+19%)
	35	215	260 (+44%)	263 (+45%)	280 (+55%)

At 20 kW/m^2 incident heat flux, PPM had a 10% higher time to ignition in comparison to unmodified PP while CM and CN had similar times to ignition. At 30 and 35 kW/m^2, PPN and PPM had similar times to ignition while CM had a higher one than CN.

PPM had an 18% higher peak heat release rate than PPN at 20 kW/m^2 heat flux. However, CM showed a 26% lower heat release rate than PPM and an 8% lower heat release rate than PPN. At 30 kW/m^2 heat flux, PPM proved to have a 36% increase in the peak heat release rate when compared to PPN. However, CM displayed a 37 % lower peak heat release rate than PPM and 14% lower than PPN. At 35 kW/m^2 heat flux, CN and PPN had similar peak heat release rates.

In this scenario, PPM showed a 36% higher peak heat release rate than PPN whereas for CM this was only 2% higher.

In terms of the mean heat release rate, at 20 kW/m^2, PPM had a value similar to PPN. CM and CN displayed 36% and 44% higher mean heat release rates, respectively. At 30 and 35 kW/m^2, PPN showed the lowest mean heat release rate while PPM, CN, and CM proved to have higher mean heat release rate values than PPN.

6.5 Discussion

6.5.1 Thermal conductivity of different fibre lengths

Fibre reinforcement exists in different lengths ranging from milled fibre all the way to continuous fibres. Typically structural requirements and manufacturing considerations drive the choice of fibre. With the results presented in this paper, it is now possible to assess how the choice of fibre length affects the fibre performance in terms of its contribution to the fire behaviour of PP. The effect of fibre length on this thermal conductivity is investigated analytically in this section in order to look at the sensitivity of the various composites to such thermal conductivity.

When assessing the fibre length effect on fire performance, one of the main material parameters to investigate is the thermal conductivity of composites. While the individual thermal properties of the fibre and the matrix can be found in the datasheets, the thermal properties of composite materials are more challenging to discover for many reasons. First, the fibre volume fraction varies. Second, different fibres have different thermal conductivities. Finally, the thermal conductivity is influenced by the composite manufacturing method through the alignment of the fibres.

Thermal conductivity of fibre reinforced composites can be estimated theoretically using Equation 6.1 as follows [38]:

$$Kc = Km\left[\frac{1+f(S-1)C}{1+fC}\right] \tag{6.1}$$

where,

$$C = \frac{(1 - Km^{-1}Kf)}{(1 + SKm^{-1}Kf - S)} \tag{6.2}$$

$$S = 1 - \frac{AR}{(AR^2 - 1)^{\frac{3}{2}}} \left[AR\sqrt{(AR^2 - 1)} - \cosh^{-1} AR\right] \tag{6.3}$$

Kc is the thermal conductivity of the composite. Km is the thermal conductivity of the matrix, Kf is the thermal conductivity of the fibre, f is the fibre volume fraction, and AR is the aspect ratio of the fabric.

Using Equation 6.1, the thermal conductivity of glass fibre reinforced PP can be estimated. Kf = 1 W/m K for E-glass fibre. Km=0.2 W/m K for polypropylene. Figure 6.8 shows the thermal conductivity for glass fibre reinforced PP for different fibre volume fractions and aspect ratios.

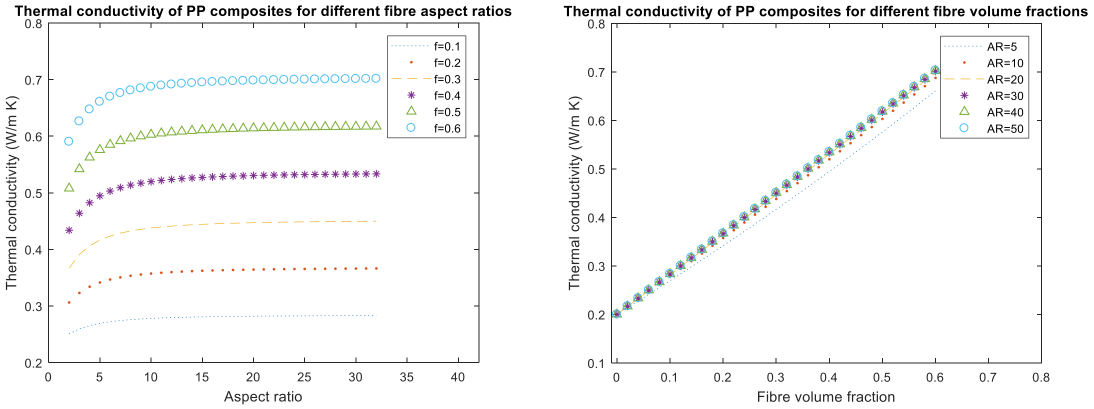

Figure 6.8: Thermal conductivity of glass fibre reinforced PP at different aspect ratios and different fibre volume fractions

6.5.2 The effect of fibre length on fire properties

The effect of fibre length on the performance of PP is somewhat unexpected. While the effect of fibre length on mechanical and thermal properties is linear, no trend was observed correlating the fibre length to the fire performance of PP. In addition, the presence of fibre reinforcement had no significant effect on either the mass loss or the time to ignition of the PP matrix.

Fibre reinforcement usually has a remarkable effect on the mass loss rate and time to ignition [10]. Yet, in this research, no effect of the fibre was observed on these. This can be explained by the change in thermal conductivity of the fibre. Thermal conductivity is a function of the fibre type, length, and volume fraction. In this study, the weight fraction of the fibre was 30%. Hence the fibre volume fraction was 13% (the densities of the fibre and matrix were 2600 and 900 kg/m^3 respectively). Figure 6.8 shows that for a fibre volume fraction lower than 20%, the thermal conductivity of glass fibre composites is similar for a fibre aspect ratio higher than 5. The fibre lengths investigated were 3 mm, 12 mm, and 100 mm, leading to aspect ratios around

6, 24, and 200. Thus, all fibre reinforced composites are expected to have similar thermal conductivities, leading to a negligible influence of the fibre length on the fire performance of glass fibre composites having a low fibre volume fraction. It is important to note that this will not be the case if a fibre with a higher thermal conductivity is used or if the fibre volume fraction is increased.

An interesting finding is that the 12 mm fibre reinforced PP had the worst fire performance in terms of the peak heat release rate and mass loss rate, despite having a comparable thermal conductivity, weight fraction, and matrix to the other two composites. After further investigation, it was found that for this composite, fibres lofted during the cone calorimeter test. This resulted in an increased out of plane angle of the fibres. This is a direct consequence of the lack of char produced by PP. We postulate that the lofting and consequent out of plane angle increased the through thickness heat transfer and also facilitated gas transfer from/to the burning front.

Figure 6.9 shows an image of the long 12mm fibre reinforced PP post fire testing. When fibres make such an angle, the in depth thermal conductivity can be increased up to 10 times [39]. An increase in thermal conductivity is, to some extent, favourable as it leads to equal distribution of the heat over the sample. However, when the thermal conductivity is too high, fire will travel very fast all over the sample, causing a higher peak heat release rate and a higher mass loss rate. In addition, fibre lofting can facilitate the gas transfer from and to the burning front. 3mm fibres are nested more finely and therefore do not loft to the same extent (Figure 6.10). Hence no change in the thermal conductivity of 3mm fibre reinforced PP is expected. Continuous fibre reinforced PP is long enough to be held down by the grill so its thermal properties are also not expected to be changed.

Figure 6.9: Long 12mm fibre reinforced PP post fire testing

Figure 6.10: Short 3mm fibre reinforced PP post fire testing

6.5.3 The influence of matrix modification

In general, MH modification of PP increased the time to ignition at 20 kW/m^2 heat flux while it had no effect on the time to ignition at higher heat fluxes. In terms of the heat release rate, MH modification impacted negatively by increasing this. The effect of MH modification on the heat release rate of PP became more critical with the increase in heat flux. While the MH modification caused an 18% increase in the peak heat release rate of the unmodified PP at 20 kW/m^2, the peak heat release rate was increased by 23% and 36% at 30 kW/m^2 and 35 kW/m^2, respectively. However, the negative effect of MH on the heat release rate was completely reversed when a glass fibre composite was made using the MH modified PP; and, in some cases, an overall improvement on the PP composite's performance was noticed.

The effect of MH on the fire performance of PP is surprising. The most likely explanation is that this is a result of improved adhesion between the fibre and the PP matrix. If this is true, then in cases where fire performance is a design parameter, a fibre/matrix compatibilizer that does not reduce the fire performance of the matrix but also promotes strong matrix fibre adhesion would proof beneficial. These findings might provide a new direction for the optimization and development of modified compounds.

6.6 Conclusion

Fibre reinforced composites are influenced by many factors, including fibre length, fibre volume fraction, and adhesion between the fibre and the matrix.

The effect of fibre length is highly dependent on the volume fraction and the type of fibre. The lower the fibre volume fraction, the lower the influence of fibre length on the fire performance of composites.

Fibre type plays an important role because fibres often have a thermal conductivity much higher than that of the matrix. If a fibre with a high thermal conductivity is used (e.g. carbon fibre), this will impact the thermal conductivity of the matrix even at a low fibre volume fraction and the composite will be more sensitive to the fibre aspect ratio. On the other hand, fibres with a relatively low thermal conductivity (e.g. glass fibre) will not have an impact on composite thermal properties at a low fibre volume fraction and they will be less sensitive to the fibre aspect ratio.

The alignment of the fibre before and during fire testing is one of the major factors influencing the fire performance of composites. When fibres are lofted, they cause an out of plane angle during fire testing. This effect will be particularly pronounced for low charring matrix materials with long enough fibres. The resulting increases in thermal conductivity and gas transfer consequently affect the fire performance.

Matrix modification can have a positive effect if it results in better adhesion between the fibre and the matrix. The improved adhesion significantly improves the fire performance of the composite material. However, if the adhesion enhancing compatibilizer has a poor fire performance, this will counteract the gains seen. Therefore, the choice of fibre/matrix compatibilizer with respect not only to interface promotion but also fire performance is critical and should be considered more frequently when optimizing the formulation of composite compounds.

In this chapter, the analysis was performed with a non-charring matrix and a low conductivity fibre. The findings are very likely different for a charring matrix or a high conductivity fibre and hence, similar experiments should be performed with different choices of matrices and fibres.

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Chapter 7

The effect of fibre length and fibre type on the fire performance of thermoplastic composites: The behaviour of polycarbonate as an example of a charring matrix

Motivation

A study of the fire performance of PP composites showed that the fibre length's effect on fire performance is not linear; this is believed to be a result of lofting. In this chapter, the effect of the fibre length on fire performance is studied for a charring matrix. Because it is known that thermal conductivity affects the fire performance of PP, different fibres are considered with different thermal conductivities in addition to glass fibre. Formulations are controlled so that the fibre length or fibre type is the only parameter tested.

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The effect of fibre length and fibre type on the fire performance of thermoplastic composites: The behaviour of polycarbonate as an example of a charring matrix

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Abstract

This study was performed to investigate the effect of fibre length and fibre type on the fire performance of a polymer with an intermediate char yield, polycarbonate (PC). Glass, basalt and carbon fibre reinforced PC with 6 mm, 12 mm, and 20 mm long fibres were tested. Samples were manufactured via compression moulding from pre-compounded PC pellets containing the reinforcing fibres of given lengths. Cone calorimetry tests with incident heat fluxes of 35 kW/m^2, 50 kW/m^2, and 70 kW/m^2 were used to investigate the fire properties of the PC glass fibre composites. Flame spread tests and thermal conductivity measurements were also performed. Transient plane thermal conductivity measurements were taken from 30°C to 160°C to determine the in-plane and out-of-plane thermal conductivity. Flame spread testing was conducted to measure the flame spread rate and critical heat flux for the flame spread. This rare complementary information provides a more complete picture of factors driving the various fire performance aspects. The results show that the role of fibre length in fire performance is more significant when the fibre used has a high thermal conductivity. Knowing the role of the fibre length and type on fire performance can help in the design of composite materials for optimised fire performance.

Author contribution percentages (Chapter 7)

Author	Sample manufacturing	Testing	Data Analysis	Paper writing	Paper editing
Yousof Ghazzawi	90%	100%	60%	100%	-
Michael Heitzmann	10%	-	10%	-	70%
Andres Osorio	-	-	30%	-	30%

7. The effect of fibre length and fibre type on the fire performance of thermoplastic composites: The behaviour of polycarbonate as an example of a charring matrix

7.1 Introduction

Fibre reinforced polymer composites are common in aerospace, construction, and transportation industries. The popularity of fibre reinforced composites is driven by its light weighting potential, favourable mechanical properties, and relatively low cost. Polycarbonate (PC) is among the most commonly used thermoplastic matrices. Compared to other engineering thermoplastics, PC has a high char yield of approximately 20-25% [1, 2]. This makes the matrix a regular choice for applications where fire performance is a consideration.

Fire retardants are usually added to polymer matrices to significantly improve the fire performance of the composite host material [3-17]. However, there are three major drawbacks of using fire retardants. First, adding fire retardant causes a drop in the mechanical properties [18-20]. Second, including such a retardant adds a significant cost [21]. Third, there are environmental concerns about a number of effective fire retardants and these substances consequently face increasingly stringent regulations [22].

The mechanical properties of composite materials are widely known and, over the past 50 years, methods to predict mechanical properties from their constituent materials' properties have been developed and validated [23-31]. The same cannot be said for the prediction of fire performance. To date, for composite materials no decision and prediction framework exists that would enable fire performance factors to be determined from the constituent properties of the matrix and fibre. In order to develop such a framework, constituent properties and their effect on the resulting composite fire performance need to be thoroughly investigated.

The literature regarding the effect of fibre length and fibre type on the fire performance of composite materials is inconclusive. The majority of prior studies are focused on continuous fibres and thermosetting resins [32-37]. For reinforced thermoplastic matrices, an investigation of short/chopped fibres is more relevant as the majority of commercially relevant applications/processes employ this form of reinforcement. A key factor leading to the lack of clarity regarding the fire performance of short fibre composites is associated with the fact that comparison between individual studies is made difficult due to the large number of permutations possible [3, 38-43]. In other words, few studies use material combinations and experimental conditions that allow a cross-comparison of results.

For example, one study suggested that an increase in fibre length may lead to better fire properties [38], whereas the present work suggests that a longer fibre length is only favourable under certain conditions and in fact can have a negative effect in some cases.

The same ambiguity is also found when looking at the effect of the fibre type on the fire performance of PP. While it is well accepted that carbon fibre has a higher thermal conductivity than glass fibre [44], this does not necessarily mean that its fire performance is better than that of glass fibre (as suggested by Patel, P., et al. [39]). More precisely, as shown in this chapter, the choice of fibre with a high thermal conductivity is only beneficial for certain fire performance aspects and may prove disadvantageous in other circumstances.

From the literature the following gaps can be identified:

- Most of the work reported has been performed on composites containing fire retardants. This makes it hard to resolve the effect of the matrix and fibre.
- The compound formulation of short fibre compounds is often not adequately controlled and/or reported, making it difficult to compare results and studies.
- Thermal properties (heat capacity, thermal conductivity) are rarely measured. Knowing these properties is a crucial factor in determining fire performance from constituent properties.

To address the above gaps, this study attempts to rigorously control and measure the critical aspects often omitted in earlier studies. This involves the manufacture of purposely compounded PC composites where the only varying parameter is the reinforcement type and fibre length. The selected fibre types are glass fibre, basalt fibre, and carbon fibre with fibre lengths of 6 mm, 12 mm, and 20 mm. This represents the most significant permutations from an industry standpoint. Both thermal properties and fire performance are investigated. The transient plane source (TPS) thermal conductivity test is used to measure the effect of fibre length and type on the in-plane and out-of-plane thermal conductivity of the composites. Cone calorimetry tests and a flame spread test are performed to compare the effect of the fibre type and fibre length with respect to fire performance.

7.2 Materials

Lotte Advanced Materials Infino SC-1220R Polycarbonate with a melt index of 22 g/10 min and density of 1.2 g/cm3 was used as the matrix. The 6 mm and 12 mm, and 20 mm chopped fibre reinforced PC pellets were made via pultrusion. All PC composites have a nominal fibre weight fraction of 30%. It is rare to find 6, 12, and 20 mm fibre compounds where only the fibre length changes. For this reason, Plasticomp (Winona, USA) was commissioned to produce the compounds where the only parameters varied were the fibre lengths (6, 12 and 20mm) and fibre types (E-glass, IM-carbon and basalt).

7.3 Manufacturing methods

7.3.1 Composite sample fabrication

The compound pellets were dried for 4 h at 100ºC and compression moulded at 270ºC under a constant pressure of 1.5 MPa for 10 min. Samples were cooled to 50ºC while maintaining pressure prior to releasing the press. Pellets were moulded into 250 x 250 mm plates.

Samples were manufactured according to the combinations shown in Table 7.1. The purpose of the test matrix was to study the effect of the fibre length and type on the fire performance of the composite. All compression moulded plates had a nominal thickness of 6 mm and were waterjet cut into 100 x 100 mm samples for cone calorimeter tests. The 600 x 100 mm samples for flame spread testing were manufactured by butt welding 200 mm x 100mm sections together. Samples for thermal conductivity measurements were cut into 30 x 6 mm disks for the glass and basalt fibre reinforced PC, and 50 x 10 mm disks for the carbon fibre reinforced PC.

Table 7.1: Testing sample configurations

Sample	PC	PCG6	PCG12	PCG20	PCB6	PCB12	PCB20	PCC6	PCC12	PCC20
Fibre type	N/A	Glass	Glass	Glass	Basalt	Basalt	Basalt	Carbon	Carbon	Carbon
Fibre length (mm)	N/A	6	12	20	6	12	20	6	12	20
Fibre loading (%)	N/A	30	30	30	30	30	30	30	30	30

7.4 Experimental method

7.4.1 Thermogravimetric analysis (TGA)

Perkin Elmer STA 6000 equipment was used to perform the TGA on the unreinforced PC samples in both N_2 and air. The sample quantities ranged from 9-13mg and the heating rate was 10°C/min. Tests were performed from room temperature to 900 °C.

7.4.2 Cone calorimetry

Samples were tested using a Fire Testing Technology, iCone Calorimeter, following ISO 5660-1. The heat release rate (HRR), time to ignition (t_{ig}), mass loss rate (MLR), and critical heat flux (CHF) were the fire properties of interest. The heat release rate is defined as the amount of heat energy released by sample per unit area. The time to ignition is defined as the time required for the material to ignite when it is exposed to a heat source. The mass loss rate is the rate at which the material is losing mass. The critical heat flux is the minimum heat flux the material requires to ignite. The back and sides of the sample were wrapped by aluminium foil. The sample's back face was insulated using an inorganic insulation in order to minimise heat losses. An ISO 5660-1 standard retainer frame was used to restrain the exposed surface of the sample and prevent contact with the heating element.

Incident heat fluxes of 35, 50, and 70 kW/m^2 were used. Piloted ignition of the samples was accomplished using an electric spark located 10 mm above them.

7.4.3 Flame spread rate

Horizontal flame spread tests were conducted using an apparatus based on ASTM E1321. Different heat fluxes were applied over the sample length ranging from 26 kW/m^2 to 10 kW/m^2 in order to obtain the flame spread velocity over the sample length, the flame spread parameter, and the critical heat flux for flame spreading. An ASTM1321 standard retainer frame was used to retain the sample. The back and sides of the sample were wrapped in aluminium foil. The samples were heated using a radiant heat panel.

7.4.4 Thermal conductivity

A Hot Disk Instruments TPS 1500 thermal conductivity meter was used to measure in-plane and out-of-plane thermal conductivity following ISO 22007-1. The testing was conducted in an oven at 30ºC, 80ºC, 130°C, and 160°C. A high temperature PEEK sensor holder was used. A 5465 Kapton sensor with a 3.2 mm radius was used to measure the thermal conductivity of the unreinforced PC, glass fibre reinforced PC, and basalt fibre reinforced PC samples. A 5501 Kapton sensor with a 6.4 mm radius was used to measure the thermal conductivity of the carbon fibre reinforced PC samples. 40 s measurement time was applied for all samples. The heating power varied according to the temperature applied to maintain a measurement time above 0.4 s and a total temperature increase above 3°C and below 4.5°C.

7.4.5 Test matrix

Table 7.2 provides an overview of the test matrix and lists the number of samples tested for each test method.

Table 7.2: Overview of test matrix and number of samples tested

Test method	PC	PCG6	PCG12	PCG20	PCB6	PCB12	PCB20	PCC6	PCC12	PCC20
TGA (air)	2	2	x	x	2	x	x	2	x	x
TGA (N_2)	2	2	x	x	2	x	x	2	x	x
Cone cal.	9*	9*	9*	9*	3	3	3	3	3	3
Flame spread	x	2	2	2	x	x	x	2	2	2
Thermal cond.	3	3	3	3	3	3	3	3	3	3

* 3 repeats each for heat flux 35 kW/m^2, 50 kW/m^2 and 75 kW/m^2

7.5 Results

Naming conventions are as shown in Table 7.1. Results are reported with a 90% confidence interval.

7.5.1 Thermogravemetric analysis (TGA)

TGA was completed for the unreinforced PC, glass, carbon, and basalt fibre reinforced PC compounds. Figure 7.1 shows that for unreinforced PC a residual mass of around 22% remained when measured in nitrogen, while no residual mass resulted in air. The onset of degradation occurred at ~375 °C with the peak degradation being observed at 500 °C.

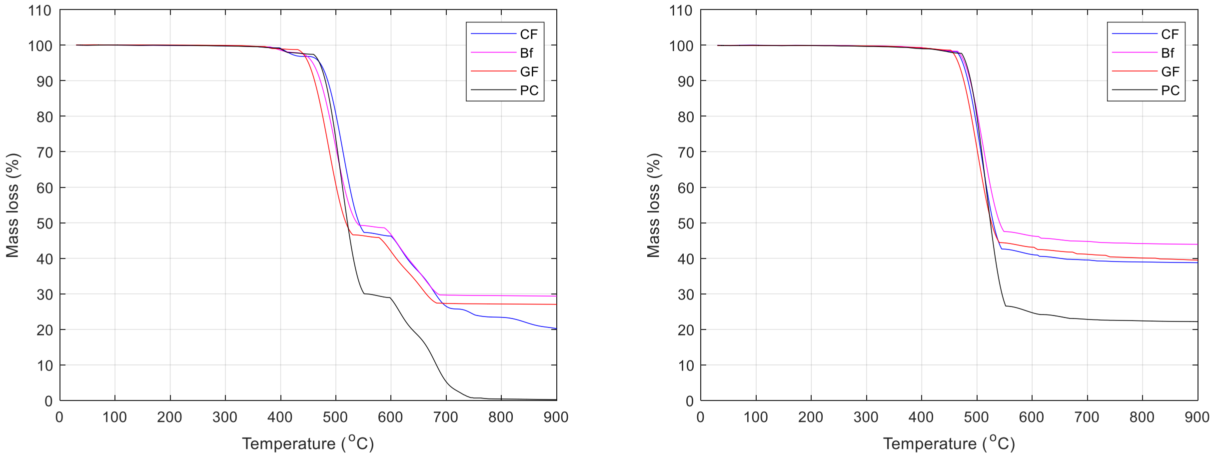

Figure 7.1: TGA results for PC and fibre reinforced PC in air (left) and N_2 (right)

7.5.2 Cone calorimetry test

Figure 7.2 shows the heat release curves for the glass fibre reinforced compounds at heat fluxes of 35 kW/m^2, 50 kW/m^2 and 75 kW/m^2. Table 7.3 shows the cone calorimetry test results for the PC and glass fibre reinforced PC for different fibre lengths and different heat fluxes.

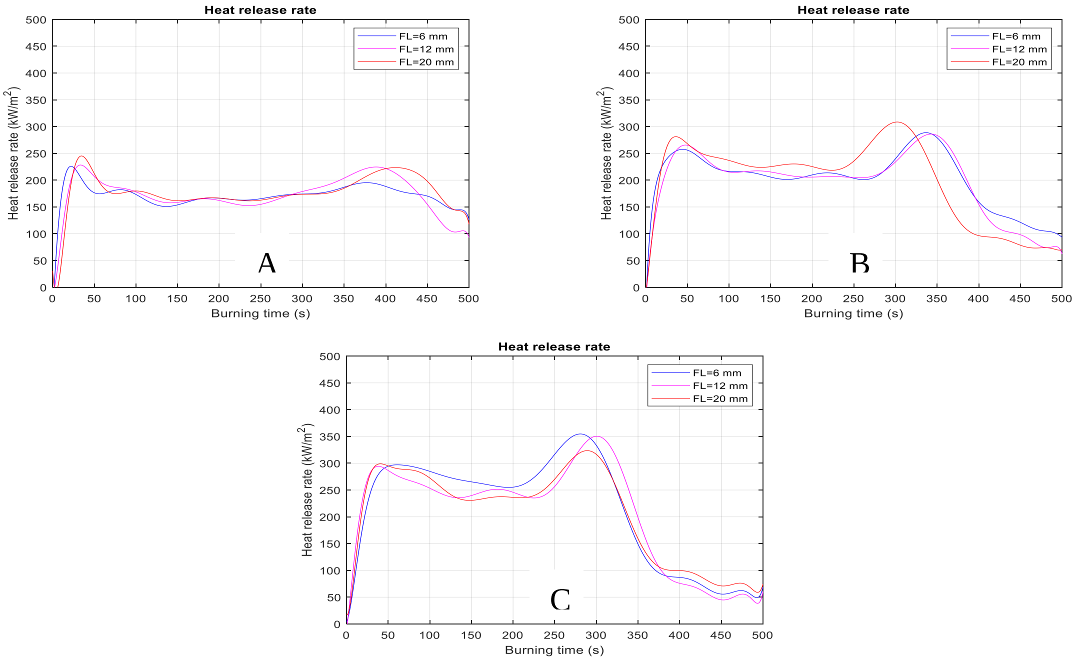

Figure 7.2: HRR vs burning time for composites at A) 35kW/m^2, B) 50kW/m^2, C) 70 kW/m^2

Table 7.3: Cone calorimetry test results for PC and glass fibre reinforced PC

@ 35 kW/m^2		PC	PCG6	PCG12	PCG20
Initial mass	g	71.26 ± 2.70	83.96 ± 3.30	85.35 ± 1.78	84.17 ± 2.21
Thickness	mm	5.94 ± 0.22	5.83 ± 0.23	5.93 ± 0.12	5.85 ± 0.15
Residual mass	g	26.78 ± 4.30	44.96 ± 1.55	47.22 ± 1.67	46.68 ± 4.89
Residual mass	%	37.55 ± 4.98	53.55 ± 0.29	55.33 ± 1.47	55.44 ± 4.77
Time to ignition	s	192.33 ± 18.95	211.07 ± 20.06	205.67 ± 17.05	191.67 ± 11.23
Burning time	s	495.33 ± 52.38	545.00 ± 103.77	538.33 ± 84.30	515.67 ± 108
Mean HRR	kW/m^2	200.07 ± 10.73	175.60 ± 16.23	171.32 ± 4.91	172.68 ± 9.15
Peak HRR	kW/m^2	283.67 ± 7.79	259.33 ± 17.55	273.67 ± 27.46	269.00 ± 22.11
Total heat release	MJ/ m^2	100.59 ± 6.13	94.99 ± 13.20	92.19 ± 13.75	88.82 ± 14.48
MLR (x10^3)	g/s	89.90 ± 4.01	72.05 ± 11.12	71.30 ± 13.14	73.16 ± 9.37
EHC	kJ/kg	22.62 ± 0.91	24.33 ± 2.26	24.22 ± 4.45	23.66 ± 1.82
@ 50 kW/m^2		PC	PCG6	PCG12	PCG20
Initial mass	g	70.73 ± 4.56	84.26 + 1.16	84.69 ± 1.21	84.05 ± 1.75
Thickness	mm	5.89 ± 0.38	5.85 ± 0.08	5.88 ± 0.08	5.84 ± 0.12
Residual mass	g	22.89 ± 0.64	42.49 ± 0.44	44.56 ± 0.05	44.10 ± 2.80
Residual mass %	%	32.39 ± 1.72	50.43 ± 1.14	52.61 ± 0.81	52.47 ± 2.82
Time to ignition	s	90.33 ± 4.24	90.00 ± 6.08	93.00 ± 7.73	90.67 ± 4.87
Burning time	s	422.33 ± 47.72	461.67 ± 62.29	417.67 ± 55.15	417.33 ± 35.13
Mean HRR	kW/m^2	278.38 ± 45.51	208.51 ± 5.17	210.64 ± 15.19	220.72 ± 10.88
Peak HRR	kW/m^2	377.00 ± 33.59	304.00 ± 11.05	300.00 ± 43.34	307.67 ± 20.39
Total heat release	MJ/ m^2	113.56 ± 14.04	96.19 ± 11.06	89.19 ± 8.08	92.03 ± 3.97
MLR (x10^3)	g/s	113.37 ± 5.83	90.92 ± 14.56	96.44 ± 11.26	95.76 ± 2.73
EHC	kJ/kg	23.73 ± 1.26	23.05 ± 3.17	22.21 ± 1.35	23.05 ± 0.75
@ 70 kW/m^2		PC	PCG6	PCG12	PCG20
Initial mass	g	69.69 ± 2.69	83.70 ± 2.65	84.79 ± 1.15	83.44 ± 2.45
Thickness	mm	5.90 ± 0.00	5.88 ± 0.13	5.88 ± 0.05	5.87 ± 0.05
Residual mass	g	21.74 ± 2.21	40.91 ± 1.56	43.11 ± 0.90	43.18 ± 1.39
Residual mass %	%	31.18 ± 2.59	48.88 ± 1.17	50.84 ± 0.40	51.75 ± 1.69
Time to ignition	s	48.33 ± 5.92	42.00 ± 5.84	49.67 ± 5.42	50.00 ± 1.69
Burning time	s	393.67 ± 87.05	381.00 ± 5.84	376.00 ± 16.08	382.00 ± 43.93
Mean HRR	kW/m^2	255.98 ± 38.22	258.86 ± 6.58	250.42 ± 1.25	241.53 ± 28.77
Peak HRR	kW/m^2	444.67 ± 41.65	397.67 ± 38.23	374.00 ± 40.14	371.00 ± 23.84
Total heat release	MJ/ m^2	104.90 ± 15.57	98.63 ± 2.54	94.16 ± 3.68	91.98 ± 3.55
MLR (x10^3)	g/s	123.00 ± 23.04	112.32 ± 5.17	110.89 ± 4.10	105.84 ± 16.81
EHC	kJ/kg	21.85 ± 2.39	23.05 ± 0.73	22.59 ± 0.75	22.84 ± 0.89

Table 7.4 shows the cone calorimetry test results for the basalt fibre reinforced PC for different fibre lengths and Table 7.5 shows the cone calorimetry results for the carbon fibre reinforced PC for different fibre lengths. Figure 7.3 shows the effect of the fibre length on the mass loss rate and the heat release rate for the glass fibre reinforced PC. Figure 7.4 shows the effect of the fibre length on these for the basalt fibre reinforced PC. Figure 7.5 shows the similar effect for the carbon fibre reinforced PC.

Table 7.4: Cone calorimetry test results for basalt fibre reinforced PC

		PCB6	PCB12	PCB20
Initial mass	g	83.91 ± 1.38	83.26 ± 0.66	83.41 ± 1.66
Thickness	mm	5.87 ± 0.1	5.82 ± 0.05	5.83 ± 0.12
Residual mass	g	44.71 ± 1.36	45.98 ± 1.69	48.04 ± 1.14
Residual mass %	%	53.29 ± 2.11	55.23 ± 1.66	57.60 ± 1.50
Time to ignition	s	229.00 ± 20.44	238.33 ± 19.97	240.00 ± 31.49
Burning time	s	499.67 ± 75.44	514.67 ± 53.53	502.00 ± 46.99
Mean HRR	kW/m^2	183.20 ± 12.20	180.34 ± 7.24	173.12 ± 3.79
Peak HRR	kW/m^2	238.67 ± 31.64	259.33 ± 39.76	303.67 ± 66.93
Total heat release	MJ/ m^2	91.15 ± 7.76	92.27 ± 10.51	86.42 ± 6.89
MLR (x10^6)	g/s	78.73 ± 7.79	72.57 ± 5.56	70.54 ± 3.47
EHC kJ/Kg	kJ/kg	23.24 ± 0.77	24.74 ± 2.07	24.42 ± 1.08

Table 7.5: Cone calorimetry test results for carbon fibre reinforced PC

		PCC6	PCC12	PCC20
Initial mass	g	76.83 ± 1.81	77.19 ± 0.77	77.40 ± 3.18
Thickness	mm	5.82 0.14	5.85 ± 0.06	5.86 ± 0.24
Residual mass	g	42.78 ± 1.80	46.94 ± 0.52	47.80 ± 2.95
Residual mass %	%	55.67 ± 1.33	60.81 ± 0.90	61.75 ± 1.32
Time to ignition	s	252.67 ± 38.34	261.33 ± 37.94	335.67 ± 30.59
Burning time	s	408.00 ± 43.93	471.00 ± 38.15	469.00 ± 4.46
Mean HRR	kW/m^2	198.07 ± 2.96	153.74 ± 16.48	153.12 ± 7.79
Peak HRR	kW/m^2	251.67 ± 9.59	258.67 ± 79.65	327.00 ± 91.15
Total heat release	MJ/ m^2	80.33 ± 7.69	76.76 ± 9.65	71.35 ± 3.09
MLR (x10^6)	g/s	83.67 ± 8.04	60.55 ± 11.24	63.11 ± 1.15
EHC kJ/Kg	kJ/kg	23.58 ± 1.96	25.36 ± 2.79	24.11 ± 0.83

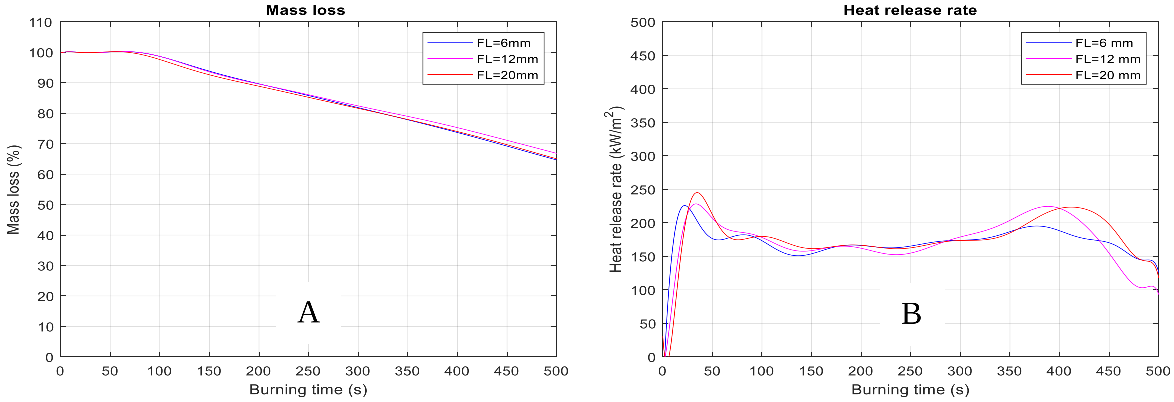

Figure 7.3: Mass loss rate (A) and heat release rate (B) of glass fibre reinforced PC

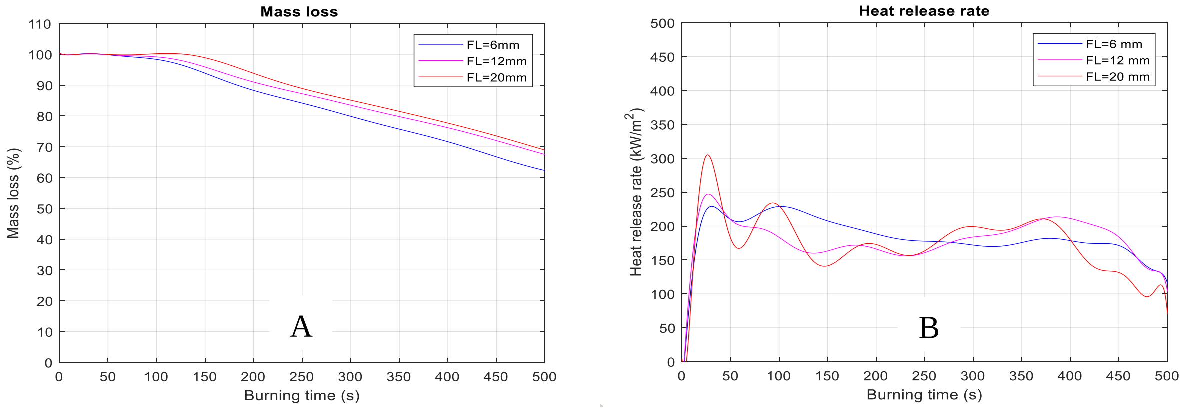

Figure 7.4: Mass loss rate (A) and heat release rate (B) of basalt fibre reinforced PC

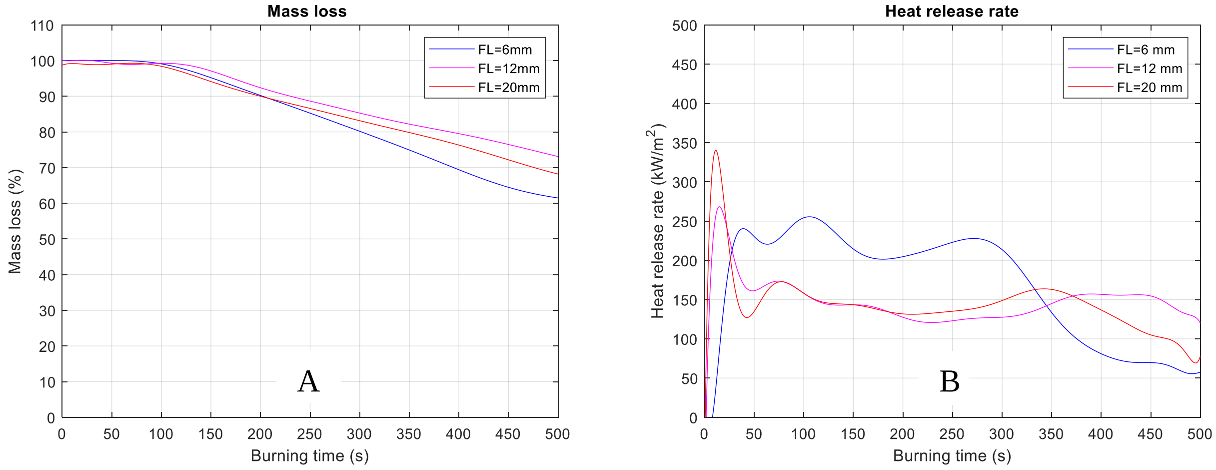

Figure 7.5: Mass loss rate (A) and heat release rate (B) of carbon fibre reinforced PC

7.5.3 Flame spread test

Glass fibre reinforced PC samples were heated for 140 to 150 s, while carbon fibre reinforced PC samples were heated for 180 to 210 s (the time to ignition was determined using cone calorimetry) before using the torch to pilot ignite the sample at the leading edge. The flame spread velocity was determined by measuring the flame travel time for every 25 mm of the sample starting from the sample's leading edge.

The flame spread test was not possible for unreinforced PC due to its high critical heat flux. Figure 7.6 shows an unsuccessful test of unreinforced PC. The leading edge of the sample melted and collapsed, and a flame spread measurement could not be obtained.

Figure 7.6: A failed attempt of flame spread test for unreinforced PC

Successful tests were conducted on glass and carbon fibre reinforced PC. Figure 7.7s show the carbon fibre reinforced PC sample intact until the point of ignition, where the temperature reached 662^o C after ignition. Figure 7.8 shows ignition at 445^{o}C and the onset of the flame spread. It can be seen that the integrity of the carbon fibre reinforced PC sample is maintained while the flame is spreading.

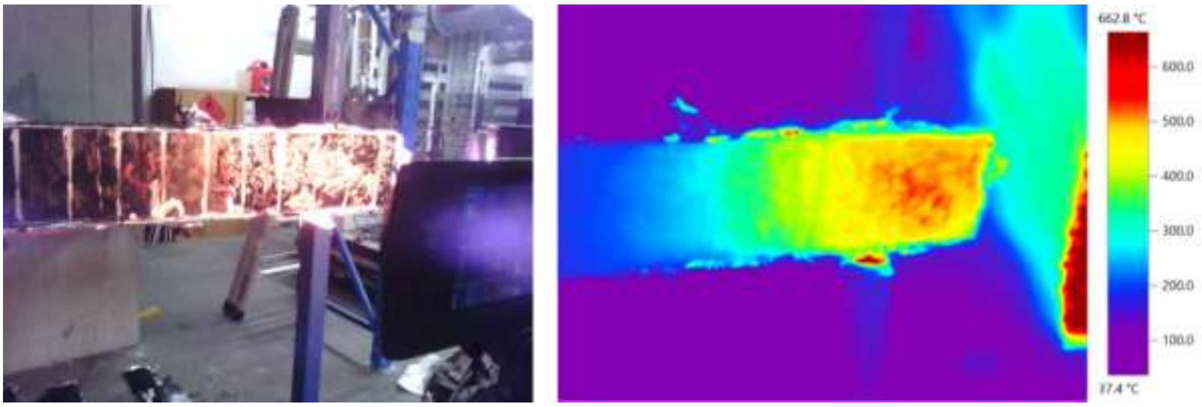

Figure 7.7: Images of carbon fibre reinforced PC just before ignition

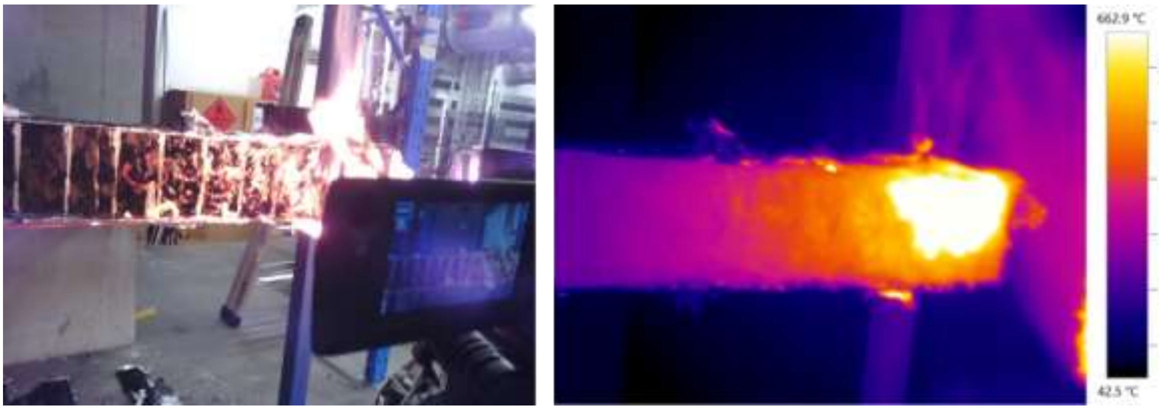

Figure 7.8: Flame spread images of carbon fibre reinforced PC

All samples were tested for the flame spread velocity, flame spread parameter, ignition temperature, and critical heat flux for the flame spread. The flame spread velocities were calculated by image processing of the test videos. These velocities were found to be similar for all samples. The ignition temperature was determined by using a thermal camera as shown in Figure 7.8 and it was found to be around 445°C for all samples. The critical heat flux for the flame spread was found by measuring the flame spread velocity across the sample length and it was identified at the point where the flame spread velocity was less than 0.3 mm/s. The critical heat flux for the flame spread was around 10 kW/m^2 for the glass fibre reinforced PC and ranged from 16 to 19 kW/m^2 for the carbon fibre reinforced PC. Figure 7.9 shows the applied heat flux versus the flame spread velocity of the glass fibre reinforced PC and the carbon fibre reinforced PC for different fibre lengths.

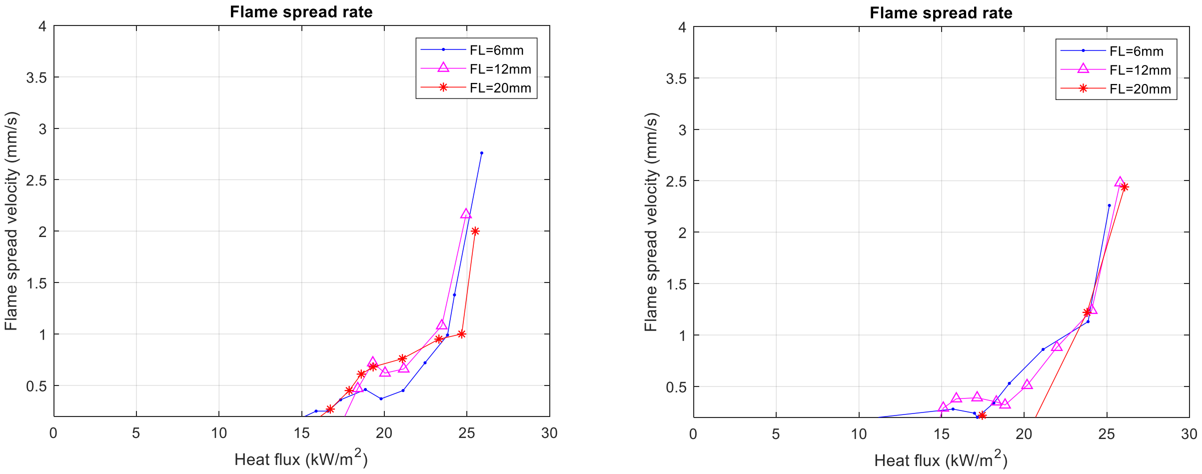

Figure 7.9: Heat flux versus flame spread velocity for glass fibre reinforced PC (left) and carbon fibre reinforced PC (right)

7.5.4 Transient plane thermal conductivity test

Table 7.6 shows the results of the thermal conductivity test conducted on glass, basalt and carbon fibre reinforced PC. Carbon fibre reinforced PC samples were tested from 30°C to 160°C for all fibre lengths due to their high thermal conductivity variation. Glass and basalt fibre reinforced PC samples were tested from 30°C to 160°C using the 12 mm long fibre reinforcement only. 6 mm and 20 mm long glass and basalt fibre reinforced PC samples were only tested at 30°C.

Table 7.6: Transient plane thermal conductivity test results

		Thermal conductivity (W/m K) In-plane/out-of-plane			
Material	Fibre length	@30ºC	@80ºC	@130ºC	@160ºC
Polycarbonate	xxx	0.244	0.256	0.272	0.2655
CF reinforced PC	6mm	1.085/0.337	1.204/0.321	1.289/0.343	1.260/0.333
	12mm	1.119/0.297	1.271/0.326	1.377/0.362	1.460/0.335
	20mm	1.189/0.312	1.378/0.332	1.546/.0364	1.645/0.343
GF reinforced PC	6mm	0.340/0.280	xxx	xxx	xxx
	12mm	0.360/0.281	0.400/0.300	0.459/0.301	0.528/0.255
	20mm	0.363/0.279	xxx	xxx	xxx
BF reinforced PC	6mm	0.363/0.269	xxx	xxx	xxx
	12mm	0.374/0.280	0.391/0.300	0.439/0.306	0.451/0.270
	20mm	0.377/0.281			

7.6 Discussion

The TGA results show that the char yield of the PC grade used in this study is 22% when measured in N_2. This correlates well with results previously reported [1, 2]. When the TGA is performed in air, the char yield above 750ºC is close to zero. This can be explained by the volatilisation of the char as a consequence of oxidative processes. The same principle is seen for compounds containing carbon fibres. As shown in Figure 7.1, gradual oxidation of the carbon fibres occurs above 700 ºC.

When comparing the results of the cone calorimetry, flame spread test and thermal conductivity measurements, it becomes evident that the major constituting factor affecting the fire performance is thermal conductivity. For this reason, this behaviour is discussed in more detail, distinguishing between the low thermal conductivity composites (containing E-glass and basalt fibres) and the high thermal conductivity composites (containing carbon fibres). It is also worth noting that lofting of the fibres was not observed in this study. This is in contrast to a similar previously performed study where a non-charring polypropylene matrix was used instead of

PC. Clearly, the char yield of 22% is sufficient to prevent the lofting of the fibres. Preventing lofting not only improves the overall fire performance but also improves the repeatability of the experiments. When lofting is encountered, the variability of the measurements is typically due to the erratic nature of the lofting phenomena.

7.6.1 Composites with low thermal conductivity

Fibre length did not seem to have a major effect on the fire performance of the glass and basalt fibre reinforced PC. The cone calorimetry results in Tables 7.3 and 7.4 show that, when tested to an incident heat flux of 35 kW/m^2, the change in fibre length had a negligible effect on the fire performance of the glass fibre composite in terms of the time to ignition, mean heat release rate, mass loss rate, and peak heat release rate. The basalt fibre composite followed the same trend in terms of the time to ignition and mean heat release rate, with minor differences observed for the mass loss rate and peak heat release rate. The mass loss rate reduced by 10% when the fibre length increased from 6 to 20 mm. The mean heat release rate increased by 5% when the fibre length extended from 6 to 20 mm. At incident heat flux of 70 kW/m^2, the effect of the fibre length started to become more apparent, even for glass fibre composites. The time to ignition, mean heat release rate and peak heat release rate increased/decreased by -10%, +2%, and +4%, respectively, when the fibre length was changed from 6 to 20 mm.

The negligible effect of the fibre length on the fire performance of the glass and basalt fibre reinforced PC can be explained by the low thermal conductivity of both. As seen in Table 7.6, the effect of the fibre length on the thermal conductivity of glass and basalt composites does not exceed 6% in-plane, and almost no change in out-of-plane thermal conductivity was observed among the 6 mm, 12mm and 20 mm fibre composites for both types of composites.

7.6.2 Composites with high thermal conductivity

The fibre length has a major effect on the thermal conductivity of the carbon fibre reinforced PC due to the much higher thermal conductivity of the fibre when compared to glass and basalt. The cone calorimetry results in Table 7.5 exhibit an increase in the residual mass, time to ignition, mass loss rate, and burning time in addition to an increase in the peak heat release rate when 6 mm and 20 mm long carbon fibre reinforced PC are compared. The increases/decreases in the fire performance parameters ranged from 20% to 40%, which is significantly higher than what was observed for the glass and basalt composites.

The significant effect of the fibre length on the fire performance of the carbon fibre reinforced PC can be related to its high thermal conductivity. As also shown in Table 7.5, the difference in the in-plane thermal conductivity between 6 mm and 20 mm long fibre composites ranged from 9% at room temperature to over 25% at 160°C because both the polymer and the fibre increase in thermal conductivity when the temperature increases. Out-of-plane thermal conductivity drops between 130°C and 160°C because the PC undergoes a phase change at 147°C. Out-of-plane thermal conductivity is also matrix dominated. In-plane thermal conductivity does not reduce because it is fibre dominated; the fibres do not undergo phase changes at such a low temperature. The influence of thermal conductivity in fire performance can be explained by employing the equations provided by Drysdale [45]:

$$I = k\rho c \tag{7.1}$$

$$\alpha = \frac{K}{\rho c} \tag{7.2}$$

$$t_{ig} = I \,. \left(\frac{T_{ig} - T_0}{q_{in}}\right)^2 \tag{7.3}$$

where, I is thermal inertia, K is thermal conductivity, ρ is material density, c is specific heat capacity, and T_{ig} is ignition temperature.

The increase in thermal conductivity directly leads to an increase in thermal inertia and thermal diffusivity. This results in a longer time to ignition and also affects the flame spread rate, the latter of which is discussed in the next section. An increase in thermal inertia also influences the heat release rate and mass loss rate. However, the effect of thermal inertia on the heat release rate and mass loss rate is more complicated and will not be discussed further in this chapter.

7.6.3 Flame spread rate

The flame spread test could not be carried out for the unreinforced PC due to the significant difference between the PC processing temperature (260ºC) and the critical heat flux for piloted ignition (~ 445ºC). As a consequence of this large temperature difference, the sample will melt and drip before ignition is achieved (see Figure 7.6). In the hope that the fibre will hold the PC together and prevent it from collapsing, a trial was conducted on the glass and carbon fibre reinforced PC with different fibre lengths. The tests on the fibre reinforced PC were successfully performed. The improved structural rigidity and melt strength provided by both kinds of fibre prevented the collapse of the sample. To the best knowledge of the author, these flame spread test results mark the first time that this test was successfully performed for PC composites. Using data from Figure 7.9 and the ignition temperatures from Figure 7.7, the flame spread parameter can be derived from [47]:

$$V = \frac{l_h}{t_{ig}} \tag{7.4}$$

where

$$\emptyset = q_{in}^2 . l_h \tag{7.5}$$

substituting 7.3 and 7.4 into 7.5 yields

$$V = \frac{\emptyset}{I\,.\,(T_{ig} - T_0)} \tag{7.6}$$

with

$$h_T = \frac{q_{ig}}{T_{ig} - T_0} \tag{7.7}$$

$$V = \frac{\emptyset^2 h_T^2}{\mathrm{I}\,.\left(\mathrm{q_{ig}} - q_{ext}\right)^2} \tag{7.8}$$

$$\frac{1}{\sqrt{V}} = \sqrt{\frac{I}{\emptyset h_T^2}}\,.\,(q_{crit} - q_{ext}) \tag{7.9}$$

$\sqrt{\frac{I}{\emptyset h_T^2}}$ is the slope, then $\emptyset$ can be rewritten as

$$\emptyset = \frac{\mathrm{I}}{\mathrm{m}^2 h_t^2} \tag{7.10}$$

Where $\emptyset$ is the flame spread parameter, V is the flame spread speed, T_0 is the ambient temperature, q_{in} is the critical heat flux for ignition, q_{ext} is the external applied heat flux, m is the slope of q_{ext} vs $\frac{1}{\sqrt{V}}$, and h_T is the total convective heat transfer parameter. Using Equation (7.7), h_T was found to be 52.38 W/m^2 K.

Because it is a function of the critical heat flux and ignition temperature, h_T is a matrix property and hence its value is unaffected by the fibre length or type. The results of the flame spread testing are shown in Table 7.7. Calculating the flame spread parameter is important to determine the difference in flame spread behaviour between the glass and carbon fibre reinforced PC for the different fibre lengths. It can also be employed to determine a parameter that can be used to compare the flame spread behaviour of PC composites for other materials in the literature. This is not easily done for PC using other means.

Table 7.7: Flame spread test results

	Fibre length	q_{crit} (kW/m^2)	Ø (kW^2/m^3)	m ($m^{3/2}s^{1/2}/kW$)	I ($kJ/mKs^{1/2}$)	t_{ig}* (s)	t_{ig2}** (s)
CF	6mm	16.32	7.13	6.70	0.88	180	180.10
reinforced	12mm	16.98	12.43	5.35	0.98	200	181.16
PC	20mm	18.89	15.65	4.89	1.03	210	185.49
GF	6mm	10.23	5.26	7.12	0.73	150	175.76
reinforced	12mm	9.92	5.66	6.86	0.73	150	175.76
PC	20mm	10.1	6.98	6.18	0.73	150	175.76

*Time to ignition @26kW/m^2 heat flux applied on sample leading edge. Time to ignition was estimated by using data obtained from cone calorimetry test

** Calculated using Equation (7.3)

As seen in the results, the type of fibre used has a major effect on the flame spread. While the fibre length does not seem to have much effect on the flame spread behaviour of the glass fibre reinforced PC, a 110% increase in flame spread is noticed when the fibre length of carbon fibre reinforced PC is increased from 6 mm to 20 mm. This variation in flame spread properties between glass and carbon fibre reinforced PC is due to the difference in thermal inertia which is greatly influenced by thermal conductivity and the volumetric specific heat capacity. An interesting finding is that critical heat flux for the flame spread of glass fibre composites is lower than carbon fibre composites despite the latter having a higher flame spread.

By only looking at Table 7.7, this might suggest that the glass fibre composites exhibit a worse performance than carbon fibre composites since fire travels for longer in glass. However, Figure 7.10 shows that the reason for the early extinguishing of carbon fibre composite samples is the melting and consequent loss of material that is responsible for terminating the test.

Figure 7.10: A picture of burnt 12mm long CF (right) and GF (left) reinforced PC after flame spread test

Equation (7.3) uses thermal conductivity to calculate the time to ignition. However, it does not account for in-plane thermal conductivity which must have an effect. Although for many materials in-plane and out-of-plane thermal conductivity are similar, materials such as the carbon fibre composite used in this research has an in-plane thermal conductivity four times greater than the out-of-plane thermal conductivity. This represents a challenge that is not captured in the model discussed above. When the model is used in its current form using the values measured in in Table 7.6 it appears that glass and carbon fibre reinforced composites have a comparable time to ignition. However, from the cone calorimetry test results in Table 7.3, Table 7.4, and Table 7.5, it is easy to notice that the fibre type has a significant effect on the time to ignition of composite materials as seen in Table 7.7.

It is worth noting that all the convective heat transfer parameters and flame spread parameters for unreinforced PC shown in Table 7.7 differ significantly from results reported in previous literature [47]. These earlier reported values in other research employed a theoretical approximation based on a mathematical model to determine the flame spread. The estimation of the flame spread for PC in the present work is much higher than the values determined in the prior study using mathematical modelling [47]. Although some difference is expected since the results in Table 7.7 are determined for fibre reinforced PC, the ignition temperature and the total convective heat transfer are material properties and consequently should be comparable. This suggests that, for this class of material, theoretical approximation might not be an accurate way of determining the flame spread parameter and that the presented experimental method likely yields more reliable values.

7.7 Conclusion

The results presented above have shown that thermal properties are the key driver of fire performance for the fibre reinforced PC composites analysed in this research. Factors such as the fibre type, fibre length, matrix type, and the material temperature have an effect on the thermal properties. The level at which the fibre length influences thermal properties is dependent on the thermal properties of the fibre. For fibres with low thermal conductivity, only a minor effect of fibre length is observed. On the other hand, for fibres with high thermal conductivity, the fibre length has a major influence, especially on in-plane thermal conductivity. It is concluded that thermal properties can, to a certain extent, be used to estimate fire performance aspects, i.e. the time to ignition, heat release rate, thermal conductivity, and mass loss rate, using the approach described in this chapter. Determining the thermal properties of a composite material based on its constituents is relatively straightforward and can be, for example, achieved analytically by employing the model proposed by C. Chen [44] or numerically by using a representative volume element approach. Predicting a composite material's flame spread behaviour from its constituent properties remains challenging. A promising, albeit complicated approach, is the combination of a general pyrolysis model (e.g. GPYRO) [48] and a fire dynamics simulator.

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Chapter 8

Fire and post fire properties of two glass fibre reinforced materials: an epoxy and a polycarbonate composite: A comparative study

Motivation

After having studied the fire performance of a thermoplastic composite, a comparison with a similar thermoset matrix will help to give a general idea of the fire performance of thermoplastics vs. thermoset composites

TWENTY-SECOND INTERNATIONAL CONFERENCE ON COMPOSITE MATERIALS (ICCM22)

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FIRE AND POST FIRE PROPERTIES OF GLASS FIBER REINFORCED EPOXY AND POLYCARBONATE COMPOSITE: A COMPARATIVE STUDY

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Abstract

The fire performance of a continuous glass fibre reinforced polycarbonate (PC) thermoplastic composite is evaluated against the fire performance of a continuous glass fibre reinforced epoxy thermoset composite. Both composites had a fibre volume fraction of 47% and a nominal thickness of 3.9 mm. A plain weave fabric was used for both composites. The PC composite was manufactured using film stacking while the epoxy composite was manufactured using light resin transfer moulding. The fire performances of the two composites were compared at incident heat fluxes of 25 kW/m^2, 35 kW/m^2, and 50 kW/m^2. Post fire, four point bending testing was used to investigate the post fire residual mechanical properties.

Author contribution percentages (Chapter 8)

Author	Sample manufacturing	Testing	Data Analysis	Paper writing	Paper editing
Yousof Ghazzawi	70%	70%	90%	100%	-
Michael Heitzmann	-	-	-	-	60%
Andres Osorio	-	-	-	-	20%
Asanka Basnyake	30%	30%	10%	-	-
Juan Hidalgo	-	-	-	-	20%

8. Fire and Post Fire Properties of Two Glass Fibre Reinforced Materials: An Epoxy and a Polycarbonate Composite, a Comparative Study

8.1 Introduction

Fibre reinforced composites are considered for a large variety of applications such as the aerospace, construction, railway, and automotive industries. Due to their well-known properties and processing conditions, thermoset composites still dominate the composite market, with over 90% of the continuous fibre composite market share. However, thermoplastic composites are increasingly replacing thermosets in applications where low cost, high impact strength, and recyclability are desired.

This is due to the fact that thermosets are more mature products and have been used by industry for some time. Some investigation has been undertaken into the fire performance of thermoplastic composites. Nonetheless, due to its current low market share and a large diversity in the matrix choices for thermoplastics, the research for this group of composites is less comprehensive. A large proportion of the work is focused around chopped fibre composites [1-8].

There are only a few articles comparing the fire performance of thermosets to thermoplastics and these have mostly been done on high performance composites [9].

This study aims to compare the fire performance of an engineering thermoplastic, polycarbonate (PC), to the fire performance of a thermoset with a similar classification, Bisphenol A based epoxy resin. To ensure a reasonable basis for this comparison, both composites have the same fibre volume fraction, similar densities, comparable thicknesses, and are tested under the same conditions.

Cone calorimetry is used to investigate the fire performance of the glass fibre reinforced PC and epoxy. The two composites are compared in terms of their heat release rate, burning time, time to ignition, critical heat flux, mass loss rate, and char yield.

Four point bending tests are performed to compare the post fire mechanical properties of the epoxy and PC composites in terms of their bending strength and flexural modulus.

8.2 Materials

SABIC PC 2200 polycarbonate copolymer with a melt index of 22 g per 10 min, density of 1200 kg/m3, and glass transition temperature of 147ºC was used to make the thermoplastic composite in the study. Ampreg 22 epoxy was used with a fast hardener. The glass transition temperature of the epoxy and hardener mix was 115ºC and the density was 1147 kg/m^3.

The glass fibre reinforced polycarbonate composites were manufactured using film stacking. The films were dried for 4h at 100ºC. After drying, the fabrics were laid up with the films interleaved and compression moulded at 270ºC under a constant pressure of 2 MPa for 10 min. Samples were cooled to 50ºC while maintaining pressure prior to releasing the press. The glass fibre reinforced epoxy composites were manufactured using light resin transfer moulding. The resin was cured at room temperature for 24 hours under vacuum then post cured at 50ºC for 16 hours. 17 layers of plain weave fabric with an areal weight of 280 g/m^2 were used to make 250 x 250 mm plates of both the PC and epoxy composites. The plates had a nominal thickness of 6 mm and were cut into 100 x 100 mm samples for the cone calorimeter test using waterjet cutting.

8.3 Experimentation

A cone calorimetry (Fire Testing Technology, Icone Calorimeter) test was conducted according to ISO 5660-1 to compare the fire performance of the two composites in terms of their heat release rate (HRR), time to ignition (t_{ig}), mass loss, and critical heat flux (CHF). The test was carried out at heat flux values of 25 kW/m^2, 35 kW/m^2, and 50 kW/m^2. Sample size was 100 x 100 mm. So as to minimise radiation heat losses and prevent spurious mass loss readings due to melting and dripping, the edge and rear faces were wrapped with aluminium foil. The sample's back face was insulated using ceramic wool to minimise heat losses. As suggested in ISO 5660-1, a retaining frame used to restrain the exposed surface of the sample and prevent it from being in contact with the heating element.

Four point bending tests were performed, in accordance with ASTM D6272, to investigate the pre and post fire mechanical properties of the composite samples. The sample size was 100 x 10 mm. Samples were taken from different areas of the burned 100 x 100 mm samples.

8.4 Results

This section summarises the results of the cone calorimeter and flexural bending tests performed on the two composite types.

8.4.1 Fire testing

Fire testing was carried out for three specimens for each composite at the three different incident heat fluxes to compare the glass fibre reinforced epoxy composite (GFREC) to the glass fibre reinforced PC composite (GFRPC) in terms of their time to ignition (t_{ig}), peak heat release rate (pHRR), mean heat release rate (mHRR), total heat release (tHR), char yield (CY), critical heat flux (CHF) . Results are reported with a 90% confidence interval as shown in Table 8.1.

Table 8.1: Fire testing results for PC and epoxy composites

		HF (kW/m2)	GFRPC	GFREC
		25	618.67 ± 55.57	183.00 ± 5.84
tig	(S)	35	248.00 ± 2.92	107.00 ± 4.46
		50	116.00 ± 0.00	59.00 ± 2.92
		25	122.92 ± 10.54	381.29 ± 58.90
pHRR	(kW/m2)	35	165.28 ± 29.48	423.00 ± 47.70
		50	195.51 ± 21.46	467.78 ± 17.06
		25	85.52 ± 8.75	222.55 ± 15.43
mHRR	(kW/m2)	35	117.09 ± 18.49	226.18 ± 25.19
		50	123.25 ± 7.50	257.18 ± 1.16
		25	30.79 ± 3.15	67.88 ± 4.71
tHR	(MJ/m2)	35	39.81 ± 6.29	65.59 ± 7.30
		50	38.21 ± 2.32	65.58 ± 0.30
		25	34.99 ± 5.63	7.81 ± 1.53
CY	(%)	35	24.76 ± 4.36	8.00 ± 2.23
		50	19.32 ± 0.78	7.18 ± 1.59
CHF	(kW/m2)	-	23	11

In terms of the time to ignition, the polycarbonate composite took at least twice as much time as the epoxy. For instance, at 25 kW/m^2 incident heat flux, the polycarbonate required around 618 s to ignite, which is over three times as long as the epoxy, at 183 s.

As far as the heat release rate is concerned, the polycarbonate composite exhibited less than half the rate compared to the epoxy composite. For example, at an incident heat flux of 35 kW/m^2, the polycarbonate composite had an average pHRR of 165.28 kW/m^2 while for the epoxy composite this was 467.78 kW/m^2. Figure 8.1 shows the heat release rates for the PC and epoxy glass fibre composites.

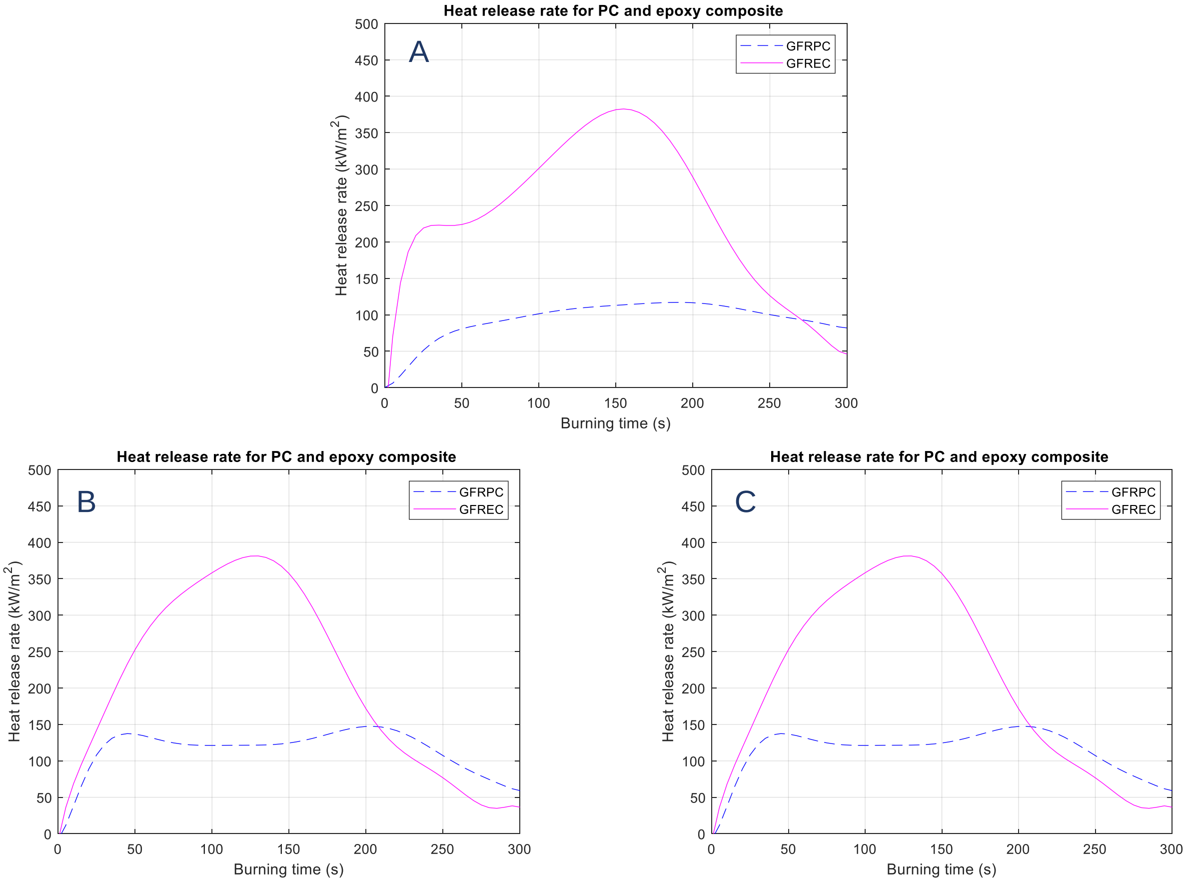

Figure 8.1: Heat release rate for PC and epoxy composites at an incident heat flux of A) 25 kW/m^2, B) 35 kW/m^2, C) 50 kW/m^2

The char yield of the polycarbonate was much higher than for the epoxy. While the polycarbonate's char yield ranged from 35% at 25 kW/m^2 heat flux to 19% at 50kW/m^2 heat flux, the epoxy had a very low char yield of about 8 %.

As for the critical heat flux, the PC composite samples ignited at an incident heat flux of 23 kW/m^2 while the epoxy composite samples ignited at 11 kW/m^2.

With regard to the mass loss rate, As seen in Figure 8.2, the epoxy composite samples started losing mass very rapidly, right from the onset of ignition, while for the PC composite samples the onset of the mass loss only became pronounced after 50 to 100 s from the time to ignition, depending on the incident heat flux.

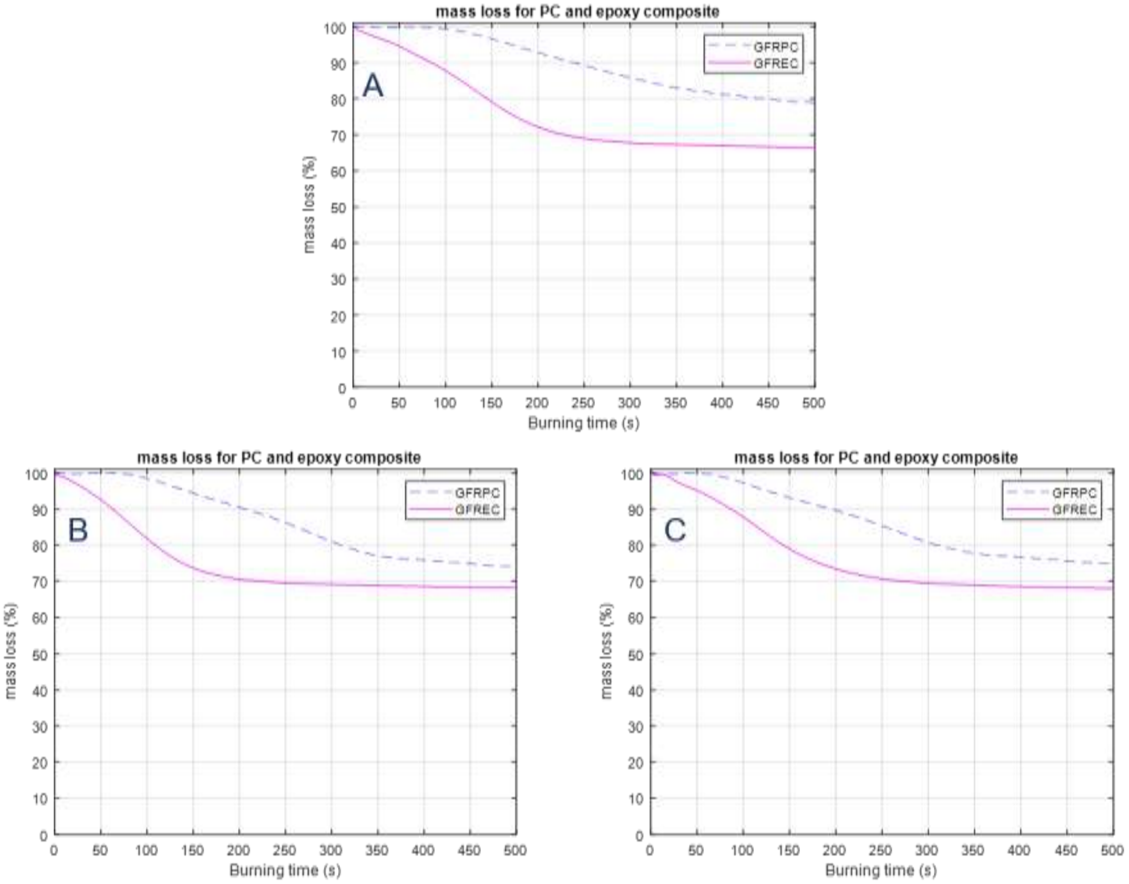

Figure 8.2: Mass loss for PC and epoxy composites at an incident heat flux of A) 25 kW/m^2, B) 35 kW/m^2, C) 50 kW/m^2

8.4.3 Flexural test

Figure 8.3 demonstrates the flexural test results for the glass fibre reinforced PC prior to and post fire exposure. Samples were taken from different parts of the burned samples from the Icone test. The glass fibre reinforced epoxy composite sample did not have any strength left after exposure to fire while the glass fibre reinforced PC samples had post fire mechanical properties of 7% when tested at 25kW/m^2. When tested at higher incident heat fluxes, the post fire mechanical properties of the PC composite were found to be less than 5% at 35 kW/m^2 and almost 0% at 50kW/m^2. As shown in Figure 8.3, the remaining performances of the post fire flexural test samples were heavily influenced by the sampling locations. At 25 kW/m^2 heat flux, the strength reduced by more than 70% from the edge of the specimen to the centre.

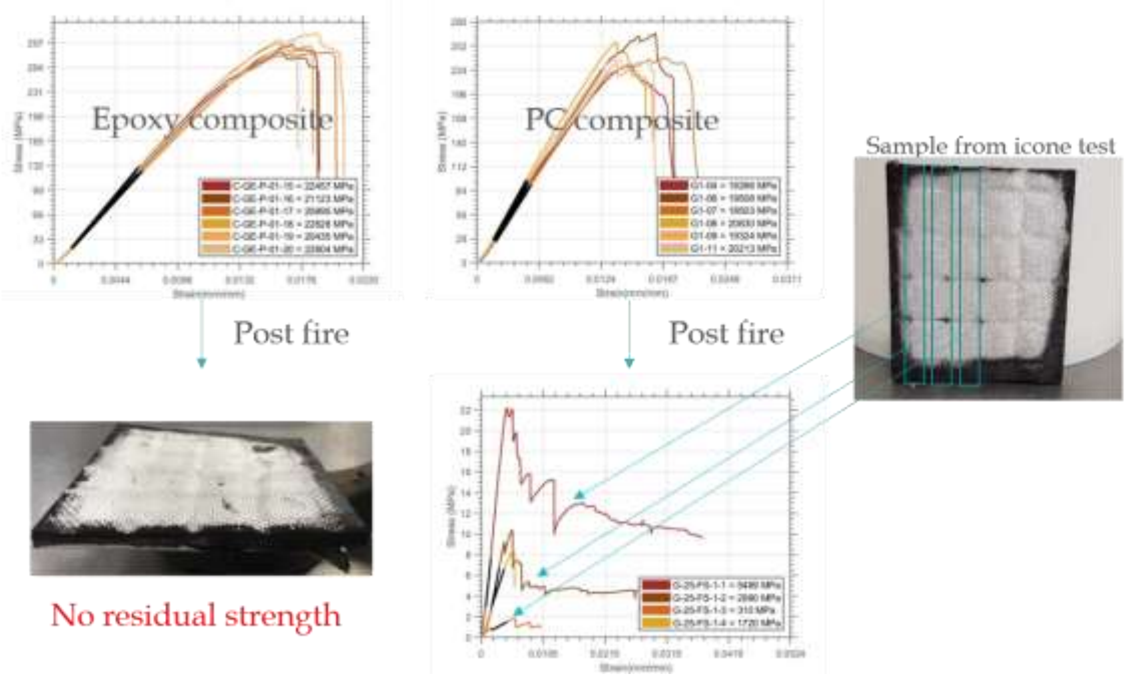

Figure 8.3: Prior to and post fire flexural properties of glass fibre reinforced epoxy/PC

8.5 Discussion

8.5.1 Fire performance of glass fibre reinforced epoxy/PC composite

As shown in Table 8.1, the PC composite was superior to the epoxy composite in terms of its fire performance. The PC composite had a lower rates for mean heat release, peak heat release, and mass loss. In addition, the PC composite samples took at least twice as much time to ignite when compared to the epoxy composite samples at similar incident heat fluxes. The critical heat flux of the polycarbonate was 23 kW/m^2; while it was 11 kW/m^2 for the epoxy. This means that the epoxy composite would ignite at approximately 220ºC while the PC would ignite only when exposed to temperatures around 400ºC or higher. The significant difference in fire performance between the two resins is remarkable considering they have a similar chemical structure. This suggests that knowing the chemical structure of a polymer is not enough to estimate its fire performance.

8.5.2 Post fire mechanical properties

As indicated in Figure 8.3, the PC composite had a post fire flexural strength of around 7% when tested at an incident heat flux of 25%. This is believed to be a result of the PC having a char yield of 35 % at this heat flux. It is worth noting that the char yield is greatly affected by the heat flux and reduces from 35% at 25 kW/m^2 heat flux to 19% at 50kW/m^2. The epoxy composite had no post fire mechanical properties left after testing. This is a result of the much lower char yield of the epoxy resin, which was only measured at around 8%, very low when compared to the PC. Figure 8.4 is an SEM image for the PC composite after fire testing. The image shows that some char is still attached to the fabric, indicating some residual strength remaining in the PC composite.

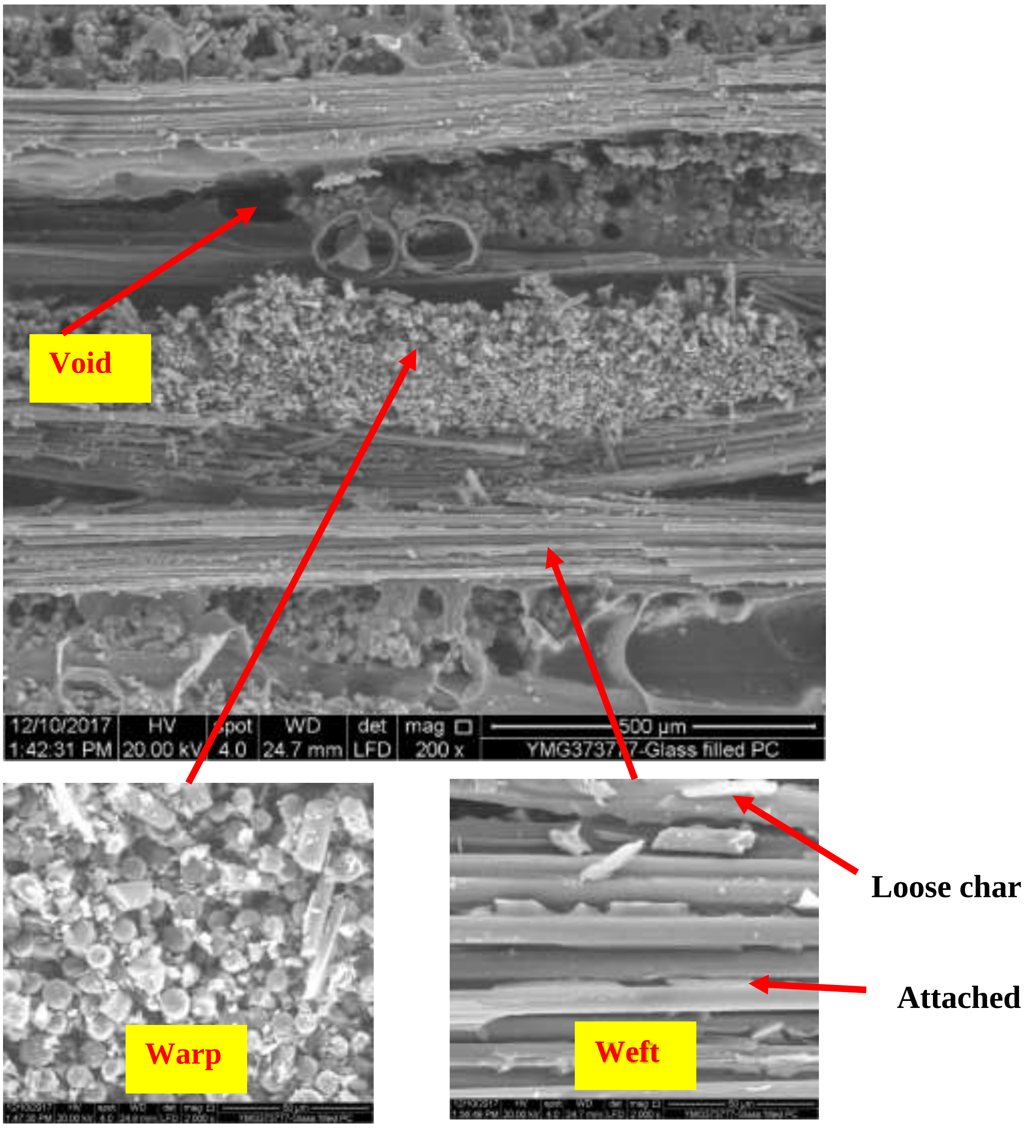

Figure 8.4: SEM images for PC reinforced samples after cone calorimeter testing

8.6 Conclusion

In this study, the glass fibre reinforced PC (thermoplastic composite) has been found to be superior to the glass fibre reinforced epoxy (thermoset composite) in terms of its fire performance. Despite a comparable fibre volume fraction, the PC composite samples have a better time to ignition, heat release rate, and critical heat flux than the epoxy composite samples when exposed to similar conditions. This difference between the epoxy and PC composite is extraordinary considering the similarities in the chemical backbone of the two resins, both being made of BisphenolA monomer.

Unsurprisingly, the char yield has an effect on post fire mechanical properties. For the lowest heat flux tested, the PC retained 7% of its flexural strength. It is worth noting that the post fire performance is greatly affected by the sample location and the heat flux. For more realistic fire scenarios, this highlights an interesting point: the residual structural performance is not just a simple function of the char yield, but is a rather complex function of the thermal history of the sample during the fire event.

In this study, the analysis was performed on a certain epoxy matrix (Bisphenol A resin and Polyoxyalkyleneamine/cyclohexylamine hardener). However, clearly, many different epoxy resin chemistries exist and, consequently, their performance could differ greatly to the system compared here.

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9. Conclusion: Critical aspects of composite materials design for fire performance

9.1 Introduction

The importance of composite materials has become well recognized across many industries including in aerospace, building and construction, marine, transports, or oil and gas. The discussion has moved from whether composites can replace metals and common engineering materials to how to leverage composites' constituent properties to optimize for better composite performance. An area of particular concern is the fire performance of composites. Although composites surpass metals in many areas, including light weight and mechanical properties, metals have typically much better fire performance compared to composites.

The fire properties for virgin plastics are not complicated to study and are well known [1-10]. On the other hand, due to the near infinite choice of fibre and matrix materials, it is very challenging to study and predict the fire performance for composite materials based on their constituents' properties. A lack of consideration of fire performance requirements can lead to situations where mature designs fail to meet fire performance requirements and result in costly iterative engineering loops to meet structural and fire performance stipulations simultaneously. Figure 9.1 shows the possible composite design choices in terms of fire performance.

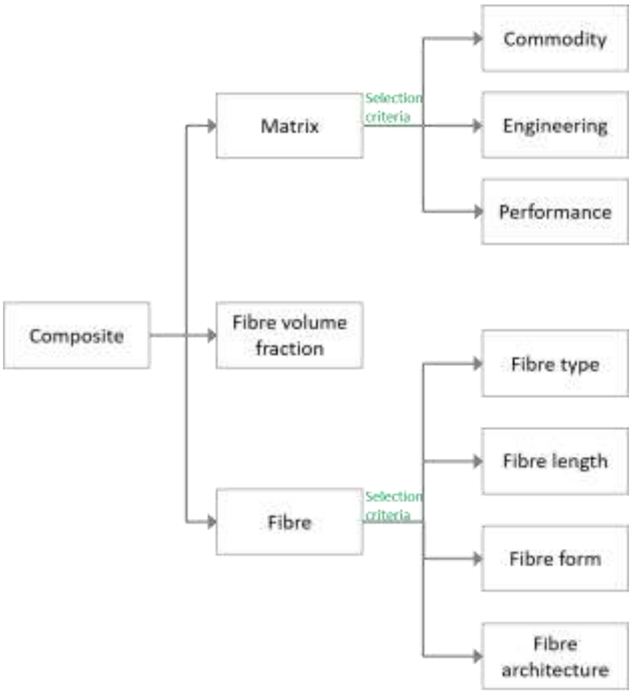

Figure 9.1: Composite design choices

Improving the composite's fire performance is most commonly achieved through the addition of fire retardants [11-25]. However, when a fire retardant is added to the matrix, this typically causes a significant drop in its mechanical properties. In addition, a number of effective fire retardants also have a major impact on the environment [26-30].

A majority of prior research into relationships between constituents has been focused on thermosetting fibre reinforced plastics. Thermoplastic composites, particularly short and long fibre compounds, have received far less attention. Possibly the most commonly used form of thermoplastic, polymer matrix composites, have largely been ignored. In addition, results from prior studies are often difficult to compare due to the variety and the lack of control in matrix grades and additives.

In this chapter, data from Chapters 4, 5, 6, 7, and 8 is used to discuss constituent contributions on fire performance and to derive a decision framework. Where appropriate, results from the literature are used to extend or justify the proposed framework's applicability beyond the materials tested in this research.

9.2 Composite fire performance parameters

The fire performance of composite materials is regularly characterised based on measures such as time to ignition, heat release rate, flame spread rate, and mass loss rate. Numeric equations to estimate these parameters were introduced in Chapter 7 where they were derived in detail. For convenience, they are summarized again below [31, 32]:

$$HRR = MLR\ x\ EHC \tag{9.1}$$

$$t_{ig} = I\,.\left(\frac{T_{ig} - T_0}{q_{in}}\right)^2 \tag{9.2}$$

Where

$$I = k\rho c_p \tag{9.3}$$

$$\frac{1}{\sqrt{V}} = \sqrt{\frac{I}{\emptyset h_T^2}} \cdot (q_{crit} - q_{ext}) \tag{9.4}$$

$\sqrt{\frac{I}{\emptyset h_T^2}}$ is the slope, then $\emptyset$ can be rewritten as

$$\emptyset = \frac{\mathrm{I}}{\mathrm{m}^2 h_t^2} \tag{9.5}$$

Where HRR is the mean heat release rate, EHC is the effective heat of combustion, MLR is the mass loss rate, I is the thermal inertia, K is the thermal conductivity, ρ is the material density, c is the specific heat capacity, T_{ig} is the ignition temperature, T_0 is the ambient temperature, $\emptyset$ is the flame spread parameter, V is the flame spread speed, q_{in} is the critical heat flux for ignition, q_{ext} is the external applied heat flux, m is the slope of q_{ext} vs $\frac{1}{\sqrt{V}}$, and h_T is the total convective heat transfer parameter.

9.3 Factors affecting the fire performance of composites

As Chapters 2 to 8 have indicated, the most significant factors affecting the fire performance of composites are: char yield, specific heat capacity (CP), density, effective heat of combustion, thermal conductivity, and other factors such as fibre volume fraction, lofting, and fibre architecture.

For composite materials, both matrix and fibre affect the fire performance. However, sensitivity to the factors mentioned above varies between fibres and matrices. Matrices greatly influence the fire performance of composites through the CP, heat of combustion, and char yield values; while fibres mainly affect the fire performance of composites through variations in the thermal conductivity and density between common fibres used in fibre reinforced composites. In the following sections the key contributions of this research study are summarized and the decision framework is developed and demonstrated in Figure 9.12.

9.3.1 Char yield

This is a very important, if not the most important property of the matrix. Char reduces the speed of a fire's spread as it acts as a buffering layer with low thermal conductivity.

As presented in Chapters 5 and 6, a polymer with a high char yield (PC) is characterised by a higher time to ignition, slower mass loss rate and lower heat release rate when compared to one with a low char yield (PP). Figure 9.2 illustrates that a PC has a far lower heat release rate than PP when the same heat flux is applied (35 kW/m^2).

As shown in Figure 9.3, for diverse kinds of polymers, the tendency is for heat of combustion and char yield to be inversely proportional. Matrices with a high char yield in general have a lower heat of combustion. This trend can be explained through the fact that for charring matrices not all material is consumed and turned into combustible volatiles. Hence, less heat energy is produced by the matrix [32]. In addition, as shown in Chapter 8, lofting of fibres is less likely to occur in a composite with a high char yield matrix since the char helps to hold fibres in place (Figure 8.4). Due to its poor thermal conductivity, char also has insulation and barrier properties, which limits the temperature transfer between composite layers and helps to supress fire growth. As emphasised in Chapter 8, char yield is sensitive to the heat flux applied on the matrix. In general, the temperature at which the char yield of a matrix is measured is not standardized and it can range from 300 to 1000°C. However, as per our research findings, when a high heat flux was applied, the polymer's char yield was lower than when a lower heat flux was applied to the same polymer (Table 9.1). Therefore, it is important when reporting the tested char yield of the matrix, to also mention the extent of heat flux applied. This is something that is generally overlooked in the literature and results describing this behaviour are rarely recorded.

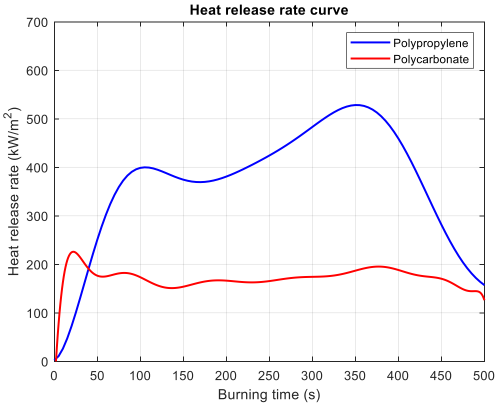

Figure 9.2: Heat release rate for PP and PC

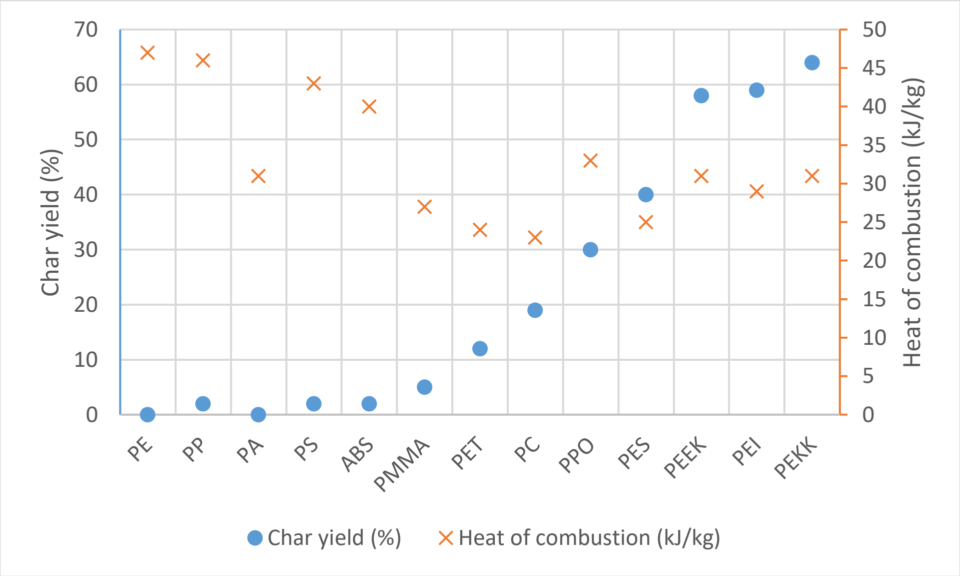

Figure 9.3: Char yield vs. heat of combustion of various polymers [33-35]

9.3.2 Effective heat of combustion

The heat of combustion is a material property. In most fire scenarios, only the matrix’s heat of combustion is considered. Figure 9.4 shows the TGA for a PC matrix and fibre reinforced PC in both air and nitrogen. As seen in Figure 9.4, fibres do not degrade or oxidize much at low temperatures when the test in done in a nitrogen environment. Since the fire test environment is close to nitrogen in TGA (as concluded in Chapter 6), the heat generated from fibres in these cases is minimal. Yet carbon fibres play an important part here. Their oxidization began at about 500°C and is exothermic, thus influencing fire performance. Nevertheless, findings indicate that for the specific heat fluxes and surface/flame temperatures explored in this research, the carbon fibre reinforced compounds’ mass loss was similar to the mass loss curves of testing conducted in an inert atmosphere (as Figure 7.5 illustrates).

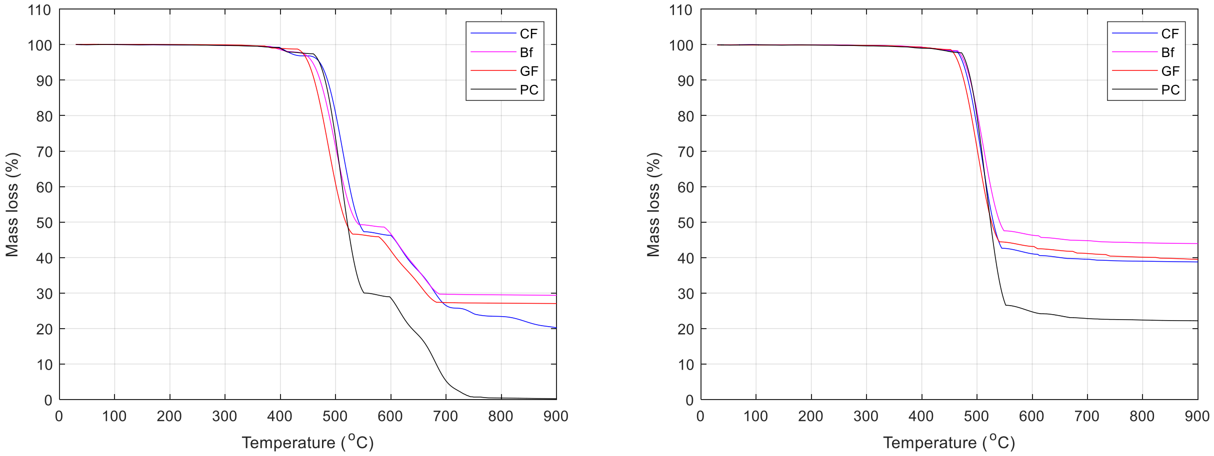

Figure 9.4: TGA for PC and PC composites at air (left) and nitrogen (right)

Matrices with a high heat of combustion also burn more rapidly than those with a low heat of combustion. As shown in Chapter 5, for a fibre reinforced thermoplastic composite, the fibres have merely a diluting effect (except for highly conductive fibres). Irrespective of whether the matrix is charring, the total heat release corresponded to the burned amount of the matrix. The total amount of heat energy generated by the composite is low when compared to the virgin matrix. In Figure 9.5, both PC and PC composite have the same thickness of 4 mm. However, the total heat energy released by the composite was 46 MJ/m^2; while the virgin PC released 105 MJ/m^2 of heat energy, which is more than double that of the composite. This is because the nominal fibre volume fraction of the composite is 50%. This suggests that the effect of an inert fibre is simply one of dilution. Consequently the total heat released for the composite material can be calculated when knowing the effective heat of combustion of the matrix material and the fibre volume fraction.

Table 9.1 shows typical heat of combustion values for different matrices. The heat of combustion has a direct effect on the heat release rate as seen in Equation (9.1). Both the char yield and heat of combustion are influenced by the chemical structure of the matrix. As seen in Figure 9.3, the heat of combustion follows an opposite trend to the char yield. With the exception of a few polymers, when the char yield is high, the heat of combustion is low and vice versa.

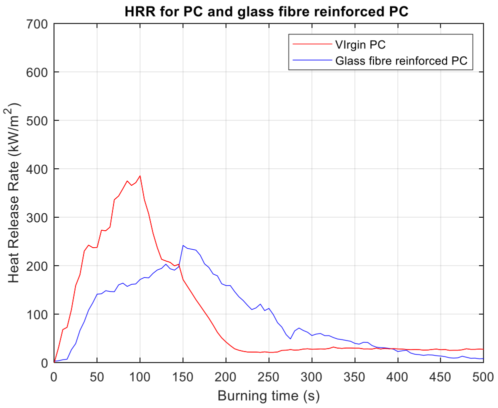

Figure 9.5: A comparison between virgin PC and glass fibre reinforced PC

9.3.3 Specific heat capacity

Specific heat capacity (CP) is influenced by both the matrix and fibre. For matrices, the CP typically varied between 1000 and 2000 kJ/Kg K; while for fibres, it varied between 700 and 900 kJ/Kg K, as seen in Table 9.1. The CP for composites can be determined using the role of mixture as per Equation 9.6:

$$CP_{mix} = \frac{m_f}{m_{mix}} CP_f + \frac{m_{mat}}{m_{mix}} CP_{mix} \qquad [9.6]$$

CP is very sensitive to temperature, especially when a phase change occurs. When matrices are heated, the CP gradually increases. However, when the matrix reaches the melting point for semi-crystalline matrices or he glass transition point for amorphous matrices, a step increase in the value of the CP occurs. Figure 9.6 shows the change in CP as a function of the temperature for PC. The change in the value of CP for matrices when they reached the melting point varied between 15 to 40% as seen in Table 9.1.

CP affects the fire performance of composites through thermal inertia as shown in Equation (9.3). Thermal inertia is the product of CP, density, and thermal conductivity. The choice of the matrix or fibre can affect the value of CP since every matrix or fibre has a unique CP. At room temperature, most common fibres such as glass, basalt, and carbon fibre have a comparable CP, while matrices vary a lot in CP value as seen in Table 9.1.

The selection of the matrix or fibre is not the only way CP influences thermal inertia. CP is temperature sensitive. The amount with which the CP changes the thermal inertia as a result of temperature change depends on the matrix used and varied from 15% and reached up to 40%

for matrices on melting or glass transition (as Table 9.1 illustrates). This is quite high, especially because thermal inertia plays an important role in many aspects of fire performance. The CP of the fibre is less sensitive to temperature variation due to the fact that the maximum service temperature the composite typically reaches during fire is far less than the temperature required to cause a phase change to fibres (Figure 7.8).

Table 9.1: Properties of common fibres and matrices [33-35]

		CP (solid) J/g K	CP (liquid) J/g K	Density g/cm^3	Thermal conductivity W/m K	Heat of combustion MJ/Kg	Ignition temperature ºC	Char yield %
Fibres	Basalt	0.840	-	2.75	1.1	-	-	-
	Glass	0.80	-	2.56	1.00	-	-	-
	Carbon	0.71	-	1.70	10.00	-	-	-
Matrices	PVC	1.00	1.2	1.40	0.19	20.00	385	18.00
	PC	1.25	1.69	1.20	0.24	22	425	22.00
	PMMA	1.50	1.99	1.18	0.22	25	300	1.70
	PE	1.90	2.58	0.98	0.40	47	340	0.20
	PP	1.92	2.47	0.90	0.20	46	320	0.00

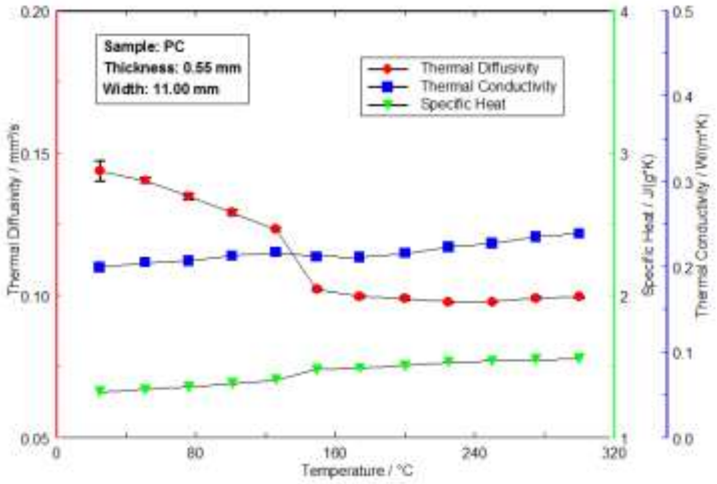

Figure 9.6: CP values for PC at different temperatures [36]

9.3.4 Density

As shown in Equation (9.3), the densities of fibre and matrix influence composites' fire performance through thermal inertia. Densities of the fibres varied between 1.70 and 2.75 g/cm^3 and for matrices between 0.90 and 1.40 g/cm^3.

Table 9.1 shows the densities of common fibres and matrices. The effect of temperature on density has its limitations. At melting point, the density of a matrix typically drops by around 10% [37]. The selection of fibre and matrix is critical to composite density since they vary considerably in their properties (Table 9.1). Density is far less sensitive to temperature change with up to a 10% total drop in density at melting point for a matrix and almost no change for fibres since they have a much higher melting temperature. It is important to notice that, as per Table 9.1, matrices that have a high CP also have a low density and vice versa, with exception of very few matrices. The same rule does not apply to fibres.

9.3.5 Thermal conductivity

Thermal conductivity is a key design parameter for the optimized fire performance of composites. Although the thermal conductivity of matrices is low and usually ranges from 0.2 to 0.3 W/m K (Table 9.1), thermal conductivity for highly graphitic carbon fibres can reach 800 W/m K (e.g., NGF XN100). The table also indicates that the thermal conductivity for basalt and glass fibres ranges from 0.8 to 1.2 W/m K and from 5 to 15 W/m K for PAN based carbon fibre (Table 9.1). Therefore, thermal conductivity of composites is mainly driven by fibres. Thermal conductivity’s impact on fire performance was unclear and thus investigated and described in Chapters 6 and 7.

In Chapter 7, thermal conductivity of different fibre types and for a PC matrix at different temperatures has been examined and results are presented in Table 9.2. Considering the critical importance of thermal conductivity, it is somewhat surprising that this property is not more regularly measured and reported.

By looking at Equations (9.1-9.5), it can be seen that thermal conductivity greatly influences fire performance through thermal inertia; which then influences time to ignition, heat release rate, flame spread rate, and mass loss rate. Since the thermal conductivity of matrices is generally low (Table 9.1), the main effect of thermal conductivity comes from fibres. Fibre type, fibre length, fibre orientation, and fibre volume fraction all have an impact on the thermal conductivity of composites. The extent to which the fibre affects thermal conductivity is highly dependent on the temperature. Thermal conductivity can be measured at different temperatures using a transient plane thermal conductivity test as seen in Table 9.2. Thermal conductivity can also be estimated mathematically relatively easy from the constituent properties of the composite (see Chapter 6).

Although mathematical estimation does not estimate the thermal conductivity as a function of temperature, fibres such as glass and basalt have a relatively low thermal conductivity and are less sensitive to temperature change (Table 9.2). Therefore, mathematical modelling will be helpful. However, when fibres with high thermal conductivity such as carbon fibre are used, mathematical modelling becomes increasingly difficult for various reasons.

First, fibres with high thermal conductivity are sensitive to temperature change, hence the change in thermal conductivity as a function of temperature will be significant, especially if the fibre volume fraction is high. Second, fibres such as carbon fibres come in many grades and forms. Each grade has its unique thermal conductivity. In fact, carbon fibre can have a thermal conductivity starting from 10 W/m K for PAN based carbon fibre and exceeding 800 W/m K for pitch based carbon fibre (e.g., NGF XN100). Third, fibres with high thermal conductivity will have a remarkable difference between their in plane and out of plane thermal conductivity. The majority of current mathematical modelling is only able to estimate out of plane thermal conductivity. Due to these complications, it is suggested that a representative volume element approach might be the more appropriate way to predict the thermal conductivity/diffusivity of a composite material.

Table 9.2: Influence of fibre length and type on thermal conductivity
Thermal Conductivity (W/m K)
In plane/out of plane

Material	Fibre length	@30ºC	@80ºC	@130ºC	@160ºC
Polycarbonate	-	0.244	0.256	0.272	0.2655
CF reinforced PC	6mm	1.085/0.337	1.204/0.321	1.289/0.343	1.260/0.333
	12mm	1.119/0.297	1.271/0.326	1.377/0.362	1.460/0.335
	20mm	1.189/0.312	1.378/0.332	1.546/.0364	1.645/0.343
GF reinforced PC	6mm	0.340/0.280	-	-	-
	12mm	0.360/0.281	0.400/0.300	0.459/0.301	0.528/0.255
	20mm	0.363/0.279	-	-	-
BF reinforced PC	6mm	0.363/0.269	-	-	-
	12mm	0.374/0.280	0.391/0.300	0.439/0.306	0.451/0.270
	20mm	0.377/0.281	-	-	-

9.3.5.1 Fibre type

Fibre type has a major effect on fire performance. While glass fibre has a very low thermal conductivity of 1 W/m K, carbon fibre has a very high thermal conductivity of around 10 W/m K (Table 9.1). The impact of fibre type on thermal conductivity was undetermined so it was examined and presented in Chapters 7.

In Chapter 7, the fire performance of different fibre types is measured. Figure 9.7 shows the time to ignition, burning time, and peak heat release rates for glass, basalt and carbon fibre reinforced PC.

Fibre type affects the fire performance through thermal conductivity. An increase in thermal conductivity causes the thermal inertia to rise, as seen in Equation (9.3) and Table 9.2. When this happens, the time to ignition is also extended, which is favourable. However, the composite will also release more heat and burn more rapidly. Figure 9.7 presents some data for this. Carbon fibre reinforced PC composite has the longest time to ignition but the highest peak heat release rate and less burning time when compared to the other fibre materials in this figure.

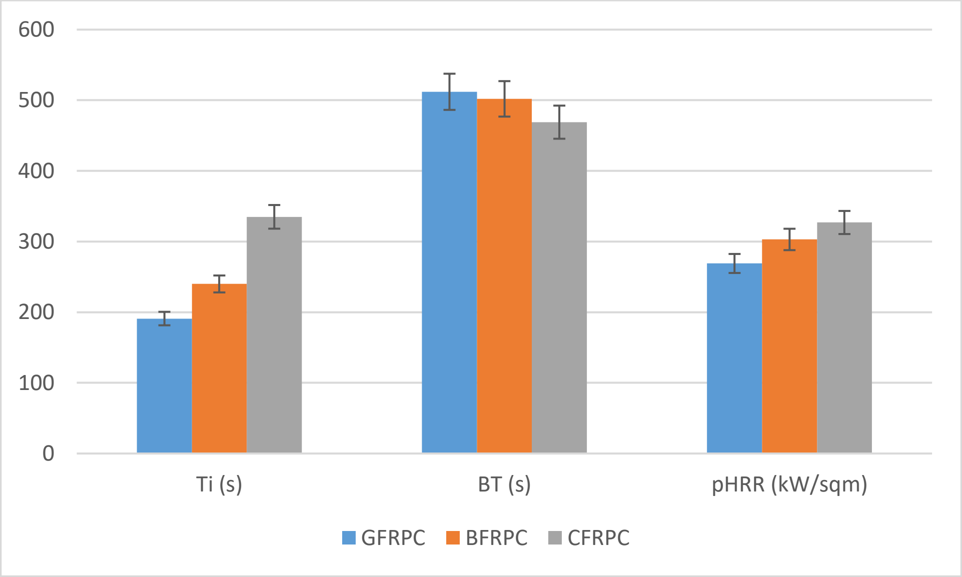

Figure 9.7: Fire performance comparison between glass, basalt, and carbon fibre composites

9.3.5.2 Fibre length

Another factor affecting the fire performance of composites is fibre length, especially when a highly conductive fibre such as carbon fibre is used. Details to clarify this effect were presented in Chapters 6 and 7.

In Chapter 7, the effect of fibre length on fire performance of composites was shown. Table 9.3 shows the effect of fibre length on the fire performance of carbon fibre reinforced PC.

The increase in fibre length results in an increase in thermal conductivity. The rate of increase in thermal conductivity as a function of fibre length depends on the inherent thermal conductivity of the fibre. The higher the inherent thermal conductivity of the fibre, the more sensitive is the composite to fibre length change.

Table 9.3: Fire performance of different fibre types and lengths

@ 35 kW/m^2		PCG6	PCG20	PCB6	PCB20	PCC6	PCC20
Initial mass	g	83.96	84.17	83.91	83.41	76.83	77.40
Thickness	mm	5.83	5.85	5.87	5.83	5.82	5.86
Residual mass	g	44.96	46.68	44.71	48.04	42.78	47.80
Residual mass	%	53.55	55.44	53.29	57.60	55.67	61.75
Time to ignition	s	211.07	191.67	229.00	240.00	252.67	335.67
Burning time	s	545.00	515.67	499.67	502.00	408.00	469.00
Mean HRR	kW/m^2	175.60	172.68	183.20	173.12	198.07	153.12
Peak HRR	kW/m^2	259.33	269.00	238.67	303.67	251.67	327.00
Total heat release	MJ/ m^2	94.99	88.82	91.15	86.42	80.33	71.35
MLR (x10^3)	g/s	72.05	73.16	78.73	70.54	83.67	63.11
EHC	kJ/kg	24.33	23.66	23.24	24.42	23.58	24.11

For PCXY, X: Fibre type where G: Glass, B: Basalt, and C: Carbon. Y: Fibre length in mm

9.3.6 Fibre volume fraction

One of the major composite design criteria is fibre volume fraction. When fibre volume is high, it generally means that the fibre's influence in composite is also high, leading to a higher diluting of the matrix dominated properties and higher thermal conductivity.

In a relevant research, the effect of fibre volume fraction on thermal conductivity has been studied [38]. Table 9.9 shows the impact of fibre content on the fire performance of carbon fibre reinforced polypropylene. The increase in fibre volume fraction resulted in a lower peak heat release rate, lower heat energy release, less burning time, and higher mass residue due the diluting effect of the fibre content.

Table 9.4: Effect of fibre content on fire performance [38]

		PPC0	PPC5	PPC10	PPC20	PPC30
Burning time	S	1120	1102	975	815	503
Peak HRR	kW/m^2	190	182	155	148	133
Total heat release	MJ/ m^2	99	94	86	81	61
Residue	%	24	31	37	41	47

For PPCX, X: fibre mass content %, C: carbon fibre

9.3.7 Lofting

While fibres reinforce matrices, the role of the matrix is to hold fibres together in a predefined orientation. When part of the matrix is consumed in a fire, its ability to maintain the fibre orientation decreases, which may results in lofting of fibre. The effect of lofting has not been totally understood in earlier investigations. This is why the lofting effect due to matrix consumption was explored, with findings provided in Chapter 6.

As described in Chapter 6, a CT image was taken for PP composites with different fibre lengths showing the fibre formation of the sample before exposure to fire (see Figure 9.8). After burning, the PP sample with 12 mm long fibres lofted (Figure 9.9). Table 9.5 shows the fire performance of PP composites with different fibre lengths.

It was found that PP composite with a fibre length of 12 mm ignited the most quickly and had the highest HRR of the PP composites examined. Our findings showed that an intermediate fibre length (between 5 and 20 mm) was where fibres were more vulnerable to loft. Thus, steering clear of this range can significantly change fire performance, especially for non-charring matrices. For those matrices with a high char yield, lofting is less problematic. As Figure 9.8 illustrates, the char keeps the fibres together, giving the composite some residual strength, therefore reducing lofting.

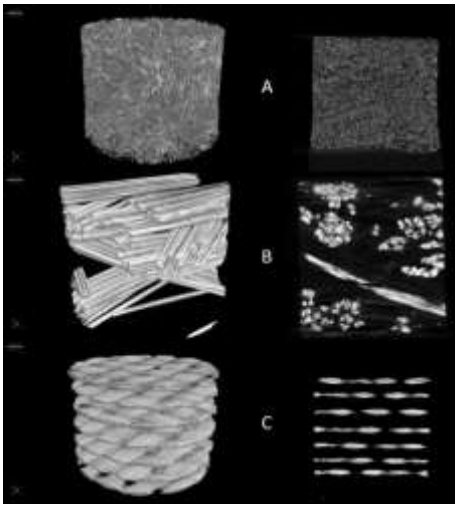

Figure 9.8: CT image of PP composites with 3 mm fibres (A), 12 mm fibres (B), and continuous fibres (C)

Figure 9.9: Lofting of 12 mm long glass fibres as a result of composite exposure to fire

Table 9.5: Fire performance of PP composites with different fibre lengths

		PP	PPG3	PPG12	PPGC
Time to ignition	S	209	233	209	238
Flameout	S	948	1166	1025	1073
Mean HRR	kW/m^2	139	183	194	189
Peak HRR	kW/m^2	418	390	473	325

For PPGX, G: Glass fibre, X: fibre length, C: refers to continuous fibre

9.3.8 Fibre architecture

When continuous fibres are used, they are used predominantly in fabric forms, where they are either woven together in a (typically) biaxial weave (e.g. twill, satin, plain) or held together by a fixing strand (UD fabrics). The effect of the fibre architecture was not clear and was therefore investigated in Chapter 5.

In Chapter 5, the effect of fabric architecture for the most common fabric types (plain, twill and UD) on the fire performance of composites was studied. Figure 9.10 shows the heat release rate curve of PC composites where plain, twill, and UD fabrics are tested.

Fibre architecture mainly affects the fire performance of composites through the peak heat release where the UD fabric has around a 25% lower peak heat release rate than other fabrics. The differences in other fire performance parameters were found negligible.

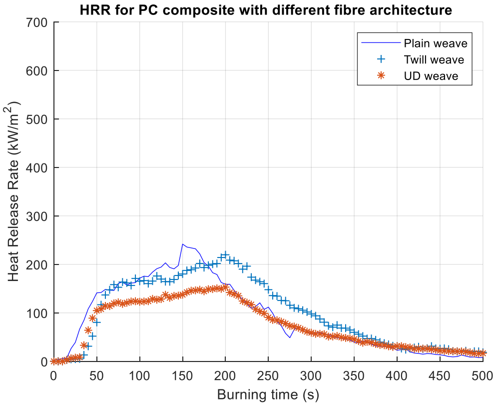

Figure 9.10: The effect of fibre architecture on the fire performance of composites

9.4 Conclusion: Critical aspects of composite design

Figure 9.11 provides a summary plot showing how the fire performance parameters are affected by composite material design choices. Both the matrix and fibre affect the fire performance of composites. The matrix influences the fire performance of composites through the char yield, specific heat capacity, and effective heat of combustion while fibres affect the fire performance through the thermal conductivity, fibre architecture, and fibre volume fraction. Broadly speaking, for the matrix the most important aspect is the char yield, while for the fibres it is thermal conductivity. A decision framework has to be based on the properties of both the matrix and the fibre in order to optimize the best design.

Fibre effect on fire performance is more complicated than the matrix. The selection of fibre type and length depends on the application since it is priority based (see Figure 9.12). Fibres with a high thermal conductivity are favourable for a higher ignition delay time. However, high thermal conductivity also results in higher HRR and MLR. On the other hand, fibres with a low thermal conductivity will ignite sooner but will also have lower HRR and MLR. The effect of fibre length depends on the type of fibre and matrix. If a non-charring matrix is used, the intermediate fibre length between 5 and 20 mm should be avoided in order to prevent lofting (Figure 9.10). However, if a charring matrix is used, then a longer fibre will lead to a higher time to ignition but also a higher HRR, MLR, and flame spread rate. This is especially so if a fibre with a high thermal conductivity is used.

For practical applications, fire retardants are often employed because, as the current findings indicate, fine tuning the fire and matrix constituent properties reaps restricted gains and the processes frequently act against each other for the following reasons:

1. Irrespective of the addition of a fire retardant, the influence of the fibres discussed are still relevant and the same trends will apply.
2. The need to understand thermal properties of both the fibres and matrix should be expanded to include the fire retardant's properties, but again, the same trends as discussed here will apply favourably.
3. Understanding of the contribution of the matrix and the interactions with the fibres is also relevant (or can help) in selecting the right fire retardant.

Figure 9.12 is a decision plot showing how composite material can be designed for optimized fire performance.

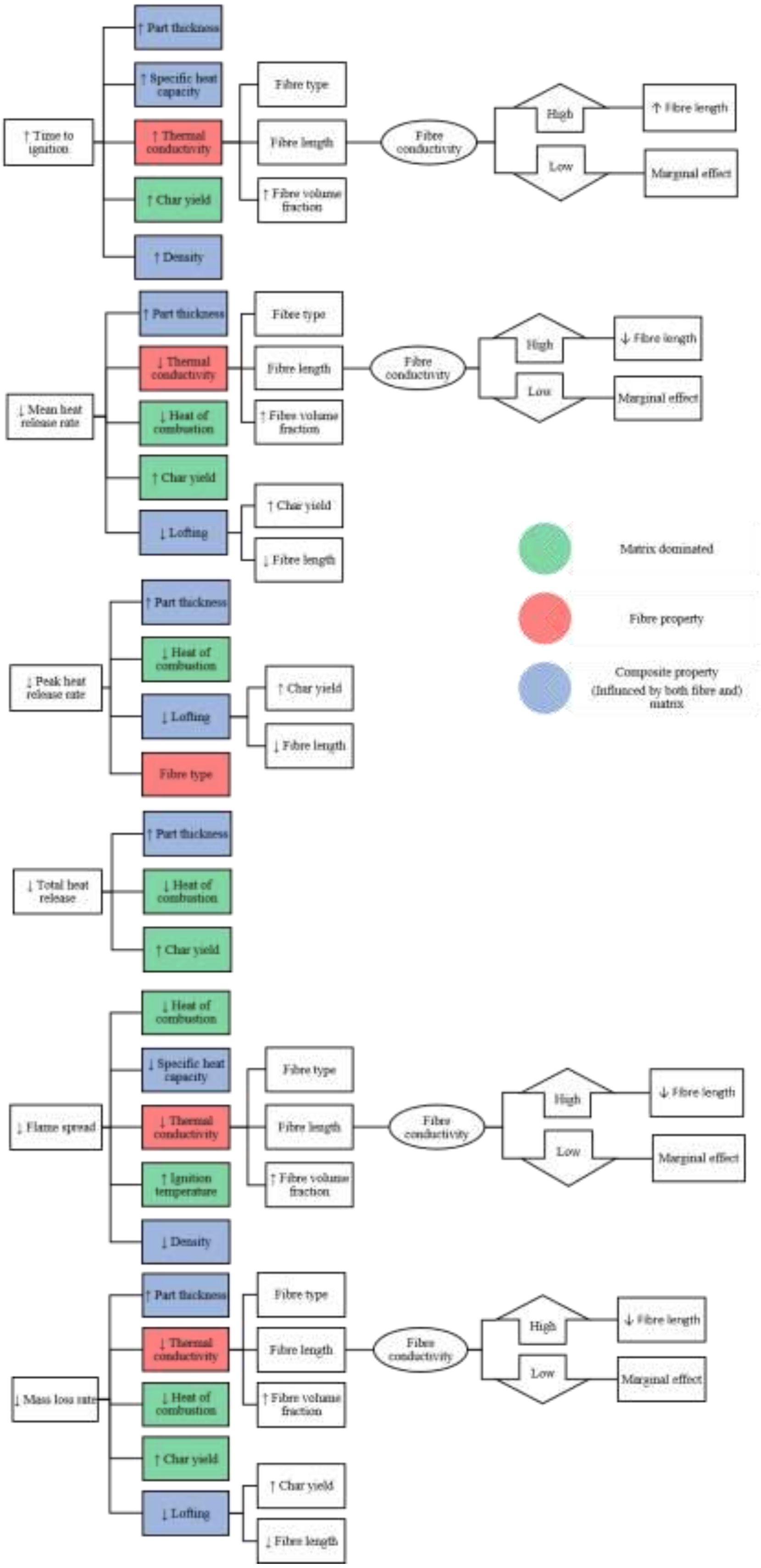

Figure 9.11: Summary plot – Qualitative frame work

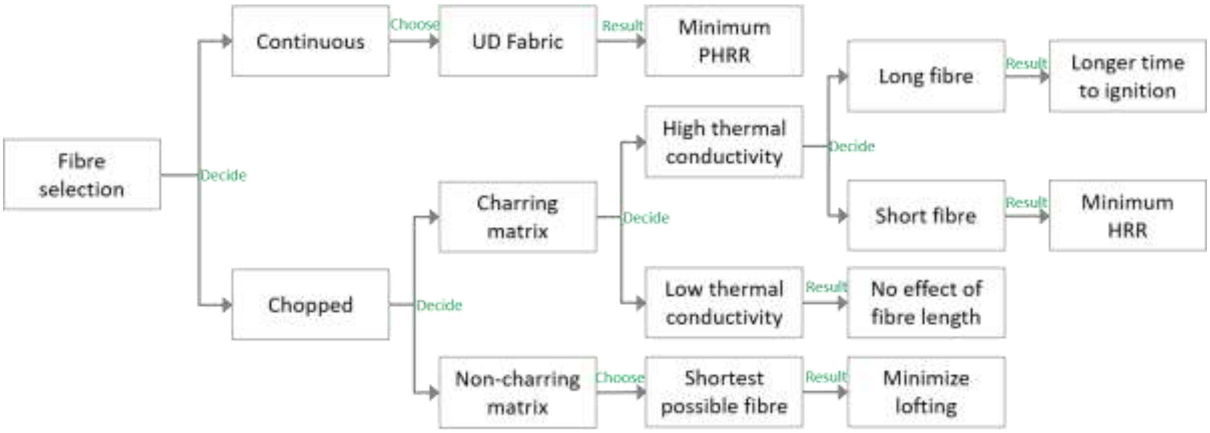

Figure 9.12: Composite design decision plot for optimized fire performance

9.5 Suggested directions for future research

The current study aimed to systematically explore the effect of composite design choices on the fire performance of thermoplastic composites. A qualitative decision framework to select constituents for cases where the fire performance of the composite is of concern was proposed. Thermal conductivity was found to be a key to connect the constituent properties to the fire performance of composites. Lofting of fibres was connected to char yield of the matrix.

Due to time constraints and equipment limitations, some research questions which arose in the course of this study remain unanswered.

Thermal conductivity of the fibre was found to be one of the most important fire performance parameters. Fire properties such as the time to ignition, heat release rate, flame spread rate, and mass loss rate are all significantly influenced by thermal conductivity. In this research, thermal conductivity of the composite was measured only up to the glass transition point of the matrix. Measuring thermal conductivity beyond the glass transition point for thermoplastic composites requires a special mould to maintain the composites' structure and prevent the flow of the thermoplastic matrix. It is believed that thermal conductivity has to be measured far beyond glass transition point, at the very least up to ignition point. This is a research focus to be considered in the future.

The current models to predict the fire performance of composites are limited. For instance, the equations used to predict the thermal inertia are isotropic and only take into account the out of plane thermal conductivity. For highly conductive fibres, this needs to be addressed since their in plane thermal conductivity is too high to ignore. In addition, the current models cannot accurately predict key fire performance parameters such as the flame spread rate and mass loss rate.

Two matrices (PC, PP) and three fibres (GF, BF, CF) were investigated in this research. The selection was based on char yield, thermal conductivity, and popularity in industry. There is room for other matrices and fibres needs to be similarly examined.

Other questions to consider in the future are as follows:

- The change in CP across the temperature range has been largely ignored.
- Fibre orientation and length for short fibre depends on processing conditions and consequently this needs to be considered.
- The relationship between the peak heat release rate and fibre type/geometry beyond thermal conductivity should be explored.
- An in depth study of the role of fibre architecture on fire performance of composites is recommended.
- Smoke and toxicity resulting from the burning of thermoplastic composites needs to be analysed.
- The effect of different fibre architectures on the surface of compressed moulding composites vs injection moulded composites

Understanding and covering the above research gaps will further help in improving the composite materials fire performance and limit the use of fire retardants which have major economical and environmental impacts.

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11. Appendix

A digital record of measurement data and calculations is made available through the UQ e-Space. The records entitled ‘Data for Chapter 5’ ‘Data for Chapter 6’ ‘Data for Chapter 7’ contains the following additional information:

- Raw data for cone calorimetry test results (Chapter 5)
- Raw data for cone calorimetry test results (Chapter 6)
- The estimation of thermal conductivity of fibre reinforced composites and related calculations (Chapter 6)
- Detailed calculations used (Chapter 6)
- Thermal conductivity measurements in details (Chapter 7)
- Flame spread rate detailed test results and calculations (Chapter 7)
- Detailed calculations used (Chapter 7)