Non-halogenated fire protective coatings for structural applications

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2020

Ng, Y. H. (2020). Non-halogenated fire protective coatings for structural applications.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/144334>

<https://doi.org/10.32657/10356/144334>

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**NANYANG
TECHNOLOGICAL
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SINGAPORE

**NON-HALOGENATED FIRE PROTECTIVE
COATINGS FOR STRUCTURAL
APPLICATIONS**

**NG YAN HAO
SCHOOL OF CIVIL AND ENVIRONMENTAL
ENGINEERING**

2020

Non-halogenated fire protective coatings for structural applications

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School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University in partial fulfilment of the
requirement for the degree of Doctor of Philosophy

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

10-01-2020

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13/01/2020

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal in which I am listed as an author.

Chapter 4 is published as Yan Hao Ng, Aravind Dasari, Kang Hai Tan and Lijun Qian. Intumescent fire-retardant acrylic coatings: Effects of additive loading ratio and scale of testing. *Progress in Organic Coatings* **150**, 105985 (2021). DOI: <https://doi.org/10.1016/j.porgcoat.2020.105985>.

The contributions of the co-authors are as follows:

- Professor Tan and Associate Professor Dasari provided the initial project direction and edited the manuscript drafts.
- The manuscript drafts were prepared by me.
- The laboratory work at the School of Civil and Environmental Engineering and School of Materials Science and Engineering was conducted by me. This includes sample preparation, characterisation, testing and data analysis.
- Professor Qian revised the manuscript drafts.

Chapter 5 is published as Yan Hao Ng, Indraneel Suhas Zope, Aravind Dasari, Kang Hai Tan. Correlating the performance of a fire-retardant coating across different scales of testing. *Polymers* **2020**, 12, 2271. DOI: <https://doi.org/10.3390/polym12102271>.

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- The laboratory work at the School of Civil and Environmental Engineering and School of Materials Science and Engineering was conducted by me. This includes sample preparation, characterisation, testing and data analysis.
- Dr Zope assisted with laboratory work conducted in the School of Material Science and Engineering.

Chapter 7 is published as Yan Hao Ng, Anil Suri, Aravind Dasari, and Kang Hai Tan. Thermal decomposition and fire response of non-halogenated polymer-based thermal

coatings for concrete structures. *Surface and Coatings Technology* **320**, 396 – 403 (2017).
DOI: <https://doi.org/10.1016/j.surfcoat.2016.12.015>.

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- The laboratory work at the School of Civil and Environmental Engineering and School of Materials Science and Engineering was conducted by me. This includes sample preparation, characterisation, testing, numerical simulation and data analysis.
- Dr Anil Suri assisted with data analysis and revised the manuscript drafts.

This thesis also contains materials from 2 technology disclosures in which I am listed as a co-inventor. The technology disclosures are as follows:

- Non-halogenated fire-resistant coatings for concrete structures, Technology Disclosure, Ref.: TD/194/16, June 22, 2016, NTUitive Pte Ltd., Nanyang Technological University, Singapore.
- Fire retardant coatings for steel structures, Technology Disclosure, Ref.: TD/293/17, October 26, 2017, NTUitive Pte Ltd., Nanyang Technological University, Singapore.

The contributions to the technology disclosures are as follows:

- Professor Tan and Associate Professor Dasari provided the initial project direction.
- The laboratory work at the School of Civil and Environmental Engineering and School of Materials Science and Engineering was conducted by me, together with Dr Indraneel Suhas Zope. This includes sample preparation, characterisation, testing and data analysis.

29/10/20

Date

Ng Yan Hao

Acknowledgement

I am very grateful to have had the opportunity to work with two great supervisors, who have provided me with unwavering support, warm encouragement and valuable guidance throughout my Ph.D. First and foremost, I would like to express my sincere gratitude and appreciation to my supervisor, Professor Tan Kang Hai, whose expertise and persistent support have been invaluable in the course of my PhD research activities and development of this thesis. I would also like to extend my appreciation to my co-supervisor, Associate Professor Dasari Aravind, for his mentorship and guidance in my research. Not only were our discussions critical to my understanding of flame-retardant polymers and materials science, but they also supported my coherent articulation and development of this thesis.

My sincere appreciation is also extended to Dr Indraneel Suhas Zope for his enthusiasm and generosity in sharing his knowledge on flame-retardant polymers with me, reinforcing the basic foundations of my understanding on the subject and further broadening my knowledge throughout the course of this program. I would also like to thank Mr Sheik Mohamed Anees, Mr Seah Geng Jie Dean, and Mr Jonathan Siow Jun Yang for their kind assistance in various series and iterations of laboratory work through the course of my Ph.D, as well as Professor Qian Lijun of Beijing Technology and Business University for his kind assistance on cone calorimeter tests and hospitality when I was in Beijing. I am also thankful to the laboratory staff in MSE, FACTS and CEE for their help and support.

I would also like to extend my sincerest gratitude to my colleagues, whose collaborative attitudes and stimulating discussions have also helped sustain a positive atmosphere and working environment. Most particularly, Dr Nguyen Minh Phuong for his constructive comments and assistance in my research work, as well as Mr Du Panwei, Mr Fan Shengxin, Ms Nguyen Thi Nguyet Hang, and Mr Zhang Dong for their encouragement throughout my Ph.D.

Finally, I am indebted to the love and unconditional support from my parents, Mr Ng Keng Siang and Mrs Aw Wai Meng, my sister, Ms Ng Ting Yong, and my brother-in-law, Mr Yao Yikai. I would also like to acknowledge Ms Theresa Tung for her unwavering encouragement throughout my Ph.D.

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Abstract

Modern high-rise buildings are typically constructed with reinforced concrete-, or steel-framed structures. As fire incidents in a building threaten the lives of the people and inflict severe damages to the infrastructure, it is a regulatory requirement to protect steel structures with fire protective coatings. It is also practical to apply fire protective coatings on existing concrete structures if there are changes to fire-resistance rating.

Therefore, the thesis focuses on the development of fire protective coatings, with particular emphasis on steel as the substrate due to their prevalence in the industry. The fire-retardant mechanism of the developed coating formulations is discussed in detail, and it was found that the expansion of expandable graphite formed an insulating barrier that is capable of reducing heat transfer to the substrate. Expandable graphite depends heavily on the physical flame-retardant mechanism as it does not react with the additives or the resin.

Although studies on mechanism explain the reason behind the improved flame-retardant performance at the materials-scale, it is difficult to correlate the findings with the performance of the coatings at structural-scale. In the literature, this aspect is not well-studied, and the work performed in this thesis will bridge the gap between materials- and structural-scale experiments. It was found that the flammability characteristics obtained through materials-scale tests correlate to the initial 10 to 15 min of a structural-scale fire test. After the initial stage, materials-scale tests do not provide much insights on the performance of a coating and will require the use of bulk-scale fire tests. Thermal conductivity of the residue was also identified to be one of the key parameters that govern the rise in temperature at the later stage of a structural-scale fire test.

The effective thermal conductivity of the coatings based on the structural-scale fire test was calculated and validated with numerical simulations. This provides a reference for the measured conductivity values and calculated effective thermal conductivity values from a bulk-scale cone calorimeter test. The effective thermal conductivity values obtained from the bulk-scale cone calorimeter were in agreement with the effective thermal conductivity values from the structural-scale fire test. It highlights the potential of using effective conductivity values to predict the performance of other coatings before conducting a structural-scale fire test. Based on the work performed on steel substrates, a generic flowchart to design fire protective coatings was proposed. The developed fire

protective coatings were also extended to concrete structures and the results on performance were highlighted towards the end in this thesis.

In conclusion, the work in this thesis provides a critical understanding of different parameters that contribute to performance at structural-scale. Correlating the materials-scale behaviour of the coatings to bulk- and structural-scale is a *critical contribution* of this work to the field. This is made possible through the knowledge gleaned from two engineering disciplines, which is currently lacking in the literature on fire-protective coating systems.

List of Publications

Journal Publications

1. Yan Hao Ng, Anil Suri, Aravind Dasari, Kang Hai Tan. Thermal decomposition and fire response of non-halogenated polymer-based thermal coatings for concrete structures. *Surface & Coatings Technology*. 2017, 320, 396-403.
2. Yan Hao Ng, Indraneel Suhas Zope, Aravind Dasari, Kang Hai Tan. Correlating the performance of a fire-retardant coating across different scales of testing. *Submitted*.

Conference Publications / Presentations

1. Yan Hao Ng, Aravind Dasari, Kang Hai Tan, Fire-retardant coatings for concrete substrate: A comparison between one-dimensional and two-dimensional heat transfer, *10th International Conference on Structures in Fire*, Belfast, 2018
2. Yan Hao Ng, Minh Phuong Nguyen, Kang Hai Tan, Kian Wee Ng. A case study on the evacuation of deep mega underground in Singapore, *2nd International Fire Safety Symposium*, Naples, 2017

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List of Abbreviations

Abbreviation	Description
APP	Ammonia polyphosphate
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
BS	British Standards
CSH	Calcium-silicate hydrate
CSTB	Centre Scientifique et Technique du Batiment
DMA	Dynamic mechanical analyser
DSC	Differential scanning calorimetry
EC	Eurocode
EG	Expandable graphite
EN	European Norm
FIGRA	Fire growth rate
FPI	Fire performance index
FR	Flame-retardant
FTIR	Fourier transform infrared spectrometer
HCC	Heat of complete combustion
HRC	Heat release capacity
HRR	Heat release rate
IR	Infrared
ISO	International organization for standardization
LOI	Limiting oxygen index
MCC	Microcalorimeter
MDSC	Modulated differential scanning calorimetry
MEL	Melamine
MMA	Methyl methacrylate
MTPS	Modified transient plane source
PCFC	Pyrolysis combustion flow chamber
PER	Pentaerythritol
PMMA	Poly (methyl methacrylate)
PP	Polypropylene

RABT	Richtlinien für die Ausstattung und den Betrieb von Straßentunneln
RWS	Rijkswaterstaat
SEM	Scanning electron microscopy
TG	Thermogravimetric
TGA	Thermogravimetric analysis
TG-IR	Thermogravimetric analysis coupled with infrared Spectrometer
THR	Total heat release
TSP	Total smoke produce
UB	Universal beam
UL	Underwriter Laboratories

List of Symbols

Symbol	Description
ΔM	Difference between experimental residual weight and theoretical residual weight
M_{exp}	Residual weight of a composition
M_T	Theoretical residual weight
$M_{exp,r}$	Experimental residual weight of resin
$M_{exp,1}$	Experimental residual weight of additive 1
$M_{exp,2}$	Experimental residual weight of additive 2
$M_{exp,3}$	Experimental residual weight of additive 3
W_T	Total solid weight of the composition
W_r	Solid weight of resin in the composition
W_1	Solid weight of additive 1 in the composition
W_2	Solid weight of additive 2 in the composition
W_3	Solid weight of additive 3 in the composition
η_c	Heat release capacity
$h_{c,s}^0$	Heat of combustion of fuel gases per unit initial mass of solid
E_a	Global activation energy for pyrolysis
e	Natural number
R	Gas constant
T_p	Temperature of maximum pyrolysis (mass loss) rate
$\Delta\theta_{s,t}$	Rise in steel section temperature over time step
$\theta_{s,t}$	Steel section temperature
$\Delta\theta_{a,t}$	Rise in furnace temperature over time step
θ_t	Furnace temperature
$\theta_{p,t}$	Temperature of coating on steel section at time t
$\lambda_{p,t}$	Thermal conductivity of coating on steel section at time t
λ_{p,θ_p}	Thermal conductivity of coating on steel section with respect to coating's temperature
d_p	Dry film thickness of coating

$\frac{A_p}{V}$	Steel section factor
c_s	Specific heat capacity of steel
ρ_s	Density of steel
Δt	Time increment
Q_w	Heat loss from steel to wool
Q_c	Heat flow from the cone to surface of coating (i.e. heat flux of cone heater)
λ_w	Thermal conductivity of wool
k_p	Thermal conductivity of coating in cone calorimeter test
ΔT_s	Rise in steel plate temperature over time
T_s	Temperature of steel plate at time t
T_w	Temperature of wool at time t
ΔT_{ss}	Rise in coating surface temperature in cone calorimeter test
T_{ss}	Surface temperature of coating in cone calorimeter test at time t
T_c	Temperature of cone heater at time t
d_w	Thickness of wool
d_s	Thickness of steel
ρ_p	Density of coating
c_p	Specific heat capacity of coating in cone calorimeter test
ε	Emissivity
σ	Stefan-Boltzman constant
h_c	Convection coefficient
T_g	Glass transition temperature

Chapter 1 Introduction

This chapter presents an overview of the research work in this thesis. It highlights the importance of protecting construction materials, particularly load-bearing structural elements, against fire. This chapter also points to some of the existing and widely used passive protection strategies, with specific emphasis on intumescent coatings, which is the main focus of the thesis. The research presented in this thesis focuses on the development of chemical compositions for a fire protective coating and correlating the behaviour from materials-scale, through bulk-scale, to structural-scale. The integrated approach is relatively absent in the literature. Research outcome is summarised, and the last section of this chapter describes the organisation of the thesis.

1.1 Research overview

Fire incidents in buildings are considered hazardous as they threaten the lives of people and inflict severe damages to the structure. According to a historical survey, there are 22 cases of fire-induced collapse events from 1970 to 2002. Among the 22 cases, 7 of them involved the collapse of concrete buildings, while 6 cases involved the collapse of steel buildings [1]. Hence, it is a regulatory requirement to protect structural members in an event of a fire. For structural steel sections, this can be achieved with typical passive fire protection systems such as gypsum boards, cementitious spray and concrete encasement. These systems may not be aesthetically pleasing and become vulnerable to damage during installation. Intumescent coatings gradually became the market leader as it is easier for off-site applications, reducing overall construction time and better quality control [2]. Moreover, intumescent coatings are more aesthetically pleasing and may also offer corrosion protection to a certain extent when compared to other protection systems. The intumescent phenomenon is a result of simultaneous reactions between three main chemical additives (i.e. an acid source, a char forming agent and a spumific or blowing agent) incorporated into a suitable polymer resin. Reaction between these chemical additives forms a thick porous carbonaceous char structure, which reduces heat transfer to the substrate due to its low thermal conductivity and consequently reduces the rate at which temperature of the substrate increases.

Although the use of passive fire protection on concrete is currently not stipulated in regulations, there soon may be a need to adopt some form of fire protection for concrete structures. This is because high-performance concrete, which is slowly gaining popularity in industry, tends to exhibit explosive spalling when exposed to fire. This occurrence

results in excessive damage to concrete structures as reinforcement bars [3] are exposed and large pieces of concrete blocks are dislodged. Thermal barriers or fire protective coatings can help to mitigate this effect and prevent excessive damage to concrete structures. Another more common strategy is to include polypropylene fibres into the concrete mix for high strength concrete.

Over the years, development in flame-retardant (FR) polymers has helped to identify various additives (e.g. ammonium polyphosphate (APP), pentaerythritol (PER), titanium dioxide, etc) that enhance intumescent behaviour or its char structure. Expandable graphite (EG) has been one of these additives that demonstrate superior performance in improving flame-retardancy of various polymer matrix, e.g. polyurethane foams, acrylonitrile-butadiene-styrene copolymer, linear low-density polyethylene, poly(ethylene terephthalate), etc. Moreover, EG reduces costs of intumescent formulation and does not require extensive method for preparation [4]. However, the use of EG to replace the blowing agent in a fire protective coating is not widely reported in literature and the market is still dominated by intumescent coating based on conventional formulation (APP, PER and melamine). In addition, the tests used to assess the performance of new EG-based systems typically focus on flame-retardant performance and are hardly related to its performance as a protective coating.

Apart from elucidating the mechanism of EG in an acrylic-based system, this work aims to correlate the test results and FR behaviour of the coating from materials- to structural-scale. This is important for the development of new fire-protective coatings as results from materials-scale tests do not necessarily reflect results obtained in structural-scale fire tests.

1.2 Research objectives and scope

This research focuses on the development of non-halogenated fire protective coatings for structural applications. It requires knowledge from two engineering disciplines, namely materials science engineering and structural fire engineering. The knowledge from materials science will help to shed light on flame-retardancy of polymer systems, while the knowledge from structural fire engineering will help to understand the condition in which the coating will be exposed to in a fire.

The FR mechanism to form carbonaceous char is necessary as it has been reported to improve the FR performance of most polymers systems in the condensed phase and even

in the gas-phase. However, FR mechanism will vary with the change in formulations and polymer systems and there is a need to understand the effects and the role of each additive that is present in the system. The knowledge is beneficial as it can be used to optimise fire protective formulations or even flame-retardant formulations for other applications. Hence, the following scope of work is proposed to meet the research objectives of this study.

1. Investigate the chemical, physical and thermal mechanisms behind the fire-retardant performance.
2. Conduct fire tests on coated steel columns to assess the performance of the developed coating.
3. Correlate the relationships between different scales of testing and their implications on the performance of fire protective coating.

1.3 Research novelty and outcome

The outcome of this research addresses issues related to the development of non-halogenated fire protective coatings and can be summarised as follows:

1. The FR mechanism of EG-based coating has been shown to be largely physical, with no chemical interaction between the additives or resin with EG. The exfoliated graphite network that adheres to the substrate at high temperature reduces heat transfer to the substrate, which highlights that thermal conductivity of the char governs its performance as a thermal barrier.
2. Apart from the design and development of fire protection coatings, the emphasis on correlating the materials-scale behaviour of the coatings to bulk- and structural-scale is a critical contribution of this work to the field. This is made possible through the knowledge gleaned from two engineering disciplines. This is clearly lacking in the literature and current research on protective coating systems.
3. Research work on materials science engineering focuses on the materials- and bulk-scale tests to elucidate underlying mechanisms and identify the optimal formulations. However, fire protective coating needs to be assessed at a structural-scale and results and performance measured from smaller scale testing does not necessarily reflect the performance at a large scale. This aspect is not well-studied at all and the work performed in this thesis will allow researchers to correlate the performance of a fire protective coating right from the materials-scale to the

structural-scale, bridging the gap between materials- and structural-scale experiments.

4. In this process, the performance of the developed coating is correlated across different scales of testing. This provided critical understanding of different intrinsic and extrinsic parameters that contribute to performance. The intrinsic parameters such as flammability characteristics affect time-temperature development of a steel-substrate in the initial stage of the test, while extrinsic parameters such as cohesion affect the end stage of the test.

1.4 Organisation of this thesis

This thesis comprises eight chapters. An introduction to the research background to formulate the objectives and lay down the scope is presented in Chapter 1. A summary of novelty and research outcomes has also been briefly presented.

Chapter 2 provides a comprehensive review of relevant research work carried out in the past. An overview of the microstructure changes of steel and concrete under fire exposure will be presented to help readers understand inherent changes at the materials-scale that are irreversible. Flame-retardant mechanisms and the use of different FR additives will be discussed in detail, before focusing on the recent research work on fire protective coatings such as intumescent coating. An understanding of these topics is required to be engaged in ensuing discussions of subsequent chapters.

Chapter 3 introduces the resin and additives before explaining the different characterisation and experimental techniques used to analyse coatings. This allows the readers to appreciate the importance of different parameters evaluated in each test and their limitations.

Chapter 4 begins with thermal stability of additives used in the coatings and flammability characteristic of the coating. An in-depth study of the flame-retardant mechanism will subsequently be discussed.

Chapter 5 starts with the performance of the developed coating at bulk- and structural-scale before consolidating the results and insights obtained from the tests conducted across three different scales (i.e. materials-, bulk- and structural-scale). Relationship between the tests at different scales will be elaborated and a method to predict performance of the fire protective coating at structural-scale will be proposed.

Chapter 6 presents the basic thermal properties (i.e. thermal conductivity and specific heat capacity) of the coating, along with numerical work to highlight the effects of certain thermal properties. This helps to corroborate the FR mechanism discussed in Chapter 4 and shows that thermal conductivity governs the performance of the coating at bulk- and structural-scale.

Chapter 7 highlights the applicability of the developed coatings to concrete substrates. It considers the mechanism of key flame-retardant additives discussed in Chapters 4 to 6. It should be noted that the specific compositions developed for concrete are filed as a technical disclosure and the discussion in this thesis will mainly focus on the performance of the coating. Chapter 8 concludes the work done on fire protective coatings in this thesis and propose future work based on the limitations of this work.

Chapter 2 Literature review

This chapter provides a comprehensive review of the effects of fire on construction materials, methods used to protect them and the mechanisms and issues behind some of the most commonly used protection systems. This review begins with the influence of fire on steel and concrete materials and it highlights irreversible changes that subsequently lead to a reduction in their mechanical properties and load-bearing capacity. Subsequently, passive fire protection methodologies will be discussed to enhance performance of steel and concrete in a fire scenario. Specific emphases will be on intumescent coatings, the materials and mechanisms behind their performance, and correlations of the performance at different scales (materials to structural). Despite the importance of correlations at different length scales, the literature on this topic is extremely limited. Lastly, research work on modelling intumescent coatings is discussed as it remains as one of the conventional and well-accepted methods used to predict fire performance through heat transfer analysis.

2.1 Fire

The occurrence of a fire in buildings is common as seen in selected examples in Table 2-1. It is capable of destroying properties, result in huge monetary losses, and the toxic fumes produced can be fatal to the occupants.

Table 2-1: A brief review of fire statistics in five different countries.

Country	Year	Number of building fires	Fatalities	Losses	Currency	Reference
United States of America	2016	475,500	3390	13 billion	USD	[5]
United Kingdom	2016	37,740	328	N.A.	-	[6]
Australia	2014	19,524	98	~ 702 million	AUD	[7]
New Zealand	2014	5,294	100	71.55 million	NZD	
Singapore	2018	2,926	4	N.A.	-	[8]

Note:

1: Also equivalent to 0.22 per 100,00 head of population

N.A.: data not available

The development of a fire in a building, otherwise known as a compartment fire, has been well-studied. The beginning of a fire within a ventilated compartment involves the

ignition of materials (Figure 2-1). At this stage, smoke and toxic gases from the ignited materials rises to the ceiling and does not have much effect on the compartment. If the fire is left unattended, it continues to burn, and hot gases start to accumulate at the upper layer of the compartment. Heat is radiated from the burning fire and accumulated gases back to the compartment walls and floors. As the temperature of the hot gases and smoke reaches a critical temperature, a flashover fire develops as shown in Figure 2-1, resulting in a sudden increase in temperature within the compartment causing all combustible materials in the compartment to burn. The temperature within the compartment continues to rise and will decrease (decay stage) when all combustible materials have been consumed in the fire.

Figure 2-1: Representation of fire growth in a compartment. Adapted from [9, 10].

Image from [11].

It should be noted that the assessment of structural members under fire condition is typically conducted through standard tests. The ISO 834 standard cellulosic fire curve is one of the most widely used time-temperature profiles [9] to assess structural performance. Other time-temperature profiles such as hydrocarbon curve, *Rijkswaterstaat* (RWS) and *Richtlijnen für die Ausstattung und den Betrieb von StraBentunneln* (RABT) fire curves are used to simulate the fire intensity in a tunnel. The ISO 834 standard fire curve originated from the estimated temperature profile of fire tests carried out in the early 1900 – 1910s [12]. At that time, researchers consolidated available time-temperature profiles of other fire tests conducted and plotted an idealisation of these curves as the standard fire curve. It has been shown that the standard fire curve has limited similarity with the

temperature profile of a compartment fire [9]. The lack of fire decay (cooling branch) in the standard fire curve is one of its drawbacks in depicting a natural fire curve, along with the lack of parameters that affect fire behaviour. Despite these shortcomings, the standard fire curve is the stipulated fire curve in Euro-Codes and British Standards. Fire protective coatings on structural members will also be assessed using this fire curve.

Figure 2-2: (a) Time-temperature profiles for different typical standard fire scenarios and (b) historical time-temperature profiles of different furnace tests. Figures adapted from [12].

The time-temperature profiles are important as they describe the temperature which the materials (i.e. fire protective coating and substrate) will be exposed to. The behaviour of the steel and concrete are governed by the changes in temperature which will be discussed in Section 2.2.

2.2 Effects of fire on steel and concrete

2.2.1 Steel

The chemical compositions of carbon steel typically consist of iron, carbon, manganese, silicon, sulphur, phosphorus, and alloying elements such as chromium and vanadium. These elements constitute the structure of carbon steel as they form ferrite, pearlite, austenite, and cementite during the heat treatment process. The formation of these structures depends on the type of heat treatment adopted (such as annealing, normalising, and tempering) and the amount of the alloying elements present [13].

Varying the composition of steel can affect its thermal properties such as thermal conductivity [14]. This is relevant considering the changes in microstructure as the temperature of steel increases, and the corresponding changes in thermal conductivity. Microstructural changes in a typical carbon steel, depending on the carbon content, can

include (i) tempering and resultant precipitation of cementite and other carbides, (ii) increase in grain size and simultaneous decrease in the grain boundary area per unit volume, and (iii) change of phase from ferrite to austenite (generally, above 710 °C).

Structural steels used in construction typically contain a mixed ferrite-pearlite microstructure. The ultimate tensile strength of ferrite-pearlite steels is influenced by the carbon content, ratio of dual phases, and also the pearlite grain size [15]. For engineers to use structural steels in practice, extensive research work has been conducted to determine the behaviour of steels under different temperatures. The stress-strain relationship is arguably one of the most important parameters as deterioration of strength with temperature plays a significant role in structural fire designs [9]. Experiments to quantify stress-strain relationships of different types of steel [16-18] have been reported and this data is used to support the development of steel material model in a code of practice. For example, stress-strain relationship of carbon steel, along with respective reduction factor for yield strength, elastic modulus and proportional limit (Figure 2-3) are included in EC3-1-2 [19] and are widely used as design parameters for performance-based design of steel structures in a fire condition.

Figure 2-3: (a) Stress-strain relationship and (b) reduction factors for stress-strain relationship of carbon steel at elevated temperatures. Figures from EC3-1-2 [19].

The mechanical properties of steel are important for the development of fire protective coating as they allow researchers to set a realistic performance benchmark for the developed coating. Critical temperatures of 500 °C to 600 °C can be derived from Figure 2-3b as a reduction in yield strength is already 50 %. It may not be necessary to set a performance benchmark at a higher temperature as a sharp decrease in the yield strength of steel material is observed after 500 °C to 600 °C.

There is also extensive research to enhance fire performance of steel by altering their compositions. Nippon fire-resistant steel consists of niobium and molybdenum. Microstructural studies [20] showed that the fire-resistant steel contains very fine distribution of metal carbide precipitates, which consequently allows high lattice friction stresses to be maintained up to 600 °C.

Table 2-2: Composition of fire-resistant steel and a summary of their yield strength at ambient and elevated temperatures. Adapted from [21].

Steel	Weight Percentage							
	A	B	C	D	E	F	G	H
C	0.11	0.12	0.12	0.13	0.13	0.12	0.17	0.25
Mn	1.02	1.02	1.08	0.99	1.00	0.96	0.74	1.42
Si	0.35	0.35	0.29	0.31	0.31	0.3	0.31	0.056
S	0.022	0.032	0.029	0.025	0.026	0.025	0.034	0.024
P	0.019	0.025	0.027	0.021	0.022	0.021	0.027	0.024
Cr	0.31	0.29	0.4	0.38	0.39	0.38	0.54	0.55
Mo	0.26	0.2	0.14	0.26	0.26	0.26	0.22	0.00
Nb	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.00
V	0.00	0.00	0.00	0.00	0.07	0.12	0.00	0.00
Al	0.0033	0.099	0.097	0.0034	0.0039	0.0039	0.052	0.004
N	0.0042	0.0063	0.0067	0.0047	0.0047	0.007	0.0124	0.0075
Mechanical properties								
AYS	287	293	298	338	293	415	320	624
EYS	219	191	188	279	250	280	214	419
RF	0.24	0.35	0.37	0.17	0.15	0.33	0.33	0.33

Note:

AYS = Ambient yield stress (MPa)

EYS = Yield stress at elevated temperature (600 °C) (MPa)

RF = Reduction factor of stress at elevated temperatures compared to ambient temperature. Lower reduction factor indicates better performance.

The influence of other alloying elements (chromium, molybdenum, niobium, and vanadium) on yield strength of steel at elevated temperatures (Table 2-2) has also been reported [21]. Compared to the reduction factor stated in EC2 (i.e. 0.47 at 600 °C), fire-resistant steel that includes alloying elements demonstrates better strength retention at 600 °C. The addition of chromium and molybdenum were reported to stabilise cementite of pearlite at high temperature, while the loss of strength for niobium and vanadium is minimal at high temperature. Moreover, precipitation hardening of niobium and vanadium (Steel D and E) also helps to improve stability of microstructure at higher temperatures and prevents significant reduction in yield strength.

The first structure built with a fire-resistant steel frame is the Nippon Steel Corporation Number 2 Building (Figure 2-4a). Designers showed that the temperature of the steel reached a maximum of 600°C after 2 h at a particular storey in the building [22]. However, there was no information on how the time-temperature curve was derived. Fire protection to the steel was still required, but a noticeable reduction ($1/3$) in fire protection thickness is allowed compared to ordinary steel. The second fire-resistant steel frame building was the Tobihata building (Figure 2-4b) and fire protection was not warranted as it was shown with fire engineering calculations that the temperature would not exceed 600°C within the stipulated time.

Figure 2-4: Photographs of (a) Nippon Steel Corporation Number 2 Building and (b) Tobihata Building. Image from [22].

Although the use of fire-resistant steel is an excellent idea as it reduces or eliminates the need for fire protection of steel buildings, such use is not common at all. The material cost of using fire-resistant steel is much higher compared to ordinary structural steel due to additional processes required. The additional cost cannot be negated with elimination or reduction in fire protection materials and hence is not economically viable. This also suggested that there is still a need to continue the development of fire protective coatings for ordinary steel.

2.2.2 Concrete

Conventionally, protecting concrete structures is not necessary according to Euro-Code regulatory standards as designers can specify an axis distance (similar to concrete cover) corresponding to a required fire resistance. Enhancing their performance is much easier compared to steel as it can be easily achieved with increased cross-sectional area or number of reinforcing bars within the concrete element. The lower thermal conductivity and higher specific heat capacity of concrete (Figure 2-5) compared to structural steel also help with the former's performance in fire.

Figure 2-5: (a) Thermal conductivity of concrete and steel and (b) specific heat capacity of concrete and steel. Based on EC 2, Part 1-2 [23] and EC 3, Part 1-2 [24].

Despite this, it does not mean that concrete material is stable under high temperature. Exposing concrete to a fire results in complex physicochemical changes [25] and these changes determine the behaviour and mechanical properties of concrete during a fire. Many studies on the physiochemical changes in concrete with increase in temperature were published, and a general overview [26-28] is summarised in Table 2-3.

Table 2-3: Effect of heating on concrete microstructure.

Temperature	Hydrated Cement Paste	Aggregate
On heating to 300 °C	Loss of evaporable water	
	Dehydration of gypsum and ettringite.	-
	Thermal expansion of cement paste is restricted by shrinkage as interlayer CSH water evaporates, creating severe cracking.	-
400 to 550 °C	Calcium hydroxide dissociates to form free calcium oxide. Dehydroxylation of calcium hydroxide (Portlandite).	-
500 to 900 °C	Decomposition of CSH Dissociation of calcium carbonate (700 to 900 °C)	Quartz undergoes sudden expansion (up to 1.85 %) at 573 °C
		De-carbonation reaction of carbonate rocks.
		Limestone expand steadily
		Decomposition of limestone with the liberation of carbon dioxide.

The compressive strength of concrete, one of the most important design parameters, understood by civil engineers, is governed by calcium-silicate-hydrate (CSH). This corroborates with a reduction profile of compressive strength reported in EC 2-1-2 [23]

and in literature. A survey of more than 40 publications [29] concluded that the compressive strength of concrete remains constant from ambient to 300 °C. A decrease in compressive strength is observed between 300 °C to 800 °C, with a clear reduction from 600 °C, before approaching zero at 800 °C. Morphological studies show degradation of concrete microstructure with elevated temperatures [30, 31]. The degradation begins at 300 °C, and an increase to 500 °C results in a matrix that is dominated by microcracks and intermingled with voids [30]. Calcium hydroxide and CSH phase boundaries are distorted at 600 °C. The changes in microstructure corroborate with the reduction in compressive strength and they are irreversible. This is also the reason behind replacing fire-induced concrete structures as strength cannot be recovered.

Nonetheless, the low thermal conductivity and high specific heat capacity of concrete provide time for an entire concrete section to reach thermal equilibrium and the required time increases with an increase in cross-sectional dimensions. In spite of this, there may be a need to apply some form of fire protection on existing concrete members to mitigate fire effect on concrete structures and to alleviate fire-induced spalling. This may be due to a change in occupancy in a building with increased fire load and corresponding increase in fire resistance rating. Alternatively, there may be alteration and addition work to be carried out in a building in accordance to the latest building or fire code, which usually specifies more stringent requirements for fire protection.

Research continues to push the frontier of concrete materials (e.g. high performance and ultra-high performance concrete) and allows the development of concrete with enhancing durability, ductility, strength and other aspects such as self-cleaning [32]. The term high-performance concrete was coined to describe these group of concrete materials and high-strength concrete is one of the high-performance concretes. The increase in strength is welcomed by designers as cross-sectional dimensions can be reduced to achieve the same load-bearing capacity. However, high-strength concrete is prone to explosive spalling [33] when exposed to fire and the destructive nature may lead to complete failure of a concrete member [34, 35], which is detrimental to structural integrity.

It has been widely accepted that explosive spalling is typically associated with two main physical processes, namely, thermo-mechanical and thermo-hydral [36]. The thermo-mechanical process is a result of temperature gradients induced by surrounding temperature. Strain incompatibilities between expanding aggregates and shrinking

cement paste due to dehydration generate tensile stresses across the heated surface. Due to transfer of water in liquid and vapour phase, formation of pressure gradients (thermo-hydral process) allows pore pressure to accumulate, and an abrupt release of pressure causes explosive spalling. This understanding allows researchers to propose methods to alleviate explosive spalling and addition of polypropylene (PP) fibres is one of the common methods [35, 37, 38]. It should be noted that this method is only applicable to new concrete structures. For enhancing fire resistance of existing concrete members, the most effective way is to apply a protective coating system.

Table 2-4: Summary of preventive measures against concrete spalling. Adapted from [39].

Method	Description	Targeted spalling mechanism
Aggregate type	Use small size aggregates with low thermal expansion and porosity	Thermal stress spalling
Polypropylene fibres	Add fibres into concrete mix	Pore pressure spalling
Air-entraining agent	Form air voids in concrete matrix	Pore pressure spalling
Moisture content control	Reduce vapour pressure	Pore pressure spalling
Compressive stress control	Concrete matrix with increased permeability due to reduced compressive strength	Pore pressure spalling
Supplementary reinforcement	Increase tensile capacity of concrete locally	Thermal stress spalling
Thermal barriers	Reduce the heat flow to concrete and steel reinforcement	Thermal stress and pore pressure spalling

The exact mechanism of PP fibres mitigating the severity of spalling is still being debated, and several possible mechanisms (formation of discontinuous reservoirs during mixing, formation of micro-cracks due to thermal expansion of fibres [37], and formation of continuous channels in the concrete matrix) have been proposed [40]. Although experimental work did demonstrate the effectiveness of PP fibres in mitigating the severity of spalling [41], occurrence of spalling has not been completely eliminated. This is supported by a comprehensive literature review conducted by Hedayati, *et al* [42], in which fibres (steel, polypropylene, or a mixture of both) were reported to reduce the extent of spalling. Moreover, the addition of PP fibres in a concrete mix is not always beneficial as there would be a reduction of workability associated with high PP fibre

content. Alternative measures to mitigate spalling require changes to the concrete mix design. These measures (moisture content and compressive strength control) may result in a reduction of concrete strength as they specifically reduce pore pressure spalling with an increase in permeability. Among the methods proposed in Table 2-4, it can be concluded that thermal barrier is the most effective measure against fire and resistance to spalling [39]. It prevents the rise in temperature of the concrete, ultimately preventing the loss in structural strength.

2.2.3 Non-reactive passive fire protection systems

Non-reactive passive fire protection systems are a type of thermal barriers that are typically used in tunnels to protect concrete linings from fire-induced spalling and strength loss [43] under extremely intense fire conditions (RWS, RABT, or hydrocarbon fire curve). Conventional cementitious coatings are typically vermiculate-based with addition of inorganic minerals (cement, gypsum, etc.). Improvement to cementitious-based coatings have been reported as more stable coatings (e.g. geopolymer-based) have been developed [44-46].

The performance of cementitious-based thermal barriers on the concrete substrate is promising as the temperature of concrete substrate is kept low after 2 to 3 hours of fire exposure. There is even a publication [45] that reports good performance for potassium-based geopolymer under successive fire tests. Although the performance of these thermal barriers is promising, there are some practical issues that need to be considered. For example, the synthesis of geopolymer requires a curing condition of 70 °C over a period of 2 days. This requirement might not be practical in an actual construction site as heaters need to be deployed. In addition, cementitious-barriers are prone to fire-induced spalling. Although spalling might not be explosive in nature, a reduction in thickness will occur in the event of spalling and may reduce the performance of the coating. This is because the performance of thermal barriers is mainly governed by their low thermal conductivity. A reduction in thickness results in an increase in heat transfer as conductivity values of thermal barrier remain largely the same.

Gypsum panels also rely on low thermal conductivity to reduce the increase in temperature on a substrate. Furthermore, it dehydrates and releases chemically bound water upon exposure to elevated temperatures (100 °C and 200 °C) [47]. Gypsum boards are usually used to protect steel structures by encasing steel members in a box-up

configuration. However, they usually require mechanical fixing around a member and can be brittle and difficult to install on-site.

Table 2-5: Summary of cementitious-based thermal barriers on concrete substrate.

Reference	[48]	[49]	[50]	[46]	[44]
Material	Cementitious-based	Volcanic-ash-cementitious-based	Bottom-ash-cementitious-based	Sodium-based geopolymer	Potassium-based geopolymer
Thickness (mm)	49	30, 35, 45	20, 30, 40	50	50
Substrate	Concrete				
Fire Curve	ISO 834	ZTV-ING	RABT	ISO 834	RWS
Duration (hours)	3	3	3	2	2
Concrete temperature (°C)	100	290, 250, 175	700*, 500, 200	103	250
Remarks	-	Cracking on the surface of barrier	* Spalling of barrier	Steel anchors may be required to improve adhesion	

2.3 Effects of fire on polymers

Polymers have become indispensable in today's industry as they are being used in many industries. However, thermal performance of polymers remains an issue that needs to be addressed. The combustion mechanism of polymers has been studied and various flame-retardant (FR) strategies (e.g. intumescent system) have been proposed to enhance their performance.

2.3.1 Combustion of polymers

As heat from an external source causes thermal degradation of a polymer, volatile gaseous products are produced. In the presence of oxygen and heat, the volatile products undergo combustion, which further promote thermal degradation of the polymer. This 'self-sustaining' cycle [51] is expected to continue until the heat source can no longer degrade the polymer, or volatile products are no longer produced, i.e. all organic materials are combusted or formed thermally-stable char residues.

Flame-retardant strategies target the gas phase or the condensed phase of the polymer during combustion. Gas phase additives rely on free radicals scavenging and prevent the branching of radical chain reaction within a flame. Alternatively, gas-phase additives may produce inert gases that dilute flammable volatiles or decompose endothermically and absorb heat from the flame. Condensed-phase-active FRs typically rely on the formation of char that is promoted by chemical reactions of the additives, physical retention of

polymers, catalysis, or oxidative dehydrogenation. The chemical structure of a polymer plays an important role in the charring process as cross-linking, aromatization, fusion of aromatic rings, and graphitization need to develop in a sequential manner during thermal decomposition [52].

Figure 2-6: Combustion of a polymer. Adapted from [51].

2.3.2 Halogenated flame retardants

The main mechanism of halogenated FR is generally accepted to be gas-phase-active. They are typically brominated or chlorinated organic compounds incorporated into the polymer matrix in the form of additives, or introduced into the polymer chain by copolymerization [53]. Improved FR performance of textiles [54] and polymers [55, 56] due to the addition of halogenated compounds have been widely reported.

Synergistic actions of antimony trioxide (Sb_2O_3) with halogenated compounds are well-documented in the literature. Early studies on the mechanism of such systems showed that antimony trioxide played a significant role as they reduced hydrogen concentration much better than halogenated compounds [57]. It was later shown that Sb_2O_3 promoted the evolution of hydrogen halide that was responsible for radical scavenging, and retained halogens in the flame region with a ‘mist’ of fine antimony oxide (SbO) particles [52, 53].

In 2001, 39% of FR additives used in electronics are brominated compounds as they are able to reduce flammability of thermoplastic housing that encases electronic boards. However, they posed an environmental issue when the appliances were not disposed of properly [58]. Improper combustion of these systems would result in the formation of dioxins and furans, which are persistent organic pollutants and will find their way into rivers as pollutants, and eventually end up as food intake [59]. Studies showed that exposure to these chemicals is detrimental to the health of mankind and wildlife [60]. Therefore, it is necessary to find alternatives that are environmentally benign and exhibit satisfactory FR performance.

2.3.3 Phosphorus-based flame retardant.

Amidst the growing environmental concerns, phosphorus-based additives gained traction as an alternative to halogenated-based additives. This class of additives typically promote char formation in polymers, which is considered as a condensed-phase mode of action. Phosphorus compounds can be used to flame retard polymers with different key functional groups. For example, some phosphorus compounds with cellulose components (e.g. wood, and textile fibre) form cellulose phosphate through phosphorylation (addition of phosphate group, PO_4^{3-}). The formation of polyphosphates followed by crosslinking and aromatization promoted charring in samples. Polyphosphoric acid could also form a film on the surface that acts as a thermal barrier and stops flame propagation [61].

Phosphorus-based FR additives in thermoplastics (such as polyamides, polystyrene, and poly (methyl methacrylate)) also act mainly in the condensed-phase as the improved fire retardancy is a result of char formation [62, 63]. Resorcinol bis(diphenyl phosphate) typically contains 60 % to 75 % of phosphate species [64], and its ability to impart flame retardant properties to polymers by acting in the condensed-phase was reported. Char formation increased [65] when resorcinol bis(diphenyl phosphate) was added to polyphenylene oxide and polystyrene blend. It releases phenol -OH groups during thermal decomposition that generated crosslink polyphenylene oxide chains and increased char residue. The additive also acted as a catalyst and promoted the evolution of phenol groups in polyphenylene oxide and cross-linking. Similar FR mechanism was reported with polycarbonate and acrylonitrile-butadiene-styrene blend [66].

Red phosphorus is another phosphorus-based FR additive and its dominating FR mechanism depends on the polymer matrix. Its ability to form char in polyamide-6 is related to the phosphorus content [67] present in resin as the resultant charring was

attributed to the formation of phosphoric esters during thermal decomposition. However, red phosphorus was reported to increase the gas phase action in low-density polyethylene wood composite [68]. Decomposition of red phosphorus releases high concentration of phosphorus oxide radicals into the flaming zone that could also trap active radicals.

Char forming additives do not necessarily only act on condensed-phase mechanism and combined FR mechanism for phosphorus-based polymers (such as methyl methacrylate) are also available [63, 69]. To a certain extent, the formation of char on the surface helps to trap volatile products that contribute to the combustion of flame as shown in Figure 2-6.

2.3.4 Intumescent system

Intumescent system relies on a combination of FR mechanisms. It promotes char formation and expands during heating and this likely protects the underlying layers from further decomposition. Intumescent systems do not require thick coatings and can be simply applied as a type of paint. The use of intumescent coatings became prevalent in 2001 (Figure 2-7) and started to dominate the steel fire protection market in 2005. Its market share was estimated to reach \$918.2 million in 2018 [2].

Figure 2-7: Trends in structural fire protection from 1992 to 2014. Image adapted from [2].

A typical intumescent system relies on the combination of an acid source, a carbonising agent, and a foaming agent. However, depending on the polymer matrix, carbonising and foaming agents may not be required to promote intumescence behaviour. For example, thermal degradation of APP and polyamide-6 mixture produces 5-amidopenthyl polyphosphate between 260 °C to 315 °C [70], which is a precursor of char. Decomposition products of 5-amidopenthyl polyphosphate and APP are responsible for the intumescence phenomenon. In PP matrix, APP and PER are able to produce intumescence due to the formation of thermally-stable crosslinked polyaromatic structure [71, 72] and evolution of high yield gaseous products as PER phosphate decomposes [73]. Intumescence behaviour can be further enhanced with the introduction of blowing agents such as melamine or urea. These three additives, namely, APP, PER and melamine form the conventional intumescent system.

Figure 2-8: Picture of char formation in intumescent systems and its schematic representation. Image from [74].

In a typical intumescent coating subjected to fire, as it reaches a critical temperature, acid released from phosphorus-based FR (APP) causes char forming agent (PER) to dehydrate. The char-forming agent releases water (or other by-products) to form the building blocks of char (double C=C bond). Meanwhile, blowing agents (melamine) decompose to produce copious amounts of gases that cause expansion [74]. The formation of carbonaceous char with low thermal conductivity acts as an insulator between the fire and the substrate or unreacted virgin materials (Figure 2-8). Char structure can impede the diffusion of volatile pyrolysis products and reduce the amount of pyrolysis product in the combustion process [52], acting in the condensed- and gas-phase mode.

2.3.5 Factors affecting the performance of intumescence

There are various factors that affect the performance of an intumescent coating. Some of these are described in Section 2.3.5.1 to 2.3.5.4.

2.3.5.1 Ratio of additives

Apart from studying the intumescent mechanism, other aspects were also investigated to optimise FR performance. The weight ratio of additives present is one of these aspects that has been widely investigated and optimal weight ratios of 3:1:1 between APP, PER and MEL combination in polyamide [75], 2.7:1:1.1 between APP, PER and MEL combination in acrylic, 3:1 and 2:1 between APP and PER in polypropylene [76], have been suggested. Compared to PER and MEL, the content of APP in the system is important as it participates over a wider temperature range in forming char [77]. The degradation products of APP are the main factor affecting the properties of the char structure [78]. In polypropylene (PP), the effects of varying the ratio of intumescent additives such as APP, PER, MEL on limiting oxygen index (LOI) values have been studied and reported in the form of an infographic plot (Figure 2-9) [73]. There is no substantial increase in LOI values even with changes in the ratio of different additives when total loading is kept to 10 and 20 weight percent. The maximum LOI value was achieved with an optimum ratio when the total loading of FR additives was 30 %.

Figure 2-9: Relationship between LOI and different ratio of APP, PER, and MEL in polypropylene. Adapted from [73].

The optimum ratio, based on maximum LOI values, is determined to be 1:0.5:0.3. It is also apparent from Figure 2-9 that higher LOI values are achieved with a higher concentration of APP or PER weight ratio when total loading is kept at 30 weight percent. The difference in FR performance with varying ratio is not surprising as the ratio between APP and PER was reported to influence the properties of carbonaceous foam formed in PP [78]. This corroborates with the findings of Camino, *et al* [72] in which stability of polyphosphate chain and crosslinked structures formed varies with APP:PER ratio.

2.3.5.2 Polymer matrix

Apart from the additives, it should be noted that the polymer matrix also plays a crucial role in FR performance. The chemical structure of the polymer [73] will influence FR performance as it may react with the additive to form char and the formation of crosslinked phosphate ester char between the cured epoxy resin and APP [79] serves as an example. Formation of a more stable char structure has been reported for phosphate monomers (from APP) with styrene-acrylic copolymers [80], but the work also showed the importance of melt viscosity in intumescent systems.

A polymer matrix with high crosslinking degree can restrict intumescence behaviour [80] and lead to poor thermal performance. Excessive PER will likely increase the ‘stiffness’ of the molten char structure [72], making intumescence difficult and consequently restrict expansion. The temperature at which polymer matrix and additive degrades can also affect char structure since it is usually formed with the decomposition product of matrix and additives. More importantly, the melt viscosity of the polymer should not be too low (< 2000 Pa.s) nor too high (> 14,000 Pa.s) [81] during decomposition of intumescent additives [82]. Low melt viscosity allows trapped gases to escape with ease leading to slump and cohesive failure of char structure, while high melt viscosity restrains gases from being formed and consequently restricts expansion of the carbonaceous structure.

2.3.5.3 Expansion

Expansion is crucial to the performance of an intumescent coating. Typically, a coating with higher expansion ratio (assuming the char has the same thermal properties) will perform better. This can be achieved with MEL or urea which releases gases during decomposition that remain trapped in the viscosity melt flow. Alternatives to blowing agents have been reported and expandable graphite (EG) has been highlighted as one of the novel FR additives [4, 74] in recent years (2014 – 2015).

EG is a pseudo-2D solid like layered compound (Figure 2-10). It consists of carbon atoms arranged in the form of hexagonal cells and held together with covalent bonds. The hexagonal cells are organised within a layered nano-sheet to form a carbon layer joined together with weak van der Waals forces. The carbon layers are intercalated with oxidants such as sulphuric acid, hydrogen peroxide and/or potassium permanganate. When heated, sulphur dioxide is released in a redox reaction (Equation 2-1) that causes exfoliation of the graphite layers [4].

This exfoliation occurs along the c-axis of the crystal structure, forming a puffed-up material of low density with a worm-like structure. The irreversible expansion of EG forms an insulative layer that shields the virgin polymer or substrate from the heat source. They show a different chemistry/mechanism compared to formulations based on acid source, carbonisation compounds, and blowing agents [4]. EG has demonstrated its ability to provide good retardancy to various polymer matrices such as polyethylene, epoxy, unsaturated polyester [4] and polyurethane foams [83]. These works focus on improving the FR performance of polymer systems but do not discuss the performance of EG as an additive for fire protective coating.

Figure 2-10. Structure of expandable graphite. Adapted from [84].

The use of EG in fire protective coating was reported in 2007 [85], but it served as a supplementary material that was included into a conventional intumescent formulation (i.e. APP, PER and MEL system). As expected, EG did improve the performance of the conventional intumescent system. However, it is interesting to note that EG also improves the durability of the coatings based on water immersion test results. The parallel arrangement of the graphite layers increased the diffusion path for water ions through the coating and reduced the migration of FR additives out of the coating. Hence, reduction in fire performance is not as significant as the coating without any EG additives.

2.3.5.4 Cohesive char structure

However, the incorporation of EG into coatings may not be as straight-forward as the exfoliated graphite network is soft and may not generate a cohesive char structure. Additives such as calcium carbonate and clay can be introduced to improve thermal stability of silicone matrix while EG and the choice of resin (e.g. silicone-based) may also need to play a role [86]. If the char structure is stabilised, it can have a comparable performance with a commercial intumescent system. For conventional intumescent systems, additives such as titanium dioxide [87, 88] can be added to improve mechanical property and stability of char. This is achieved with the formation of titanium pyrophosphate (TiP_2O_7), a ceramic-like layer, which is more thermally-stable compared to carbonaceous char structure. However, good FR performance is only achieved with good dispersion of titanium dioxide in the polymer system [88], which may be difficult to achieve at times.

2.3.6 Issues with intumescent coatings

As the additives used in most of the intumescent formulations are susceptible to weathering, the use of a topcoat is one of the easiest solutions to alleviate adverse effects of weathering on the intumescent coating. This may help to control the leaching of additives and in turn help to maintain the fire retardant performance of the coatings even after subjecting them to accelerated weathering conditions [76]. Particles such as synthetic and natural clay platelets and nanoparticles can be incorporated to increase the diffusion pathway of water and reduce the rate at which the additives are leached out of the system. These methods do not eliminate the issue but reduce the rate at which the coating deteriorates.

Another issue with intumescent coatings is the lack of adhesion between the char and the substrate, which may limit their performance. Adhesive failure of intumescent char has been reported in magazines [89], technical reports (Figure 2-11a) [90, 91] and publications [92, 93]. This results in a sudden increase in temperature as seen in Lines 2 and 3 in Figure 2-11b, which is detrimental to the performance of an intumescent coating. Improvement in adhesion of char to steel substrate has been reported [94] when boric acid and APP were added, and the temperature of the substrate increased at a constant rate since the char did not detach from the substrate during heating. The authors did not study the mechanism behind improved adhesion, but it was postulated that a reaction between boric acid and APP derivative during thermal decomposition promoted adhesion between the char and the steel substrate [94]. Nonetheless, the test highlighted the importance of a char structure that is cohesive and can adhere to a substrate under elevated temperatures.

Figure 2-11: (a) Slumping of intumescent coating in a fire test. Image from [90]. Time-temperature profiles on the unexposed surface for different coating compositions.

Adapted from [94].

The issue of adhesion between intumescent char and substrate is not limited to steel. Delamination between the intumescent coating and the concrete substrate, followed by extensive spalling of the soffit of the concrete slab (Figure 2-12), caused a concrete slab to reach premature failure [95]. The reason behind the delamination was not elucidated further. It was postulated that the coating has prevented evaporation of water from the surface of the concrete that eventually resulted in spalling. Another hypothesis was that the presence of intumescent coating within the surface voids and pores contributed to spalling as the coating itself expanded under temperature.

Figure 2-12: Spalling of concrete slab protected with intumescent coating. Image from [95].

Adhesion failure of intumescent coating could be attributed to the weight of the char as slumping of char can occur during a fire test [90]. This is expected as the polymeric content degrades during heating and reduces the surface contact between the coating and the substrate. The degradation of the polymer matrix also results in softening and the weight of char causes slumping behaviour as seen in Figure 2-11. To prevent adhesion failure of the char structure, the conventional formulation can be modified.

2.4 Testing fire protective coatings

The review on FR thus far touches on the behaviour and performance of intumescent coatings. Different types of tests such as cone calorimeter [96-98] and furnace tests [85, 99, 100] were used to evaluate the behaviour and performance of coatings at different scales. However, the tests used to evaluate FR behaviour may not be representative of an actual fire resistance test due to the difference in scale of specimens. In fact, there are many publications that characterise FR performance of polymers and coatings through materials-scale and bulk-scale tests, but very few papers [101] on their performance in an actual fire resistance test.

Correlations between limiting oxygen index (LOI) test, UL94 test, microscale combustion calorimetry (MCC, or otherwise known as PCFC) and cone calorimeter test for FR cables have been reported [102]. Parameters related to flammability (e.g. total heat release, char yield and fire growth index) were compared [102] and certain interesting trends have been identified. For example, FR polymers with V-0 rating in UL94 test will have 30% LOI values and FR polymers with a total heat release rate below 21 kJ/g and heat release capacity smaller than 380 J/(gK) have higher chances of obtaining V-0 rating in UL94

test [102]. Correlating test results conducted at different scales (e.g. MCC and cone calorimeter) becomes more complex as the FR mechanism captured in the tests differs. A cone calorimeter can simulate flame-inhibiting reactions better as samples in MCC are subjected to complete combustion. This resulted in poor correlation of total heat release for halogenated FR polymers.

There are publications that correlate mechanical properties of intumescent coating with furnace tests (Figure 2-13) [103]. A higher time to failure in a furnace test is directly related to the expansion ratio and mechanical resistance of char. It was also proposed that high complex viscosity will indicate a high mechanical resistance of char, while high remaining mass in TGA relates to high expansion ratio in a rheometer.

Figure 2-13: Correlation between mechanical parameters and time to failure in a bulk-scale fire test. Adapted from [103].

However, the relationship proposed is largely qualitative and does not relate to the fire resistance rating. Moreover, char with high mechanical resistance may be heavy and rigid and can result in delamination as discussed in Section 2.3.6. The structural-scale fire test is also different from the bulk-scale furnace test discussed in work by Jimenez, *et al* [103]. This technique will be beneficial in preliminary stages where changes to composition are expected. Thus far, there is only one publication [101] that suggested the use of cone calorimeter to predict the performance of an intumescent coating in a structural-scale fire test. Principle of heat transfer was used to calculate the required heat flux as a function of time in the cone calorimeter test and time-temperature profile of the steel section in cone calorimeter test was compared with the time-temperature profile of a steel section.

Figure 2-14: Time-temperature profiles of (a) thermocouple in I-section and (b) I-section and sample in cone calorimeter test. (c) Time-heat flux relationship. Image from [101].

However, variations between the thermocouples are apparent at the early stages of the I-section fire test (Figure 2-14a). This implies uneven thickness due to poor applications or uneven heating due to poor experimental setup, both of which were detrimental to its performance. The time-temperature profile was also validated with different thicknesses of the intumescent coating as seen in Figure 2-14b and the initial ramp of the sample (2.7mm sample) in the cone calorimeter tests differed from the temperature profile of the I-section in the structural-sale fire test. Moreover, this technique stipulated a time-heat flux relationship (Figure 2-14c) which might not be feasible for all cone calorimeter tests.

2.5 Modelling intumescent coatings

As seen in Section 2.4, experimental tests to assess the performance of intumescent coatings can be challenging and time-consuming. This is the reason behind the development of numerical models to predict performance of intumescent coatings. Relevant parameters such as thermal properties and physical properties serve as input data to the models, and they are usually obtained from material tests. Early models for intumescent systems were based on physical processes such as the expansion of intumescent coatings under thermal loads. Anderson and Wauters [104] developed a 1-dimensional heat transfer model that depicted heat transfer through an intumescent system to a metal substrate as shown in Figure 2-15a. The expansion of intumescent char was assumed to be a function of the quantity of gaseous products released, represented by changes in the mass during thermal decomposition.

The changes in mass were obtained through thermogravimetric analysis (TGA) and expressed using Fourier series to facilitate numerical simulations. As shown in Figure 2-15b, the model does not agree well with the experimental data. The authors explained that the expansion factor proposed in the publication might not be accurate as the expansion of coatings only accounted for mass loss. This resulted in inaccuracy as the expansion of coatings would be a function of mass loss rate and temperature, which were not incorporated into the model.

Figure 2-15: (a) Schematic representation of the model and (b) results computed using the model compared with experimental data. Image from [104].

Over the years, improvements to modelling were made to account for various aspects of an intumescent coating. This includes predicting the rate of swelling [105], accounting for degradation through Arrhenius equation [106, 107] and the effect of polymer viscosity [108]. Although these models can be considerably accurate in predicting heat transfer through an intumescent coating, there are still drawbacks. For example, conventional models capture intumescent behaviour through the expansion of little bubbles produced during the thermal degradation of polymer and trapping of inert gases released from the reactions.

This may not be applicable if the reaction mechanism changes and the expansion is no longer related to the release of gases. Expansion of bubbles is also assumed to follow ideal gas law [107] which may not accurately describe the behaviour of the volatiles released during decomposition. This is because the volatiles can exist as radicals and it will be difficult to ascertain the appropriate values for the parameters (i.e. pressure,

temperature and number of moles) in ideal gas law. Moreover, these models typically rely on thermal conductivity of air to predict heat transfer across the thickness of the coating and do not account for thermal conductivity of the molten char or any chemical mechanism that may be present during decomposition. Lastly, most models [104, 107, 109-111] reviewed can only predict the performance of intumescent coatings based on a one-dimensional heat transfer. This may not be realistic along the edges of a structural member as expansion around the edges may not be as straight-forward.

Figure 2-16: (a) Bubbles in the model expanding in a 3-dimensional manner. (b) Geometry of expanding bubble with a thermal gradient. (c) Cross-sectional view of the model at different stages of expansion, with topmost being the start of the experiment.

Image from [105].

2.6 Summary and gaps in the literature

The review presented in this chapter covers the importance of fire protection to structural elements (both concrete and steel) and available fire protection strategies. Emphasis is placed on passive protection technologies like coatings. Fire-resistance polymer-based coatings exhibit promising performance but research work conducted seldom relate the fire tests on coatings to fire resistance rating. Moreover, research work on fire-resistance coatings mainly focuses on the fire performance (i.e. flammability) of small-scale samples that may not be an accurate representation at structural scale. In conclusion, the following research gaps have been identified:

1. Notwithstanding dominating passive fire protection market, there are various issues with the current intumescent coating formulations.

2. Fire protective coatings are a viable solution to prevent (a) fire damage of concrete and steel materials and (b) fire-induced spalling of concrete. However, research work for structural fire protection systems is largely based on traditional intumescent formation.
3. FR polymers are characterised using materials-scale samples that are typically measured in milligrams. The behaviour of the FR polymers in bulk (measured in gram) cannot be captured through materials-scale tests, making it difficult to relate the results obtained from materials-scale tests to their actual performance in bulk- or structural-scale tests. The available literature on correlating fire protective coatings across different scales are rather limited and require more validation.
4. Models for intumescent coatings are typically based on air voids produced during the decomposition process.

Chapter 3 Materials, characterisation and fire tests

It is important to understand the basic structure of the resin and additives and how different aspects of the proposed coating are evaluated. This chapter begins with a description of basic characteristics of the resin and additives used in the coating. This is followed by a description of the different characterisation techniques adopted in this thesis. The rationale behind the techniques and parameters used during the tests are also discussed. Lastly, the experimental setups for three different fire tests to assess the performance of the proposed coating are discussed.

3.1 Materials

3.1.1 Resin

Acrylic emulsion polymer (water-based) is used as the binder in this thesis due to its characteristic features of emitting less VOCs and superior exterior durability [112]. The resin is supplied by Synthomer and its product name is Plextol R 4180. The resin has a relative density of 0.9 kg/m³ to 1.1 kg/m³ and a solid content of approximately 50%. At room temperature, it remains as an aqueous dispersion and it can dry up and form a film. The typical chemical structure of the resin is shown in Figure 3-1.

Figure 3-1: Schematic of the acrylic chemical structure.

3.1.2 Ammonium polyphosphate

Ammonium polyphosphate is an inorganic salt of polyphosphoric acid and can be represented with the chemical formula, $[\text{NH}_4.\text{PO}_3]_n$. A schematic of APP chemical structure is shown in Figure 3-2.

Figure 3-2: Schematic of APP chemical structure.

It can be prepared by reacting ammonia with concentrated phosphoric acid [113]. As a commercial product, APP comes in different molecular weights (Phase I, Phase II, etc). In this work, Phase II APP is used as one of the additives in the coating. The APP is obtained from McKinn International Pte Ltd and appears as fine white powder.

3.1.3 Pentaerythritol

Pentaerythritol (PER) with the chemical formula of C₅H₁₂O₄ is used as a carbonizing agent in this work. This polyol is purchased from Sigma-Aldrich and remains as a white powder at room temperature. A schematic of PER chemical structure is shown in Figure 3-3.

Figure 3-3: Schematic of PER chemical structure.

3.1.4 Expandable graphite

Chemical structure and general details regarding EG can be found in Section 2.3.5.3. In this work, EG is provided by Shijiazhuang ADT Carbonic Material Factory. The product name is EG ADT 150 and is reported to have an expansion volume of more than 150 ml/g. Scanning electron microscopy (SEM) and particle size distribution are presented in Figure 3-4.

Figure 3-4: SEM micrographs of (a) EG flakes and (b) intercalated layers of EG platelets [114]. (c) Distribution of EG ADT 150 particle size.

Scanning electron microscopy (SEM) was used to characterise its surface morphology (Figure 3-4a) and intercalated layers (Figure 3-4b) before its expansion upon heating. The particle size of EG ADT 150 is measured using a particle size analyser (Malvern Instruments, Mastersizer 2000). The EG particles were suspended in water and their particle sizes were determined based on laser diffraction technique. The particle size ranges from 103 (0.1 percentile) to 593 (0.9 percentile) μm , with a mean particle size of 282 (0.5 percentile) μm (Figure 3-4c).

3.1.5 Preparation of coating mixture

The additives described in Section 3.1.1 to 3.1.4 are used without further modification. Required amounts of the additives¹ (in terms of weight) were measured and added into the water-based acrylic resin in a sequential manner (i.e. APP, PER, EG). The mixture

¹ Please refer to Section 4.3, Table 4-3 and Chapter 7, Table 7-1 for details regarding composition of coatings.

was mixed using an overhead stirrer (IKA RW 20 digital attached with 4-bladed propeller stirrer) with a minimum of 1000 rpm for at least 3 min, after each additive was added.

An apparent increase in viscosity was expected when APP was added into the resin, while viscosity increase with the addition of PER and EG was not as significant unless its weight ratio dominates. That is, excess PER and EG (e.g. more than 21 g of the additive in 100 g of resin) will lead to an apparent increase in viscosity of the mixture. Visual observation on the mixture was required throughout the mixing process to ensure that agglomeration of additives did not occur. Water was added to the mixture to control the viscosity of the mixture and ensure it was suitable for spraying.

3.1.6 Spraying of coating

The coating could be sprayed onto a substrate using a spray gun. Air spray gun with a nozzle diameter of 3.5 mm and a line pressure of 3 MPa was used to spray the mixture for the materials- and bulk-scale specimens (Figure 3-5a). Air-pressurised spray gun (Figure 3-5b) did not require large quantities of coating for spraying, which was more manageable during development stages.

(a)

(b)

Figure 3-5: (a) Air-pressurised spray gun and (b) industrial airless spray gun.

Subsequent layers were sprayed or applied until the desired thickness was achieved once the coating was touch-dry. The touch-dry time for each layer of coating was approximately 2 h. Curing occurred at ambient room temperature and typically took approximately 5 h. In a structural-scale test, an industrial airless spray gun was used to coat the steel sections. The airless spray gun could produce a maximum line pressure of 3600 psi and a customised spraying tip was used. Despite the differences, the same composition could be used with a slight adjustment to the viscosity of the mixture.

3.1.7 Thickness measurement

It is important to measure the thickness of fire protective coating as this parameter is often used to compare their performances with other coatings. A coating thickness gauge is one of the non-destructive methods as it applies electromagnetic induction principle to measure the thickness of a non-magnetic coating on a magnetic substrate. In this work, Elcometer 456 is used to measure the thickness of the developed coating on steel substrates. A total of 15 to 25 readings from different regions of a steel plate are usually measured and the average of those readings is given in this thesis.

3.2 Characterisation techniques and testing

3.2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Figure 3-6) is one of the most commonly used methods to evaluate thermal degradation of a material in different atmospheres like nitrogen / argon or air to simulate pyrolysis or oxidative conditions, respectively.

Figure 3-6: Schematic of TGA instrument. Image from [115].

The instrument consists of a precision balance, programmable furnace and selectable gas input. This provides the data to interpret thermal stability of a coating material under

different environments. The residual weight percent of a sample, which is also referred to as a mass loss curve, is obtained with respect to temperature.

Employed instrument details and parameters:

TA Instruments SDT Q600 and TA Instruments Q500 were used in this work. Samples with a weight of 8 mg to 10 mg were placed in an alumina cup and heated up to 1000 °C at a heating rate of 0.33 K/s. Tests were conducted in both oxidative (air) and pyrolysis (nitrogen) environments. The data presented in the thesis is based on 1 data and the samples were repeated once to ensure repeatability.

3.2.1.1 Theoretical thermogravimetric curves

Theoretical TG curves were computed to further understand the role of each additive on thermal stability of the matrix. A positive ΔM shows that weight loss is lower than expected, suggesting an interaction between additives and matrix that results in an increase in thermal stability, while a negative ΔM indicates otherwise [99].

$$\Delta M = M_{exp} - M_T \quad \text{Equation 3-1}$$

$$M_T = \frac{W_r}{W_T} M_{exp,r} + \frac{W_1}{W_T} M_{exp,1} + \frac{W_2}{W_T} M_{exp,2} + \frac{W_3}{W_T} M_{exp,3} \quad \text{Equation 3-2}$$

where

- ΔM : difference between experimental residual weight [%] and theoretical residual weight [%]
- M_{exp} : residual weight [%] of a composition
- M_T : theoretical residual weight [%] computed using residual weight [%] of each additive present in the composition (Equation 3-2)
- $M_{exp,r}$: experimental residual weight [%] of resin
- $M_{exp,1}$: experimental residual weight [%] of additive 1
- $M_{exp,2}$: experimental residual weight [%] of additive 2
- $M_{exp,3}$: experimental residual weight [%] of additive 3
- W_T : total solid weight of the composition [g]
- W_r : solid weight of resin in the composition [g]
- W_1 : solid weight of additive 1 in the composition [g]
- W_2 : solid weight of additive 2 in the composition [g]
- W_3 : solid weight of additive 3 in the composition [g]

Note:

In this work, additive 1, 2 or 3 refers to APP, PER or EG, respectively

3.2.2 Fourier transform infrared spectrometer (FTIR)

FTIR collects the infrared spectrum of a sample [116]. This is produced by emitting an infrared source through an interferometer and measuring the light beams after it interacts with the sample using a detector (Figure 3-7a).

Figure 3-7: Illustration of (a) interferometer and (b) reflectance of infrared beam in FTIR / ATR – FTIR equipment. Image from [116].

An infrared spectrum is usually presented as absorbance (light intensity) versus wavenumber (property of light). Through many years of extensive research, relationships between molecular vibrations and wavenumber have been established. This means that a peak position at a certain wavenumber can be used to help identify molecules in a sample. An attenuated total reflectance (ATR) accessory can be used with an FTIR equipment. ATR is based on internal reflectance (Figure 3-7b) where an infrared beam is passed through a crystal and reflected off the surface of the sample before entering the detector [116]. This technique is useful in identifying molecules on a solid sample which is unlikely for the infrared beam to pass through. However, it should be noted that the depth of penetration is limited to a few microns of the sample.

Employed instrument details and parameters:

The samples were heated with the TGA instrument from ambient to certain temperature intervals (i.e. 150 °C, 200 °C, 250 °C, 275 °C, 300 °C, 400 °C, & 600 °C) at a heating rate of 20 °C/min. The desired temperature was maintained for 5 min before the furnace was cooled to ambient. Spectra of the residue were collected in ATR mode using Perkin-Elmer Frontier Spectrometer. The spectra collected were in the range of 4000 to 600 cm^{-1} with a resolution of 2 cm^{-1} and 32 scans per condition. The data presented in this thesis is based on 1 sample for each temperature interval.

3.2.3 Thermogravimetric analysis coupled with infrared spectrometer (TG-IR)

Thermogravimetric analysis can be coupled with an infrared spectrometer and the working principles of each equipment still apply (Figure 3-8).

Figure 3-8: Setup of TG-IR equipment. Adapted from [117].

The difference lies in the state of the samples as TG-IR focuses on identifying the molecules of gaseous products formed during the decomposition process. As the sample decomposes, a pump directs the volatiles through a line connecting the TGA equipment to an infrared (IR) cell and the line is kept at a constant temperature (Figure 3-8) to reduce the condensation of volatiles in the pipeline itself. The spectrometer will continuously collect an IR spectrum of the gaseous product throughout the test and a complete spectrum of intensity versus wavenumber versus temperature can be obtained. This allows the identification of molecules in volatiles at a specific temperature range.

Employed instrument details and parameters:

Perkin-Elmer TGA 4000 was coupled to Perkin-Elmer Frontier Spectrometer through an IR cell as shown in Figure 3-8. The airflow and temperature of the IR cell and connecting line were controlled using Perkin-Elmer TL 8000. The samples (8 to 10 mg) were placed in the TGA equipment and heated from ambient to 900 °C at a heating rate of 20 °C/min. An airflow of 40 ml/min was maintained along with an IR cell and line temperature of 300 °C. Spectra of volatiles were continuously collected, and they fell within the range of 4000 cm⁻¹ to 450 cm⁻¹ with a resolution of 8 cm⁻¹ and 1 accumulation. The data presented in this thesis is based on 1 sample and selected samples were repeated once to ensure repeatability.

3.2.4 Rheological studies

Visco-elastic measurements (complex viscosity) of the coatings are carried out across a temperature range to understand the rheological changes during thermal degradation (Figure 3-9).

Figure 3-9: Experimental setup for rheological studies.

The polymeric material is pressed between two plates (conical or parallel configuration) and a rotational force is applied onto the sample by the top plate. When coupled with a furnace, the polymeric material softens (and melts depending on the nature of the polymer) upon heating and melt viscosity will be determined based on the shear stress of the molten material. A typical test procedure begins with applying a certain torque and a minimum force (to allow contact) on a cured coating sample. The torque and force are maintained throughout the test. The thickness of the sample is measured and referred to as the gap between the shaft and stage. As heat is applied, reactions within the sample result in decomposition and expansion. These physical changes alter complex viscosity and the gap between the stage and the shaft, and the changes will be recorded by the rheometer.

Employed instrument details and parameters:

MCR 501 from Anton Paar, coupled with its furnace accessory CDT 600, was used in this work. Disc-shaped samples with a diameter of 25 mm were prepared and a 25 mm diameter parallel plate was used as the measuring system. The samples were heated at a heating rate of 5 °C/min from ambient to 400 °C. A strain amplitude of 2% with a

frequency of 10 Hz were applied to the samples during heating. The data presented in this thesis is based on an average of 2 to 3 samples.

3.2.5 Viscoelastic properties

The viscoelastic properties (e.g. storage modulus, loss modulus and tan delta) of a sample are determined using a dynamic mechanical analysis (DMA) instrument. The instrument characterises the viscoelastic property of a sample by applying deformations in different modes such as three-point bending, compression or tension with an oscillatory behaviour. The deformations of a sample, with known geometry, are related to its stiffness. The relationship between the applied sinusoidal stress to strain can be recorded [118] and an example is shown in Figure 3-10.

Figure 3-10: Relationship between applied sinusoidal stress to strain of a sample in DMA test. Image adapted from [118].

The modulus is derived from the in-phase component while the storage modulus is derived from the out-of-phase component. The tan delta property, which is also known as damping, is the ratio of the loss modulus to storage modulus. It offers an understanding of the glass-transition temperature and curing behaviour of the sample.

Employed instrument details and parameters:

A TA Instruments DMA Q800 was used in this work. The film tension clamp setup was used, and the samples were prepared as thin films. The samples had an approximate length of 30 mm and a width 5 mm and thicknesses ranging from 0.8 mm to 1.2 mm. The samples were cooled to -10°C before they were heated with a heating rate of $5^{\circ}\text{C}/\text{min}$ to 100°C . An amplitude of $15\ \mu\text{m}$ with a frequency of 1 Hz was applied during the test. The data presented in this thesis is based on an average of 2 to 3 samples.

3.2.6 Pyrolysis combustion flow calorimeter (PCFC)

The amount of heat released during the combustion of the material is considered as one of the most important parameters to determine how flammable the material is in a fire [119]. Pyrolysis combustion flow calorimeter has been developed as a laboratory-scale test to measure heat release rate of materials in a controlled condition. The instrument consists of a pyrolysis chamber as well as a combustion chamber (Figure 3-11).

Figure 3-11: Schematic of burning sample and PCFC. Image from [119].

A few milligrams of the material, similar to TGA, is enough for evaluation in a PCFC. The material is first placed in the pyrolysis chamber, where it is exposed to heat in an inert environment and volatiles released from the material will be directed into the combustion chamber. The concentration of oxygen available in the combustion chamber is monitored continuously as the volatiles are combusted. The heat release rate is computed based on the reduction in oxygen concentration within the combustion chamber, which is the reason that this technique is also known as oxygen consumption calorimetry, that is, the heat release per unit oxygen consumed is equal to 13.1 kJ/g.

Employed instrument details and parameters:

The tests were performed using a Fire Testing Technology (FTT) Micro Calorimeter in with reference to ASTM D7309 [120]. Weighing between 6 to 17 mg, the samples were heated with a heating rate of 0.33 K/s and 1 K/s from ambient to 600 °C in the pyrolysis chamber while a temperature of 900 °C was maintained in the combustion chamber. The total heat release rate and heat release capacity were calculated using MCC Curve Fit 1.7 software. The data presented in this thesis is based on an average of 2 to 3 samples.

3.2.7 Cone calorimeter

The cone calorimeter is a bench-scale test that can also be used to measure heat release rate of a material. This is also based on the oxygen consumption principle similar to PCFC. This equipment was developed by NIST in the 1980s and its primary role is to quantify the heat release rate of products at bench-scale and estimate their contribution to a fire in a room [121]. A schematic of cone calorimeter is shown in Figure 3-12.

Figure 3-12: Schematic of cone calorimeter. Image from [122].

A sample (100 by 100 mm in surface area) is typically placed horizontally under a conical radiant heater and the surface of the material will be exposed to a constant irradiance. Although a cone calorimeter also depends on oxygen consumption calorimetry to determine the heat release rate of the material, the material is placed in an environment where there is ample supply of ambient air and oxidative thermal decomposition of the material is expected. However, once the sample ignites, within the flame zone, oxygen is depleted, and pyrolysis-dominated degradation is mostly expected. The sample scale and

the decomposition environment set it apart from PCFC. Other fire response parameters such as mass loss, smoke production and carbon monoxide production can be measured during the test [10]. Fire growth rate index (FIGRA) or fire performance index (FPI) [123] can be deduced analytically from the data obtained from the cone calorimeter for better comparison among samples. The assessment of intumescent coating with cone calorimeter should be done with caution. This is because significant swelling of the coating will affect irradiation imposed on the surface and placement of mesh is required to restrict expansion [121].

Employed instrument details and parameters:

The flammability of the samples was characterised using an FTT cone calorimeter, in accordance to ISO 5660-1 [124]. Samples were prepared by spraying over a steel plate of 90 mm x 90 mm x 4 mm. The slight reduction in the dimensions of the steel plate ensured that the coatings which overflow along the edges are also exposed to heat. The irradiance on the sample surface was calibrated at 35 kW/m² and 50 kW/m². Depending on the objective of the test, a metal mesh with an aperture size of 1 mm was used to constrain the expansion of the sample during heating. This helps to maintain a constant heat flux across the surface of the sample. The data presented in this thesis is based on 1 sample and selected samples were repeated once to ensure repeatability.

3.2.8 Modified Transient Plane Source (MTPS)

Thermal conductivity is an intrinsic material property that determines the rate at which heat is conducted through the material. Equipment using steady-state and transient methods have been developed to measure thermal conductivity of materials [125]. Thermal equilibrium between the sensors and the sample must be achieved in a steady-state method, which is often time consuming. Equipment such as transient plane source uses transient method to determine conductivity in a shorter time. The sensor of a transient plane source equipment will be sandwiched by two identical materials. An electrical current is supplied to the sensor, which results in heat generated from the sensor to the surrounding materials. The increase in temperature is determined based on the electrical resistance of the sensor and it allows thermal conductivity to be inversely calculated with changes in resistive voltage [125, 126]. A modified transient plane source, developed by Mathis Instrument, is based on transient plane source method and it reduces the need to sandwich the sample around the sensor as it employs a one-dimensional heat flow into

the material. This method does not require users to optimise power output, time or even sensor size to ensure repeatability in results.

Employed instrument details and parameters:

Thermal conductivity of the samples was determined using C-Therm TCi MTPS equipment. The equipment allows different test calibration methods to be selected. Polymer and foam test methods were adopted for this test. Polymer test method was used for samples that were heated up to 200 °C while foam test method was used for samples heated from 300 °C to 700 °C. This is because the coating was dominated by polymer below 200 °C. The expansion of EG after 200 °C and the decomposition of polymer will introduce air voids into the system. Hence, the foam test method was deemed more appropriate after 300 °C. The samples were heated to the desired temperature (i.e. 100 to 900 °C, with a 100 °C interval) and kept isothermal for 5 min in a furnace (measured using a thermocouple). The samples were removed from the furnace and allowed to cool to ambient before placing it on the sensor. Changes in packing density of char were not expected during cooling and were deemed beneficial at low temperatures (100 °C to 300 °C). This was because the resin decomposed within this temperature range and was likely to be in its molten state, which is difficult to handle. The data presented in this thesis is based on an average of 2 samples.

3.2.9 Modulated Differential Scanning Calorimetry (MDSC)

Differential Scanning Calorimetry measures the difference in the heat flow of a sample with a reference sample when subjected to a temperature programme. The enthalpy differences allow the identification of the type of reactions (i.e. exothermic or endothermic) occurring at different temperatures and relate them to certain changes in a polymer system. Modulated differential scanning calorimetry imposes a temperature ramp that incorporates a sinusoidal temperature oscillation and allows specific heat capacity of a material to be determined.

Employed instrument details and parameters:

Modulated differential scanning calorimetry was conducted using TA Discovery DSC. Samples of 3 to 5 mg were placed in Tzero aluminium hermetic pans as the coating expands under heating and may damage standard pans. A heating rate of 10 °C/min, with an amplitude of ± 1.523 °C and a period of 60 s, was used in the test. The sample was

heated from 20 °C to 400 °C. The data presented in this thesis is based on the average of 2 samples.

3.3 Fire tests

3.3.1 Direct flame torching test

Direct flame torching test was conducted to investigate the performance of a coating subjected to a flame. This is required as fire protective coating on concrete walls is subjected to a large-scale single item burning test such as EN 13501-1 / EN 13823. The direct torching test setup is illustrated in Figure 3-13.

Figure 3-13: Digital photograph of torching test conducted in a controlled environment and (b) an illustration of the experimental set-up for direct flame torching of coatings.

The direct flame torching experiment was conducted using a methane burner in a chamber to ensure a constant atmospheric environment and heating conditions (flame temperature and flame length). The flame temperature was calibrated to be 750 ± 50 °C, with an estimated flame length of approximately 40 to 50 mm. The coatings were applied over a type-K thermocouple (Thermocouple 1 in Figure 3-13b) that was embedded into a 50 mm thick concrete block. The thermocouple was flushed with the surface of the concrete, and it recorded temperature of the concrete block. An additional type-K thermocouple (Thermocouple 2 in Figure 3-13b) was used to measure the temperature of the unexposed surface. The burner was placed such that the flame would be heating the area directly above the thermocouple. A laminar flame with minor flicking was produced using the burner, and the same area was heated consistently.

3.3.2 Rapid heating furnace

The rapid heating furnace located in the School of Civil and Environmental Engineering Fire Annex and the experimental setup for 1D bulk-scale furnace test are shown in Figure 3-14.

Figure 3-14: (a) Digital photograph of rapid heating furnace. (b) Schematic of gypsum board setup. Digital photographs of (c) exposed surface and (d) furnace in operation. (e) Schematic drawing showing the location of the thermocouple.

The rapid heating furnace (Figure 3-14a) has an internal dimension of 1.7 m long by 0.7 m wide by 0.85 m high and was used to assess the coatings at bulk-scale with ISO 834 time-temperature profile. Heat is produced via electrical heating elements located alongside the furnace. Two openings are located at each end of the furnace and the opening has dimensions of 0.38 by 0.38m. A gypsum board setup was designed to hold the coated substrate at the opening. The setup consisted of 3 boards with dimensions of 0.38 m by 0.38 m and gaps between the setup and the openings were filled with thermal

wool. The first and third boards, with an opening of 0.15 m by 0.15m, were used to hold the sample and prevent it from falling forward or backwards. The second board with an opening of 0.16 m by 0.16 m was used to support the four sides of the substrate. Bolts with threaded rods were placed at four corners of the setup to secure the three boards together (Figure 3-14b and c). The surface of the coating was exposed to one-dimensional heating (Figure 3-14d). This condition has been evaluated in preliminary setups with the use of four thermocouples and has been presented in a previous publication [100]. A type K-thermocouple was placed between the interface of the coating and substrate for temperature measurement (Figure 3-14e).

3.3.3 Nabertherm muffle furnace

Isothermal thermal tests can be conducted using a muffle furnace, which is located in the School of Materials Science and Engineering. This was achieved with a Nabertherm muffle furnace shown in Figure 3-15.

(a)

(b)

(c)

Figure 3-15: Digital photographs of (a) muffle furnace, (b) in-house modification was done to accommodate the setup and (c) gypsum board setup for muffle furnace test.

In an isothermal test, the furnace was used to heat samples for thermal conductivity testing (Section 3.2.8). A similar one-dimensional heat transfer setup was also used with a Nabertherm muffle furnace. Modifications were made to the furnace door to accommodate the setup (Figure 3-15b and c). It is worth noting that the back surface of the sample will not be exposed to ambient, which differs from the setup described in Figure 3-14d. This setup was used to investigate FR mechanism of the coatings with different additive ratios.

3.3.3.1 Estimating thickness of char structure after furnace test

The thickness of char is estimated using Image J software. The method requires digital photographs of char formation after the furnace test and an upright ruler for calibration. An example of the char structure after the furnace test and photograph for calibration and analysis are presented in Figure 3-16.

Figure 3-16: Digital photographs of (a) exfoliated EG network after the furnace test, (b) char and scale for calibration purpose and (c) example of measurement analysis.

The expansion of char is rather uniform across a vertical plane due to 1D experimental setup. Hence, the photographs of two random sides were acquired and the thicknesses were analysed using ImageJ software (Figure 3-16a). The photographs include the expanded char network and a scale (Figure 3-16b). This allows the relationship between photograph resolution / pixel and distance to be determined in ImageJ. Vertical lines were subsequently drawn from the top of the steel plate to the top of the char structure and the length of these lines were measured based on the relationship established earlier (Figure 3-16c). A series of 11 to 15 lines were drawn in random to capture char thickness and the average thickness of all lines from both sides of the photographs were used to estimate the thickness of char formation after the furnace test.

3.3.4 Gas-fuelled furnace

In a structural-scale fire test, a coated structural member will be subjected to mechanical and thermal loads. Mechanical loads depend on the loading conditions that the member will be subjected to when used in a building, while thermal loads are defined as the time-temperature profiles of the heated gas in an enclosed furnace. Heat exposure to a member is dependent on the type of members (viz. columns, beams, slabs or walls). One-dimensional heat transfer is applicable for slabs, while heat exposure to beams and columns can be 2-, 3-, or 4-face, respectively. All structural-scale tests were conducted in *Centre Scientifique et Technique du Batiment* (CSTB), France. The specimen used in the furnace test, the furnace itself, and the test setup are shown in Figure 3-17.

The steel section, Universal Beam (UB) 406 x 178 x 67 kg/m (Figure 3-17a), had a length of 1 m and was coated all around (Figure 3-17c). It had a section factor of 175 m^{-1} . The furnace was 4 m long by 3 m wide by 2.2 m deep (Figure 3-17b). The steel sections were mounted onto a concrete slab, which was supported by the perimeter of the furnace. In this setup, the columns would be exposed to heat from all sides and would be representative of a column section (4-face exposure). As shown in Figure 3-17e, there were four type-K thermocouples (diameter 1.8 mm) used to record the temperature of both flanges (two thermocouples for each flange) and one type-K thermocouple to record the web temperature. The thermocouples were located at the middle of the top and bottom of the steel section (500 mm from the top) and the middle of the flange and web.

Figure 3-17: Digital photographs of (a) steel column before coating, (b) test furnace, (c) coated steel column, (d) column setup for furnace test and (e) schematic drawing showing locations of thermocouple.

Chapter 4 Thermal stability and flame-retardant mechanism of developed coating

This chapter elucidates the thermal stability, flammability properties and fire performance of the developed coatings. The FR mechanism will be thoroughly investigated based on the effects of varying the ratio of each additive.

4.1 Thermal decomposition of resin

Weight loss curves and corresponding derivative weight loss plots of the acrylic resin in both N_2 and air environments are shown in Figure 4-1. A summary of the TGA data is also listed in Table 4-1 for ease of reference.

Figure 4-1: (a) Mass loss curves and (b) derivative weight loss curves of resin in oxidative and pyrolysis environments.

Table 4-1: Summary of TGA results for resin.

Notation	T _{5%} ($^{\circ}C$)	T _{50%} ($^{\circ}C$)	Residual weight %	Environment
ACR N_2	352	399	0	Pyrolysis
ACR Air	303	371	0	Air

Note:

T_{5%} = onset temperature, defined as the temperature at which 5% mass loss occurs

T_{50%} = maximum decomposition temperature, defined as the temperature at which 50% mass loss occurs.

Thermal decomposition of neat acrylic resin binder (ACR) in nitrogen occurred over a single step between 300 $^{\circ}C$ to 400 $^{\circ}C$ (Figure 4-1a). Random C–C scission along the main chain was expected to be the dominant thermal degradation mechanism in the acrylic system [127]. Mass loss behaviour in oxidative condition was similar as well except that the decomposition occurred earlier, as expected (T_{5%} and T_{50%} in Table 4-1). A plausible

explanation is the formation of unstable hydroperoxides from radicals and oxygen, which breaks down rapidly to produce more free radicals and causes the decomposition to occur at a lower temperature. In thermal oxidative decomposition, hydrogen atom abstraction was the main reason behind main-chain scission of acrylic system.

(a)

(b)

Figure 4-2: TG-IR plots of ACR in (a) oxidative and (b) pyrolysis environments.

The TG-IR plots (Figure 4-2a and b) show peaks detected from 300 °C to 400 °C. The peaks between 1800 cm^{-1} to 1600 cm^{-1} in Figure 4-2 could be attributed to C=O bonds while the peaks between 1500 cm^{-1} to 1200 cm^{-1} and 1200 cm^{-1} to 1000 cm^{-1} could be attributed to O=CH-CH₂ and ester linkages, respectively. The peaks between 3200 cm^{-1} to 2800 cm^{-1} could be assigned to C-H stretch, which indicated the presence of methane gas, while carbon monoxide (CO) was assigned to the two peaks between 2400 cm^{-1} to 2200 cm^{-1} . The presence of monomer MMA, methane and carbon monoxide gases were typical decomposition products of this resin [127].

4.2 Thermal decomposition of additives

The mass loss curves and derivative mass loss curves of the additives (i.e. APP, PER and EG) in oxidative environments are presented in Figure 4-3a and b, while the 3D TG-IR contour plot of APP and its corresponding 2D map are presented in Figure 4-3c and d. A summary of the TGA results for the additives is presented in Table 4-2.

Figure 4-3: (a) Mass loss curves and (b) derivative mass loss curves of additives in oxidative environment. (c) 3D TG-IR contour plot of APP and (d) its corresponding 2D map of wavenumber versus temperature.

Table 4-2: Summary of TGA results for additives in air environment.

Notation	T _{5%} (°C)	T _{50%} (°C)	Residual weight %
APP	345	643	11
PER	252	303	0
EG	208	816	35

Note:

T_{5%} = onset temperature, defined as the temperature at which 5% mass loss occurs

T_{50%} = maximum decomposition temperature, defined as the temperature at which 50% mass loss occurs.

Thermal degradation of APP in air occurred over two main steps (Figure 4-3a). The first degradation step of APP between 300 °C to 400 °C corresponded to the evolution of ammonia gas and water vapour while the evaporation of phosphoric acid (H₃PO₄) and the dehydration of acid in phosphorus pentoxide (P₄O₁₀) occurred at the second step between 550 °C to 700 °C [128]. The TG-IR plots (3D surface and 2D contour map of APP) in Figure 4-3c and d corroborated with the decomposition products of APP additives. At 300 °C, peaks at 3300 cm⁻¹, 1600 cm⁻¹ and 1000 cm⁻¹ to 900 cm⁻¹ could be attributed to NH₃ (ammonia gas). The two definitive peaks between 1000 cm⁻¹ to 900 cm⁻¹ which corresponds to ammonia gas is also apparent in Figure 4-3c at 300 °C. After 600 °C, peaks between 1300 cm⁻¹ to 1000 cm⁻¹ can be assigned to P=O, while the broad peak between 3600 cm⁻¹ to 2600 cm⁻¹ can be assigned to O-H bonds.

The single mass loss step of PER powder seen in Figure 4-3a and b showed that it volatilised without decomposition on heating [129]. The decomposition process started slightly after 200 °C and was completed before 350 °C. The release of carbon dioxide and water vapour is expected during decomposition of PER. The first decomposition step of EG resulted in a mass loss of around 15% at approximately 210 °C. This was attributed to the exfoliation of graphite platelets caused by a redox reaction (Equation 2-1). The second decomposition step of EG occurred at 742 °C and it was attributed to the oxidation of graphite platelets.

4.3 Compositions for mechanism study

As discussed in Section 2.3.5.1, the weight ratio of the additives can affect the performance of a fire-protective coating and there were many publications that suggested an optimum weight ratio for conventional intumescent systems was 3:1:1 (APP:PER:MEL). Hence, the weight ratio of the dominating additive was kept at 3:1:1

and individual additive was varied to study its role in improving the FR performance of the polymer resin. A summary of the compositions in this study is shown in Table 4-3.

Table 4-3: Summary of FR compositions.

Notation	APP	PER	EG	Wet resin	H ₂ O
	Units in gram [g]				
3A	21	7	7	100	10
3P	7	21	7	100	10
3E	7	7	21	100	10

As seen in Table 4-3, the notation of each composition corresponds to the dominating additive. That is, if APP is the dominating additive, the composition is designated as 3A. The total weight ratio of the additive was kept constant for all three compositions at 35 g per 100 g of wet resin (50 g of dry resin), which represented a loading weight percent of ~ 41.2 %.

4.4 Flame-retardant mechanism of the coating

4.4.1 Thermal stability

The mass loss curves and derivative mass loss curves of the neat resin and the different intumescent coatings are shown in Figure 4-4 and a summary of the TGA results is also presented in Table 4-4.

Figure 4-4: (a) Mass loss and (b) derivate weight of neat resin and FR composition in air environment.

Table 4-4: Summary of TGA results for neat resin and FR compositions in air environment.

Notation	T _{5%} (°C)	T _{50%} (°C)	Residual weight (%) at 1000 °C	Mass loss (%)	
				200 °C to 300 °C	300 °C to 400 °C
ACR	303	371	0	2.8	85.5
3A	246	381	6	7.4	52.6
3P	240	351	6	18.0	55.7
3E	237	368	11	10.5	51.5

As explained in Section 4.1, acrylic decomposes in one main step mostly by chain scission mechanism between 300 °C to 400 °C to yield volatiles [127]. Even in the intumescent systems, the bulk of the mass loss is dominated by the decomposition of acrylic resin in between 300 °C to 400 °C. The lack of significant changes in the degradation temperatures (T_{50%} in Table 4-4) and mass loss profile in all the systems (Figure 4-4a) compared to the neat resin suggest the lack of predominant interactions among the additives and the resin. However, by comparing the mass loss between 200 °C to 400 °C (Figure 4-4), it was apparent that APP and EG dominated systems behaved rather differently. This suggested that acrylic resin might have had interactions with APP to a smaller extent [128].

In general, the reaction of the acidic species from the APP (orthophosphates / phosphoric acid / polyphosphoric acid) with PER takes place above 280 °C with formation of esters in intumescent systems [72, 74]. Subsequent carbonisation process occurs *via* the Diels-Alder reaction and a free radical process resulting in the formation of aromatic structures. Finally, a blowing agent such as melamine (or even the polymer resin) decomposes to yield volatiles that swells the char [130]. However, in the current case, since EG expands at between 180 °C to 200 °C (Figure 4-3a), which was lower than the degradation temperature of the resin (303 °C) or APP and PER (345 °C and 252 °C, respectively), the swelling efficiency of the resin is expected to be significantly influenced. Also, as seen in Figure 4-4a, with a higher amount of PER, degradation started slightly earlier (from 250 °C). No residue was left for ACR, but the intumescent formulations 3A and 3P with higher loading levels of APP and PER, respectively, showed the same amount of residue (~10%) at 900 °C. Composition 3E showed the highest residue at 900 °C, but after 900 °C, the oxidation of graphite (carbon) seemed to dominate under these thermo-oxidative conditions.

The theoretical TG curve is shown in Figure 4-5 and it illustrates thermal stability of the resin in the presence of the additives. Readers may refer to Section 3.2.1.1 for more information regarding the calculations of the theoretical curves.

Figure 4-5: Difference between experimental mass loss curves and theoretical TG curves.

As seen in Figure 4-5, there are three different temperature zones that can be identified from the curves, 200 °C to 300 °C, 300 °C to 400 °C, and 500 °C to 700 °C. In the 200 °C to 300 °C, the negative ΔM values for all the 3 compositions corresponded to a reduction in thermal stability. The large negative ΔM value seen in 3P was understandable due to the lack of sufficient APP in the system resulting in a higher rate of volatilization of higher amounts of PER. In between 300 °C to 400 °C, an increase in thermal stability could be observed in 3A while a further reduction in thermal stability could be observed in 3P and 3E. This suggested that the reaction between excess APP and PER or resin increased thermal stability of the resin between 300 °C to 400 °C, but it only occurred when excess APP was present (e.g. 3A).

An increase in thermal stability was seen in 3P and 3E between 500 °C to 700 °C. However, the negative ΔM between 550 °C to 700 °C in 3A indicated the oxidation of char formed. The reduction in thermal stability may also be attributed to an antagonistic effect between APP and EG that was also reported by Meng, *et al* [131]. The antagonistic effect occurred as the exfoliated graphite structure increased the interface between phosphoric acid and the environment, resulting in accelerated decomposition of the acid. It may also be postulated that excess APP that did not participate in any reaction was decomposing and resulted in negative ΔM values between 550 °C to 700 °C in 3A. This

is because the second decomposition step of APP, as seen in Figure 4-3a, also occurs between 500 °C to 700 °C. In 3E and 3P, there was no dominant interaction between the additives and the formation of carbonaceous char. Therefore, it can be seen that the thermal stability of the samples is dominated by EG. Complex viscosity (both real and imaginary) variations and measured thickness with temperature for neat resin and FR compositions were measured and shown in Figure 4-6.

Figure 4-6: (a) Complex viscosity and (b) gap measurement of samples.

Generally, in a typical intumescent formulation, the gases evolved from the blowing agent are expected to be trapped inside the system and slowly diffuse out through the highly viscous resin melt. This creates a porous barrier influencing thermal conductivity and in turn, improving the fire resistance duration. However, in the present systems, since the EG was expanding, it had to push the viscous melt to create this barrier. Therefore, the viscosity of the resin should correlate with the temperature at which EG expands. As seen in Figure 4-6b, expansion of EG typically occurred after 180 °C, where the resin was softened as it had a complex viscosity less than 1000 Pa.s. The complex viscosity of FR compositions at ambient is lower compared to the neat resin suggesting a significant influence on the resin curing behaviour in the presence of additives (Figure 4-6a). The curing behaviour of the resin and composition can be characterised with the glass transition temperature (T_g). This was achieved by identifying the temperature that corresponds to the peak tan delta profile, shown in Figure 4-7.

Figure 4-7: Tan delta profile of coatings.

The T_g of the neat resin is 36.3 °C, while the T_g for 3A, 3P and 3E are 41.6 °C, 39.4 °C, 43.6 °C, respectively. However, the matrix resin viscosity drops dramatically after ~45 °C (which is slightly after the T_g of the polymer). The drop corresponds to the increase in mobility of the chains and free volume. Beyond this temperature, a major change was seen around the temperatures corresponding to the expansion of EG (180 °C to 250 °C). As a result of the physical expansion of an FR sample, correspondingly, its viscosity also increases. In typical intumescent formulations (without EG), the viscosity decreases very rapidly during the matrix degradation temperature range. But after this, an increase will be seen due to the carbonisation process, where the liquid phase resin completely disappears (degrades) and a carbonaceous char is formed. The reaction between APP and PER will also influence the viscosity between 250 °C to 330 °C.

4.4.2 Changes in chemical bonds – ATR-FTIR

The ATR-FTIR spectra of the additives and the FR compositions at ambient temperature are presented in Figure 4-8. The spectra of three different compositions at ambient condition were similar as it was unlikely for any chemical reaction to take place among the additives or resin during mechanical stirring. Irrespective of the composition, the ATR-FTIR spectra in Figure 4-8b were similar and dominated by the peaks from the resin. The definitive peak between 1800 cm^{-1} to 1750 cm^{-1} with a peak maximum at 1727 cm^{-1} corresponds to C=O stretching in carbonyl groups, while the peaks between 3100 cm^{-1} to 2800 cm^{-1} with a maximum at 2956 cm^{-1} indicated the presence of aliphatic groups (CH_3 from methyl groups) in acrylic resin. The peaks at 1450 cm^{-1} to 1400 cm^{-1} , 1250 cm^{-1} , and 1170 cm^{-1} to 1150 cm^{-1} could be attributed to the presence of C-O bonds.

Figure 4-8: FTIR spectra of (a) individual additives and (b) samples 3A, 3P and 3E additives at ambient temperature.

A slight difference could be observed at 800 cm⁻¹ as a small peak was seen in 3A but was not apparent in 3E and 3P. Composition 3A was dominated by APP and when comparing its spectra with the APP powder spectra in Figure 4-8b, it is clear that the peak at 800 cm⁻¹ could be attributed to NH₃⁺ bond. The FTIR spectra of the different compositions were dominated by the peaks from the resin. The changes in ATR-FTIR spectra of the compositions were insignificant between 150 °C to 275 °C and it corroborated well with the spectra in TGA and TG-IR analysis. Mass loss in TGA between 150 °C to 250 °C (Figure 4-4a) were within 5% for the three compositions and volatiles were observed to start evolving after 300 °C. The ATR-FTIR spectra of the 3 different FR compositions at 300 °C to 600 °C, at selected intervals, are presented in Figure 4-9.

Figure 4-9: (a) ATR-FTIR spectra of composition residue at (a) 300 °C, (b) 325 °C, (c) 350 °C, (d) 375 °C, (e) 400 °C, (f) 600 °C.

The peaks between 900 cm^{-1} to 880 cm^{-1} in 3A at 350 °C (Figure 4-9c) could be assigned to P–O–P bonds [128] and it could be attributed to the polyphosphate chains in APP. This peak was absent beyond 350 °C in all compositions and it suggested that APP had decomposed. In addition, the peaks 1020 cm^{-1} and 880 cm^{-1} were attributed to C–OH (stretch) and its absence beyond 350 °C suggested that PER had decomposed. The relative

intensity of carbonyl peaks (1750 cm^{-1}) in 3A remained similar as the temperature increased from $350\text{ }^{\circ}\text{C}$ to $375\text{ }^{\circ}\text{C}$ while a gradual reduction could be observed in 3E as temperature increased from $325\text{ }^{\circ}\text{C}$ to $375\text{ }^{\circ}\text{C}$. The carbonyl peaks (1750 cm^{-1}) in 3P at $350\text{ }^{\circ}\text{C}$ (Figure 4-9c) remained as the dominant peak but reduced significantly at $375\text{ }^{\circ}\text{C}$ (Figure 4-9d). Comparing the reduction of carbonyl peaks for the three compositions, it can be explained that APP dominated composition (3A) accelerated the degradation of the resin to form a stable structure [128] that subsequently delayed the decomposition of resin. Above $350\text{ }^{\circ}\text{C}$, the appearance of peaks 1650 cm^{-1} to 1600 cm^{-1} and 1090 cm^{-1} to 920 cm^{-1} could be attributed to P–OH and P–O–C aliphatic esters, respectively, indicating a reaction between APP and PER or APP and the resin and the formation of a thermally stable structure.

The peak between 1350 cm^{-1} to 1150 cm^{-1} and between 1100 cm^{-1} to 800 cm^{-1} indicated P=O stretching and P–O–P stretching bonds [128], respectively. These peaks were clearly defined in 3A and 3P at $400\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ (Figure 4-9e & f) and it suggested the formation of a thermally stable phosphate char structure after $400\text{ }^{\circ}\text{C}$. The ATR-FTIR spectra of 3E at $400\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ were largely different from 3A and 3P as it matched the spectra of EG particles at ambient. Visual observation of 3E residue after the TGA tests seemed to only consider exfoliated graphite flakes due to its brittle and flaky nature. This was supported by the ATR-FTIR spectra of 3E as carbonyl and MMA peaks were not prominent in the spectra at $400\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$. Instead, the spectra at $400\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ indicated the presence of C=C stretching (attributed to EG) at peaks 2200 cm^{-1} to 2000 cm^{-1} while only traces of P–O–C stretching bonds was visible at $400\text{ }^{\circ}\text{C}$ (Figure 4-9e). This implied that expandable graphite did not react with APP, PER, or the resin.

4.4.3 Changes in chemical bonds – TG-IR

The TG-IR spectra of the 3 different FR compositions from $300\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$, at selected intervals, are presented in Figure 4-10.

Figure 4-10: TG-IR spectra of 3A, 3P, and 3E at (a) 300 °C, (b) 325 °C, (c) 350 °C, (d) 375 °C, (e) 400 °C, (f) 600 °C.

As shown in Figure 4-9a, peaks corresponding to NH_3^+ in 3A were absent at 300 °C. This corroborated well with the TG-IR spectra of 3A (Figure 4-10a) as two sharp peaks between 1000 cm^{-1} to 900 cm^{-1} (attributed to ammonia gas) were detected at 300 °C. Since APP was the dominating additive in 3A, it was expected to see that the relative intensity of ammonia gas evolved was much higher in 3A when compared with 3P and 3E. However, the remaining volatiles that corresponded to the decomposition products of

resin was seen with much higher intensity in 3P and 3E. The peaks between 3000 cm^{-1} to 2800 cm^{-1} and 1400 cm^{-1} to 1200 cm^{-1} can be assigned to C–H bonds from aliphatic compounds. The peaks between 1800 cm^{-1} to 1600 cm^{-1} are attributed to C=O bond, which suggests ketone related degradation products. Carbon monoxide (CO) gas, represented by two sharp peaks between 2400 cm^{-1} to 2200 cm^{-1} , was also observed in Figure 4-10a and the relative intensity of the CO peaks in 3P and 3E was higher compared to 3A. These three decomposition products are typically found in the decomposition of poly (methyl methacrylate) [127, 132].

The peaks between 2400 cm^{-1} to 2200 cm^{-1} and 800 cm^{-1} to 750 cm^{-1} in Figure 4-10b-f indicated the presence of CO_2 volatiles. Since the CO_2 volatile was also part of the decomposition products of the resin, it was not surprising to see the peaks appearing at $350\text{ }^{\circ}\text{C}$ and started to dominate the spectra at higher temperatures. However, as seen in Figure 4-10f, these peaks dominated the spectra for all compositions at $600\text{ }^{\circ}\text{C}$. This was not the case when compared to 3D TG-IR plot of neat resin as it would have already completely decomposed (0% residual weight in Figure 4-4a). Hence, the presence of CO_2 volatiles was likely attributed to the oxidation of the phosphorus-carbonaceous material or the oxidation of graphite.

4.4.4 Flammability characteristics

Cone calorimeter tests were used to characterise the flammability of the different compositions. In this test series, a mesh was used to restrain the expansion of the graphite char so that the incident heat flux on the surface of the coating was kept constant throughout the test. A summary of the results obtained in cone calorimeters tests at an incident heat flux of 50 kW/m^2 is presented in Table 4-5. Heat release rate (HRR), total heat release (THR) and total smoke produced (TSP) plots of the samples are shown in Figure 4-11.

Table 4-5: Summary of cone calorimeter test results.

Notation	Peak HRR (kW/m^2)	Area under curve		Total heat release (MJ/m^2)	Mass lost (g)
		1 st peak	2 nd peak		
ACR	467.9	-	-	88.1	28.5
3A	108.1	11.4	33.0	44.4	19.8
3P	116.8	11.1	41.8	52.9	20.3
3E	84.2	4.1	28.6	32.7	16.5

Figure 4-11: (a) Heat release rate, (b) total heat release rate, and (c) total smoke produced of samples in cone calorimeter test.

The HRR curve of ACR (Figure 4-11a) corresponded to the typical burning behaviour of a thick non-charring sample [10]. A sharp increase in HRR was observed in the initial stage after the ignition of the sample and it reached a peak value before plateauing for a short period of time. This was followed by a sharp decline in HRR curve from the peak value to almost zero. This showed that the entire resin participated in combustion and was consumed within a short period of time (around 300 s), which also corroborated with the lack of residue after the test.

The HRR curve of 3A, 3P and 3E (Figure 4-11a) corresponded to the typical behaviour of a thick charring sample and a significant reduction in peak HRR could be observed for all three compositions. The initial increase in HRR, THR and TSP was expected due to the decomposition of the top few layers of the samples upon exposure to the conical heater, while EG expanded and formed an entangled and inter-twined insulating layer. The formation of the insulating layers led to a reduction in the decomposition of the samples

as evident from a drop in HRR or a plateau in the THR curves after ~ 70 s. The reduction in HRR curve is more significant for 3E due to the higher loading of EG present. This allows the formation of an exfoliated graphite network that is more compact and effective compared to 3A and 3P. As heat continues to be transferred to the underlying layers, decomposition occurred and contributed to the rise in HRR, which was represented by the second board peak after 200 s (Figure 4-11a).

A clear reduction in peak HRR could be seen when comparing the FR samples with ACR (Table 4-5). A reduction of 82 % was observed for 3E, which was the highest among the FR samples. However, among the FR samples, the differences in the peak HRR varied from 7 % to 25 %, with 3E showing the best performance. Besides, THR of 3E was the lowest (Table 4-5). The differences in the THR of the samples confirmed that pyrolysis of the entire sample was absent in 3E due to protection offered by the expanded graphite. This was also reflected in the least mass loss value of 3E (Table 4-5) indicating an effective delay of decomposition of the resin. The mass loss (initial mass – final mass) of the samples were calculated and it corroborated well with the THR values.

The difference in the peak HRR, delay in the complete combustion of the resin, and reduction in THR values suggested that the performance was dominated by physical barrier property of EG similar to polymer/clay nanocomposites [133, 134] and polymer/CNT composites [135, 136]. Apart from EG, APP dominated system (3A) performed relatively well compared to PER dominated system (3P). This signified the phosphorylation and char formation in the presence of excess APP improved flammability resistance of the neat polymer resin, which was similar to reported studies that suggested better flammability performance (LOI values or UL 94 ratings) with higher loading of APP in the polymer matrix [78, 137, 138].

A considerable reduction in TSP was observed in 3E when compared to 3A and 3P (Figure 4-11c) and this corroborated with findings reported in literature that EG acted as an efficient smoke suppressant. In addition to the graphite network formed, the graphite layers remained thermally stable at high temperature and did not decompose to create volatiles that contributed to smoke creation unlike APP or the resin. This explained the gradual increase in smoke production of 3E between 250 s to 400 s compared to 3A and 3P. The increase in smoke production after 300 s in 3P was likely associated with the decomposition of resin or unreacted PER. Similarly, the gradual increase in 3A showed that it could better delay the decomposition of the resin compared to 3P. Heat release rate

can also be measured using PCFC and the HRR of the neat resin and FR compositions in PCFC test are presented in Figure 4-12.

Figure 4-12: Heat release rate of the samples in PCFC test.

In a cone calorimeter test, the expansion of EG forms a thermal barrier between the substrate and the heat source and prevents the whole sample from participating in decomposition. However, in the PCFC experiments, formation of an effective barrier is unlikely since heat was applied in all directions and only milligrams of samples were used. Hence, HRR peaks of the three compositions were mostly narrow (Figure 4-12). This is because the entire thickness of the sample would be participating in the pyrolysis process per unit time. However, the reduction in peak of HRR was also apparent in the PCFC data with EG based systems. In sample 3P, a rather distinct additional broad peak around 200 °C to 300 °C is seen, which was a result of the presence of excessive PER. In 3A and 3E samples, the peaks around 200 °C to 300 °C were also apparent, but the intensity was very small.

4.4.5 Dominating FR mechanism

As demonstrated by Sonnier, *et al* [139], comparing the total heat release rate of the neat and FR systems obtained from PCFC and cone calorimeter could help to identify the dominating FR mechanism. This is because physical FR mechanism is expected to dominate in a cone calorimeter test, while gas-phase mechanism is expected to dominate in PCFC tests. The THR values and the reduction of THR values based on ACR for PCFC and cone calorimeter are summarised in Table 4-6.

Table 4-6: Summary of THR values and reduction in THR values.

Notation	Total Heat Release (MJ/m ²)		Reduction in THR (%)	
	PCFC	Cone calorimeter	PCFC	Cone calorimeter
ACR	26.0	88.1	-	-
3A	15.4	44.4	40.8	49.6
3P	17.0	52.9	34.6	39.9
3E	15.9	32.7	38.7	62.9

The reduction in THR values based on cone calorimeter was more apparent compared to the reduction in THR values based on PCFC, which was expected as gas-phase FR mechanism did not dominate in these systems. It was also clear that the addition of EG allowed the physical FR mechanism to dominate, which was observed in 3E where the reduction in THR based on cone calorimeter was the largest among the three compositions. This further corroborated that the samples were dominated by physical FR mechanism.

4.4.6 Preliminary assessment of the compositions in a furnace test

The samples were exposed to a one-dimensional heat transfer test to investigate its behaviour in a furnace simulating an ISO 834 fire curve (Section 3.3.3). A summary of the test results and the thickness of the coatings are presented in Table 4-7. It should be noted that the estimated average thickness of residue was obtained with ImageJ analysis software. Readers can refer to Section 3.3.3.1 for more information.

Table 4-7: Summary of preliminary one-dimensional heat transfer test.

Description	Control – bare steel plate	3A	3P	3E
Time to 200 °C (min)	11.5	20.6	19.6	24.9
Initial average thickness of coating (mm)	N.A.	2.49	2.55	2.50
Estimated average thickness of residue (mm)	N.A.	20.5	21.4	52.3
Expansion factor	N.A.	8.2	8.3	20.9

Compared to the control, the coated steel plate with 3A, 3P and 3E showed that it required a longer time for the steel plate to reach 200 °C and among the three coated samples, 3E provided the best protection. Similar performance has been seen by Gardelle, *et al* [86] who have used silicone matrix with a 25 weight percent loading of EG. However, as the thickness of the coating in [86] was ~1 mm compared to ~2.5 mm in this work, the rise

in temperature of the steel is high. For instance, the temperature of steel substrate in [86] reached 200 °C in ~ 7.5 min. Nonetheless, the furnace tests showed that the expansion of EG was critical in delaying the thermal diffusion through the coating (expanded char). It should also be noted that despite the conclusion on the performance of EG network, EG dominated composition (3E) would not necessarily provide the best fire performance when tested at the structural level. The lack of cohesion and the fluffy/fragile nature of the residue could result in cracking, fall off and delamination of the expanded graphitic char during the test on an I-section. This was observed with 3A (Figure 4-13), which had a smaller expansion factor compared to 3E and it was postulated that cohesive failure along the flange of a steel I-section would be more severe if expansion factor was greater. It should be noted that preliminary steel I-section tests for 3P and 3E were not conducted.

Figure 4-13: Digital photograph of 3A in preliminary steel I-section test.

The observations (red arrows in Figure 4-13) confirmed that cracking along the edges of I-section was a result of rapid and non-directional expansion of EG at micro-scale. Also, as a result of higher heat fluxes experienced by the edges of the steel section and cracking along the edges, the time for the steel substrate to reach 200 °C was ~ 9.2 min, shorter compared to any of the composition in the 1D test (Table 4-7). Based on the insights derived in Chapter 4, composition 3A was selected for further studies at structural-scale. Composition 3E was not selected as excessive expansion lead to cracking along the flanges which is detrimental to the fire performance of the coating. Composition 3P was not selected as the HRR was greater compared to 3A and had a similar expansion factor.

4.5 Conclusion

This chapter investigates the FR mechanism of APP, PER and EG additives in acrylic polymer system. The FR mechanism of the compositions are as follows;

- The additives can improve the thermal stability of the resin as shown in the thermogravimetric analysis.
- The complex viscosity of the acrylic matrix does not influence the expansion of the EG, which differs from conventional intumescent (APP/PER/MEL) system. The expansion of EG forms worm-like network rather than blowing of carbonaceous char.
- The presence of APP accelerates the decomposition of the acrylic polymer matrix and the formation of a thermally stable phosphate char structure is identified after 400 °C through the ATR-FTIR analysis. Chemical reaction between EG and the resin / additive is not identified through the ATR-FTIR and TG-IR analysis.
- The cone calorimeter tests demonstrate improved flammability characteristic of the acrylic resin. This is due to the expansion of EG that forms an insulating layer and the reaction between APP, PER and the resin that leads to char formation. Since EG does not react with the additives or the resin, physical FR mechanism dominates, and it is corroborated by comparing the reduction in THR values obtained from PCFC and cone calorimeter tests.
- As discussed in Section 4.4.6, the increase in EG content will not necessarily provide best fire performance as exfoliated graphite network due to poor cohesion to the steel I-section. Excess PER content is also not beneficial to the performance of the coating as it increases HRR of the coating. In view of this, char formation between APP and PER or APP and resin is still required and composition 3A will be used in further studies at structural level.
- The importance of the scale of testing needs to be investigated. It is clear that the changes in the ratios or loading levels have a significant influence on inherent characteristics of the materials, but when the scale of testing gets larger, other parameters might play a determining role in the performance.

Chapter 5 Correlating the performance of developed coating across different scales of testing

The flame-retardant (FR) mechanism discussed in Section 4.5, was based on materials-scale tests. However, it is difficult to correlate the results and insights obtained from the materials-scale tests with structural-scale fire tests, which is a regulatory requirement before the fire protective coating can be used as a commercial product. A protected steel member has to meet certain fire resistance criteria (e.g. deflection limits and/or critical temperature) with the imposed mechanical and thermal loadings according to standard fire tests such as BS 476 Part 21, ASTM E119 or EN 13381-8. However, such structural-scale fire tests are usually time-consuming, expensive and require a lot of resources. In this context, many questions arise on the usefulness and validity of materials- and structural-scale tests, and their correlations to characterise the performance of coatings at structural level.

At materials-scale, tests such as Underwriter Laboratories (UL) 94, limiting oxygen index (LOI), thermogravimetric analysis (TGA), and pyrolysis combustion flow calorimetry (PCFC) are a few commonly used techniques to characterise parameters relating to thermal stability and flammability. TGA and PCFC data are based on milligrams of a sample, whereas LOI and UL 94 tests are limited to small rectangular strips of 125 mm × 12.5 mm × (0.8 to 3.2) mm exposed to a small candle-like flame. For example, in the vertical burning UL94 test, a flame source (with a 20 mm flame height) is applied to the bottom of the specimen for 10 s for two applications, and local ignition of the sample, its self-extinguishing and dripping behaviour (melt and flame) are monitored. But such tests only give qualitative data and as expected, the performance of the sample is thickness dependent. In the tests for LOI, the minimum oxygen requirement for a sample to sustain a flame is measured, while PCFC provides information on heat release rate and in turn, combustibility of volatiles generated during pyrolysis. However, PCFC does not consider mechanistic features such as dripping, swelling, shrinking, or intumescent effect.

This is also true in a forced-combustion bulk-scale test such as a cone calorimeter test, which provides heat release rate data along with other important information like ignition time, smoke production rate, and total heat released. Although the cone calorimeter data is influenced by the development of a physical barrier during the combustion process, thus registering a broader heat release rate plot, this test does not give any information on

the gas phase mechanisms. Orientation (horizontal or vertical) and confinement of samples (restrained or unrestrained) are other parameters that have to be considered in this test. Conducting the cone calorimeter test for a particular system is important as the different types of test can provide valuable insight into its combustion behaviour [140], which is essential for its development as a fire-retardant coating.

Importantly, the key question to be addressed is whether the inherent flammability and thermal characteristics of the materials that determine the performance criterion in these different materials- and bulk- scale tests can be correlated to a component-level aggressive scenario (e.g. single burning item fire test in EN13501-1 / EN13823) and structural-scale tests like BS 476-21 or EN13381-8. Figure 5-1 illustrates the concepts behind the different types of tests and highlights some of the correlations that have been found among the different tests from the literature.

Figure 5-1: Concepts behind UL 94, LOI, cone calorimeter, PCFC and TGA [102].

There were some studies correlating the behaviour of samples observed in materials-and bulk-scale tests, like PCFC with UL 94 and LOI tests with cone calorimeter tests [102, 139, 141-143]. As seen in Figure 5-1, the relationships identified by Lin, *et al* [102] are only applicable to flame-retardant (FR) polymers and it highlights the potential of achieving V-0 rating in UL 94 tests based on flammability characteristics obtained in LOI or PCFC tests. For example, FR polymers with LOI above 30 % would achieve a V-0 rating in UL94 tests (R1) and a sample with THR below 21 kJ/g, HRC below 380 J/g and T@PSHRR below 499 °C in a PCFC test would likely obtain V-0 rating in a UL94 test (R2). The flammability limits in R2 (i.e. THR below 21 kJ/g, HRC below 380 J/g and T@PSHRR below 499 °C obtained from PCFC) and R4 are useful as they provide an indication on the performance of the sample in a UL 94 test even before the test is conducted.

The notation R3 showing char formation in non-halogenated FR compounds is also important in LOI test as it prevents more materials from sustaining combustion, which is related to char yield obtained in PCFC and cone calorimeter tests. The notation R5 shows that samples with low THR values in PCFC are likely to exhibit low FIGRA values in cone calorimeter test, but a quantitative relationship is not established. This information may be useful if FIGRA is an important test criterion and PCFC can provide a primary indication of the FIGRA value before the cone calorimeter test is conducted. Despite the useful information established by Lin, *et al* [102], it is clear from Figure 5-1 that relationships relevant to the performance of fire-retardant coatings from materials- to structural-scale are lacking. For example, it was not mentioned if a fire-retardant coating with low THR in PCFC or V-0 rating in UL 94 would ensure a specific fire resistance rating.

Although there are extensive publications on the studies of different fire retardant polymer-based coatings used on small panels [85, 94, 99, 144], and very limited research articles that correlate different materials-scale flammability tests with bulk-scale tests [139], beyond this scale, there seems to be very little information in the literature correlating materials performance with structural fire resistance. This is particularly important and relevant as structural-scale fire resistance tests are usually much more expensive compared to materials- or bulk-scale tests. Even so,

- is it reasonable to correlate structural-scale behaviour of fire-protective coatings on steel members based on materials-scale tests? More importantly, is there any

evidence to correlate the results from a laboratory type furnace with coated steel substrates in one-dimensional set up with their behaviour in structural-scale fire tests where all four sides of the member are exposed to the same time-temperature curve such as ISO 834 fire curve?

- to what extent does the materials' inherent flammability characteristics obtained at materials-scale (mg) indicate the likely performance at bulk- (g) or even structural-scale (kg) tests?

These critical questions form the basis of this chapter, which aims to correlate the test data at different scales with one another and investigate if any of the materials- or bulk-scale tests can provide an early indication of the performance of the coating in a structural-scale fire test, which is far more expensive compared to materials- or bulk-scale tests. In this chapter, the current work will focus on intrinsic parameters of the coating such as its flammability behaviour and thermal stability, while extrinsic parameters such as cohesion and adhesion of char are not considered.

In addition, the emphasis will be on identifying the performance data from different tests, particularly if the materials-scale tests can be correlated to the performance in 1D bulk-scale electrical heating furnace tests, and ultimately to structural-scale fire tests. In the structural-scale tests, protected members are exposed to heating on all four sides and heat transfer occurs in all directions. Hence, the scale of the protected sample will also play an important role. Nonetheless, it should be noted that in materials-scale tests such as TGA and PCFC with a few milligrams of the polymer sample quantity, complete combustion of the polymer is expected, while in UL94 or LOI, this is not possible. Therefore, correlating FR properties such as heat release capacity (HRC) from PCFC with UL94 data (particularly with samples showing condensed phase phenomenon) is not reasonable, and so, in this context, UL94 and LOI tests will not be considered.

5.1 Test parameters

In this chapter, the fire-retardant coating system 3A was assessed using five types of test (i.e. TGA, PCFC, cone calorimeter, furnace tests and structural-scale fire test) conducted at three different scales (i.e. materials-, bulk- and structural-scale). The composition of coating 3A includes APP, PER and EG with a ratio of 3:1:1, at a total loading level of about 41 %. The composition of coating 3A is presented in Section 4.3 and its FR mechanism is discussed in Section 4.5. Neat acrylic resin (ACR) was assessed only with

TGA and PCFC tests. A summary of the parameters for the five types of test is shown in Table 5-1.

Table 5-1: Summary of parameters for tests at different scales.

Scale	Type of tests	Sample size	Average dry film thickness	Substrate size	Heating regime	Heat source	Decomposition Atmosphere	Section for test description
Materials-scale	TGA	8 mg to 10 mg	N.A.	N.A.	0.33 K/s	Electric furnace	Air and nitrogen	3.2.1
	PCFC	6 mg to 17 mg	N.A.		0.33 K/s and 1 K/s	Electric furnace	Nitrogen (pyrolysis chamber) and air (combustion chamber)	3.2.5
Bulk-scale	Cone calorimeter with substrate temperature measurements	Coated steel plate	2.65 mm & 5.25 mm	90 mm by 90 mm by 4 mm	35 kW/m ² & 50 kW/m ²	Radiant heating	Air	3.2.6
	Heat transfer tests	Coated steel plate	2.71 mm & 5.07 mm	160 mm by 160 mm by 6 mm	ISO 834 ¹	Electric furnace	Air	3.3.2
Structural-scale	Heat transfer test	Coated steel column	5.2 mm	Universal Beam 406 x 178 x 67 kg/m of 1 m	ISO 834	Gas-fuelled (CSTB)	Air	3.3.4

Note:

1. Please refer to Figure 2-2a for the time-temperature profile of ISO 834 standard fire curve

Chapter 3 outlined the different tests, of which specific details are provided under the various sections at the right most column of Table 5-1. Readers may refer to them for more complete information. The average dry film thicknesses are presented in Table 5-1 and minor deviations from the target dry film thickness of 2.5 mm and 5 mm were observed. For ease of comparison between the bulk- and structural-scale tests, the coatings will be referred to as 2.5 mm and 5 mm instead of the average dry film thickness.

The heating rates and sample weight differ with different scales of testing, which is due to limitations of different instruments and test protocols. It should also be noted that materials-scale tests only involve the fire-retardant coating and does not involve a substrate. This is because the objective of the test is to characterise a single material and the sample holder is not designed to account for the size and mass of a steel substrate. In addition to the test parameters presented in Table 5-1, the following points regarding the PCFC and cone calorimeter tests are highlighted;

- The sample mass in a PCFC test was adjusted to ensure that the minimum oxygen concentration level in the combustion zone reduced to 10 ± 3 % during the test,

as recommended by the manufacturer. However, the PCFC test involving composition 3A at 0.33 K/s has a minimum oxygen concentration level of 16 %. To meet the required minimum oxygen concentration level of 10 ± 3 %, the mass of the sample will have to be increased to at least 30 mg. This will result in an excessive volume of volatiles to be released and result in inaccurate results. Moreover, the size of the alumina cup is unable to contain a sample of 30 mg as expansion may damage the equipment. Hence, for the sample 3A at 0.33 K/s, the minimum oxygen concentration level is not used as a validity check.

- There were 2 different series of cone calorimeter tests conducted and the test results were compared within each series to minimise calibration or instrumentation errors. Thus, the 50 kW/m² heat flux tests were conducted in both series. For the first series, an irradiance flux of 50 kW/m² was imposed onto the coating surface of the samples and the test was stopped when HRR was stabilised. In the second series of tests, irradiance of both 35 kW/m² and 50 kW/m² were used, but the tests were stopped after 1 h of heat exposure. The two heat fluxes were selected in an attempt to investigate if the time-temperature profile of the steel substrate in the cone calorimeter, bulk- or structural-scale furnace test would be similar.
- In both series of the cone calorimeter tests, the steel substrate temperature was continuously measured with K-type thermocouples embedded onto the steel plate and connected to a data-logger. Despite the expected changes in heat flux experienced by the samples, expansion of the coating was allowed to simulate more realistic temperature rise of the steel substrate for both series of tests.

5.2 Correlating TGA, PCFC and fire test with ISO 834 standard fire curve

The HRR profiles, obtained from PCFC tests at 0.33 K/s and 1 K/s, 3A and ACR are shown in Figure 5-2a. The mass loss curve and the derivative mass loss profile of 3A in air and nitrogen environments, obtained from TGA tests at 0.33 K/s, are shown in Figure 5-2b.

Figure 5-2: (a) PCFC data of ACR and 3A at different heating rates. (b) TGA mass loss and derivative mass loss profiles of 3A in air and nitrogen environments.

From the PCFC data of ACR and 3A (Figure 5-2a), as expected, an increase in the peak HRR and a slight shift of the temperature corresponding to peak HRR towards higher temperature were noted with an increase in the heating rate. Composition 3A showed an increase of peak HRR from 81 W/g to 219 W/g when the heating rate was increased from 0.33 K/s to 1 K/s. The corresponding temperature increased from 366 °C to 408 °C. The same was also true for ACR (166 W/g at 0.33 K/s to 464 W/g at 1 K/s, with the corresponding temperature increased from 383 °C to 409 °C, respectively). Therefore, these changes could not be attributed to inherent chemical or physical nature of the materials. Similar behaviour was also observed in many other systems [141, 143, 145, 146]. This suggests that there is a direct correlation between the imposed heating rate and the rate of pyrolysis.

The heat release capacity (η_c) is a function of the heat of combustion of fuel gases per unit initial mass of solid ($h_{c,s}^0$), global activation energy for pyrolysis (E_a), natural number (e), gas constant (R), temperature of maximum pyrolysis (mass loss) rate (T_p) [119, 146], that is,

$$\eta_c = \frac{h_{c,s}^0 E_a}{e R T_p^2} \quad \text{Equation 5-1}$$

The HRC (η_c), as shown in Equation 5-1, is viewed to be a time- and rate-independent material property [119]. In line with this, in the current study, there were minimal differences in the HRC (obtained from software) of 3A, ~249 J/(gK) at 0.33 K/s compared to ~243 J/(gK) at 1 K/s. Even for ACR, variations in the HRC values variations were minimal, viz. 521 J/(gK) at 0.33 K/s to 517 J/(gK) at 1 K/s. In fact, Lyon and Walters

[147] after evaluating different polymer systems in a PCFC, proposed a linear relation between the maximum specific heat release rate and the heating rate until ~5 K/s. Beyond 5 K/s, the linear relation was no longer valid due to a significant thermal lag between the sample and the quartz tube that held the sample.

However, it was interesting to note that despite the higher peak HRR of ACR, irrespective of heating rate, the heat of complete combustion values suggested otherwise. The heat of complete combustion (HCC) values obtained from PCFC test for 3A were 19.5 kJ/g at 0.33 K/s and 18.9 kJ/g at 1 K/s, while for ACR, were 16.2 kJ/g at 0.33 K/s and 15.5 kJ/g at 1 K/s (normalised with respect to the resin content). Though small, the differences suggest a change in the volatiles released during the pyrolysis of 3A compared to ACR. This might possibly be due to secondary reactions between APP and ACR, apart from the primary intumescent reaction between PER and APP. Nonetheless, the temperature of the peak HRR obtained from PCFC matched well with the peak decomposition temperature in TGA (in both nitrogen and oxygen environments) (Figure 5-2b). This was irrespective of the heating rates within each TGA or PCFC tests. This suggested that the mass pyrolysed was combustible in the temperature range of 300 °C to 400 °C. If there were to be wide differences between the temperature for the peak heat release rate from PCFC and temperature for the maximum derivative mass loss from TGA, it would suggest that the mass lost in TGA did not lead to combustible volatiles, which was not the case with 3A and ACR. Oxidation of the char, as identified in TGA in the temperature range of 500 °C to 600 °C (Figure 5-2b) in the air environment, understandably, would not be picked up in PCFC test. Another similarity was the residual masses of the samples for these two tests; the residual mass in PCFC for the intumescent coating when conducted at 0.33 K/s and 1 K/s was 23 % and 20 %, respectively, while in TGA in air and nitrogen at 600 °C, it was 20 % and 22 %, respectively. The residual masses of PCFC and TGA at 600 °C were similar and it suggested that decomposition of resin was the main reason behind the majority of mass lost by 3A in TGA. The deviation in mass loss curves for air and nitrogen environment in Figure 5-2b after 700 °C was due to oxidation of EG char (Figure 5-2b). The apparent reduction in mass in air was not observed in nitrogen as oxidation did not occur in pyrolysis environment.

Before correlating the results from PCFC and TGA with the ISO 834 standard fire curve (Figure 2-2a), it is important to compare the heating rates among the different tests, which are presented in Table 5-2.

Table 5-2: Heating rates comparison among the different tests.

ISO 834 standard fire curve		PCFC	TGA
Time duration	Heating rate (K/s)	Constant heating rate throughout the test (K/s)	
Between 0 to 1 min	5.47	0.33 K/s & 1 K/s (imposed in this study)	0.33 K/s (imposed in this study)
Between 1 to 2 min	1.59		
Between 2 to 5 min	0.73		
Between 5 to 10 min	0.34		
Between 10 to 15 min	0.20		

The imposed heating rate of 1 K/s in PCFC corresponds fairly to the heating rate of ISO 834 standard fire curve between 2 to 5 min, while 0.33 K/s in PCFC and TGA corresponds to the heating rate of ISO 834 standard fire curve between 5 to 10 min. In view of the similarities in heating rates and the discussion in Section 5.2, following findings that correlate PCFC and TGA results with the ISO 834 standard fire curve (Figure 2-2a) are listed as follows:

- The high heating rates from the ISO 834 fire curve scenario, particularly during the initial 15 min (Table 5-2) suggested that a higher value of peak HRR was to be expected during the initial period. This would dictate the initial rise of temperature of the steel substrate underneath, depending on the volume (thickness) of the coating material that was involved in the pyrolysis during this period. It is important to note that in TGA and PCFC tests, only a specific heating rate was employed throughout the test, while in the ISO 834 furnace tests, the imposed heating rate (K/s) varied widely throughout the test. This aspect in combination with the intumescent phenomenon should be considered when correlating the test results from different scales. Notably, the rise in temperature of the steel substrate with time is taken as an important parameter.
- The values of peak HRR, THR and HCC are critical parameters that could affect continuous flaming of the sample, ultimately influencing the heat transfer to the steel substrate.
- Thermal stability variations of polymers (even with an increment of 30 °C to 50 °C from any polymer coating system) have negligible effect on initial heat transfer considering the high heating rate for ISO 834 fire test and the attainment of gas temperature of ~683 °C (in the first 10 min), which was well beyond the thermal decomposition temperature of most of the commonly used polymers.

5.3 Correlating TGA, PCFC and cone calorimeter test

The thickness of the sample, the mechanisms of degradation and the type of additives become more critical when changing from materials- to bulk-scale tests. This was obvious from a comparison of PCFC and TGA results (Figure 5-2a and b) with cone calorimeter data in terms of mass loss and heat release rates, as shown in Figure 5-3.

Figure 5-3: HRR curve and normalised mass loss profile obtained in cone calorimeter test for a 2.5 mm thick FR coating with an imposed heat flux of 50 kW/m^2 .

The sharp drop in mass loss, typically seen in TGA between 300°C to 400°C for ACR and 3A (Figure 5-2b), or the rapid increase in HRR seen in PCFC in similar temperature regimes (involving the entire volume of the sample) was not as obvious in the cone calorimeter tests. An example of this behaviour for 2.5 mm thick coating is seen in Figure 5-3. This did not mean that there was no rise in the temperature of the substrate or HRR. Considering the imposed heat flux of 50 kW/m^2 on the sample in the cone calorimeter test (i.e., a rapid heating rate or a high temperature gradient across the thickness of the coating), this would result in pyrolysing a huge volume of the sample in the first few minutes of the test, while a more homogeneous insulating barrier beneath the pyrolysis zone was simultaneously established.

The insulating barrier formed on the surface of the sample was due to the expansion of EG, which reduced the heat transfer to the underlying layers. It should also be noted that due to swelling of the sample, the heat flux imposed on the sample surface in the cone calorimeter test would be different from the initial heat flux. Thus, the thermal load varied

during the test. This is an important parameter that could not be considered or measured in the current work. Nonetheless, it is important to note that the behaviour of coating depends on its thickness, that is, during the initial phase of heating for thermally thin samples, the entire volume of the sample would be pyrolysed simultaneously due to absence of thermal or viscosity gradients through the coating thickness and the heat release rate profile might be very similar to that of PCFC tests. In the current scenario, thermally thick samples (2.5 mm and 5 mm) resulted in broadening of HRR curves. This was also evident in Figure 5-3, in which decreasing gradient of mass loss with increasing time, $-0.156\text{ \%}/\text{s}$ from 0 s to 400 s, $-0.0792\text{ \%}/\text{s}$ from 400 s to 600 s and $-0.0422\text{ \%}/\text{s}$ from 600 s to 1100 s was observed.

Depending on the volume of sample pyrolysed per unit time, the rise in substrate (steel) temperature would vary. The measured temperature profiles of the steel substrate in cone calorimeter along with the HRR patterns shown in Figure 5-4 confirmed the relationship between pyrolysis and rise in temperature of the steel substrate.

Figure 5-4: Correlations between HRR data in cone calorimeter, temperature of the steel substrate and derivative for steel substrate for (a) 2.5 mm thick and (b) 5 mm thick coating 3A.

As evident in Figure 5-4, by 200 s, the steel temperature in the cone calorimeter test was raised to $\sim 178\text{ }^{\circ}\text{C}$ and $\sim 98\text{ }^{\circ}\text{C}$ for 2.5 mm and 5 mm thick coatings, respectively. For example, within that 200 s, there was a 35 % mass loss for the 2.5 mm thick sample,

which also explained why the time-to-ignition of the intumescent sample (by visual observation) was ~9 s for 2.5 mm. Furthermore, the time-to-flame out (~401 s and ~848 s for 2.5 mm and 5 mm, respectively), from visual observation, differed for the two samples and confirmed that pyrolysis was responsible for the initial rise in temperature of the steel substrate.

In summary, many similarities and critical information could be drawn from the materials- (TGA/PCFC) and bulk-scale tests like cone calorimeter. The thickness of sample (coating), imposed heating rate and the volume of flammable/combustible volatiles released are a few key parameters that provide valuable insight on how the coating may behave in a structural-scale test where ISO 834 fire curve is imposed. It should be noted that the heat flux in a furnace test varies with thermal load, which differs from a cone calorimeter test where heat flux is maintained at a constant rate throughout the test.

5.4 Correlating cone calorimeter, bulk- and structural-scale furnace tests

The time-temperature profiles of the 2.5 mm and 5 mm intumescent coating in the 1D heat transfer test are shown in Figure 5-5. Interestingly, the increase in temperature of the steel substrate due to pyrolysis also hold for 1D heat transfer (bulk) test.

Figure 5-5: Time-temperature profiles and derivative curves obtained from steel substrate with 2.5 mm and 5 mm intumescent coating when exposed to ISO 834 fire curve in an electrical furnace.

As the heating rates in the first 10 min to 15 min in the ISO 834 fire curve has similarities with the imposed heating rate in PCFC, or higher temperature gradient experienced in the cone calorimeter, a higher value of peak HRR was expected in the furnace test during the initial period. This was due to the higher volume (thickness) of material involved in the pyrolysis. This results in ignition/flaming of the sample until the HRR values are lowered due to formation of an insulating barrier. Consequently, the initial steep gradient in the derivative time-temperature profiles of underneath substrate is noted in Figure 5-5. With 2.5 mm thick coating, at 15 min, the steel temperature was 214 °C, but with 5 mm thick coating, it was only 149 °C. A similar trend was observed even with the temperature profiles obtained from cone calorimeter tests as seen in Figure 5-4a and b.

After the matrix resin has been completely pyrolysed, the gradient of the time-temperature profile (furnace test) will solely depend on thermal conductivity of the char formed, and so the gradient would be constant, as the thermal load in the furnace was almost constant during this period. For example, a constant gradient of 0.0767 K/s was observed for the 2.5 mm sample between 15 min to 77 min, while 0.0675 K/s was noted for the 5 mm thick sample between 18 min and 97 min (Figure 5-5). Thermal conductivity value of the char has a significant influence on the performance of coating as it governs the rise in temperature after the initial period of 10 to 15 min. With this parameter, it is possible to predict the rise in temperature of the substrate.

Indeed, though qualitatively, the findings from cone calorimeter and furnace results were broadly similar; in Figure 5-6, the time-temperature profiles for the steel substrate obtained in the cone calorimeter, bulk-scale and structural-scale tests are presented. The time-temperature profile of the steel substrate obtained from the structural-scale fire test is based on the average time-temperature of five thermocouples readings. The time-temperature data for the five thermocouples are consistent with one another and it corroborates well with the test setup as the steel substrate is heated from all directions. Hence, only the average time-temperature profile will be shown in Figure 5-6. It should be noted that the bulk-scale furnace test (red dash line) in Figure 5-6 is the same test as the bulk-scale furnace test (red dash line) in Figure 5-5. The time-temperature profile for the bulk-scale furnace is included in Figure 5-6 again for ease of comparison.

Figure 5-6: Time-temperature profiles of steel substrate in a cone calorimeter test conducted at 35 and 50 kW/m² along with the profile of steel substrate with 5 mm thick coating in bulk- and structural-scale furnace tests.

A developing fire is characterised by an external heat flux of 20 kW/m² to 60 kW/m², while a fully developed fire is characterised by an external heat flux greater than 50 kW/m² [10]. Cone calorimeter data obtained with respective heat fluxes of 35 and 50 kW/m² are shown in Figure 5-6. It is interesting to note that the time-temperature profiles obtained with cone calorimeter (at both 35 kW/m² and 50 kW/m²) showed a parabolic nature with decreasing gradient and attained almost a plateau in temperature after 35 min into the test. The swelling of the sample and the formation of expanded graphite network resulted in a change of irradiance imposed on the sample. As the oxidation of this network seemed to be absent under the imposed conditions, it caused a constant temperature profile after 35 min. However, in the actual furnace tests (both electrical and gas-fuelled), this plateau was not present due to relatively higher temperatures and possibly higher flux imposed on the sample. Unlike the cone calorimeter tests, oxidation of char possibly took place in both furnace tests, therefore resulting in a steady rise in the temperature of the substrate. The differences in behaviour between cone calorimeter tests at 35 kW/m² and 50 kW/m² and furnace tests (ISO 834) were significant. Behaviour of structural-scale tests deviated from the heat release rate seen when comparing cone calorimeter tests. Other factors like thickness and extent of swelling might further influenced the differences while comparing cone calorimeter data with furnace data.

The complications further escalate if the discussions and observations were extended to full-scale testing of a column ranging from 1 m to 4 m length and with different section factors. Some of the extrinsic issues that can be expected include: higher heat fluxes imposed to the edges of an H or I steel section, irregular coverage of expanded char on those edges (depending on section factor) resulting in through cracks, cohesion of char across the surface area, self-weight of char, and more importantly, mechanical load imposed on the column during the fire test. In fact, preliminary investigations on different compositions of intumescent formulations even under non-load-bearing conditions have revealed that cohesion of char was poor in the EG-based systems due to rapid and non-directional expansion of EG. More importantly, delamination between the char and the substrate occurred easily due to a reduction in the contact surface area as a result of expansion of EG/char. These parameters resulted in poor performance in the structural-scale fire test, which was observed in Figure 5-6, as the temperature of steel was obviously much lower in the 1D bulk-scale test compared to the 3D structural-scale test after 30 min. Hence, the negative performance of the coating at structural scale was completely masked in 1D furnace tests. Notably, the structural-scale furnace test presents the most austere form of testing compared to the materials- and bulk-scale test, since the former is most concerned with the integrity of char formation. Clearly, structural-scale tests focus on extrinsic parameters which relate to adhesion and cohesion of char, while materials- and bulk-scale tests heavily hinge on intrinsic parameters (e.g. flammability characteristic).

5.5 Relationships identified for materials- to structural-scale tests

An attempt was made to schematically represent the time-temperature profile of the steel substrate in bulk- and structural-scale fire tests as shown in Figure 5-7.

Figure 5-7: Schematic increase in time-temperature profile of a steel substrate in a furnace test.

Based on the furnace tests conducted and the insights derived in this chapter, it is expected for three different gradients to be seen in the time-temperature profile of a protected steel substrate in bulk- and structural-scale fire tests. In the initial stage (Segment A), a rapid rise in temperature is expected and the rate of increase in temperature of the steel substrate would be the largest. This corresponds with the pyrolysis of the coating. As the test progresses, the rate of increase in temperature of the steel substrate decreases and is represented by Segment B and Segment C. The changes in temperature gradient (Segment A to C) are associated with the behaviour of the fire-retardant coating throughout the tests and certain flammability characteristics are identified with different types of tests at different scales. Table 5-3 summarises the flammability characteristics of the coating based on the corresponding segments in Figure 5-7.

Table 5-3: Summary of behaviour of coating at different stages in a structural-scale fire test and its relevance to time-temperature profile.

Segment	Dominating mechanism	Description	Relevant test(s)
A	Thermal stability & flammability	<ul style="list-style-type: none"> The initial rapid rise in the temperature of the substrate (during the first 10-15 min) is a result of higher HRR values and the volume of material participating in the pyrolysis process per unit time. <p><u>Key parameters:</u> heating rate, HRR, HRC and THR values</p>	PCFC, TGA, cone calorimeter
B		<ul style="list-style-type: none"> Extent of pyrolysis (pyrolysis depth increases), but at a slower rate, due to thermal barrier formed on the top surface. <p><u>Key parameters:</u> The magnitude of swelling of the char on the top surface of the sample and its conductivity</p>	Cone calorimeter
C	Conductivity	<ul style="list-style-type: none"> Nothing to pyrolyse, and so the temperature rise of steel would be at a constant rate. <p><u>Key parameters:</u> Conductivity of residue, char cohesion and its adhesion to the substrate</p>	Furnace test

In Segment A, the initial rapid rise in temperature of a protected steel substrate is due to the result of higher HRR values and the volume of material participating in pyrolysis process per unit time. This suggests that flammability characteristics such as HRR and THR of the fire-retardant coating will affect the rise in steel temperature in the initial 10 to 15 min of the test. Moreover, the ignition of the coating should only be limited to the top few layers during this period of time and hence is similar to the sample size of PCFC of TGA, in which only the fire-retardant materials are involved. This was also observed in cone calorimeter tests where the initial increase in steel temperature (Figure 5-4) corroborated well with the time-to-ignition values. Improving thermal stability of a polymer to reduce HRR, HRC and THR value can reduce the rise in temperature in Segment A. However, it is postulated here that even with an increase of 30 °C to 50 °C in thermal stability may not have significant enhancement due to the exceptionally high heating rate in ISO 834 fire curve.

In Segment B, the top layers will be pyrolysed and a layer of char will be formed, which will result in a reduction in the rate of the increase in temperature. The char layer formed at the top layers reduce the rate of pyrolysis of underlying layers and consequently reduce the rise in temperature of the steel substrate. Materials-scale tests such as PCFC and TGA will not provide much information on the behaviour of the coating at this stage of the test. This is because the volume of the materials involved in the materials-scale tests are not sufficient for formation of char over a thick sample to take place. Instead, the whole sample, in milligrams, is expected to participate in char formation or pyrolysis almost instantaneously. Therefore, the behaviour in Segment B will only become apparent in bulk-scale tests. Improving char formation or increasing the magnitude of swelling at this stage will help reduce pyrolysis rate and possibly alter the rise in temperature of the steel substrate. This may help to increase the performance of the fire-retardant coating.

As the test continues, the underlying layers pyrolysed and form char. A stable char residue will eventually be formed. The conductivity of the char governs the rate of increase in temperature of the steel substrate in Segment C. The increase in temperature will remain constant for the remaining duration of the test unless the char residue exhibits adhesive or cohesive failure. Since the cone calorimeter test with the horizontal test-setup will not be able to capture delamination of char residue from a substrate or cohesive failure of the char residue, this behaviour can *only be investigated in a structural-scale furnace test*.

5.6 Conclusion

This chapter dealt with the relationships between the data obtained from material-scales (TGA and PCFC), bulk-scales tests like cone calorimeter and 1D furnace and structural-scale fire test. This was carried out from the perspective of identifying key parameters across these different scales that can assist in predicting the fire-performance of coatings at structural-scale. Interesting insights were derived from the different tests carried out at different scales on the increase in temperature of the steel substrate in a furnace test imposed with an ISO 834 standard fire curve. These observations are valid within the boundaries of the assumption that the influence of parameters on fire performance is negligible (i.e. cohesion and adhesion of char is not considered). In summary, the following relationships have been identified;

- Intrinsic parameters such as flammability characteristics of the coating obtained using PCFC and cone calorimeter affect initial rise in steel temperature within the first 10 to 15 min of the bulk- and structural-scale fire test

- After the first 10 to 15 min, char was formed on the top layers, which reduces the rate of pyrolysis of the underlying materials and results in a slower rate of increase in temperature during the structural-scale fire test. Materials-scale tests no longer provide much indication of the performance of the coating at this stage.
- Lastly, the entire thickness of the fire-retardant coating forms char and further reduces the rate of increase in temperature. This stage is no longer related to the flammability characteristics of the material as conductivity of char governs the rate of increase in temperature. The rate of increase in temperature is expected to remain constant unless adhesion or cohesion failure of the char occurs. At this stage, extrinsic parameters dominate the behaviour of the coating.

Chapter 6 Thermal properties and numerical modelling of developed coating

As discussed in Section 5.5, thermal conductivity is a critical parameter that can be used to predict the performance of the FR coating in a furnace test. It will be ideal if conductivity values can be measured and used directly in a numerical model to predict the performance of the developed coating on a substrate. However, it is a challenging task to measure this property due to poor char cohesion and complex thermal and physical reactions when exposed to heat. For example, the guarded hot plate method requires the samples to be sandwiched between two heating plates, which will hinder expansion of the coating. The laser flash technique is also not applicable as it requires the use of a reference material and does not allow excessive changes in the sample dimensions and release of volatiles which will disrupt the laser sensors during measurements.

In this chapter, the measured conductivity values obtained using Modified Transient Plane Source (MTPS) technique (Section 3.2.8) and specific heat capacity values (Section 3.2.9) are compared with effective thermal conductivity values obtained from EN 13381-8. Limitations of using the measured conductivity values are discussed and an alternative method to obtain effective thermal conductivity values from cone calorimeter tests are discussed. The effective thermal conductivity values and specific heat capacity values are validated using numerical models. In addition, the effective thermal conductivity values obtained from cone calorimeter tests are used to predict the performance of the fire protective coating in a structural-scale fire test.

6.1 Thermal properties

6.1.1 Specific heat capacity

The specific heat capacity measured using the Modulated Differential Scanning Calorimetry (MDSC) (Section 3.2.9) is presented in Figure 6-1. A general increase in specific heat capacity value is observed with an increase in temperature.

Figure 6-1: Measured and selected specific heat capacity profiles of the coating with respect to temperature.

However, a sudden spike in specific heat capacity is seen between 180 °C to 200 °C, which corresponds the expansion of EG and a sudden release of volatiles (Equation 2-1) within a small volume area. This causes inaccuracy in the measurements which does not accurately represent the material property as the volatiles cannot be released fast enough from the MDSC sample holder. With excessive volatiles trapped in the pan, specific heat capacity is expected to increase as more heat is required to raise the sample and the trapped volatiles by one degree. Decomposition of the coating occurs after 200 °C and an increase in specific heat capacity is expected with a more gradual release of volatiles over 300 °C to 400 °C as seen in TGA studies (Figure 4-4a).

A slight reduction in specific heat capacity can be observed at between 300 °C and 350 °C. There are numerous phenomena occurring during this temperature range and they can be attributed to the reduction in specific heat capacity. These include chemical changes (e.g. decomposition of polymer and reactions between additives leading to release of volatiles) and physical changes (e.g. changes in melt flow and loss in mass) that occur simultaneously during this range, making it challenging to elucidate the reduction. However, the reduction in mass due to decomposition and the presence of volatiles can result in a reduction as lesser energy is required to increase the sample by a single degree. Hence, the specific heat capacity values are selected at ambient, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C and 350 °C for numerical modelling. These values are summarised in Table 6-1.

Table 6-1: Selected specific heat capacity values of 3A for numerical simulations.

Temperature ($^{\circ}\text{C}$)	Specific Heat Capacity ($\text{J}/(\text{kg}^{\circ}\text{C})$)
23	1150
100	1470
150	1523
200	1738
250	1886
300	2211
350	2069

6.1.2 Measured thermal conductivity

The test parameters and conductivity values are summarised in Table 6-2.

Table 6-2: Parameters and measured conductivity values.

Adopted test calibration method	Contact agent	Temperature ($^{\circ}\text{C}$)	Conductivity ($\text{W}/(\text{mK})$)	Weight (g)
Polymer	Grease	26	0.441	500
		100	0.412	500
		200	0.321	500
Foam	N.A.	300	0.082	380
		400	0.050	243
		500	0.050	49
		600	0.034	0
		700	0.030	0

The measured conductivity values are based on seven different isothermal tests, with two test methods (i.e. polymer and foam). The tests conducted at 200 $^{\circ}\text{C}$ and below were assessed using the polymer test method and a thin film of grease was used as the contact agent between the sensor and the sample. The use of water as a contact agent was avoided as the sample tends to absorb water and increased the inaccuracy of the data. The tests above 300 $^{\circ}\text{C}$ were conducted with foam test method since the EG clearly expanded. It is worth noting that the weight on the sample is reduced as the cohesion of char structure is poor. The weight is selected by trial and error and it is undesirable to compress the expanded graphite network during the test.

The measured conductivity value at ambient was 0.441 $\text{W}/(\text{mK})$ and minor reduction was observed at 100 $^{\circ}\text{C}$. Since mass loss was not observed in the TGA studies (Figure 4-4a), the reduction cannot be attributed to a loss in water. Instead, as gleaned from the rheological studies (Figure 4-6a), movement in polymer chains was observed between 30

$^{\circ}\text{C}$ to 100°C and may attribute to a minor reduction in conductivity value. A further reduction in conductivity can be seen at 200°C as EG expands. The sample at 200°C consists of polymer and graphite network that was partially exfoliated. It should be pointed out that the contact between the sample and the sensor was not ideal due to the rough surface area and may affect the results even with grease as the contact agent. An apparent decrease in the conductivity value was observed after 300°C as the exfoliated graphite network had formed and the matrix was dominated by air voids and char. As temperature increased from 300°C to 700°C , a minor reduction in conductivity value was observed and it fell within the range of 0.082 W/(mK) to 0.030 W/(mK) . The reduction in applied weight provided insight into the reduction of carbonaceous material in the coating. As temperature increased, the ability for the exfoliated graphite network to support weight decreased as it exhibited poor cohesion. This was also observed in TGA studies, where oxidation of char occurs between 400°C to 600°C and the temperature remains largely at plateau from 600°C to 900°C . Since the sample can hardly take any load after 600°C , it is expected that the carbonaceous material was oxidised, leaving behind exfoliated graphite network. The conductivity values were only recorded up to 700°C . Above this temperature, the remaining exfoliated graphite network tend to oxidise in the furnace and was prone to cohesive failure when handling. This hindered the sampling procedure as it broke apart before the heated sample was removed and placed on the MTPS sensor.

According to Gardelle, *et al* [99], conductivity values of EG-based silicone matrix is 0.5 W/(mK) at ambient, and it reduces to 0.21 W/(mK) at 400°C . In a fire scenario, the samples are expected to exhibit a higher expansion ratio which will result in even lower thermal conductivity values. This suggested that the measured values may not represent the thermal property of the coating in a fire test. Hence, the *effective thermal conductivity* of the coating will be calculated instead for finite element modelling of fire tests.

6.2 Method A - Effective thermal conductivity based on structural-scale fire tests

The procedure to calculate the effective thermal conductivity of a fire protective coating on a steel section exposed to ISO 834 standard fire curve is described in EN 13381-8, Annex E3. In order to obtain a characteristic conductivity value, extensive fire tests need to be conducted and the time-temperature curves of different columns with different section factors and thicknesses are required. In this thesis, two structural-scale fire tests with the same type of coating and section factor were conducted (Section 3.3.3). The

average thicknesses of the coatings were 3.7 mm and 5.2 mm. Hence, the empirically informed procedure, Variable λ method, described in EN13381-8 Annex E3 was adapted and summarised in Figure 6-2.

Figure 6-2: Flowchart showing an adapted procedure to calculate effective thermal conductivity based on fire tests.

where

$\Delta\theta_{s,t}$: rise in steel section temperature over time step [K]

$\theta_{s,t}$: steel section temperature [K]

$\Delta\theta_t$: rise in furnace temperature over time step [K]

θ_t : furnace temperature [K]

$\theta_{p,t}$: temperature of coating at time t [K]

$\lambda_{p,t}$: thermal conductivity at time t [W/(mK)]

λ_{p,θ_p} : thermal conductivity with respect to coating's temperature [W/(mK)]

d_p : dry film thickness of coating [m]

$\frac{A_p}{V}$: steel section factor [m⁻¹]

c_s : specific heat capacity of steel [J/(kgK)]

ρ_s : density of steel [kg/m³]

Δt : time increment [s]

The basic equation (Equation 6-1) in Step 1 of Figure 6-2 is based on energy balance during a given time step [148]. Before proceeding with the calculations, average temperature between two time increments is based on a linearly interpolated temperature between the start and the end of the time step. This is because a decrease in temperature can occur due to fluctuations in thermocouple readings and will result in negative increment in the data, which is not representative of the material behaviour. The thermal conductivity value for each time step (Equation 6-2) is derived from Equation 6-1 and is expressed in Step 3 of Figure 6-2. As recommended in EN 13381-8, the chosen time increment shall not be more than 80% of the critical time increment as described in Equation 6-3. This check is performed in Step 4 to ensure that the calculated variable conductivity value in Step 3 satisfies numerical stability. If the calculated critical time exceeds 30 s, the time increment for the procedure should be 30 s.

The temperature of the coating is assumed to be the average temperature of the increment in the furnace temperature and the steel temperature as expressed in Equation 6-4. This allows the temperature of the coating for every time step to be computed and it corresponds to the thermal conductivity value at the same time step. The effective conductivity value is taken to be an average of the variable conductivity values within a certain temperature interval. For example, effective conductivity value at 325 °C is the

average of elementary variable conductivity values between 300 °C to 350 °C. The calculations for Step 1 to 6 were performed using Microsoft Excel Visual Basic Application (VBA) and the code is presented in Appendix A. The last step involves verification of the calculated values using ABAQUS software.

The assumptions and limitations of the model are as follows;

1. Temperature on the surface of the coating surrounding the steel section is assumed to be the average temperature of the furnace. Shadow effect on the web caused by the flanges is not accounted for.
2. Average temperature of steel was used in the calculations to minimise differences in temperature profiles at the flanges and the web.
3. Radiation of the flame back to the coating after the sample has been ignited is not accounted for.
4. Density of coating is assumed to be constant and does not change with temperature

The effective thermal conductivity values calculated using method A, for 3.7 mm and 5.2 mm coatings, are presented Table 6-3.

Table 6-3: Summary of effective thermal conductivity values.

Temperature (°C)	Effective thermal conductivity (W/(mK))	
	3.7 mm coating	5.2 mm coating
25	0.1427	0.0550
75	0.1278	0.0873
125	0.0832	0.0714
175	0.0578	0.0541
275	0.0479	0.0471
325	0.0411	0.0458
375	0.0412	0.0416
425	0.0432	0.0477
475	0.0351	0.0379
525	0.0341	0.0333
575	0.0314	0.0316
625	0.0353	0.0303
675	0.0398	0.0389
725	0.0451	0.0492
775	0.0535	0.0594
825	0.0797	0.0718
875	0.0743	0.1104
925	0.0989	0.0975
975	0.0734	-

Note: Effective thermal conductivity values are shown to 4 significant figures.

As shown in Table 6-3, for 3.7 mm coating, the effective thermal conductivity decreased from 0.1427 W/(mK) to a minimum of 0.0314 W/(mK) at 575 °C. The effective thermal conductivity remained relatively consistent between 325 °C to 725 °C. A rise in conductivity value between 850 °C to 950 °C was observed and was likely to be caused by a decrease in the thickness of the graphite network due to oxidation or cohesive failure of the coating. A similar trend was observed for the 5.2 mm coating, except that the initial (25 °C to 100 °C) effective thermal conductivity value is even lower. The low effective thermal conductivity values at 25 °C for the 5.2 mm coating was not expected and the error could be the result of the following;

- 1) With a rapid increase in temperature, few data points were used to compute the mean conductivity value at low temperature as it required longer time for the steel substrate to heat up with a 5.2 mm thick coating. It should be noted that the effective conductivity value for 25 °C was based on 2 variable conductivity values while the effective conductivity values for 75 °C, 125 °C and 175 °C were based on 1 variable conductivity values.
- 2) The average furnace temperature was used to compute the effective thermal conductivity. Since this phenomenon is only observed at the initial stage of the test and gases in the furnaces are not uniformly heated, it is possible that the 5.2 mm coating was subjected to a slightly higher temperature curve.

6.2.1 Numerical validation of effective thermal conductivity obtained from fire tests
ABAQUS V6.14-1 was used to verify the calculated effective thermal conductivity. A 2D model depicting the steel profile Universal Beam 406 x 178 x 67 kg/m was constructed and the coating encapsulates the perimeter of the steel beam as shown in Figure 6-3. As described in Figure 3-17, the steel section was suspended in the gas furnace and the profile of the steel columns was heated from all sides. Hence, heat is mainly transferred from the surface of the steel to its core and 2D model can be used.

Figure 6-3: Typical model and result obtained from heat transfer analysis for structural fire test.

The steel beam and coating were modelled using 8-node quadratic heat transfer (DC2D8) elements and heat transfer analysis was performed. The 3.7 mm and 5.2 mm coatings were modelled using a mesh size of 1.23 mm and 1.73 mm, respectively. This allowed the coatings to be represented with 3 layers in the model. The mesh size of the steel substrate corresponded to the mesh size of the respective coatings. A tie-constraint was used to simulate perfect bond between the coating and the steel beam. The average furnace temperature was used as an input value and heat was transferred to the profile of the I-section. Since the ISO 834 standard fire curve was imposed on the specimens, a convection coefficient of $25 \text{ W/m}^2\text{K}$ was adopted in the model. The key thermal properties used to simulate heat transfer for coating and steel are summarised in Table 6-4.

Table 6-4: Summary of key parameters of coating and steel materials used in numerical model.

Parameter	Coating	Steel
Emissivity	0.92	-
Density (kg/m^3)	1100	7850
Specific heat capacity ($\text{J}/(\text{kg}^\circ\text{C})$)	Values in Table 6-1	BS EN 1993-1-2 Section 3.4.1.2
Thermal conductivity ($\text{W}/(\text{mK})$)	Values in Table 6-3	BS EN 1993-1-2 Section 3.4.1.3

Note:

1. Change in density with temperature of the coating is not accounted for in the model.
2. Specific heat capacity of coating is assumed to be constant after 350°C .
3. Thermal conductivity of coating is assumed to be constant after 700°C

The time-temperature profiles of the steel section in the numerical models for both thicknesses are compared to the experimental values as shown in Figure 6-4. It should be noted that the time-temperature profiles in Figure 6-4 are based on the average time-temperature profile of web and flanges obtained from the experimental results and numerical results. The selected points in Figure 6-3 (red arrows) correspond to the locations of the thermocouples shown in Figure 3-17e.

Figure 6-4: Comparison of time-temperature profiles of steel substrate obtained from numerical simulation with experimental results.

A minor mismatch in the results obtained for 5.2 mm coating can be seen at the initial stage of the tests and this could be attributed to the initial effective conductivity value at ambient, which has been explained in Section 6.2. However, it is clear that the time-temperature profiles for both thicknesses are in good agreement with the experimental results. The calculated effective thermal conductivity values for 3.7 mm and 5.2 mm coatings are compared with the measured thermal conductivity values obtained from

C-Therm in Figure 6-5 to assess if the measured conductivity values can be used to predict the performance of the coating in a structural-scale fire test.

Figure 6-5: Thermal conductivity calculated from fire tests and measured conductivity values from C-Therm.

To a certain extent, the measured conductivity values in Table 6-2 can be used to estimate effective conductivity values of the char formed during the structural-scale fire test. This is corroborated with good agreement in the measured and calculated conductivity values between 300 °C to 700 °C as presented in Figure 6-5. Moreover, the exfoliated graphite network is expected to remain relatively stable within this temperature range since the expansion of EG occurs at ~ 200 °C. The apparent mismatch in conductivity values from ambient to 200 °C is that the expansion of the coating differs in these two tests. The measured conductivity values assume that the sample is exposed to a uniform temperature since the test was conducted at isothermal conditions, whereas the calculated values were associated with an average incremental temperature of furnace and steel (Step 5 in Figure 6-2). This suggested that the initial effective conductivity values are not as representative since the surface of the coating will be initially exposed to a much higher temperature compared to the underlying materials.

6.3 Method B - Effective thermal conductivity based on cone calorimeter tests

The measured conductivity values can only provide an indication of the effective conductivity values between 300 °C to 700 °C. Therefore, as an alternative, effective thermal conductivity was calculated using the cone calorimeter tests results. This methodology was proposed by Wang, *et al* [110] and it uses the heat balance equation to

determine the coating surface temperature before calculating effective thermal conductivity. The experimental setup is presented in Figure 6-6.

Figure 6-6: Experimental setup and key parameters of the cone calorimeter setup.

The coating was applied over a steel plate and a thermocouple was used to measure the time-temperature profile of the coating-steel interface throughout the test. The thermal wool was placed beneath the steel plate and a second thermocouple was placed in the middle of the wool to measure its time-temperature. The effective thermal conductivity can be calculated from a heat balance equation based on energy supplied from the conical heater and into the thermal wool. This requires the time-temperature profile of the coating surface temperature (T_{ss}), which needs to be calculated before the effective thermal conductivity of the coating can be determined. The procedure to calculate effective thermal conductivity of the coating is summarised in Figure 6-7 and a MATLAB code (Appendix B) was developed to perform the calculations.

Figure 6-7: Flowchart showing the procedure to calculate effective thermal conductivity based on cone calorimeter test.

where

Q_w	: heat loss from steel to wool [W/m ²]
Q_c	: heat flow from the cone to surface of coating (i.e. heat flux of cone heater) [W/m ²]
λ_w	: thermal conductivity of wool [W/(mK)]
k_p	: thermal conductivity of coating [W/(mK)]
ΔT_s	: rise in steel temperature over time [K]
T_s	: temperature of steel at time t [K]
T_w	: temperature of wool at time t [K]
ΔT_{ss}	: rise in coating surface temperature [K]
T_{ss}	: surface temperature of coating at time t [K]
T_c	: temperature of cone heater at time t [K]
d_w	: thickness of wool [m]
d_p	: dry film thickness of coating [m]
d_s	: thickness of steel [m]
ρ_p	: density of coating [kg/m ³]
ρ_s	: density of steel [kg/m ³]
c_p	: specific heat capacity of coating [J/(kgK)]
c_s	: specific heat capacity of steel [J/(kgK)]
Δt	: time increment [s]
ε	: emissivity of coating, 0.92
σ	: Stefan-Boltzmann constant, 5.67×10^{-8} [W/(m ² K ⁴)]
h_c	: convection coefficient, 20 [W/(m ² K)]

The time-temperature profiles of steel substrate, thermal wool and radial cone heater are obtained using the test setup shown in Figure 6-6, which is described as Step 1 in Figure 6-7. It should be noted that the temperature of the steel plate needs to be incrementally obtained or unrealistic conductivity values will be derived. This typically happens at the start of the test (~ 10 to 20 s into the test depending on the thickness of the coating) where a short period of time is required for the sample and the steel to heat up. These values were omitted from the calculations. A constant specific heat capacity is assumed in Step 2 so that initial calculations can be made. An iterative approach using specific heat capacity based on average coating temperature (Step 4 to 6) is adopted to balance heat energy equation as described in Equation 6-6. This aims to improve the accuracy of the

calculated coating surface temperature. The physical meaning to the heat balance equation [110] (Equation 6-6) in Step 4 is as follows;

Heat loss from surface of coating through radiation + heat loss from surface of coating through convection = heat flux imposed by cone calorimeter – heat loss from steel plate to thermal wool – heat stored in coating – heat stored in steel plate.

The heat loss from the steel plate to thermal wool can be calculated with Equation 6-5 in Step 3. Once the coating surface temperature for each time step has been computed, thermal conductivity of the coating can be calculated using Equation 6-7, which is based on conservation of energy. The average coating temperature is calculated in Step 8 and is associated with the conductivity values of each time step.

The assumptions and limitations of the model are as follows;

1. The temperature of the coating is calculated based on the average value of T_{ss} and T_s at every time step and is associated with the respective effective thermal conductivity at the time step. Similar to the procedure in Figure 6-2, step 6, the mean value of thermal conductivity is calculated. In this case, the temperature interval for conductivity values less than 200 °C falls within a range of 20 °C, while the temperature interval conductivity values more than 200 °C falls within a range of 100 °C. For example, the mean conductivity value at 30 °C interval consists of conductivity values between 20 to 40 °C and the mean conductivity value at 250 °C interval consists of conductivity values between 200 to 300 °C.
2. Different intervals are adopted as few values are available at lower temperature and grouping the lower conductivity values with a wider temperature interval reduces the accuracy of the calculations.
3. Non-incremental rise in steel temperature has been removed to omit negative effective thermal conductivity values from the results. In view of this, effective thermal conductivity values are based on test results from ambient to maximum steel temperature measured during the test.
4. Temperature of steel was assumed to be uniform throughout the test since the thickness of the steel plate was 4 mm. Lumped mass heat capacitance assumption for the steel substrate was made.
5. Radiation of the flame back to the coating after the sample has been ignited is not accounted for.

6. Density of coating is assumed to be constant and does not change with temperature
7. Heat flux on the surface of the coating and emissivity of the coating are assumed to be constant.

The calculated surface temperature and the average coating temperature are presented in Figure 6-8.

Figure 6-8: Time-temperature profiles of calculated surface temperature and average coating temperature for (a) 3 mm coating at 35 kW/m²; (b) 3 mm coating at 50 kW/m²; (c) 5 mm coating at 35 kW/m² and (d) 5 mm coating at 50 kW/m².

The calculated surface temperature corroborated well with the test procedure used in a cone calorimeter test. The sample was placed on a sample holder and a heat shield prevented the surface from being exposed to the irradiance. When the test commenced, the heat shield was removed, and the surface was exposed to the irradiance almost instantaneously. This resulted in a sharp rise in temperature over a short period of time.

The effective thermal conductivity values calculated based on each time-step for different thicknesses and heat fluxes are shown in Figure 6-9.

Figure 6-9: Effective thermal conductivity with respect to average coating temperature for (a) 3 mm coatings and (b) 5 mm coatings. Average effective thermal conductivity with respect to average coating temperature for (a) 3 mm coatings and (b) 5 mm coatings.

A parabolic trend in the conductivity values was observed in Figure 6-9a and b. This is because there is a wide scatter of conductivity values after the average coating temperature exceeds 400 °C. The scatter of data points could be a result of temperature fluctuations recorded by the conical heater or the steel plate. Moreover, the increase in conductivity values as the average coating temperature increases might be due to cohesive failure of the exfoliated graphite network. More work is required to ascertain this phenomenon. Nonetheless, despite the wide scatter in data points, a general trend can still be observed. The calculated effective thermal conductivity values for 3 mm coating are slightly greater with a higher heat flux. This observation was also reported by Wang, *et al* [110] as they compared the conductivity values for coatings with thicknesses less than 1.2 mm. This was attributed to a shorter time the coating had to react fully at higher irradiance and hence cannot be as effective.

Considering the scatter present in Figure 6-9a and b, it is difficult to use the values for any verification using numerical simulations. Hence, as discussed in the list of assumptions and limitations, the mean values of effective thermal conductivity within a certain temperature interval were used (Figure 6-9c and d). It should be noted that the effective thermal conductivity at 1000 °C is assumed to be the same as the last effective thermal conductivity value calculated since the test is terminated before the steel plate reaches 1000 °C.

6.3.1 Numerical validation of effective thermal conductivity value obtained from cone calorimeter

ABAQUS V6.14 was used to verify the calculated effective thermal conductivity. A 3D model, shown in Figure 6-10, was constructed for heat transfer analysis.

Figure 6-10: Typical model and result obtained from heat transfer analysis for cone calorimeter tests.

The coating, steel and thermal wool were modelled using 20-node quadratic heat transfer elements (DC3D20). The thickness of wool in the model was 40 mm and had a mesh size of 2.5 mm. The thickness of steel in the model was 4 mm and had a mesh size of 0.8 mm. The thicknesses of the coatings for each test were accounted for in the model and an appropriate mesh size was selected to divide the coating into 5 layers. A tie-constraint was used to simulate perfect bond between the interface of coating and the steel substrate, and the interface of steel and wool. The time-temperature profile of the conical heater was used as the thermal load and was transferred through convection and radiation to the

surface of the coating. A convection coefficient of $20 \text{ W/m}^2\text{K}$ was used to model convective heat transfer to the surface of the coating [110]. The surrounding of the thermal wool was assumed to be at ambient temperature and heat loss from the wool to the surrounding was accounted for through convection (convection coefficient of $9 \text{ W/m}^2\text{K}$) and radiation (emissivity of 0.9). The parameters (i.e. emissivity, density, specific heat capacity) used in the ABAQUS model for coating and steel are given in Table 6-4. Thermal conductivity of steel is given in Table 6-4, while thermal conductivity of coating is shown in Figure 6-9c and d. The thermal properties of thermal wool are based on reported values in literature [149].

The experimental results for each test were verified with the time-temperature profiles of the steel substrate in the model. The time-temperature profiles obtained from the simulations are in good agreement with the experimental results (Figure 6-11).

Figure 6-11: Comparison of time-temperature profiles of steel-coating interface with experimental and simulation results.

Mismatch in the time-temperature profiles can be seen, but it typically occurs after $\sim 500 \text{ s}$. This is due to the low effective thermal conductivity values seen between $100 \text{ }^{\circ}\text{C}$ to

200 °C as a wide scatter in effective thermal conductivity values can be observed. Currently, the scatter is attributed to fluctuations in the temperature of the cone calorimeter. There can be other factors influencing the calculated values since expansion and other physical or chemical reactions occurred throughout the specimen during this temperature range. For the developed coating discussed in this thesis, a stable exfoliated char structure will only be formed when all EG has expanded after 200 °C.

The effective thermal conductivity values obtained from the cone calorimeter were used to predict the performance of the coating in a structural fire test (Figure 6-3). The results in Figure 6-12 show that the time-temperature profiles of the simulation and experiment are in good agreement, especially at 50 kW/m².

Figure 6-12: Comparison of time-temperature profiles of steel substrate using derived effective thermal conductivity values and structural-scale fire test.

Deviation in the test results based on 35 kW/m² is expected since the temperature of the steel substrate is lower and there are lower conductivity values in the coating calculated at higher temperatures. However, it should be noted that this observation may only apply to this particular coating. As seen in Equation 2-1, the expansion of EG is different from conventional intumescent systems as it occurs instantaneously. Hence, a stable char structure with consistently low thermal conductivity is expected once the coating reaches a certain critical temperature (e.g. 300 °C). This is also observed by comparing the effective thermal conductivity values in Figure 6-5 and Figure 6-9c and d. Consistent values between ~0.045 W/(mK) to ~0.03 W/(mK) can be seen after 300 °C, which is after the temperature of EG expansion.

6.4 Conclusion

This chapter has demonstrated the potential of using effective thermal conductivity values to predict the performance of a fire protective coating in a structural fire test. The effective thermal conductivity obtained from the cone calorimeter test is consistent with those obtained from the structural-scale fire test. Hence, reasonably good agreement between experimental values and simulation was observed in Figure 6-12. It seems that the effective thermal conductivity obtained from the cone calorimeter between 35 kW/m^2 and 50 kW/m^2 and the measurement obtained by C-Therm (Figure 6-5) can give preliminary indications on the performance of coating. However, it should be noted that the observations are only valid for the current coating without considering any extrinsic parameters like column edge effects, char homogeneity and cohesion on the member, etc. More work is required to ascertain the influence of the thickness, irradiance on the sample, time-heat flux relationship and formulation of the coating.

Chapter 7 Fire protective coating for concrete structures

As evident from the work presented in Chapter 4 to 6, the mechanism of flammability and fire retardancy of the developed coatings are studied and extent of fire protection offered when applied to structural steel is investigated. Insightful knowledge on the performance is obtained across different scales and a generic methodology for future development of fire protection for steel structures is proposed. To show the full potential of the developed fire protective coating, they were also extended to concrete structures as a case study, and so, only the key results on performance are highlighted in this chapter. This case study is important as there are a number of scenarios demonstrating why fire-protective coatings are required for concrete members.

The fire-resistance rating of concrete structures will change if the type of occupancy changes. For example, according to the Singapore Fire Code 2013, the minimum fire resistance rating of a typical storage room is 1 h [150]. The minimum fire resistance rating will be increased to 2 h if addition and alteration work is performed to convert the storage room to an electrical room or a battery storage room. An increase in axis distance and cross-sectional dimensional of the concrete member will be required and a new layer of concrete may need to be cast. The bond between new and old concrete might not be compatible due to differential shrinkage and stiffness between the new and old material. Durability of the concrete member will also need to be carefully considered. In such scenarios, the application of fire protective coatings on the concrete members may be a more practical solution.

Before discussing the performance of the coating, it should be noted that a polyurethane binder as well as styrene-butadiene binder were used for concrete members as they adhere well to concrete as compared to acrylic system (Table 7-1). Considering the confidentiality of the materials and compositions of coatings (filed as a technology disclosure [151]), detailed information on the chemistry of these coatings will not be discussed. Moreover, as discussed in Section 4.6, chemical interaction between EG and the resin / additives was not identified. The reduction in heat transfer to a substrate was mainly attributed to the formation of an exfoliated graphite network, held together by carbonaceous material. In view of this, a different polymer system with EG may also work as a thermal barrier. As shown in Table 7-1, two polymer systems were selected to investigate the potential of using EG. These two polymer matrices were also known for their adhesion to concrete substrate.

Table 7-1: Overview of the chemical structures of the binders used for formulating the coatings for concrete structures.

Properties	Coating A	Coating A2	Coating B	Coating B2
Base polymer matrix	Polyurethane-based		Styrene butadiene-based	
Typical chemical structure
Weight ratio of additives				
APP	-	3	-	3
PER	-	1	-	1
EG	-	1	-	1

7.1 Thermal stability

The mass loss curves and the derivative mass loss curves of the neat polymer systems (Coating A and B) and their FR polymer systems (Coating A2 and B2) are presented in Figure 7-1 and Table 7-1. A summary of the TGA results is shown in Table 7-2.

Figure 7-1: (a) Mass loss, and (b) derivative mass loss curves of coating A, A2, B and B2 in air environment.

Table 7-2: Summary of TGA results for coating A, A2, B and B2.

Properties	Coating A	Coating A2	Coating B	Coating B2
T _{5%}	134	149	310	245
T _{50%}	356	346	400	406
Residual weight at 900°C (%)	1.5	10.7	2.4	11.0

As seen in Figure 7-1a and Table 7-2, addition of FR additives slightly reduced thermal stability of base matrices. Despite the reduction in thermal stability of coatings in the presence of FR additives, the FR coatings (Coating A2 and Coating B2) showed higher residual weight at 900 °C in an oxidative environment when compared to the neat polymer system (Coating A and Coating B). However, as discussed in Section 5.6, it is important to appreciate the differences in correlating TGA results with bulk- and structural-scale fire tests. The TGA data would only provide an indication of the time-temperature profile of a substrate in the initial structural-scale fire test (Table 5-3 and Figure 5-7) and the residue amount at 900 °C does not correlate to the effectiveness of the coating as a thermal barrier in the later stage of the test.

7.2 Direct torching test

Torching test conducted provides an indication of the coatings' effectiveness in creating a temperature difference between the heat source (fire) and the substrate. It was also conducted to investigate the performance of the coatings when exposed to fire. This is important as the coatings may be applied to concrete walls and it will be subjected to large-scale flame spread tests such as EN 13501-1 / EN13823. Digital photographs of the torched samples for Coating A, A2, B and B2 are presented in Figure 7-2.

Figure 7-2: Digital photographs of (a) A, (b) A2, (c) B and (d) B2 after torching.

Coatings A (Figure 7-2a) and B (Figure 7-2c) had ignited and decomposed upon exposure to flame. The coatings were completely burned off after approximately 5 min, exposing the concrete surface (and therefore, no accurate time-temperature profiles could be obtained). Coatings A2 (Figure 7-2b) and B2 (Figure 7-2d) showed no such behaviour throughout 120 min of torching. Charring in both coatings A2 and B2 were limited to uppermost layers, while most of the underlying coating seemed unaffected, an observation that appears to be supported by the FTIR results in Section 7.3. Surrounding areas not exposed to the flame seemed to be in a pristine condition suggesting that there was absolutely no flame spread.

7.3 FTIR analysis of samples exposed to torching

Results acquired using ATR-FTIR of the condensed phase (and residue) provided an indication of the chemical changes in the coatings across different torching durations (i.e. 10 min, 30 min and 60 min). The spectra of coatings A2 and B2 are presented in Figure 7-3a and b, respectively, indicate the outstanding behaviour of the coatings even after direct flame exposure.

(b)

Figure 7-3: FTIR spectra of (a) A2 and (b) B2 after torching at different time intervals.

There were three prominent peaks (i.e. 3000 cm^{-1} to 2800 cm^{-1} , 1700 cm^{-1} to 1500 cm^{-1} and 1200 cm^{-1} to 1000 cm^{-1}) that were associated with pristine (not torched) coating A2 (Figure 7-3a). These peaks remained unchanged after 10 min of torching. As the torching duration increased to 30 min and 60 min, decomposition of methane (CH_3) compounds could be observed with a reduction in intensity of peak values between 3000 cm^{-1} to 2800 cm^{-1} . The peaks between 1800 cm^{-1} to 1300 cm^{-1} attributed to alkane C–H stretch undergo changes over the duration of torching as the polymer chains undergo thermal fragmentation. Although the changes in carbonyl peak (1700 cm^{-1} to 1600 cm^{-1}) suggested thermal decomposition of urethane bond, the functional group was even present after 60 min of torching, as corroborated by the presence of the C–O–C stretch at $\sim 1100\text{ cm}^{-1}$, as well as the combination of N–H bend and C–N stretch at $\sim 1250\text{ cm}^{-1}$ after 60 min.

Spectra of coating B2 presented in Figure 7-3b exhibited similar trends. A distinctive peak at 700 cm^{-1} , corresponding to alkene bend, could be seen across all 3 torching durations (i.e. 10 min, 30 min and 60 min). The intensity of this peak at 60 min was slightly smaller compared to the intensity at 10 min and 30 min. Two other prominent peaks observed between 3000 cm^{-1} to 2800 cm^{-1} and 1500 cm^{-1} to 1400 cm^{-1} were detected after 60 min of torching, suggesting minimal changes to the chemical composition of coating B2. Overall, the absence of any significant changes in the chemical composition of the coating as reflected in the FTIR spectra.

7.4 Performance in bulk-scale furnace

Coating A2, with a thickness of 10 mm, was exposed to ISO 834 heating curve for 210 min before the experiment was terminated. The experimental setup has been described in Section 3.3.2. The interface temperature as well as furnace temperature as a function of time are presented in Figure 7-4. The time-temperature profiles of the gas temperature in the furnace closely matches the ISO 834 standard fire curve.

Figure 7-4: Furnace gas temperature and coating-concrete interface time-temperature profiles from bulk-scale furnace test.

Coating A2 performed exceptionally well as a thermal barrier throughout the test. Although the furnace gas temperature was approximately 1114 °C after 180 min, the coating-concrete interface temperature was only 345 °C. This suggested that the coating was able to significantly increase the temperature difference and again contradicts the TGA data. This confirmed that many parameters influence the performance at different scales. It should be noted that concrete acts also as a heat sink unlike steel, and therefore, this good performance as compared to steel substrate. After removing the concrete block from the furnace, the block remained intact except for minor cracks on the surface that were not detrimental to the integrity of the specimen.

7.5 Numerical validations and simulations

Numerical heat transfer simulation using ABAQUS software was used to assess the effectiveness of coating A2 on a concrete slab as a prequel to conducting a structural-scale fire test. Heat transfer analysis in the simulation model accounts for conduction,

convection and radiation and the input parameters for the simulation model were obtained from Eurocode. The relevant clauses are summarised in Table 7-3.

Table 7-3: Input parameters for modelling heat transfer in concrete.

Parameter	Reference to code	Input values	Temperature
Emissivity	BS EN 1992-1-2 Section 2.2(2)	0.7	-
Density (kg/m ³)	BS EN 1992-1-2 Section 3.3.2	2400	-
Specific heat capacity (J/(kg°C))	BS EN 1992-1-2 Section 3.3.2	900	20 °C ≤ θ ≤ 100 °C
		900 + (θ – 100)	100 °C ≤ θ ≤ 200 °C
		1000 + [(θ – 200)/2]	200 °C ≤ θ ≤ 400 °C
		1100	400 °C ≤ θ ≤ 1200 °C
Thermal conductivity (W/(mK))	BS EN 1992-1-2 Section 3.3.3	$2 - 0.2451 \frac{\theta}{100} + 0.0107 \left(\frac{\theta}{100}\right)^2$	20 °C ≤ θ ≤ 1200 °C

The numerical model assumed a 1D heat transfer condition, with one surface of the slab exposed to heating in the form of convection and radiation based on ISO 834 time-temperature curve as illustrated in Figure 7-5.

Figure 7-5: Illustration of heat transfer model used for validation.

Heat conducted across the thickness of the slab was computed based on the specific heat capacity and thermal conductivity of concrete. The concrete slab model in Figure 7-5 was simulated using 8-node linear heat transfer elements (DC3D8) with a thickness of 200 mm and a mesh size of 10 mm. Heat transfer to the heated surface is accounted for as convection and radiation. The convection coefficient and emissivity adopted in the model are 25 kW/m² and 0.7, respectively. The results obtained from the heat transfer analysis were validated using the R240 temperature profile in Figure A.2 of Eurocode 2 (EC2).

The temperature profile obtained from the model was compared with the temperature profile depicted in EC2 and presented in Figure 7-6.

Figure 7-6: Comparison of time-temperature profiles in EC2, Part 1-2 (as Figure A2, Curve R240) with results from validation model.

Results from the model demonstrated good agreement with the temperature profile in EC2. The upper limit of thermal conductivity of normal weight concrete was used in the model, which resulted in slight variations in temperature after 70 mm. This showed that the model and the input parameters could simulate heat transfer across concrete accurately.

7.5.1 Heat transfer analysis

Two numerical models with the same thickness (120 mm) were used as a case study to assess the effectiveness of coating A2 and the models are illustrated in Figure 7-7. The concrete slab model in Figure 7-7 was modelled using 8-node linear heat transfer element (DC3D8) and has a mesh size of 10 mm. Similar to the model described in Figure 7-5, convection (convection coefficient of 25 kW/m^2) and radiation (emissivity of 0.7) are used to simulate heat transfer from the gas of the furnace to the surface of the slab (Figure 7-7).

Figure 7-7: Illustration of (a) Model 1 (unprotected concrete slab) and (b) Model 2 (protected concrete slab).

Heat transfer analysis for Model 1 (Figure 7-7a) was performed using convection and radiation based on ISO 834 heating curve for a duration of 180 min, depicting a concrete section without fire-protective coating. Similar to the model used for validation, thermal conductivity and specific heat capacity were used to compute the heat conducted across the concrete slab. Heat transfer analysis for Model 2 (Figure 7-7b) was performed using the coating-concrete interface temperature profile obtained (Red dash line in Figure 7-4) from the experiment as an input for a duration of 180 min and it depicts a concrete section with fire-protective coating. The time-temperature profiles of the two numerical models are presented in Figure 7-8.

Figure 7-8: Comparison of time-temperature profiles obtained with Model 1 and 2.

The temperature at the unexposed surface for Model 1 was computed to be 278.2 °C while the temperature for Model 2 was computed to be 90.2 °C, a difference of 188 °C. Heat transfer has been drastically reduced due to the presence of the coating, which resulted in a slow increase in temperature across the concrete block. This created a remarkable reduction in maximum temperature at the end of 180 min and highlights the potential of coating A2 as a thermal barrier.

7.6 Conclusion

Thermo-oxidative and fire performance of the PU-based fire-protective coating for concrete was discussed in this chapter. The coating is non-halogenated and demonstrated remarkable good performance when exposed to direct flame over 120 min. The temperature of the concrete reached 66 °C and 117 °C, for coating A2 and B2, respectively. Even the area exposed to fire on the sample was localised with no flame spread throughout the torching duration. Besides, analysis of the residue after direct flame torching of the coatings for different durations indicated the presence of polymer peaks even after 60 min of torching. In the bulk-scale furnace test, coating A2 performed well as a passive fire protection system on a concrete substrate. With a thickness of 10 mm, temperature at the concrete-coating interface was recorded to be 345 °C at the end of 180 min. Simulation results also validated the effectiveness of coating A2 on a normal grade concrete slab.

Chapter 8 Developing a fire protective coating for structural application

The FR mechanism, flammability characteristic and performance of an EG-based coating as a thermal barrier was studied in this thesis. It covers the development of the coating from the materials-, to bulk- and to structural-scales, providing critical and valuable insights that are currently lacking in the literature. Based on the results and understanding obtained from Chapter 4 to 7, a methodology that aids the development of a fire protective coating for steel structure is proposed.

8.1 Proposed methodology

The methodology is summarised in a flowchart and presented in Figure 8-1.

Figure 8-1: Proposed flowchart to design a fire protective coating for steel substrate.

The first step is to understand the type of FR mechanism required. Fire protective coatings for structures are exposed to a thermal load that follows a certain time-temperature profile. These profiles typically do not account for the decay in a fire as they are usually based on

ISO 834 standard fire curve. This implies that the gas-phase mechanism will not be as effective as the condensed-phase mechanism since dilution or free radical scavenging will not disrupt the combustion cycle of the polymer or reduce the temperature or intensity of the applied thermal load. The effect of gas-phase mechanism is likely to be negated as a certain time-temperature profile has to be sustained. The gas-phase mechanism will only aid in the early stage of the test, but the condensed-phase in terms of forming a char network with low conductivity values, is still required for the remaining test duration. This allows the subsequent step, which is choosing the right additives with the appropriate polymer matrix to achieve the desired FR mechanism.

As discussed in Chapter 5, the intrinsic properties such as flammability and thermal stability were found to influence the initial stage of a fire test. Reducing the rate of pyrolysis or the amount of materials to be pyrolysed consequently means that a stable char residue with low thermal conductivity is formed at an earlier stage in the test. This prolongs the time required for the steel substrate to reach the critical cut-off temperature, hence increasing the fire resistance. The extrinsic properties such as cohesion of char have also been discussed in Chapter 5. This is important as it can have detrimental effect on the performance of the coating and may be masked in a 1D bulk-scale furnace test. It is recommended to conduct preliminary bulk-scale tests with small section sections of different geometries (e.g. I-sections, circular and rectangular sections), and the sample should be placed within the furnace so that heat is transferred from all faces.

Numerical modelling of the coating is useful before a structural-scale fire test is conducted. However, it requires thermal properties, especially thermal conductivity and specific heat capacity to be measured. It allows parametric studies to be conducted with different thicknesses of the coating and different types of steel sections. Measuring the thermal conductivity is challenging due to complex reactions that occur during expansion and decomposition of the coating. Although the two methods discussed in Chapter 6 have their limitations, numerical modelling can be used to provide indicative performance of the coating in future fire tests.

8.2 Future work

8.2.1 Improve the composition of developed coating and conduct structural fire tests with mechanical loading.

Considering the problems associated with the cohesion of graphite network and other factors discussed in Chapter 4 and 5, more work has been done to improve the

composition of the coating. The work conducted to improve the composition has been filed under the technology disclosures [152], described in the authorship attribution statement of this thesis. The work also includes preparation of a second series of structural-scale fire tests with mechanical loading applied to steel sections. The test programme for concrete is also required to determine the thickness required to achieve a certain fire resistance rating for a concrete member with certain dimensions. This information will be very useful for structural fire engineers.

8.2.2 Correlate intrinsic property with time-temperature profile

A relationship between the flammability characteristic of the coating and the fire test has been identified. However, there is insufficient data to quantify the relationship. In an ideal scenario, researchers should be able to calculate the rise in temperature with a few parameters related to flammability, such as peak HRR or THR values. This will increase the significance of conducting PCFC and cone calorimeter tests for fire protective coatings. To achieve this, the time-heat flux profile on the surface of the coating in a fire test has to be measured. This profile can then be simulated in a cone calorimeter test and correlated with the temperature of a steel substrate and HRR curve of the coating.

In addition, the work in Chapter 5 established certain relationships between different scales of fire tests but work to correlate bulk-scale torching test with large-scale flame spread tests (e.g. EN 13823) was not discussed. It is a regulatory requirement to assess polymer-based coatings with flame spread tests such as EN 13501-1 / EN 13823. The EN 13823 test is also known as the room corner fire tests and it involves large-sized samples (1 panel that is 1.5 m in height and width and 1 panel that is 1.5 m in height and 1 m in width).

8.2.3 Measure apparent thermal conductivity

The time-heat flux profile is also useful in calculating the apparent conductivity of the coating. The apparent conductivity will be more useful than effective conductivity since it does not only apply to a particular thermal load and thickness. Expansion of the coating poses another challenge that needs to be measured before a more generalised thermal conductivity value can be obtained. Preliminary work was conducted to evaluate the expansion of EG-based coating in a cone calorimeter test.

This involves the use of the MATLAB Image Analysis module (Appendix C) and a video recording of a cone calorimeter test. The video of the coating expansion during the cone

calorimeter test can be separated from digital photographs and correlated to time and steel temperature. In each photograph, colour intensity values along the image width are recorded and relationship between colour intensity values and image height at selected image width can be obtained as shown in Figure 8-2. Thermal wool is white in colour and is represented by high intensity values that are larger than 150. The expanded residue is black in colour and is represented by low intensity values that are lower than 100. The stark contrast in colour intensity allows the thickness of the coating to be identified and this information can be collected along the image width. By comparing the relationship between colour intensity and image height along the image width for each photograph, the change in thickness of the coating can be determined.

Figure 8-2: Relationship between colour intensity and image height for a selected image width (a,b) before and (c,d) after a cone calorimeter test.

However, there are some issues that need to be addressed with this experimental setup. For example, ignition of the sample causes the camera to lose focus and return an image that is almost entirely black in colour. These images cannot be analysed as there is minimal contrast between colour intensity values. Also, it can be seen in Figure 8-2b and d that the initial colour of the coating is grey, and the residue is black, which are both close to the colour of the conical heater (Figure 8-2a). Hence, a few trials are required to

select the appropriate intensity value for calculation so that other colours that are similar to the residue are not accounted for. Lastly, expansion of the coating into the conical heater cannot be accounted for since the view will be blocked by the conical heater.

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Appendix A

**Microsoft Excel Visual Basic Application (VBA) code to calculate
effective thermal conductivity**

Thickness (mm)		5.2	Ap/V (m ⁻¹)	155	Conductivity_Max Thickness VBA											
Coating	Specific (J/(kg.K))	1150	V/Ap (m ⁻¹)	0.006451613												
density (kg/m ³)		1100	Count Row	242	VBA - Calculated											
Furnace				Steel												
ΔT (s)	Average (°C)	Average (K)	Increment (K)	Average (°C)	Average (K)	Increment (K)	Specific Heat Capacity of Steel	Lumda	Coating Temperature	Critical Time Step	STEP 7	STEP 7 - Interval	Data points	Calculated Mean	Std. Dev	
	22.18	295.3328571		19.95	293.1											
30	29.13	302.2842857	6.951428571	20.05	293.2	0.1	439.8371593	0.042503156	22.82928571	2180.228571	0	25	2	0.055031578	0.017717864	
30	76.83	349.9842857	47.7	21.025	294.175	0.975	440.5258924	0.06756	36.76089286	1373.767033	50	75	1	0.087298538	0	
30	157.55	430.7028571	80.71857143	24.025	297.175	3	442.6266412	0.087298538	69.85928571	1068.222857	100	125	1	0.071348148	0	
30	269.69	542.8385714	112.1357143	28.425	301.575	4.4	445.6580241	0.071348148	119.9228571	1315.983117	150	175	1	0.054061395	0	
30	412.89	686.04	143.2014286	33.625	306.775	5.2	449.1657418	0.054061395	186.1571429	1750.453846	200	225	0	0	0	
30	542.04	815.19	129.15	39.575	312.725	5.95	453.0822289	0.047098625	257.0325	2026.74958	250	275	1	0.047098625	0	
30	631.30	904.4528571	89.26285714	46	319.15	6.425	457.1980459	0.044057201	314.7294643	2186.345303	300	325	6	0.045835145	0.002089441	
30	660.81	933.9628571	29.51	52.75	325.9	6.75	461.3990714	0.044962667	347.7164286	2162.00127	350	375	7	0.041598563	0.002660774	
30	644.41	917.5628571	0.105714286	59.475	332.625	6.725	465.4632216	0.046977292	354.3626786	2087.510568	400	425	9	0.047707104	0.001588587	
30	616.55	889.6957143	0.105714286	65.975	339.125	6.5	469.2801271	0.048635396	346.6021429	2032.876484	450	475	15	0.037905972	0.002777721	
30	602.47	875.6228571	0.105714286	72.1	345.25	6.125	472.780055	0.047929621	339.2733929	2078.195685	500	525	13	0.033261912	0.000759779	
30	605.12	878.2685714	0.105714286	77.9	351.05	5.8	476.0105458	0.045969938	339.3978571	2181.594089	550	575	19	0.031548255	0.00121557	
30	615.59	888.7428571	0.105714286	83.4	356.55	5.5	479.0011116	0.043456047	345.5028571	2322.296104	600	625	18	0.030329499	0.001445259	
30	628.73	901.8785714	0.105714286	88.7	361.85	5.3	481.8179622	0.041510902	354.1053571	2445.412399	650	675	20	0.038885368	0.002703543	
30	644.53	917.68	0.105714286	93.9	367.05	5.2	484.5216331	0.040167675	363.9646429	2541.369231	700	725	23	0.04915461	0.002963964	
30	661.66	934.8085714	17.12857143	99.075	372.225	5.175	487.1551421	0.039337852	374.7908929	2609.08323	750	775	25	0.059392226	0.002812582	
30	674.88	948.0328571	13.22428571	104.35	377.5	5.275	489.7827661	0.039752583	384.9916071	2595.789303	800	825	32	0.071812931	0.006180868	
30	683.28	956.4257143	8.392857143	109.725	382.875	5.375	492.4032564	0.040508635	393.0583929	2560.970631	850	875	37	0.110380745	0.030480184	
30	684.74	957.8928571	1.467142857	115.35	388.5	5.625	495.0863119	0.042935001	398.2733929	2429.409524	900	925	11	0.097474615	0.005262303	
30	684.80	957.9528571	0.06	121.2	394.35	5.85	497.8148459	0.045359742	401.5239286	2312.21685	950	975	0	0	0	
30	686.05	959.2	1.247142857	127.25	400.4	6.05	500.5731373	0.047575851	404.8257143	2216.727273	1000					
30	690.69	963.8371429	4.637142857	133.425	406.575	6.175	503.3248383	0.048960499	409.3530357	2165.877154						
30	697.45	970.5985714	6.761428571	139.65	412.8	6.225	506.0369695	0.049575175	415.3026786	2150.548709						
30	706.14	979.2871429	8.688571429	145.8	418.95	6.15	508.6585763	0.04900858	422.2589286	2186.681533						
30	715.06	988.21	8.922857143	151.925	425.075	6.125	511.2154665	0.048810989	429.7305357	2206.569796						
30	723.10	996.2528571	8.042857143	157.95	431.1	6.025	513.68095	0.048073377	437.0094643	2251.231298						
30	729.99	1003.137143	6.884285714	163.775	436.925	5.825	516.0205187	0.046601916	443.70375	2332.891232						
30	735.63	1008.78	5.642857143	169.425	442.575	5.65	518.2509226	0.045397808	449.7042857	2405.118584						
30	741.68	1014.827143	6.047142857	174.7	447.85	5.275	520.3008765	0.042494382	455.3580357	2579.611645						
30	747.02	1020.168571	5.341428571	179.775	452.925	5.075	522.2454287	0.041016742	460.7926786	2682.531175						
30	750.85	1023.998571	3.83	184.7	457.85	4.925	524.1082247	0.040023664	465.5855357	2758.896592						
30	753.62	1026.774286	2.775714286	189.525	462.675	4.825	525.9115516	0.039488854	469.6744643	2805.882457						
30	754.33	1027.475714	0.701428571	194.2	467.35	4.675	527.6398037	0.038659275	472.91875	2875.511688						
30	754.72	1027.874286	0.398571429	198.85	472	4.65	529.3416132	0.038871603	475.525	2869.028571						
30	755.18	1028.328571	0.454285714	203.4	476.55	4.55	530.9915088	0.038437417	478.0382143	2910.480377						
30	755.15	1028.301429	0.403809524	207.85	481	4.45	532.591703	0.038014377	480.395	2951.738042						
30	755.01	1028.164286	0.403809524	212.15	485.3	4.3	534.126443	0.03713995	482.5414286	3029.940199						
30	756.39	1029.54	1.375714286	216.425	489.575	4.275	535.6421007	0.037227619	484.9948214	3031.382456						
30	757.41	1030.56	1.02	220.525	493.675	4.1	537.087164	0.036005381	487.6875	3142.741463						
30	757.66	1030.807143	0.247142857	224.6	497.75	4.075	538.5160417	0.036138701	490.0480357	3139.477651						
30	758.67	1031.82	1.012857143	228.575	501.725	3.975	539.9036349	0.035540188	492.3755357	3200.573585						
30	760.69	1033.841429	2.021428571	232.45	505.6	3.875	541.2512124	0.034854445	495.0966071	3271.688848						
30	761.65	1034.802857	0.961428571	236.275	509.425	3.825	542.5772196	0.034676981	497.7673214	3296.488515						
30	764.49	1037.635714	2.832857143	240.1	513.25	3.825	543.8998207	0.034827279	500.6283929	3290.263305						
30	767.87	1041.022857	3.387142857	243.85	517	3.75	545.1939005	0.034249329	504.0771429	3353.746286						
30	770.38	1043.528571	2.505714286	247.575	520.725	3.725	546.4775151	0.034180631	507.4191071	3368.398849						
30	776.77	1049.922857	6.394285714	251.275	524.425	3.7	547.7513827	0.033855895	511.5003571	3408.634749						

```

Module1 - 1

Sub Interpolate()
Dim T_Input() As Double 'Input data for interpolation
Dim T_In() As Double 'Corrected Increment
Dim T_Temp() As Double

Worksheets("S3 - Interpolate").Activate
'Count total number of row
irow_all = ActiveSheet.UsedRange.Rows.Count
'Account for header
irow = irow_all - 1

'Array
ReDim T_Input(irow)
For i = 1 To irow
T_Input(i) = Cells(i + 1, 1)
Next i

'Calculate increment
ReDim T_In(irow)
For i = 2 To irow
T_In(i) = T_Input(i) - T_Input(i - 1)
Next i

'Output increment
For i = 2 To irow
Cells(i + 1, 2) = T_In(i)
Next

'limit counter for search
'To increase if not enough
n = 20
'check negative values and count
For i = 2 To irow
If T_In(i) < 0 Then
T_Data = T_Input(i - 1)
'Initialise counter
counter = 0#

For j = 0 To n
If T_Input(i + j) - T_Data < 0 Then
counter = counter + 1
Else
Exit For
End If
Next

'Correct value
In_Value = (T_Input(i + counter) - T_Input(i - 1)) / (counter + 1)
For n = 0 To counter
T_In(i + n) = In_Value
Next
End If
Next

'Output Increment
For i = 2 To irow
Cells(i + 1, 3) = T_In(i)
Next

ReDim T_Temp(irow)
'Correct temperature based on increment
T_Temp(1) = T_Input(1)
For i = 2 To irow
T_Temp(i) = T_Temp(i - 1) + T_In(i)
Next

For i = 1 To irow
Cells(i + 1, 4) = T_Temp(i)
Next

End Sub

```

Module1 - 1

```

Sub Cond_Min()
Dim lumda_p_t() As Double 'thermal conductivity [Watts per metre per degree Kelvin]
Dim delta_t As Single 'time step [seconds]
Dim irow As Single
Dim coat_temp() As Double
Dim crt_temp_in() As Double

'steel property variable
Dim steel_sec_factor As Double 'section factor [m-1]
Dim steel_ts() As Double 'steel temperature increase over time step [kelvin]
Dim steel_den As Double 'steel density [kg/m3]
Dim steel_shc() As Double 'steel specific heat capacity [joules per kilogram per kelvin]
Dim steel_t() As Double 'steel temperature[Celsius]
'furnace variable
Dim fur_ts() As Double 'furnance temperature increase over time step [Kelvin]
Dim fur_t() As Double 'furnace temperature [Celsius]
'coating variable
Dim coat_t As Double 'coating thickness [m]
Dim coat_shc As Double 'coating specific heat capacity [J/(kg.K)]
Dim coat_den As Double 'coating density [kg/m3]
'Range variable
Dim Mean_Range() As Double
Dim R_Bound() As Double
Dim R_Temp() As Double
Dim Range_counter() As Integer
Dim Mean() As Double
Dim Std_Dev() As Double

delta_t = 30
Worksheets("Cond_Min").Activate

'Input
coat_t = Cells(1, 3) * 0.001 'need to convert to metre
coat_shc = Cells(2, 3)
coat_den = Cells(3, 3)
steel_sec_factor = Cells(1, 5)
irow = Cells(3, 5)
steel_den = 7850

'Dimension set
ReDim lumda_p_t(irow)
ReDim steel_ts(irow)
ReDim steel_shc(irow)
ReDim steel_t(irow)
ReDim fur_ts(irow)
ReDim fur_t(irow)
ReDim coat_temp(irow)

For i = 1 To irow
    fur_t(i) = Cells(i + 6, 2)
    fur_ts(i) = Cells(i + 6, 4)
    steel_t(i) = Cells(i + 6, 5)
    steel_ts(i) = Cells(i + 6, 7)
Next

initial_fur_t = Cells(6, 2)
initial_steel_t = Cells(6, 5)
'Specific heat of carbon steel baed on EC3-2 - 3.4.1.2

For i = 1 To irow - 1
    If steel_t(i) >= 20 And steel_t(i) < 600 Then
        steel_shc(i) = 425 + (0.773 * steel_t(i)) - (0.00169 * (steel_t(i) ^ 2)) + (0.00000222 * (steel_t(i) ^ 3))
    ElseIf steel_t(i) >= 600 And steel_t(i) < 735 Then
        steel_shc(i) = 666 + (13002 / (738 - steel_t(i)))
    ElseIf steel_t(i) >= 735 And steel_t(i) < 900 Then
        steel_shc(i) = 545 + (17820 / (steel_t(i) - 731))
    ElseIf steel_t(i) > 900 Then
        steel_shc(i) = 650
    End If

    Cells(i + 6, 8) = steel_shc(i)

    lumda_p_t(i) = coat_t * (1 / steel_sec_factor) * steel_shc(i) * steel_den * (1 / ((fur_t(i) - steel_t(i)) * delta_t)) * steel_ts(i)

```



```

Module1 - 2

Cells(i + 6, 9) = lumda_p_t(i)

Next

For i = 1 To irow - 1
If i = 1 Then
coat_temp(i) = (((initial_fur_t + fur_t(i)) / 2) + ((initial_steel_t + steel_t(i)) / 2)) / 2
Else
coat_temp(i) = (((fur_t(i - 1) + fur_t(i)) / 2) + ((steel_t(i - 1) + steel_t(i)) / 2)) / 2
End If

Cells(i + 6, 10) = coat_temp(i)
Next

'Calculate critical time increment
ReDim crt_temp_in(irow)
For i = 1 To irow - 1
    crt_temp_in(i) = 0.8 * ((steel_shc(i) * steel_den) / (lumda_p_t(i) / coat_t)) * (1 / steel_sec_factor)
    Cells(i + 6, 11) = crt_temp_in(i)
Next

'Calculate arithmetical mean values of lumda for temp with 50 OC.
'Range allocation
n = 1000 / 50
ReDim R_Bound(n + 1)
R_Bound(0) = 0
For i = 0 To n
    R_Bound(i + 1) = R_Bound(i) + 50
    Cells(i + 7, 12) = R_Bound(i)
Next
ReDim R_Temp(n)
For i = 1 To n
    R_Temp(i) = (R_Bound(i) + R_Bound(i - 1)) / 2
    Cells(i + 6, 13) = R_Temp(i)
Next

ReDim Range_counter(n + 1)
ReDim Mean_Range(n + 1, irow)
ReDim Mean(n)
ReDim Std_Dev(n)

'Identify number of data within an interval
For j = 0 To n
    rc = 0#
    For i = 1 To irow
        If coat_temp(i) > R_Bound(j) And coat_temp(i) < R_Bound(j + 1) Then
            rc = rc + 1
        End If
    Next
    Range_counter(j + 1) = rc
Next

'Output number of data points within an interval
For i = 1 To n
    Cells(i + 6, 14) = Range_counter(i)
Next

'Data arranged in array for calculation
For j = 0 To n
    For i = 1 To irow
        If coat_temp(i) > R_Bound(j) And coat_temp(i) < R_Bound(j + 1) Then
            Mean_Range(j + 1, i) = lumda_p_t(i)
        End If
    Next
Next

'Calculate mean value
For j = 1 To n
    If Range_counter(j) <> 0 Then
        Total_Sum = 0#
        For i = 1 To irow
            Total_Sum = Total_Sum + Mean_Range(j, i)
        Next
        Mean(j) = Total_Sum / Range_counter(j)
    Else

```

```
Module1 - 3

    Mean(j) = 0
End If
Cells(j + 6, 15) = Mean(j)
Next
'Calculate standard deviation
For j = 1 To n
    If Range_counter(j) > 1 Then
        SumSq = 0#
        For i = 1 To irow
            If Mean_Range(j, i) <> 0 Then
                SumSq = SumSq + (Mean_Range(j, i) - Mean(j)) ^ 2
            End If
        Next
        Std_Dev(j) = Sqr(SumSq / (Range_counter(j) - 1))
    Else
        Std_Dev(j) = 0
    End If
    Cells(j + 6, 16) = Std_Dev(j)
Next
End Sub
```

Appendix B

MATLAB Code to calculate effective thermal conductivity

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```

clc;
clear all; %clear all variables in workspace

% import steel temperature
d_input = csvread('CSTB G1-5M-3-50-RI.csv', 1, 0);
[irow,icol]=size(d_input);% no of data points in row and col
d_input_c=num2cell(d_input);%convert steel temperature to array
%check thickness and heat flux

%check for steel increment
for i = 2:irow
    if d_input_c{i,2}<=d_input_c{i,1}
        fprintf('Steel temperature not incremental');
        return
    else
        break
    end
end

%allocate cell array
for i = 1:irow
    steel_temp_k{i,1} = d_input_c{i,2}+273.15;
    wool_temp_k{i,1} = d_input_c{i,3}+273.15;
    cone_temp{i,1} = d_input_c{i,4};
end

%calculate time step
for i = 2:irow
    t_s{i,1} = d_input_c{i,1} - d_input_c{i-1,1};
end

%variables for wool
wool_t = 0.02; %m
%Variables for coating
coat_t = 5.091*10^-3; %m
coat_den = 1100; %kg/m-3
%initialise specific heat capacity array
for i=1:irow
    coat_h_c {i,1} = 1150; %J.kg-1.K-1
end
%General variables
sbc = 5.67 * 10^-8; %W.M-2.K-4
e = 0.92;
hc = 20; %W.M-2.K
%Variables for steel
steel_t = 4*10^-3; %m
steel_den = 7850; %kg/m-3

%Heat flux from cone
%Change unit to W/m-2
Q_e = 50000; %W.M-2

%calculate specific heat capacity of steel wrt temperature

```

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```

        coat_h_c{i,1} = 1150;
    elseif coat_t_avg_c{i,1}>=100 && coat_t_avg_c{i,1}<150
        coat_h_c{i,1} = 1471;
    elseif coat_t_avg_c{i,1}>=150 && coat_t_avg_c{i,1}<200
        coat_h_c{i,1} = 1523;
    elseif coat_t_avg_c{i,1}>=200 && coat_t_avg_c{i,1}<250
        coat_h_c{i,1} = 1738;
    elseif coat_t_avg_c{i,1}>=250 && coat_t_avg_c{i,1}<300
        coat_h_c{i,1} = 1886;
    elseif coat_t_avg_c{i,1}>=300 && coat_t_avg_c{i,1}<350
        coat_h_c{i,1} = 2211;
    else
        coat_h_c{i,1} = 2069;
    end
    check{j,i} = coat_t_sur_c{i,1};
    if j > 1
        err{j,i} = abs(check{j,i} - check{j-1,i});
        err_max{j} = max([err{j,:}]);
    end
end
if err_max{j} < 5 && err_max{j} > 0
break
end
end
HB_last = j;

%Calculate thermal conductivity
coat_cond{1,1} = 0;
syms cc
for i = 2:irow
    ht_eqn = cc * ((coat_t_sur_k{i,1}-steel_temp_k{i,1})/coat_t)-Q_loss{i,1} == 0;
    steel_hs{i,1};
    ht_sol = double(solve(ht_eqn,cc));
    coat_cond {i,1} = ht_sol;
    fprintf('TC %d\n',i);
end
fprintf('Calculate Thermal Conductivity Completed \n');
%Assume first % second conductivity value is the same
coat_cond{1,1} = coat_cond{2,1};

%Calculate temperature interval
r_bound{1,1} = 0;
n1=200/20;
n2 = (700 - 200)/100;
for i =1:n1
    r_bound{i+1,1} = r_bound{i,1} + 20;
end
for i=1:n2
    r_bound{n1+i+1,1} = r_bound{n1+i,1} + 100;
end
for i = 1:n1+n2
    r_temp{i,1} = (r_bound{i+1,1}+r_bound{i,1})/2;
end

```

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```
%Unit = J.kg-1.K-1
for i = 1:irow
    if d_input_c{i,2} >= 20 && d_input_c{i,2} < 600
        steel_h_c {i,1} = 425 + 0.773 * d_input_c{i,2} - 0.00169*(d_input_c{i,2}^2) + 0.00000222*(d_input_c{i,2}^3);
    elseif d_input_c{i,2} >= 600 && d_input_c{i,2} < 735
        steel_h_c {i,1} = 666 + 13002 / (738 - d_input_c{i,2});
    elseif d_input_c{i,2} >= 735 && d_input_c{i,2} < 900
        steel_h_c {i,1} = 545 + 17820 / (d_input_c{i,2}-731);
    else
        steel_h_c {i,1} = 650;
    end
end

%calculate thermal conductivity of wool [W/m.K]
for i = 1:irow
    wool_cond{i,1} = 0.03+0.2438*((wool_temp_k{i,1}/1000)^3);
end
%calculate Q_loss based on wool temperature
for i = 1:irow
    Q_loss{i,1} = wool_cond{i,1}*((steel_temp_k{i,1}-wool_temp_k{i,1})/(wool_t/2));
end
%calculate change delta steel temperature and heat stored in steel plate
delta_st {1,1} = 0;
steel_hs {1,1} = 0;
for i = 2:irow
    delta_st {i,1} = steel_temp_k{i,1}-steel_temp_k{i-1,1};
    steel_hs {i,1} = (delta_st{i,1}/t_s{i,1})*steel_h_c{i,1}*steel_den*steel_t;
end

syms cts %variable to solve heat balance equation
%initialise array
coat_t_sur_c{1,1} = d_input_c{1,2};
coat_t_sur_k{1,1} = coat_t_sur_c{1,1}+273.15;
coat_t_avg_c{1,1} = (coat_t_sur_c{1,1} + d_input_c{1,2})/2;
err_max{1} = 0; %error array
max_iteration = 100;

for j = 1:max_iteration
    for i = 2:irow
        fprintf('I %d ST %d\n',j,i);
        hb_eqn = (e * sbc * (cts^4)) + (hc*(cts-conv_temp{i,1}))+((((cts-coat_t_sur_k{i-1,1})+delta_st{i,1})/(2*t_s{i,1}))*coat_h_c{i,1}*coat_den*coat_t)== ...
            (Q_e-Q_loss{i}-steel_hs{i,1}); % solve heat balance equation
        hb_sol = double(solve(hb_eqn,cts,'Real',true)); % return only real solution since equation goes up to power 4
        coat_t_sur_solution = max(hb_sol); %choose maximum solution based on real numbers
        coat_t_sur_k{i,1} = coat_t_sur_solution; %update surface temperature for next step
        coat_t_sur_c{i,1} = coat_t_sur_k{i,1}-273.15;
        coat_t_avg_c{i,1} = (coat_t_sur_c{i,1} + d_input_c{i,2})/2; %calculate average coating temperature based on surface and steel
        if coat_t_avg_c{i,1}>=10 && coat_t_avg_c{i,1}<100
```

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```

%Identify number of data within an interval
for j= 1:n1+n2
    rc = 0;
    for i=1:irow
        if coat_t_avg_c(i,1) > r_bound{j,1} && coat_t_avg_c(i,1) < r_bound{j+1,1}
            rc = rc+1;
        end
    end
    range_counter{j,1} = rc;
end

%Arrange conductivity data for mean calculation
for j=1:n1+n2
    for i =1:irow
        if coat_t_avg_c(i,1) > r_bound{j,1} && coat_t_avg_c(i,1) < r_bound{j+1,1}
            mean_range(j,i) = coat_cond{i,1};
        end
    end
end

%Compute size of mean_range array
[mr_irow, mr_icol] = size(mean_range);

%Calculate mean conductivity value for each interval
for j = 1:mr_irow
    if range_counter {j,1} ~= 0
        total_sum = 0;
        for i = 1:irow
            total_sum = total_sum+mean_range(j,i);
        end
        coat_cond_mean{j,1} = total_sum / range_counter{j};
    else
        coat_cond_mean{j,1} = 0;
    end
end

fprintf('Heat balance completed at loop %d\n',HB_last);
fprintf('Calculate Mean Thermal Conductivity Completed \n');
fprintf('Code Complete \n');

```

Appendix C

**MATLAB Code to calculate change in thickness of developed
coating during cone calorimeter test**

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```

clc;
clear all; %clear all variables in workspace
close all; %close other windows

image_folder = uigetdir(); %prompt for image folder directory
image_list = dir([image_folder, '\*.jpeg']); %list of images and the image extension
image_number = length(image_list); % total number of images
% loop through list and import all images into MATLAB images array
fprintf('Import images into MATLAB\n');
for i = 1:image_number
    images{i} = imread([image_folder, '\', image_list(i).name]);
end
fprintf('Images import completed\n');

%height and width and colour of an image
[i_height, i_width, i_colour] = size(images{1});
i_width_half = i_width/2;

%Convert images in cell array to an array for intensity scanning
fprintf('Convert images from cells to array\n');
image_int = zeros(image_number, i_height, i_width); %preallocate image_int array
%image intensity array = (image number, height, width)
for i = 1:image_number %loop to convert images in cell array to array
    image_int(i, :, :) = images{i}(:, :, 2); %JPEG - RBG - 1 is Red, 2 is Geen, 3 is
blue
end
fprintf('Image intensity captured\n');

%Check first image and intensity

int_vert_1 = images{1}(:, i_width_half, 1);
int_vert_2 = images{image_number}(:, i_width_half, 1);
subplot(2,2,1); plot(int_vert_1, view([90,90])
grid(subplot(2,2,1), 'on');
grid(subplot(2,2,1), 'minor');
set(gca, 'YTick', [0:5:300]);
subplot(2,2,2); imshow(images{1})
subplot(2,2,3); plot(int_vert_2, view([90,90])
grid(subplot(2,2,3), 'on')
grid(subplot(2,2,3), 'minor');
set(gca, 'YTick', [0:5:300]);
subplot(2,2,4); imshow(images{image_number})
fprintf('Check if numeric value of pixel decreases with height!\n');
fprintf('Larger nuermic value should be bottom of picture!\n');

%CHECK -- numeric value of pixel decreases with height!!%

% Cutoff value for image intensity
int_cut_upper = 100;
int_cut_lower = 35;
% Calculation interval value
cal_int_val = 10;

```

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```
%Last value with ignition probe in picture
image_number_cut = 9;

%Close figure windows after cutoff value has been recorded
close all;

fprintf('Calculate slope change\n');
%loop to find change in slope from bottom up
%preallocate image slope change
image_int_slope_change = zeros(image_number,i_height,i_width);

% slope change for lower height is based on interval
for i=1:image_number %search for every image
    for k = 1:i_width %along the width of an image
        for j = i_height:-1:2 %count from bottom up
            if j > cal_int_val
                image_int_slope_change (i,j,k)= image_int(i,j,k)-image_int(i,j-1,
cal_int_val,k);
            else
                image_int_slope_change (i,j,k)= image_int(i,j,k)-image_int(i,j-1,k);
            end
        end
    end
end

image_int_slope_change_sort = sort (image_int_slope_change,2);

%preallocate image intensity cutoff
image_int_cut=zeros(image_number,i_width);
fprintf('Image intensity search\n');

%loop for intensity search based on input cutoff value - Black
for i = 1:image_number %search for every image
    fprintf('Start %d\n', i)
    if i <= image_number_cut
        for k = 1:i_width %along the width of an image
            z=0; %decreasing sort value to find best match with image_int_slope_change
array
            while image_int_cut(i,k)==0
                z=z+1;
                for j = i_height:-1:i_height/2 %count from bottom up to half of picture
                    if image_int(i,j,k)<=int_cut_upper && image_int(i,j,k) <
>int_cut_lower && image_int_slope_change (i,j,k)<= image_int_slope_change_sort(i,z,
k)
                        image_int_cut(i,k) = j; %array in number of image and width
                        break
                    end
                end
            end
        end
    else
        for k = 1:i_width %along the width of an image
            z=0; %decreasing sort value to find best match with image_int_slope_change
```

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```

array
    while image_int_cut(i,k)==0
        z=z+1;
        for j = i_height:-1:2 %count from bottom up
            if z < i_height && image_int(i,j,k)<=int_cut_upper && image_int(i,
j,k)>int_cut_lower && image_int_slope_change (i,j,k)<= image_int_slope_change_sort
(i,z,k)
                image_int_cut(i,k) = j; %array in number of image and width
            elseif z > i_height
                image_int_cut(i,k)=0.5; %arbitrary value for error point
            end
        end
    end
end
end
end
end
fprintf('Check image intensity array\n');
fprintf('Image intensity search COMPLETED\n');
%Median value for each image
arr_med_value = zeros(image_number);
for i =1:image_number
    arr_med_value(i)= median(image_int_cut(i,:));
end
med_value(1,:) = arr_med_value(i);
fprintf('Calculate median value COMPLETED\n');

% fprintf('Error check\n');
% %Average value for each image'
% arr_avg_value = zeros(image_number);
% for i=1:image_number
%     arr_avg_value (i) = mean(image_int_cut(i,:));
% end
% avg_value(1,:)= arr_avg_value(:,1);

```