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Permanent address: Assoc. Prof. Dr. Faiz Ahmad_____

Village Post Office Saukin Wind,____   Department of Mechanical Engineering,

Tehsil Parur, District Sialkot,_____   Universiti Teknologi PETRONAS_____

Pakistan_____

Date :_____   Date :_____

UNIVERSITI TEKNOLOGI PETRONAS

SYNTHESIS, CHARACHTERIZATION AND EVALUATION OF EXPANDABLE

GRAPHITE BASED INTUMESCENT FIRE RETARDANT COATING FOR

STEEL STRUCTURES

By

SAMI ULLAH

The undersigned certify that they have read and recommended to the post graduate studies program for acceptance this thesis for the fulfillment of the requirement for the degree stated.

Signature:

Main Supervisor: Assoc. Prof. Dr. Faiz Ahmad

Signature:

Head of Department: Assoc. Prof. Dr. Ahmad Majdi Bin Abdul Rani

Date:

SYNTHESIS, CHARACHTERIZATION AND EVALUATION OF EXPANDABLE GRAPHITE BASED INTUMESCENT FIRE RETARDANT COATING FOR STEEL STRUCTURES

By

SAMI ULLAH

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Signature of Author   Signature of Supervisor

Permanent address:

Village Post Office Saukin Wind,   Assoc. Prof. Dr. Faiz Ahmad

Tehsil Parur, District Sialkot,

Pakistan

Date :_____   Date :_____

I dedicate this research work to my beloved parents and to my siblings

ACKNOWLEDGEMENTS

ABSTRACT

Structural steel is an integral part of any construction such as bridges, buildings, ships, cars and off shore structures. The integrity of structural steel has pivotal role in safety of structures and human. In the case of fire, the steel starts losing its load bearing ability above 500°C and in the case of fire, the temperature of unprotected steel rises to 800°C within 10 minutes. Intumescent fire retarding coatings are designed to insulate the structural steel under the action of heat, flames or fire thus protecting their integrity.

The main objectives of this research project are to synthesis and characterization of an expandable graphite (EG) based intumescent coating formulation (ICF). An intumescent coating with considerable char expansion and flaky morphology can provide good heat shielding to the steel structures. A high residual weight of intumescent coating on exposure to fire forms a protective passive layer of char which can minimize the flow of heat to steel substrate. A range of formulations were synthesized by varying the concentration of intumescent ingredients. One formulation containing 8.5wt% expandable graphite was identified with char expansion 13.4 times. The performance of the ICF was optimized using a various particle size of EG. An ICF with 300μm particle size improved char expansion, morphology, residual weight and reduced steel substrate temperature to 367°C after 60 minutes fire test. IFC formulation containing 300μm was further studied for reinforcing inorganic fillers, Multi-walled carbon nanotubes (MWCNTs), Kaolin clay (KC) and Zirconium silicate (ZS). One formulation containing 5wt% ZS showed 24 times char expansion and residual weight was increased to 38% with respect to IF5-BA-Mel. The substrate temperature was reduced to 213°C and char was hard and adherent with substrate.

Carbolite furnace was used to study the char expansion of intumescent coating formulations at 500°C and 800°C. Heat shielding test was performed according to ASTM E119 standard test. The test was conducted for 60 minutes and the temperature

of the steel substrate was recorded at an interval of one minute. Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM) were used to study the char morphology. Thermal stability of IFCs was analysed using Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). The chemical composition of residual char was determined using X-Ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and X-Ray Photoelectron spectroscopy (XPS). The weather resistance of IFCs was measured using Q-Sun Xenon Test Chambers. The gaseous products during burning of coating samples were analyzed by Pyrolysis Gas Chromatography (Py-GC).

The examination of char morphology showed that flaky and multiporous type of char is most suitable to reduce the flow of heat to steel substrate. It was also noted that addition of ZS 5wt% in ICF modified the char morphology from flaky to multiporous and this was very helpful to minimize substrate temperature. XRD analysis of char of IFCs showed that the presence of high temperature boron based compounds i.e. borophosphate, boron oxide and borophosphate oxide which are stable at high temperature and helped to reduce the flow of heat to substrate. The presence of these compounds in the char was also confirmed by functional groups analysis using FTIR. The elemental analysis and carbon contents of selected ICFs showed high carbon contents compared to oxygen. This type of char is suitable for formation of carboneous layer on the substrate surface. TGA analysis showed a considerable increase in residual weight of IF5-BA-Mel reinforced with inorganic fillers. Py-GC analysis of gaseous products released during burning of selected ICFs showed less concentration compared to IF5-BA-Mel formulation. The weathering test of selected ICFs showed approximately 2% decrease in char expansion, however no change in char morphology was observed. Based on the results it was concluded that a ICF containing 5wt% ZS is more suitable for long term application due to high char expansion, lower substrate temperature, high residual weight and environment friendly properties.

ABSTRAK

Struktur besi merupakan satu pengukuhan dalam apa jua pembinaan seperti jambatan,banggunan, kapal, kereta dan struktur dasar laut. Keutuhan struktur besi menyumbang kepada keselamatan manusia dan struktur. Di dalam kes kebakaran, besi mulai hilang berat beban apabila suhu mencecah 500°C dan didalam kes kebakaran ini, suhu besi mencapai 800°C dalam masa 10 minit. Salutan intumescent direka untuk menebat struktur besi daripada haba, seterusnya melindungi keutuhannya.

Objektif utama penyelidikan ini adalah untuk menjalankan sintesi dan pencirian grafit yang mengembang berasakan formulasi salutan intumescent. Salutan intumescent dengan pengembangan arang yang sepadan dan morfologi pengisi boleh member penahanan haba yang baik kepada struktur besi. Berat baki salutan intumescent yang didedah kepada api membentuk lapisan dan lindungan arang dimana dapat meminimumkan aliran api ke atas besi. Beberapa formulasi telah disintesis dengan mempelbagaikan kepekatan kandungan intumescent. Satu formulasi mengandungi 8.5wt% grafit yang mengembang dan pengembangan arang diidentifikasikan sebanyak 13.4 kali. Prestasi formulasi salutan intumescent telah dioptimumkan menggunakan pelbagai saiz grafit. Salutan intumescent dengan 300μm meningkatkan pengembangan arang, morfologi,berat sisa dan mengurangkan suhu besi kepada 367°C selepas 60 minit. Formulasi salutan intumescent yang mengandungi 300μm saiz telah dimasukkan dengan menggunakan pengisi tak organic seperti karbon nanotube berdinding pelbagai, tanah liat kaolin, dan silica zirconium. Satu formulasi yang mengandungi 5wt% silica zirconium menunjukkan 24 kali pengembangan arang dan baki sisa meningkat 38%. Suhu substrat telah berkurang kepada 213°C dan arang yang dihasilkan keras dan melekat pada besi.

Relung Carbolite digunakan untuk menganalisis pengembangan salutan intumescent pada suhu 500°C dan 800°C. Ujian penahanan haba dilakukan menggunakan penyelarasan ASTM E119. Ujian dilakukan selama 60 minit dan suhu

substrat besi direkod setiap selang 1 minit. SEM dan FESEM digunakan untuk menganalisis morfologi arang. Kestabilan therma salutan intumescent dianalisis menggunakan TGA dan DTA. Komposisi kimia baki arang ditentukan dengan menggunakan XRD, FTIR dan XPS. Ketahanan terhadap cuaca salutan intumescent dilakukan dengan menggunakan Q-Sun Xenon Test Chamber. Gas yang terbebas dianalisis menggunakan Kromatogafi Gas Pirolisis.

Ujian morfologi arang menunjukkan arang mempunyai struktur berpori pelbagai dan sesuai untuk mengurangkan aliran haba ke atas substrat. Didapati juga penggunaan 5wt% silica zirconium telah mengubah morfologi arang menjadi berpori dan berguna untuk meminimumkan suhu substrat. XRD analisis menunjukkan arang salutan intumescent mengandungi boron, boron oksida dan borofosfat yang stabil pada suhu tinggi dan mengurangkan aliran udara kepada substrat. Sebatian ini ditentukan menggunakan FTIR. Analisis unsure dan karbon menunjukkan salutan intumescent mempunyai kandungan karbon yang tinggi berbanding oksigen. Ini menunjukkan arang amat sesuai membentuk lapisan karbon diatas permukaan. Analisis TGA menunjukkan peningkatan dalam baki berat IF5- BA- Mel dengan menggunakan pengisi. Ujian gas pirolisis menunjukkan gas yang terhasil semasa pembakaran salutan intumescent menunjukkan kekurangan kepekatan berbanding IF5- BA-Mel formulasi. Ujian ketahanan cuaca salutan intumescent terpilih menunjukkan salutan intumescent berkurang sebanyak 2% dalam pengembangan arang. Berdasarkan keputusan, dapat disimpulkan salutan intumescent mengandungi 5wt% silica zirconium adalah sesuai untuk penggunaan masa panjang berdasarkan kepada peningkatan pengembangan arang, suhu rendah substrat, peningkatan baki berat dan mesra alam.

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LIST OF ABBREVIATIONS

APP	Ammonium Polyphosphate
ATH	Aluminium trihydroxide
BA	Boric Acid
BPA	Bisphenol A
DTA	Differential Thermal Analysis
DTGA	Derivative of thermogravimetric Analysis
EG	Expandable Graphite
EVA	Ethyl Vinyl Acetate
FESEM	Field Emission Scanning Electron Microscopy
FR	Fire retardant
FTIR	Fourier Transform Infrared Spectroscopy
ICFs	Intumescent Coating Formulations
KC	Kaolin Clay
Mel	Melamine
MWCNTs	Multi-walled carbon nanotubes
PA6	Polyamide 6
PER	Pentaerythritol
Py-GC	Pyrolysis of Gas Chromatography
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X- ray Diffraction
ZS	Zirconium Silicate

CHAPTER 1

INTRODUCTION

1.1 Chapter Overview

This chapter presents an introduction to the research work; it consists of background of this study on fire threats on man and materials, problem statement, objective of this research work, and scope and thesis organization.

1.2 Background

Due to the great risk of fires to human and their possessions, new methods are continuously being investigated and developed to prevent fires and reduce their effects. Some additives to polymers have been known to increase the material resistance to ignition, the amount of fire stress it can withstand, retard the rate of combustion of the materials and prevent sustained burning [1]. These additives that are incorporated in the polymeric materials are called flame retardant.

Passive fire proofing materials which are composed of insulating systems (forming a carbonaceous char on the substrate on ignition) are commonly used to protect steel structures. The materials are designed to decrease heat transfer from a fire to the structure being protected. These are usually, coatings such as mineral-based or organic resin-based products, known as intumescent coatings. Intumescent coatings are designed to perform under severe condition to maintain the steel integrity between 1 to 3 hours when the temperature of the surrounding is in excess of $1100^{\circ}C$ [2-4]. This duration is considered as sufficient for evacuation of personnels and to control the fire.

Multiple risk-benefit analysis conducted over the last decade has shown that flame retardants have helped to reduce the number of severe injuries and deaths caused by fires. Legislation has become more stringent especially in the United Kingdom and in California, USA. This has led to not only tighter fire standards, but also to study on the environmental and health impact of flame retardants [5]. The use of polymeric materials, which are made of hydrocarbons mainly, in everyday life increases fire hazards. In order to make these materials safer for the consumers, flame retardants are very often incorporated into them to limit their flammability. As an example, in 2004, there were 508 fire-related deaths in the UK, compared with 593 in 2003; the usage of fire retardant had reduced 14 percent death caused by fire [6]. The highest number recorded was 1096 deaths in 1979. Through the 1980s and 1990s there was a general downward trend in fire-related deaths. This trend can be linked to strict legislation in terms of fire hazards combined with the growing use of flame retardants (global demand for flame retardant was forecasted to increase by 4.8% per year to 2.2 million metric tons in 2009) [7]. Figure 1.1 shows the statistics of fire occurrence according to the types of fire in Malaysia from January to June 2010 [8].
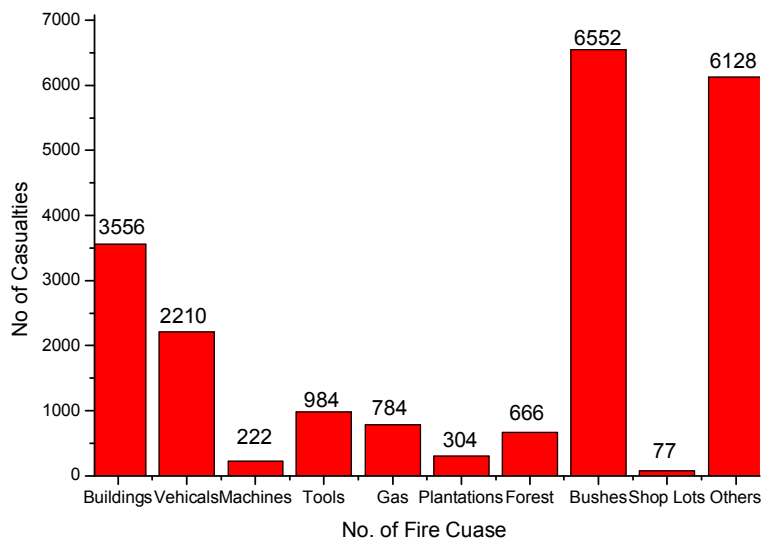
Figure 1.1: Statistics of fire causes in Malaysia from January to June 2010 [8]

1.3 Intumescent Coating

Intumescence is defined as the swelling of certain substances when they are heated. Intumescent coatings form upon heating an expanded multicellular layer, which acts as a thermal barrier that effectively protects the substrate against rapid increase of temperature, thereby maintaining the structural integrity of the substrate. Intumescent coatings contain "active" ingredients bound together by a binder. Generally, three "active" ingredients are used: an acid source (normally ammonium polyphosphate or a mineral acid), a carbon source (such as char forming polymers or polyols) and a blowing agent (e.g. melamine). Intumescent flame retardants form a foamed carbon barrier layer on the polymer surface when it is exposed to heat [9, 10]. The optimum performance of the coating in terms of physical and chemical properties in order to form an effective protective char layer is to insulate the substrate from fire [11].

Chemical interactions between the "active" ingredients in the formulation lead to the formation of the intumescent char. It is generally accepted [12] that first, the acid source breaks down to yield a mineral acid, then it takes part in the dehydration of the carbonization source to yield the carbonaceous char and finally, the blowing agent decomposes to yield gaseous products. The latter cause the char to swell and produce the insulating multi-cellular protective layer. This protective char limits both the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source, resulting in conservation of the underlying material.

This results in the expansion or foaming of the coating, sometimes up to several times of its original thickness, to form a protective carbonaceous char that acts as an insulative barrier between the fire and the substrate. The "intumescence concept" allows a balance between the fire properties and the level of additives in the material. The formulation of these coatings has to be adapted in terms of their physical and chemical properties to form an efficient protective char.

Structural steel is a material that is commonly used in the construction of bridges, boats, cars, offshore and gas platforms, and mega buildings. The structural steel work used in buildings usually requires fire protective materials to reduce the devastating cost of fire in terms of property damage and life hazard. Steel is an alloy; consists

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mostly of iron with a carbon content of 0.2 to 2.04% depending on its grade. It is a non-combustible material where when exposed to high temperature above 500ºC results in reduction of its strength and stiffness. If it has been exposed for a long time, the crystalline/metallurgical structure of the steel will undergo transformation. Unprotected steel will visibly deform, twist and buckle. The significant heating effects of the fire could permanently alter the properties of the steel material. In order to prevent this from occurring, a fire protection coating has been applied to steel structures such as spray on steel, intumescent paints or membrane/gypsum boards [13]. Steel that has not been exposed to very high temperature for a prolonged time will not be significantly deformed; its metallurgy will not be affected after cooling, and hence it will retain its original thermomechanical properties.

1.4 Problem Statement

Fire has main three classes, such as class A, class B and class C. Class A fires involve common combustibles such as wood, paper, cloth, rubber, trash and plastics. They are common in typical commercial and home settings, but can occur anywhere these types of materials are found. Class B fires involve flammable liquids, solvents, oil, gasoline, paint, lacquers, tars and other synthetic or oil-based products. Class B fires often spread rapidly and, unless properly secured, can reflash after the flames are extinguished. Class C fires involve flammable gases such as natural gas, methane and acetylene. Steel is very attractive as construction material and has vast applications in oil and gas, railways, bridges, public places and buildings. In cases of fire, the temperature of the steel can rise to $1000^{\circ}C$ within a few minutes. The limitation associated with steel based structure is that when temperature rises more than $500^{\circ}C$, it losses load bearing capability and the structure tends to fall. This causes loss of not only buildings but human lives. This problem is even more severe in off-shore environment where rescue efforts may not be that much effective which consequently results in the loss of many lives. Traditionally used fire retardants are not very effective, and they contain halogens and release toxic vapours during burning which is a very severe threat to life and environment. Generally an intumescent coating can protect a substrate from heat for a limited time. However, the duration of protection can be prolonged by using a layer of intumescent coating of a certain thickness. For a

fixed thickness of an intumescent coating, and the protection time is dependent on the thermal efficiency of the intumescent coating itself. In other words, it depends on how affective the intumescent coating is in slowing down the heat transfer from the fire to the substrate.

Therefore, in order to increase the duration for protection of substrate material, there is a need to improve the thermal insulation property of the intumescent coating. Thermal insulation property of intumescent coating can be improved by developing a formulation which may result in enhanced char expansion, char morphology, increased residual char weight and thermal conductivity. A proper selection of coating ingredients can improve char expansion and char morphology which can effectively reduce thermal conductivity of the resulting char, while the coating formulation can also affect thermal conductivity directly due to different raw materials (or different ratio) which are different fire retardant properties. Therefore, in an intumescent coating formulation, char expansion, char morphology, residual weight and heat insulation are interrelated. The effect of char morphology on thermal efficiency or thermal conductivity cannot be studied unless the coating formulation is fixed. The question now is 'how can we improve char expansion, char morphology, char residual weight and thermal conductivity or heat shielding properties with a fixed coating formulation'?

In conclusion, the challenge in improving char expansion, morphology, residual weight and thermal insulation property of intumescent coating is finding the right combination of the ingredients. One possible approach towards this is by optimizing the ingredients ratio, and subsequently further improving the protection performance of the intumescent coating by selecting ingredients particle size to expand the carboneous char and filler weight percentage.

1.5 Research objectives

Based on the problem associated with the protection of steel substrate and intumescent coatings, the following objectives are considered:

To synthesis intumescent fire retardant coating using expandable graphite (EG), and to investigate the effects of various particle size of EG to optimize fire protection performance.

To study the effect on heat shielding, residual char expansion, char morphology, char composition and thermal degradation of intumescent ingredients with the optimized particle size of expandable graphite.

The study will be further strengthened by investigating the effects of inorganic fillers reinforcement on improving the char residue, char morphology and the fire protection performance of optimized coating formulation.

To investigate the long term application of intumescent coating from the aspect of weather resistance behaviour.

1.6 Scope of work

A systematic approach adopts on the synthesis of a new formulation of intumescent fire retardant coating with expandable graphite as a carbon and char expansion source. The synthesis involves studying the effects of char expansion and char morphology of epoxy resin with each of one, two and three intumescent ingredients. A range of formulations are developed by varying the concentration of the intumescent ingredients. The effects of different particle sizes of EG on char expansion and char morphology with the objective of determining the optimize particle size that has better char expansion and char morphology. The study also investigates the effect of heat shielding, residual char expansion, char morphology, and char composition of intumescent coating formulations (ICFs). To optimize intumescent formulation with higher char expansion, char morphology, and minimum temperature of the steel substrate and high residual char weight percentage.

The optimum formulation is further reinforced by incorporating three different inorganic fillers (Multi-walled carbon nanotubes, kaolin clay and zirconium silicate). To determine the filler that gives the best fire protection performance on residual char expansion, char morphology, minimum temperature of the steel substrate, high

residual char weight percentage, high carbon content in the char residue, better weather ability and low volatile organic content.

The intumescent coating was first characterized before further evaluation using ASTM and UL standards were carried out. The intumescent coating was characterized again after the fire test. The pre-fire testing involves Thermo gravimetric Analysis (TGA), Derivative of Thermo gravimetric Analysis (DTGA) and Differential Thermal Analysis (DTA) to determine the residual weight percentage and thermal degradation of the intumescent fire retardant coating. The post-fire testing involves, carbolite furnace was used to study the char expansion of ICFs at 500°C and 800°C. Heat insulation test was performed according to ASTM E119 standard test. The morphology of char structure is analyzed by Scanning Electron Microscopy (SEM) and Field Emission Electron Microscopy (FESEM). Functional groups of the char residue are analyzed by Fourier Transform Infrared Spectroscopy (FTIR) analysis and the chemical composition of char residue is analyzed by X-Ray Diffraction (XRD). The weight percentage of the residual char element is determined by X-Ray Photoelectron Spectroscopy. The gaseous products after pyrolysis of the intumescent sample are analyzed by Pyrolysis Gas Chromatography (Py-GC). Finally, the ability of intumescent coatings to withstand weathering effects is done using Q-Sun Xenon Test Chamber. The ultimate goal of weathering studies is to provide a link between the composition of a coating or its constituents and how well it performs its macroscopic function.

1.7 Organization of the Thesis

The thesis is presented in five chapters. Chapter 1 describes the research background related to intumescent fire retardant coating, structural steel substrate, limitations associated with steel substrate and advantage of fire protection system that can overcome steel substrate limitations. The motivation of the study, research objectives and scope of the study are also presented.

Chapter 2 entitled "theory and literature review". It includes the categories of flame retardants, fire science thermal degradation, flammability and flame retardancy,

the history of flame retardants, types of flame retardants, inorganic flame retardant, halogenated flame retardants, phosphorus flame retardants, oxygenated hydrocarbon, flame retardants, metal in flame retardants, intumescent coating, expandable graphite, and weather ability of intumescent steel substrate.

Chapter 3 contains the methodology adapted for the research. Details of the materials used, intumescent coating preparation and equipment involved in the research are described. The methods used for physical, chemical and thermal tests of the developed coatings are discussed.

Chapter 4 presents the results and discussions of the tests and related analyses. Firstly, the effects each of formulation of epoxy and hardener are discussed. This is followed by the discussions on the effects of EG particle sizes on the expansion and char morphology of the intumescent coating formulations, and the effects of individual ingredients on the intumescent coating formulations. The final part covers the characterization of reinforced optimum coating formulation with best intumescent fire retardant properties. Chapter 5 presents the conclusion of this study and some recommendations for future research.

1.8 Chapter Summary

In this chapter, the introduction to this research and advantages of fire protection coating toward people safety and protection against fire has been presented. The problem statement integral to this research has been clearly addressed in order to understand the need for such research to be conducted, followed by the research objectives, scope of work and thesis organization.

In the next chapter, the theory and literature review on intumescent coating is discussed briefly. The development of intumescent coating and past work by other researchers will be presented.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Chapter overview

This chapter presents the literature review and theory of the research. It will begin with the introduction to fire science, global consumption of fire retardant, historical development of intumescent coating, definition of fillers and its function in intumescent coating. Literature review on past work related to the effect of filler in intumescent coating and effect of weather on intumescent coating is presented briefly in this chapter.

2.2 Fire science

Combustion is a rapid, oxidative process requiring fuel, an oxidizing agent (typically oxygen) and energy. In a ship, the structure and contents serve as the fuel; oxygen from the air acts as the oxidizer. The three stages to initiate combustion are heating, thermal decomposition and ignition of volatile components. The basic sources of ignition are chemical, electrical or mechanical. Chemical based sources usually lead to spontaneous combustion. Electrical fires originate from induction, dielectric processes, arcing, and/or static electricity. Mechanical sources of ignition are typically from heat due to compression or friction.

Fires can be classified by the combustion process, rate of growth, basis of ventilation, or fire stage. Material properties have a great effect on the ignition and heat released by a fire. These material properties include temperature resistance, decomposition temperature, mode of decomposition, softening temperature, flash-ignition temperature, rate of heat release, oxygen index, and heat of combustion.

Two models used to describe the combustion process (primarily used in firefighting) are the fire triangle and fire tetrahedron, shown in Figure 2.1. The three main constituents of the fire triangle are fuel, energy (such as heat), and oxidant (typically oxygen). Although the fire triangle is useful, it fails to identify the fourth, essential element of fire which is the sustaining chemical reaction as shown in Figure 2.1(b) [14].

As defined by Faraday's experiments with a candle [15], there are four types of fire processes: 1) diffusion controlled flaming, 2) smouldering 3) spontaneous and, 4) premixed flaming combustion. In typical fire scenarios, one encounters diffusion flames, spontaneous combustion and/or smouldering. A burning match or building fire are examples of diffusion controlled flaming combustion. The diffusion flame is a result of oxygen diffusing into the gaseous fuel. This type of combustion requires a pilot flame such as a flame, spark, electrical arc, or glowing wire, to initiate combustion of a material or its vapours. Smouldering combustion is the oxidation of a solid without a flame, which usually results in an increase in temperature and/or the production of smoke. Spontaneous combustion or ignition is the process by which oxygen combines slowly with the fuel, usually at its surface, with the slow evolution of heat energy [16]. The fire starts when the material reaches its ignition temperature. In a premixed flame the gases required for combustion are premixed, then ignited (e.g., an oxy-acetylene torch).
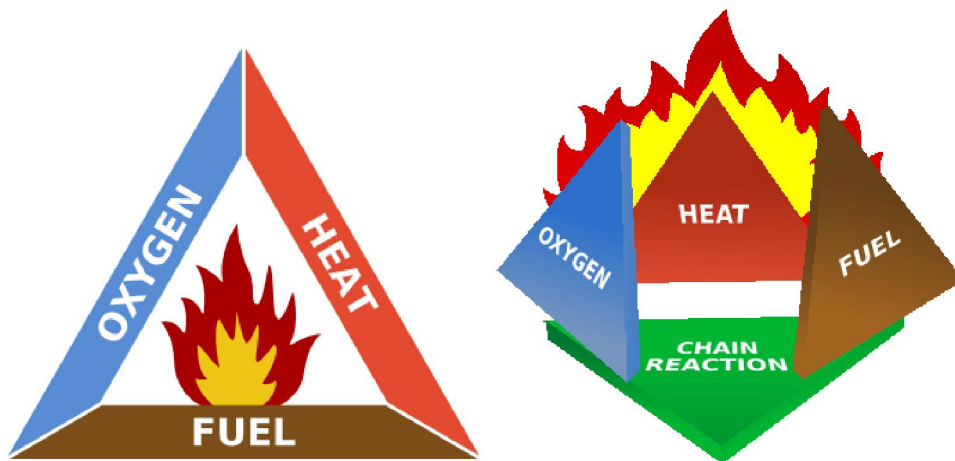
Figure 2.1: Fire models: (a) Fire Triangle, (b) Fire Tetrahedron [14]

2.3 Thermal degradation, flammability and flame retardancy

A chemical used as a coating or an element of an explosive material to reduce or eliminate a tendency to burn, which is used with paints, rubber, textiles, plastics, and other materials. Also known as fireproofing compound or a fire retardant, it is a substance other than water that decreases flammability of fuels or barrier their combustion [17].

Organic compounds degrade thermally, as is the case with polymers. If this thermal degradation of combustible materials is oxidative, and characterized by the generation and emitting of heat and light, the process is called a fire; fire is the flame, which is a visual sign and is an indication of the heat generated.

A flame retardant system is a compound or compositions added to materials, which increases a given material's resistance to combustion [17]. Effective flame retardant needs to hinder the supply of one or more of the elements required for sustained combustion [18]. The objective of the flame retardants is to lower a polymers intrinsic fire hazard by decreasing the rates of burning and flame spreading under fire conditions. The use of the flame retardants may avoid a small fire from flattering a major disaster [19]. In order for a flame retardant to be effective, it must interact and interfere with the degradation of the host polymer at the polymer's degradation temperature. The degradation temperatures for the most widely used polymers are between $200^{o}C$ and $400^{o}C$ [20]. Increased fire resistance can be achieved through several mechanisms, as can be seen in Figure 2.2.

A flame retardant is not intended to avert the material from igniting, but to keep the flame stretch rate to the least and to avoid sustained burning. Flame retardant tends to retard the spread of flames by increasing the given polymer's resistance to ignition. Ignition is unavoidable, because most substances will flame up if subjected to high enough levels of fire stress- thermal radiation [16].
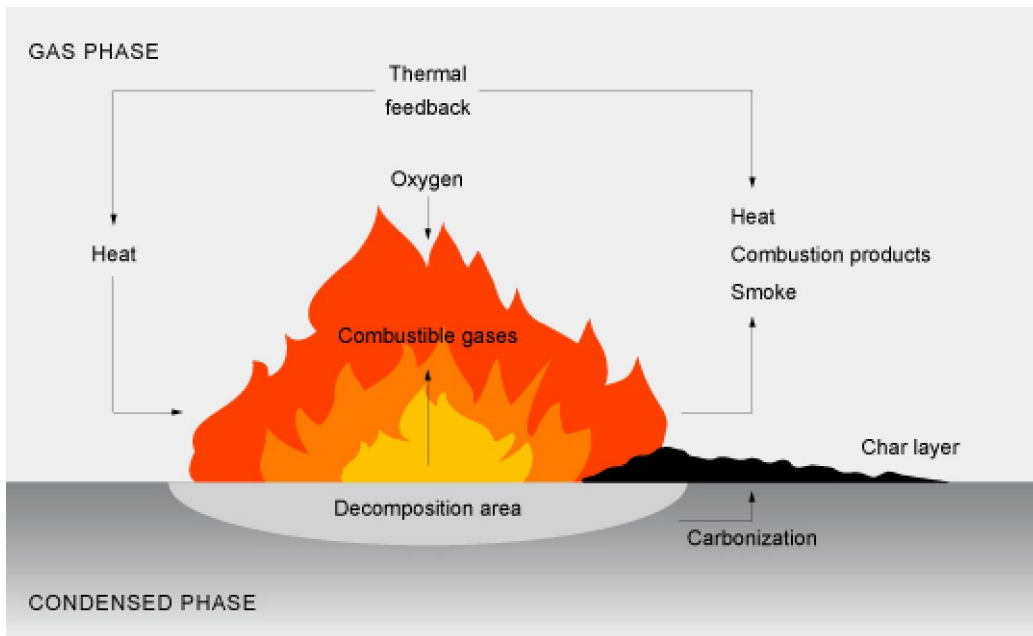
Figure 2.2: Model of combustion and flame retardance [19]

A useful and complete description of the mechanisms of general retardant systems is provided in the review article of Green [21, 22]. Different flame retardant systems can be identified, all of which function by different mechanisms. Flame retardants interfere with thermal decomposition pathway of the polymeric material. Different compositions interact differently with different polymers and flame retardant is used in this way very specific to the particular substrate for which it is designed.

Some flame retardants which form acids during combustion-like the halogens-operate through gas phase free radical inhibition. Other groups of retardants produce many non-combustible gases and dilute the amount of fuel or oxygen supplied to the fire. The formation of solid residues on the surface of the burning material is another way of reducing flame spread. Some reduce the rate of heat release during combustion by affecting the heat transfer pathway to the polymer substrate. Another group of flame retardants form a foaming char on the surface of the combusting material. These additives are called intumescent system. This system can also operate through combinations of the above mentioned mechanisms [19].

2.4 Global consumption of flame retardants

The worldwide market for halogen-free FRs is increasing strongly from US$ 1.62 billion in 2005 to $2.72 billion in 2009 as reported by the Swiss science and business consultancy firm Acon AG [23]. In addition to this, in Western Europe, the United States, and Asia, public consciousness of potential harmful halogenated products, industrial end-user initiatives and environmental legislation are jointly driving the market trend toward halogen-free products, which is an opportunity for a growing demand of intumescent products. These last products are phosphorus-based compounds which are expected, along with mineral FR's to show the fastest growth [23]. Figure 2.3 shows the global consumption of fire retardant compounds.
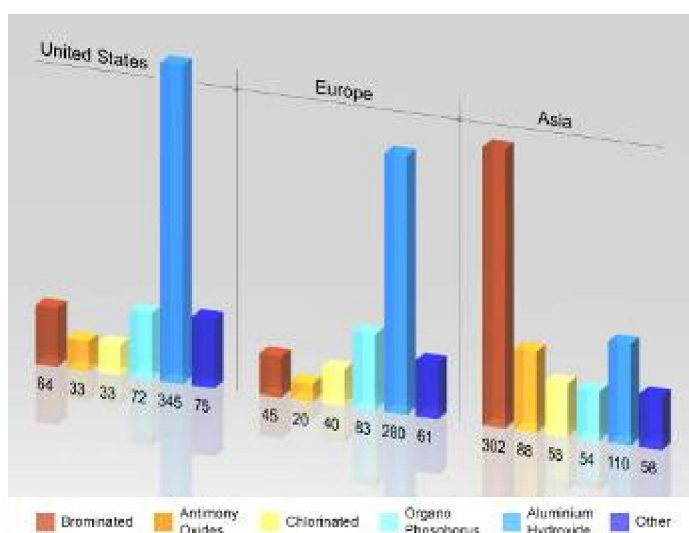
Figure 2.3: Consumption of flame retardants by region, based on volume. Figures are in 1000 tons, with a total of 1.8 million metric tons, data for 2007 [8]

2.5 The history of flame retardants

The need for fireproofing polymers became important in the nineteenth century due to the commercialization of cellulose nitrate plastic [24]. These materials are highly flammable and present a major fire risk.

In the early 1980's a mixture of pentaerythritol and melamine was used as intumescent flame retardant systems, together with additives such as phosphates [24]. Both ATH and halogenated compounds are still dominant. Antimony is now widely used with halogen compounds.

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In the early 1990's, market trends suggested that the market was beginning to move away from halogenated flame retardants [24] due to their toxic nature. These compounds work very well in most cases but release poisonous and corrosive gases when decomposing in fire, and these retardants are not readily disposable after use. In Europe especially, the environmentalists are putting more pressure on companies to produce more environmentally friendly products to protect the environment and humans [25]. The flame retardant world market for 1990 was estimated approximately 500 000 metric tons [26]. The dominant inorganic flame retardant is still ATH as it is also the least expensive flame retardant. Even though the flame retardant being used at present is based on inorganic compounds (such as ATH) and halogen containing compounds, but the use of intumescent materials is increasing [25, 27].

Different types of flame retardants, including intumescent systems with and without the additions of the fillers have been implemented with great success. Another new field of interest is the use of nano-clay composites as flame retardants [28]. In these materials the layered nano-clay is dispersed through out a polymer as exfoliated sheets, each of about 1×10^{-9} meters in thickness. Reasonable flame retardancy can be achieved at very low amount, in the order of 5%.

2.6 Basics of flame retardancy

A range of methods can be used to protect materials more successfully against attack by fire. Inherently Flame retardant (FR) polymers or high performance polymers can be used, but this implies the use of specific materials which might not have the required properties (e.g. aging, cost, etc.). Nevertheless, they exhibit very low flammability and are very efficient. The second method is to chemically modify the existing polymer to synthesize a FR polymer. In this case, specific production processes are required and very often the new FR polymer remains only synthesized at the laboratory scale. The last method is to use flame retardants directly incorporated in coating covering their surface (e.g. structural steel or textiles) [1, 29, 30]. This approach is frequently favored to recommend low flammability to polymeric materials as it is a tolerable compromise between cost and properties, it fetch great flexibility to design materials with multifunctional properties. The first two

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approaches will be briefly described in the following sections based on recent work and the last one will be fully described in terms of mechanism of action.

2.7 Types of flame retardant

Different types of flame retardants are described below.

2.7.1 Inorganic flame Retardant

Inorganic fillers act as flame retardants due to their endothermic decomposition which withdraws heat from the fire, and simultaneously releases water and inert gases such as CO_2, NH_3, etc. that dilute the oxygen and volatile fuel supplied to the fire [30, 31]. Furthermore, these inorganic compounds are non-combustible materials and thus physically dilute the amount of combustible polymers in the solid phase. Rothon (1996) [32] discussed several inorganic fillers flame retardant systems including zinc borate and magnesium hydroxide. Metal oxide residue is formed during the decomposition of inorganic systems. These metal oxides may catalyse further oxidation of the condensed phase. The later includes the carboneous residues formed during the charring step and remaining polymer [33].

2.7.2 Aluminium tri hydroxide (ATH)

In the early 1970's the main inorganic flame retardants used were aluminium tri hydroxide (ATH), zinc borate and antimony compounds [24, 32]. Although antimony was one of the most popular and frequently used compounds in the flame retardant systems over the years, it was expensive and thus used sparingly [1]. It, unfortunately, starts to decompose just above $200^{\circ}C$ and needs to be used in high dosages. $Mg(OH)_2$ systems are used when higher processing temperatures are needed [32]. Its metal oxide, which is formed on decomposition, is however a stronger char oxidation catalyst than those of ATH and leads to increased after glow [34]. For many years now, antimony based inorganic compounds have been used for flame retardants, for example Sb_2O_3, Sb_2O_5 and Na_3SbO_4 [35]. In 1990, some 20 000 metric tons of Sb_2O_3

were used in the USA as flame retardant. Unfortunately, antimony based compounds are very expensive. The basic Na_3SbO_4 is ideal for polymers which hydrolyze when processed in the presence of acidic additives. Currently antimony compounds are not used as flame retardant on their own, but are used as synergistic agent with other flame retardants. The addition of antimony compounds to halogen systems can increase their efficiency considerably and thus reduces the total additive loading in the polymer. More recent studies have shown that antimony trioxide has an inhibiting effect on char oxidation [35] when used with inorganic fillers. Unfortunately, a chemical explanation for this inhibiting effect was not given.

2.7.3 Boron compounds

Boron compounds are also widely used as flame retardant [36]. Compounds such as borax, zinc borate, barium metaborate and ammonium fluoroborate are well known fire retardant. Boron compounds act in both the condensed and vapour phase as fire suppressants. Most boron complexes are Lewis acids, which promote crosslinking of polymeric material on thermal degradation and thus minimize decomposition and volatile combustibles. Boron compounds can also react with hydroxyl group in the polymers to form glassy ester. This ester forms a char coating on the substrate surface and reduces solid-state carbon oxidation by protecting the underlying material. Moreover, it is common knowledge in commercial practice that the addition of zinc borate to metal hydroxide flame retardant systems can help to reduce the afterglow effect.

Based on the observation by Jimenez et.al. [11], there is a two step degradation mechanism in boric acid which starts with a weight loss of about 30% between 100 to $140^{o}C$, and a second step in the temperature range of $140-200^{o}C$. This step leads to the formation of a thermal stable material containing about 55% of the initial mass.

$$H_2BO_3 \longrightarrow H_2O + HBO_2 \qquad (1)$$
$$2HBO_2 \longrightarrow H_2O + B_2O_3 \qquad (2)$$
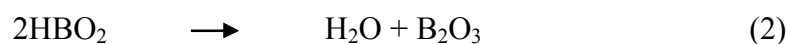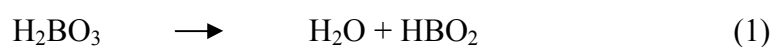
Boron oxide (B_2O_3) is a very hard glass. The crystals begin to break down at $300^{o}C$ and series of suboxides are produced with partial melting until full fusion is

reached at 700°C. High thermal stability of the compound means that the amount of char will be high. Moreover, due to the nature of boron oxide, the char will also show good mechanical resistance.

Boric acid forms hard glass with the release of water. It can play the role as blowing agent by providing a "glue" to hold the char together and provides structural integrity to the char with the substrate [37] .

2.7.4 Molybdenum

Molybdenum compounds are also used as flame retardants [36]. There are different types of molybdenum compounds which are currently used as fire retardant. Some of the compounds are molybdic oxide, molybdenum trioxide, zinc molybdate and ammonia octamolybdate. Molybdenum trioxide acts as a condensed phase retardant by increasing the char yield [38].

2.7.5 Halogenated flame retardants

The use of halogen containing flame retardants started to grow in the 1970's. The 1980's saw a large increase in the use of brominated system. Currently bromine based flame retardants are the most widely used halogen systems. In early 1990's approximately 150,000 metric tons of halogen based flame retardants were consumed annually worldwide, which is more than 25% of the total flame retardant market [26].

The use of halogen flame retardants is in the vapour phase. They decompose on heating to form halogen radicals that interfere with oxidation of the volatile fuels. Halogen radicals reduce the concentration of oxygen and hydrogen radicals when they react during fire [39].

Antimony and phosphorus based compounds are very effective synergists with halogen based flame retardants [35, 39]. These compounds help with the scavenging of free radicals and regeneration of the halogen radicals.

In the 1990's the market started to move away from halogen based flame retardants [24]. This is because they produce toxic gases (e.g hydrobromic and hydrochloric acid and fumes) and high levels of smoke. These gases are also highly corrosive. The halogen coating retardants are also difficult to dispose of, which implies that they are an environmental risk [40]. The shift to more environmentally friendly flame retardants is of interest worldwide especially in Europe. Accordingly, the majority of current research works are focusing on non-halogen scheme. However, alternative systems are usually less effective and tend to be more expensive.

2.8 Phosphorus flame retardant

Phosphorous containing flame retardants include phosphate esters and inorganic phosphate [21]. you can mention that even though phosphorus compounds are effective fire retardants but they are expensive. Taking advantage of this property but compromising on cost, phosphorus based fire retardants areThe mechanism of phosphate flame retardants varies depending on both the types of phosphorus compound and the polymer. Phosphorus-based flame retardants work in both the condensed and vapour phase (with the condensed phase being predominant), and interact accordingly to both physical and chemical mechanisms [40, 41]. Each of these mechanisms will be discussed separately. For example, they appear to function by promoting char formation, dripping of the burning polymer. It is well known that both phosphorus and phosphorus born compounds act as inhibitors of carbon oxidation [24, 42].

Even though phosphorus compounds are effective fire retardants but they are expensive [21]. Taking advantage of this property but compromising on cost, phosphorus based fire retardants are widely used as a synergistic agent for the halogen, inorganic and organic compounds. Organic fire retardants like intumescent fire retardants are relatively dependant on phosphorus compounds [43].

2.9 Condensed phase flame retardant

Two types of the reactions can take place in condensed phase flame retardant. Firstly breakdown of the rich polyhydric carbon (Polymer) by flame retardant. Secondly flame retardant can cause a carbon char layer on the polymer's surface. Different flame inhibition mechanisms have been identified in the polymer structure of materials that use phosphorus as flame retardant. Some examples of these are heat loss due the melt flow and drenched, surface barrier with char formation, acid catalyzed dehydration and char enhancement [44].

The derivatives of phosphoric acid and other phosphate decompose thermally to form strong phosphoric acid, which is a good flame retardant owing to its own low volatility [45]. The role of phosphoric acid is as a catalyst to start the dehydration in the presence of rich hydroxyl compound. Furthermore, when heated at high temperature, it forms polyphosphoric acid which. is an even better catalyst for dehydration of rich hydroxyl compound than phosphoric acid itself. In the dehydration step, char that protects the base substrate is formed, and water is released which will further reduce the heat. The formation of char is due to phosphoric acid, which will enhance the permeability and protect the char during fire [22]. The addition of nitrogen compounds in their gaseous state act in synergy with phosphorous to increase the char yield [33]. Mostly melamine, urea and dicyandiamide have been known to work well.

Initial crosslinking reaction occurs in the presence of rich phosphorus through the polymer. The phosphorus containing compounds can also catalyse the extract of the polymer chains thus reducing its molecular weight. This reduces the viscosity of the polymer, allowing it to trickle away from the fire region [45].

2.10 Vapour phase flame retardants

During thermal decomposition of the phosphorous based flame retardants, volatile phosphorous compounds are produced, which are effective flame retardants. Mass spectroscopy studies have shown that triphenyl phosphate thermally degrades to form volatile species such as P_2, PO, PO_2 and HPO_2. These phosphorous species

interfere and inhibit the branching step in the vapour phase. They extinguish the flame by reducing the hydrogen atom concentration in the vapour phase, [46]. Many phosphorous based flame retardants form water during fire. This water is volatilized forming inert water vapour. The presence of water vapour may help to extinguish the flame as it dilutes the combustibles and starves the fire of O_2 [21, 46].

The branching step, in the flame chemistry of the vapour phase, is rate cooling. In this step, hydrogen radicals react with oxygen to form hydroxyl and oxygen radicals as indicated below [19]. The hydroxyl and oxygen radicals react with the fuel and combustion is sustained.

$$H. + O_2 \quad \rightarrow \quad OH + O.$$
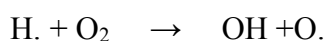
2.11 Phosphorous based Inorganic additive flame retardant

Phosphorous-containing flame retardants include inorganic phosphate, red phosphorous, organo phosphorous and chlorophosphorous compounds [21]. Adequate flame retardancy is achieved either by mechanical blending of the flame retardant compound with the polymeric substrate, or by chemical integration of the flame retardant into the polymer molecule either by copolymerization or by chemical modification of the performed polymer. Currently, synthetic polymers are made more flame retardant by adding additive. Additives are more generally used as they are usually cheaper and more widely applicable [47]. In many cases, these flame retardant mixtures can give an enhanced performance at low cost.

The synergistic effect of phosphorous- nitrogen and phosphorous –halogen are well-documented [22, 48]. Certain inorganic phosphorous compounds have been extensively used as components in intumescent system[49]. In recent years, there has been an intense research thought in the effect of nano inorganic such as clay in the polymeric systems containing phosphorous compounds, both as additives and as reactives [50].

The different types of phosphorous based flame retardants are discussed briefly in the following subsections.

2.11.1 Red phosphorous

The red allotropic form of phosphorous is moderately nontoxic and unlike white phosphorous, is not instinctively flammable. It is a polymeric form of phosphorous, thermally stable up to 450°. It has proved to be a powerful flame retardant additive. Elemental red phosphorus is a highly efficient flame retardant, especially for oxygen containing polymers such as polycarbonates and poly(ethylene terephthalate). The coated red phosphorous is used as flame retardant in nylon electrical parts, mainly in Europe and Asia [51, 52].

Red phosphorous will react with atmospheric wetness to form toxic phosphine gas, and it will ignite readily in air. As a result, commercial product is often encapsulated in an appropriate polymer matrix [52].

2.11.2 Ammonium phosphate

Ammonium phosphate was first recommended as flame retardant in theater curtains by Gay-Lussac in 1821. Mono and diammonium phosphate, or a mixture of the two, are widely used as flame retardant in a broad range of cellulosic materials such as paper, cotton and wood [53]. These salts have proven to be highly efficient at relatively low cost of application. The flame retardant formulations based on these salts are generally nondurable, because they are water soluble and, therefore, are easily susceptible to leaching out from the material matrix.

Ammonium polyphosphate (APP), on the other hand, is moderately water insoluble, nonmelting solids with very high phosphorous content up to 30%. They exist in several crystalline forms and the commercial products differ in molecular weights, particle size, solubilities and so on. They are used in intumescent paints with pentaerythritol as the carbon source and melamine as the blowing agent [52]. The intumescent coatings normally restrain resinous binder, acid source, gas source and other inorganic fillers. These systems are highly efficient as flame retardant in hydroxylated polymers.

2.11.3 Phosphates and phosphonates

There are several classes of amine phosphates commercially available as flame retardant for use in a wide variety of polymeric substrate, both natural and synthetic. A common example is the three variations of melamine phosphate i.e. melamine orthophosphate, melamine pyrophosphate and dimelamine orthophosphate.

Phosphate esters of phosphoric acid constitute an important family of organophosphorous flame retardants [43]. Triethylphosphate, a colourless liquid that has a boiling point between 209°C - 218°C, and containing 17wt% phosphorus, has been used commercially as an additive for poly ester resin and in cellulosic material. Trioctylphosphate is employed as a specialty flame retardant plasticizer for vinyl composites where low temperature flexibility is critical.

Water soluble dimethyl methylphosphonate, prepared by the Arbuzov rearrangement of trimethyl phosphite, has 25 wt % phosphorous content, the highest possible for an alkyl phosphonate ester [54]. It is used as a flame retardant in alumina trihydrate filled polyester resin and as a flame suppressant for halogenated polyesters.

2.11.4 Halogenated phosphates and phosphonates

Halogen gives flame retardancy to some extent; however this contribution is balanced by the lower phosphorous content. The halogens generally reduce vapour pressure and water solubility [39]. Tris(2-chloroethyl)phosphate, tri(1-chloroethyl)phosphate, 1,3-dichloro-2-propanol phosphate, bis(2-chloroethyl) 2-chloroethyl phosphonate are the cardinal members of this class of flame retardant. These compounds have different viscosities, solubilities, hydrolytic stabilities, and boiling points. The flame retardant efficiencies generally depend on their structural features and phosphorous halogen ratio. Tris(2-chloroethyl) phosphate is widely used in polyurethane, polyisocyanurate foams, most classes of thermosets, and in wood resin composites.

1,3-Dichloro-2-propanol phosphate has high boiling point, less water solubility and it enhances the stability of amine catalyst used in foam manufacture. It is used as

a flame retardant in butadiene, styrene and acrylic lattices for textile back coating. While bis(2-chloroethyl) 2-chloroethyl phosphonate is commercially available as a mixture of isomers. It is widely used as a flame retardant additive for rigid urethane foam, adhesives and coatings [55].

2.11.5 Reactive flame retardant

Another class of flame retardant is classified as reactive flame retardants; these are those that are covalently attached to polymer chains. The reactive flame retardants are inherently immobile within the polymer matrix. These are incorporated during the synthesis of the polymer, and also can be homogeneously dispersed throughout the polymer at molecular level. Due to, they are used in lower concentrations than comparable additives to give a desired level of flame retardancy. The incorporation of lower levels of flame retardants may bring an added advantage to the overall properties of the polymer (chemical, physical, and mechanical) are less likely to be the adversely affected when compared with those of nonflame retardant counterpart [47].

Reactive flame retardant can bring problems. The extensive reactive modification of a partly crystalline polymer is likely to lead to a significant loss of crystallinity, whereas if an additive is introduced to a partly crystalline polymer, it will most probably end up in the amorphous phase and has little impact on crystallinity [47, 52].

2.12 Intumescent fire retardant

The word "intumescence" comes from Latin "intumescere" which means "to swell up". Intumescence is defined as the swelling of certain substances when they are heated. Upon heating, intumescent coatings expand forming multicellular layer, which acts as a thermal barrier that effectively protects the substrate against rapid increase of temperature [9, 56].

Intumescent coatings contain "active" ingredients bound together by a binder. Generally, three "active" ingredients are used namely an acid source (normally

ammonium polyphosphate or a mineral acid), a carbon source (such as char forming polymers or polyols) and a blowing agent (e.g. melamine) [11, 12].

Chemical interactions between the "active" ingredients in the formulation lead to the formation of intumescent char. It is generally accepted [12] initially that the acid source breaks down to yield a mineral acid. Then it reacts with carbon source to yield carboneous char, and finally the blowing agent decomposes to yield inert gaseous products with low thermal conductivity to swell up the carbon char and produce the multicellular protective layers. These gases are trapped inside the viscous liquid due to formation of bubbles. This protective char restricts both heat transfer from the heat source to the substrate, and mass transfer from the substrate to the heat source, resulting in protection of the underlying material. In other words, to intumesce means to swell and to char. In simple terms, when exposed to heat, intumescent coating forms a thick highly insulative foam on the surface of the steel [57]. While fire retardant coatings have been used for 50 years, the incorporation of intumescent additives in polymeric materials is a comparatively new approach [58].

2.12.1 Classification of intumescent coatings

There are two different types of intumescent coatings. The first one is traditional chemical intumescent fire retardant coatings with chemical fire retardant mechanism. The second one is a new type of physical intumescent coatings containing expandable graphite with physical fire retardant mechanism.

2.12.2 Traditional intumescent coating

This type of coatings consists of three basic components: carbon, acid and gas [9, 59]. A carbon source; it can be a carbon-rich polyhydric compound, such as a glucose, starch, and pentaerythritol. An acid source is a dehydrating agent that reacts with carbon source to form carbonaceous char. This is generally a source of phosphoric acid, such as ammonium phosphate (APP), diammonium phosphate, and the other phosphates. A gas source expands the carboneous char of the coating with the release of gaseous products upon heating. This is normally a source of nitrogen or halogen

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releasing compound such as melamine and melamine phosphates, urea or chlorinated paraffin [12].

The initial intumescent coating was based on starch, APP and urea formaldehyde. This product would stink of formaldehyde, and is not percolate resistant [52]. At the present time, there is new development of intumescent coatings. For example, a new carbon source dispersed in polyurethane to improve weather durability of the coatings [59]. Significantly water-insoluble acid sources and gas sources, such as melamine pyrophosphate [60], melamine polyphosphate, as well as melamine polymetaphosphate have been studied to attain better fire retardancy [61] of intumescent coatings with these compounds.

In an earlier research [11], it has been shown that the combination of ammonium polyphosphate derivative (APP) and boric acid provides an intumescent behavior to an epoxy-based coating. It was observed that their proper blend inside the resin led to char expansion; the char that formed had good adhesion to steel plates, but this relation has not been further clarified.

Hanafin et al. [62] describes that typical intumescent coating contain at least one type of epoxy resin which functions as a binder, at least one char forming agent, at least one spumific and at least one epoxy curing agent. Char forming agent causes the formation of char when the intumescent coating is exposed to fire. Char forming agent controls the rate and mechanism of thermal decomposition of epoxy, resulting in the formation of carbonaceous char instead of the formation of carbon dioxide, carbon monoxide and water. The common component in fire retardant for char forming agent is phosphorous.

Pollak [63] has stated that there are two types of intumescent coating available either water-based or solvent-based coatings. Basically there are two materials added to support the intumescent coating which are the primer and topcoat. The purpose of the primer is to enhance adhesion of the intumescent coating to the substrate, while the topcoat is to provide a decorative appearance (e.g., color, gloss) or to enhance the durability of the coating. However, the primer and topcoat must be chemically compatible with the intumescent coating. According to Pollak, water-based products might not be able to accept an epoxy, hence will not have proper adhesion.

Jimenez et al.[11] reported that under the heat of flame, temperature of the coating surface will reach at a critical level. When this happens, the surface of the coating begins to melt and is changed into a highly gummy fluid. Concurrently, reactions are instigated that result in the release of inert gases with low thermal conductivity. The reaction leads to expansion of the carboneous char, up to several times its original coating thickness, to form a protective carbonaceous char as shown in Figure 2.4 that works as an insulative barrier between the fire and the substrate.
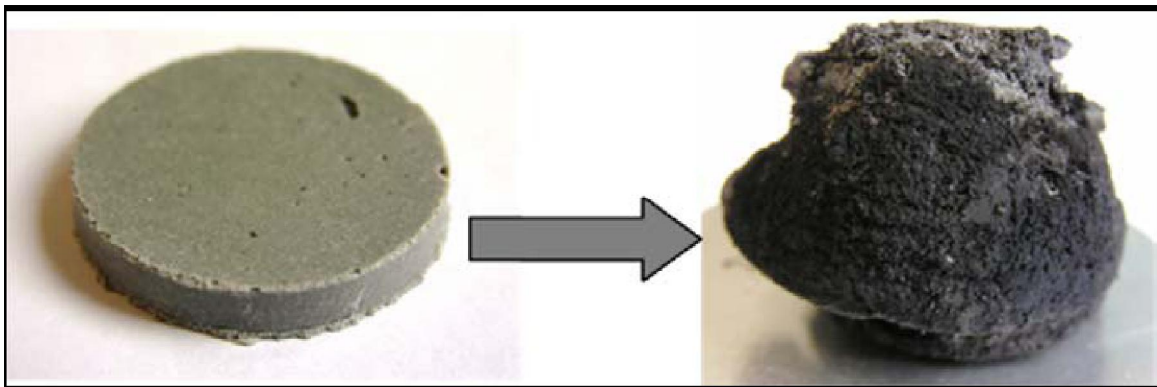
Figure 2.4: Swelling of an intumescent coating [11]

According to Underwriters Laboratories (UL) [64], intumescent fire-resistive coatings are paint like coatings that are applied to structural steel, including roof assemblies, column, beams, floor and walls. Typically, the thickness of intumescent coating ranges from 0.03-0.5 inches. As mentioned earlier three components are required to make an intumescent coating. However, Camino and Delobel [47], listed four categories of component which are necessary to provide intumescence. The respective components are an inorganic acid or a compound which generates an acid on heating between $100^{o}C$ and $250^{o}C$, a polyhydric compound (rich in carbon atoms), an amine or amide and a halogenated organic compound. Intumescence occurs only as temperature increases in the appropriate sequence to take place chemical reactions and physical processes. The rich polyhydric compound should not decompose or volatize at low temperature in order to react with the acid source, and the blowing gases should develop at the correct stage of gelation process.

It is essential for the material used in intumescent coating, to be thermally stable, provide a barrier to heat and the gasses. In order to reach this effect, a spume charred

layer has to be formed. A slow diffusion of gases in the char structure during the intumescent process allows the formation of an expanded structure as presented in Figure 2.5 [65].
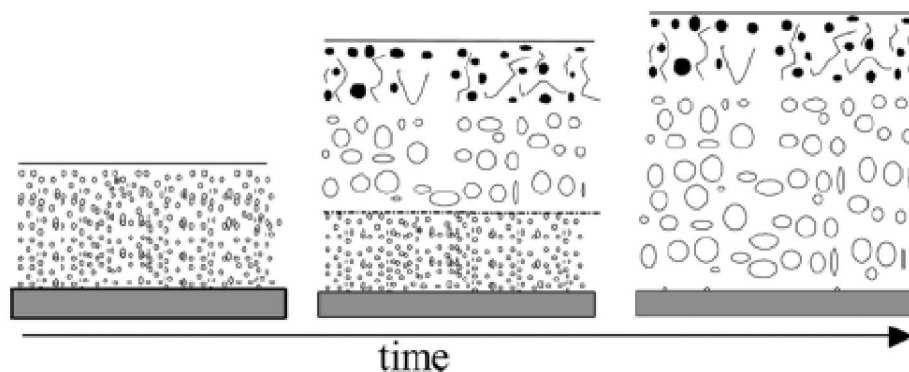
Figure 2.5: Intumescence Process [65]

The largely empirical development of intumescent coatings has led to the preferential use of certain compound in commercial systems. Ammonium polyphosphate (APP) is most commonly used of inorganic acid. Pentaerythritol (PER) and its oligomers, and water insoluble appropriate epoxy resins are polyurethane pentaerythritol examples of other polyhydric compounds. The commonly used blowing agents are nitrogen compounds such as melamine, urea, dicyandiamide and their derivatives. The halogenated compounds are also used as a blowing agent; mostly chloroparaffins are preferred as blowing agents or gas source in the intumescent coatings. There is also an inclination to avoid the introduction of halogenated compounds in intumescent systems because of their toxicity and the corrosiveness of HCl [58].

2.12.3 Expandable graphite intumescent coatings

Expandable graphite is a new generation fire retardant additive. It is formed by treating crystalline graphite with intercalates such as nitric or sulphuric acid [66, 67] .
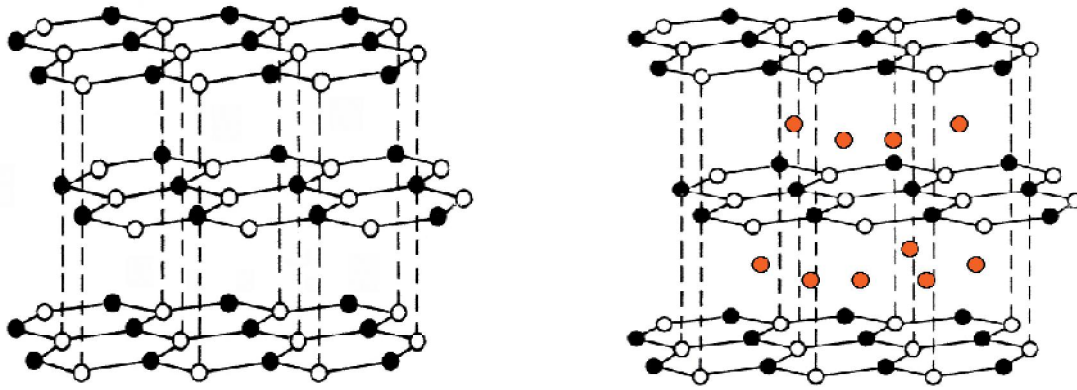
Figure 2.6: (a) Crystal structure of graphite, (b) Graphite layers with intercalated molecules

There is no covalent bonding subsist among the plane of the carbon atoms, the intercalant can be inserted into the gap and located within the graphite lattice .When the intercalated graphite is exposed to heat, the inserted molecules of acid would decompose and release gases. The graphite layer planes are forced apart by the gas and the graphite would expand. Expandable graphite coatings can expand the carboneous char to a greater degree than the traditional intumescent coatings, and thus provide better insulation to the underlying substrate [67].

Zhenyu Wang et al. (2007) [67] reported that anti-oxidation and fire resistance properties of expandable graphite coatings that contain xxx with size of 72μm are better than those of APP-PER-MEL Coating.

2.12.4 Acid source

An acid source is a dehydrating agent that reacts with carbon source to form carbonaceous char. Ammonium polyphosphate (APP) is mostly used as an acid source in the intumescent coatings. It has a high molecular weight chain phosphate. The phosphoric acid speeds up the formation of carbonaceous char and releases NH_3 gas which improves swelling [11]. So APP can be used as an acid source and a blowing agent.

The degradation mechanism of pure APP has been broadly explored. APP initiates to lose NH_3 gas at a temperature above 200^oC and highly condenses polyphosphoric

acid. Polyphosphoric acid does not show an additional weight loss below 600°C. Above 600°C, an azotropic P_4O_{10}-H_2O mixture boils and phosphorus is mislaid from the system. The lost is due to increasing loss of ammonia from 2.8 to 14.3% of the total blend weight.. The loss of NH_3 upon heating of a APP can be represented in a chemical equation as shown in the figure below [11].
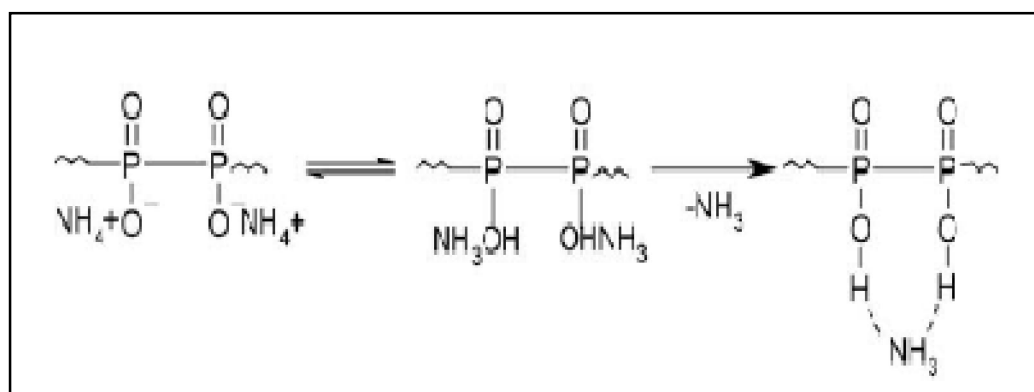
Figure 2.7: Degradation mechanism of APP[11]

Based on the research done by Camino and Delobel [58] on APP, under TGA, derivative thermogravimetric (DTG) and DSC there are few exothermic reactions involved. They observed three successive steps of weight loss in the range 260-420°C, 420-500°C and 500-600°C with corresponding weight loss of 13%, 4% and 78%. A further 3.5% of weight was slowly lost upon heating to 900°C.

It is substantial that APP is an acid source as it forms poly phosphoric acid, a gas source due to the release of NH_3, and also a carbonization source (the tris-(2-hydroxyethyl)isocyanurate) as THEIC contains carbon atoms, which provide char when heated [11].

During the first step and second step of degradation, infrared spectroscopy shows that the gases evolved from APP-PER (3:1 w/w ratio) contain ammonia and water. APP does not completely degrade to P_2O_5 due to the presence of residual ammonia, which interferes with water loss. The second step of degradation involves the elimination of water to form phosphorimidic groups [58].

NH_3 gas blows the charring layer to form a thick, hard and black charring layer. In the later stage of the experiment conducted by Jimenez et.al., [12], weight loss of

the coating is 18wt%. At the same time, high temperature and high pressure air current is formed on surface of the coating; the carbon in the charring layer is oxidized to carbon dioxide by oxygen. Due to weak adhesion, a part of the charring layer is detached [68].

Phosphorus compounds are highly diverse chemicals with different chemical properties that influence their role differently in the fire retardant mechanism. These mechanisms include the development of a glassy surface to shield the substrate structure from heat and oxygen, and free radical inhibition generally proposed for halogens [47].

Flame retardant mechanism for phosphorus depends on the type of phosphorus compound and the chemical structure of the polymer. Some phosphorus compounds will decompose thermally in the condensed phase to form phosphoric and polyphosphoric acids.

These acids can form a molten gummy surface layer to protect the substrate from fire and oxygen. The acids can dehydrate cellulose and transesterify ester polymers, and finally form significant amounts of char.

Ammonium polyphosphate is a relatively water-insoluble, nonmelting solid with high phosphorus content (30%). APP functions by decomposing to phosphoric acids, which esterifies the hydroxyl groups and the resulting cellulose ester decomposes to give char. These compounds also inhibit smoldering combustion. The flame retardancy is not permanent because of the water solubility properties [47].

2.12.5 Blowing agent

A blowing agent is an intumescent gas source that could expand the char of coating upon heating. This is typically a nitrogen or halogen releasing compound such as melamine phosphate, melamine and urea. In the patent for "Low Density, Light Weight Intumescent Coating" patented by Hanafin et al. [62], nitrogen releasing compound is also the preferred source. . According to Jimenez et al. [11], blowing agent is said to enhance foaming within char by releasing a large amount of gas

during char formation. An example of blowing agent is carbonate salts such as calcium carbonate (limestone) that will degrade to release carbon dioxide.
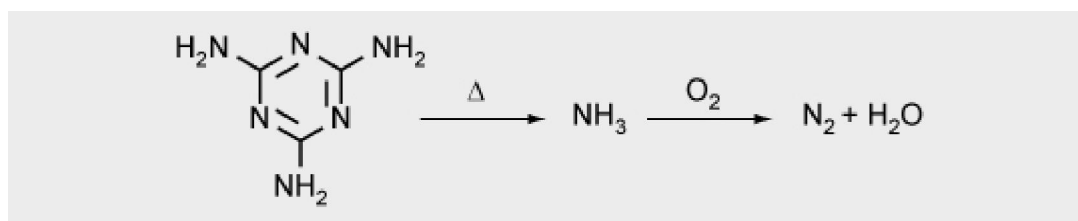
Figure 2.8: Degradation mechanism of blowing agent into gaseous products

2.12.6 Thermosets as binder

In thermoset systems, reactive flame retardant can be incorporated either in one, or more of the principal chain-forming components or in crosslinking agent. Both strategies have been employed with P-containing flame retardants in a variety of thermosets. Thermoset epoxy resins are specialty plastics in 2000, of which about 1.2 million tons were produced worldwide [69].

Epoxy resins are relatively expensive polymers and have outstanding material properties. They are used especially as coatings, adhesives, and electro casting composites for aerospace, and electro and electronic industrial applications. Like most polymers, epoxy resins are based on their flammable chemical composition, because almost all organic substances can be oxidized in an exothermic reaction with (air) oxygen to produce carbon dioxide and water[70, 71].

Flame retardants reduce the risk of fire origin and fire spread; and protect people, property and the environment. However, there are concerns regarding the use of flame retardants, especially the halogen-containing additives due to the release of toxic gases in case of fire [72]. Therefore, the focus of research in this area has shifted towards development of alternative halogen-free flame retardants. Since often both inorganic flame retardants and fillers in epoxy resin matrix or intrinsically flame-retardant resins such as phenolic resins and cyanate esters meet the high mechanical requirements, the trend is particularly on selected composite materials and resins to phosphorus-containing systems[73].

One of phosphorus-containing flame retardants, the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), has been known since 1972, is commercially available and used in many industrial applications as flame retardant in polyester fibers. In these applications, it has the required flame-retardant effect and offers the opportunity or be used as a derivative of flame retardant [74].

The major commercial alternative to DOPO and its derivatives for reactively flame retardant is epoxy resin, especially for electronic application. Amino and functional aromatic phosphates, phosphonates, and phosphine oxides have also been used as reactive components to impart flame retardancy in cured epoxy resins [72].

The three active ingredients of intumescent coating are linked together by a binder. Binder will become fundamental ingredients of the intumescent coating [4].

Gu et al. [68] reported that the matrix resins (prepared by unsaturated polyester resin and epoxy resin as two-component) manipulate the flame retardant performance of the intumescent coating. The matrix resins can well control the gas diffusion and contribute to development of the charring layer structure.

2.12.7 Char

Char is formed in the process of the thermal degradation of xxx and occurs in the expense of other reaction that may form volatiles. A typical char layer consists of an amorphous carbon along the way to graphitization. The extent of graphitization will influence the combustibility of the char layer and enhances thermal stability if the char layer contains an inorganic component in addition to carbon [33].

An X-ray diffraction (XRD) spectrum of char of the APP-PER system at a temperature above 290°C shows a single broad 2θ of about 23° which may be assigned to the conventional d002 scattering if isotropic carbon [58].

Fire resistance of coatings mostly depends on the formation of char initiated by reaction between APP, pentaerythritol (PER) and melamine; the char formation reaction is given in Figure 2.8. The interaction and decomposition of fire retardants additives and thermoplastic resin at 300-440°C establish the char formation [75].
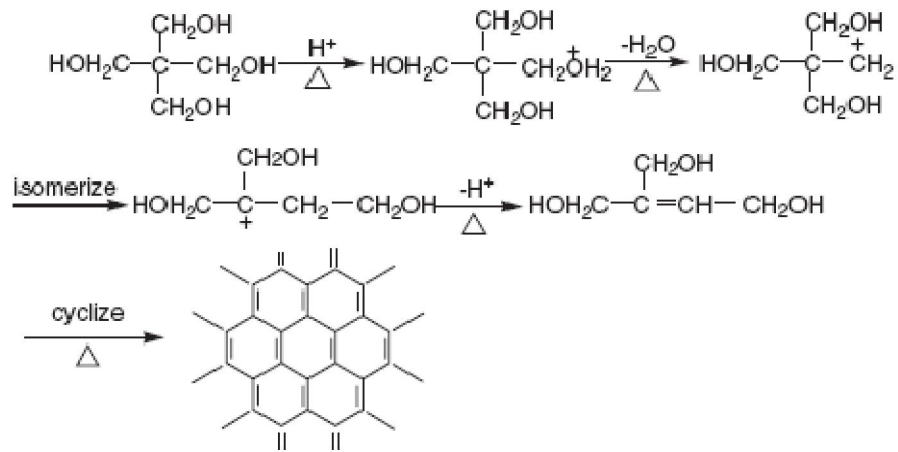
Figure 2.9: Char formation process [75]

The charring layer shield the surrounding substance and its protective property depends on the physical and chemical structure of the charring layer [76-78].

There are two perfect characteristics of charring structure that can be divided into uniform structure and asymmetric structure. Uniform structure bears the acceptable temperature gradients in the charring layer, and shelter the viscous liquid underlying the matrix material. In the non ideal structure, they have many routes and gaps that will contribute to overflow of gas and molten mass to enter the fire region due to this isolation effect of heat transfer is low-grade [75].
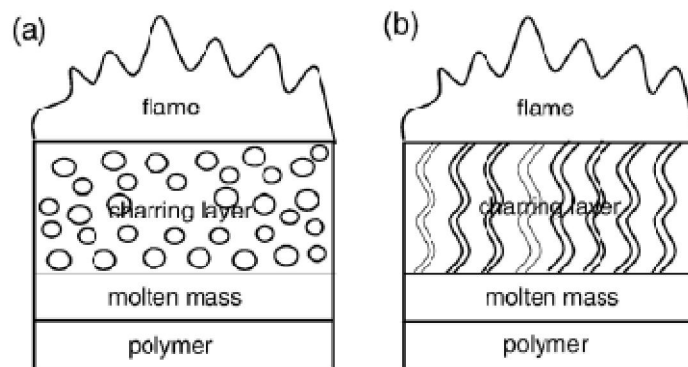
Figure 2.10: Structure of charring layer (a) uniform (b) asymmetric [75]

The greater the carbon content of a char (in the range 60-80%), the greater the thermal stability of the char. Char formation can be induced or increased by using

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additives that react with the degrading polymer and promote char formation at the expense of the formation of volatiles [79].

The promotion of char formation is perhaps the most important overall concept in fire retarding plastic materials. Char will reduce the heat of combustion from 94 000 calories per gram mol of carbon dioxide to 26 400 calories per gram mol of carbon monoxide to zero for carbon retained in the solid phase. Furthermore, formation of char will lower the smoke evolution, oxygen depletion and toxic gas evolution particularly carbon monoxide [80].

2.13 Effects of fillers towards intumescent

Fillers are non-polymeric compounding materials. Mostly, the amount of fillers used is in the range of 20-40% of the polymer mass. Fillers can be categorized as either "inert" or "active" based on their apparent smoke suppressant functions. Inert fillers lessen the quantity of smoke produced from a given mass of polymer by sinking the amount of combustible material present in the coating or by absorbing heat to decrease the burning rate of the material. Examples of such fillers are carbon black, clays, calcium carbonate ($CaCO_3$) and silica (SiO_2). It is possible that filler may be inert in one polymer system, but active in another. For example, HCl is formed during the combustion of chlorinated polymer system and will react with $CaCO_3$; however, $CaCO_3$ remains unchanged mostly during the combustion of polypropylene. Inert fillers usually give only minor contribution in flame retardancy, unless present in very high concentration[81].

'Active' fillers promote heat absorption similar as inert fillers; they absorb more heat per unit weight by endothermic process. Such as water, ammonia and carbon dioxide gases, evolved upon heating may also reduce the fuel volatiles and modify flame reactions. Currently used active fillers include aluminium tri-hydrate, magnesium hydroxide, magnesium carbonate and talcs [82]. During decomposition of polymer, water or carbon dioxide is released, generating both effects as flame retardant and smoke suppressant.

The addition of fillers has an adverse effect on the physical properties of polymers. High impact resistant polymers, for example ABS, undergo an immense decrease in impact strength due to the presence of fillers.

Chou, et al. [83] used three kinds of flame retardants in the study involving graphite powder (GP), sericite $Al_4(OH)_4(KAlSi_3O_{10})_2$ and graphite/sericite mixture. The study supports the fact that as the percentage of sericite in the flame retardant exceeds 75%, the flame proof grade of the IFRC incorporated with flame retardant is ranked the first grade fire retardant coating.

Li, et al. [84] reported that modifiers such as molybdenum disilicide ($MoSi_2$) and expandable graphite (EG) have been used to improve the performance of APP-PER-MEL coating. The largest improvement was achieved with 9 wt% $MoSi_2$ and 5 wt% EG.

A vigilant study by Scharf [85] evaluated the effect of TiO_2 and SnO_2 on the flame retardant char forming effect of APP in polypropylene, jointly with an intumescent nitrogenous resin. TiO_2 gave a stronger char yield and increased flame retardant properties. SnO_2, on the other hand, was the opposite; it made the char more porous and did not improve the char yield .The favorable reaction of TiO_2 was considered to have physical "bridging effect" but the harmful action of SnO_2 was suspected due to a useful chemical reactions with the phosphorous compound.

The synergistic effect observed by combination of traditional flame retardant with nano-fillers. A halogen free flame retardant nanocomposite using PA6, red phosphorous, montmorillonite and MgOH was reported by Tang et al. [86]. The coating that contained the nanocomposite flame retardant demonstrated better flame retardant properties than those of a traditional flame retardant PA6. Laoutid et al. [87] exchanged MgOH in flame retardant ethylene vinyl acetate by organoclays and found that the fire retardant properties of the system was enhanced. Horrocks et al. [88] verified the synergistic effect in flame retardant properties by combining APP with organoclays for PA6 polymer system.

Gu, et al. [68] synthesized an intumescent fire retardant coating by using a two component matrix resin i.e. an epoxy and an unsaturated polyester resin; they used

pentaerythritol as the carbon source, APP as the acid source, melamine as the gas source, titanium dioxide as then additive, and expandable graphite as the synergistic agent. The limit of fire-endurance achieved was 210 min with coating thickness of 2.0mm on wood matrix.

Howell [89] exploited to produce a flame retardant compound including both halogen (bromine) and phosphorous componds. These compounds range from salt of phosphonium bromide which demonstrates moderately high decomposition temperatures to bromoaryl phosphates which endure decomposition at further modest temperatures. He identified that these compounds have binary functional behaviour as flame retardants, to protect the gas phase activity related with halogen compounds, while endorsing the expansion of protective char in the solid phase.

Jimenez et al. [12] reported that ammonium polyphosphate and boric acid provide good result when they are mixed separately into resin. They used Bunsen burner test on the plate and discovered that the char produced from ammonium polyphosphate and epoxy resin puffed during the test. They also reported that bonding of char to the steel plate was very weak when ammonium polyphosphate was not added into the coating. The char formed from a blended mixture of boric acid and resin did not bond to the plate. A better result was attained when boric acid and APP were mixed together into the resin matrix. The temperature of rear of the steel plate achieved 400 °C in 29.5 min compared to 4 min when epoxy resin alone was used, and the char remained on the plate. However, the furnace test did not clarify how APP, boric acid and epoxy coating works. TGA result showed that thermal stability increased due to the interaction of additives with thermoset resin. They recommended that a reaction occurs between ammonium polyphosphate derivative and boric acid during heating which allows adhesion between char and steel substrate.

Li et al. [79] prepared an intumescent flame retardant coating using PER, APP, and MEL. Molybdenum trioxide (MoO_3) and ferric oxide (Fe_2O_3) were used as inorganic fillers to enhance the thermal properties of the APP–PER–MEL intumescent flame retardant coating. Based on the results of XPS analysis, they reported that thermal strength of the residue char of the APP–PER–MEL coating was enhanced with MoO_3 and Fe_2O_3 because the carbon contents were enhanced with 9 wt % MoO_3

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and 9 wt % Fe_2O_3 at 350 °C, 580 °C and 800 °C. SEM images of chars showed that MoO_3 and Fe_2O_3 improved the top and inner surface structure of char layer of the APP–PER–MEL coating. However, they did not explain the temperature of the substrate, and char residue composition.

2.13.1 Kaolin clay

Kaolin is a fine clay mineral with the chemical composition of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. It has two layers of crystal i.e. silicon-oxygen tetrahedral layer attached with alumina octahedral layer. Clay minerals include kaolinite, nacrite, dickite, montmorillonite, illite, chlorite, attapulgite and anauxite. Kaolin clay minerals have the same chemical compositions. They differ from each other by layers stacked on top of one another. Kaolinite is the main ingredient of kaolin. Its chemical composition is $Al_2Si_2O_5(OH)_4$ (theoretically 39.8% alumina + 46.3% silica + 13.9%) but elements are not diverted from this ideal composition.

Clay can be used as flame retardant systems. Experiments showed that the heat release rate, the most important parameter for predicting fire hazard, was reduced by 63% in the nylon-6-clay nanocomposite containing 5% of modified montmorillonite clay. The clay additive did not degrade the overall material properties and caused no increase in carbon monoxide or soot levels during combustion [28, 33].

2.13.2 Zirconium silicate

Zirconium is a chemical element with the symbol Zr. Zirconium is used as filler in intumescent coating. The use of zirconia with borate as additives in organic polymers reduces polymer flammability. When heated to temperature at which fire retardant activity is needed and exhibited, zirconia will modify to the form in which the fire retardant effect is provided. It is preferred to use powder form of zirconia such that it can be readily dispersed in the material in which it is incorporated. [90]. Zirconium acetate ($ZrC_2H_4O_2$) is used as a flame retardant for textiles. In thermal barrier coating, $ZrSiO_4$ or zircon have been extensively investigated [91].

Liu et al. [92] prepared intumescent flame-retardant poly(lactic acid) (PLA/IFR)/organo-modified α-zirconium phosphate (OZrP) nanocomposites via incorporation of charring agent (CA), ammonium polyphosphate (APP) and OZrP into PLA. OZrP was synthesized directly by a solvent thermal method. The TGA data showed that the OZrP could increase the residue and significantly improve the flame retardancy of PLA/IFR/OZrP nanocomposites, showing an excellent synergistic effect. The flame retardant mechanism of PLA/IFR/OZrP nanocomposites may correspond to the intumescent flame retardant mechanism and catalyzed carbonization mechanism caused by OZrP.

2.13.3 Multi-walled carbon nanotube

The discovery of carbon nanotube in 1991 marked the emergence of a new class of high performance polymer composites with nanotubes as the reinforcing material. The exceptional mechanical and physical properties demonstrated by carbon nanotubes, especially single wall carbon nanotubes, combined with their low density makes them an excellent candidate for composites reinforcement. These composites are being used to enhance the strength, stiffness and electrical conductivity.

Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Structurally MWCNTs consist of multiple layers of graphite superimposed and rolled in on them to form a tubular shape. The MWCNT are the most reasonable ones for commercialization as composite addictive or coating elements. They offer less attractive properties, but they can be produced on high scale at a relatively low price [93-96].

Previous research has shown that nanoparticle fillers are highly attractive for the purpose of making a material more flame retardant, because they can simultaneously improve both the physical and flammability properties of the polymer nanocomposite [75, 97-99].

2.13.3.1 Application of MCNTs as addictive

Multiwall Carbon Nanotubes are believed to be useful as flame retardant nano addictive because of their highly elongated shape, and the balance between the effect of thermal conductivity and shielding performance of external radiant flux and heat feedback from the flame. Their excellent mechanical properties combined with their nano size and low density of 2.0 g/cm^3 makes them a viable reinforcing phase in a variety of polymer, ceramic and metallic matrices in designing high-performance composite materials [100, 101]. It is also believed that CNT can provide innovative materials for thermal control application with their high thermal conductivity, and high aspect ratios as well as the mechanical strength [13]. It is also belief that the char form will be much denser [93, 98].

Florentina et al. [100] combined carbon nanotubes with fire retardant materials such as ATH (alumina trihydrate), DECA (decabromodiphnyl oxide), antimony oxide (Sb$_2$O$_3$) and resorcinol diphospate (RDP). They concluded that there is interaction between ATH and CNT which manifested in large amount of char that consequently greatly decreases the values of peak heat release. It is believed that there is some potential advantage in combining CNT with fire retardants in some polymers.

Some of us wonder why carbon nanotubes are used instead of other cheaper material such as clay and carbon nano-fibers. It was found that these particles provide material non-flammability with relatively small concentration compared to other fillers. Carbon nanotubes usually possess diameters in the range from 50 to 150nm. CNT themselves are not flame retardants – they do not put out fire [96, 102].

2.13.3.2 Advantage of MWCNT as carbon source

It is believed that MWCNT as carbon source in intumescent coating can have several advantages as discussed below.

　i.　Provide protective char on the material surface

　　　a.　The char of CNT reduces the diffusion of evaporated chemicals, and simultaneously the diffusion of oxygen from closed environment toward the surface of the material.

    b.   The char provides heat thermal barrier – reduces the rate of heat transport. This will slow down the melting of coating and its evaporation in comparison to the unprotected one.

    c.   The char produced will be much denser.

ii.   Boost mechanical strength (up to 15 to 20 times stronger than steel but 5 times lighter), thermal conductivity, electrostatic discharge features, electrical conductivity and thermal conductivity (same as that of diamond but more than five times that of copper) – all of these give significant impact on product performance and quality.

iii.   Ignite more easily (increased time for the formation of char).

iv.   The scaffold of carbon nanotubes reduces the convective movement that appears in molten material during fire and the relevant mass and heat transfer ratios are also decreased.
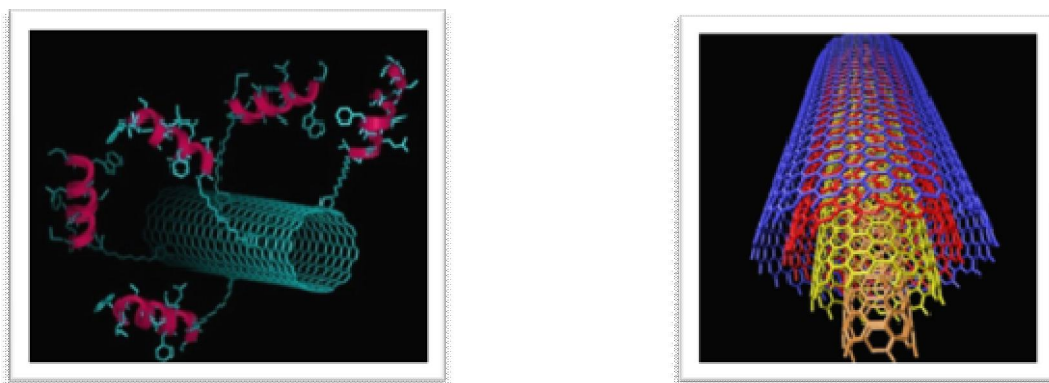
Figure 2.11: The bonding in carbon nanotubes is sp² (left) and multiwalled carbon nanotube (MWCNT) model (right)

2.14 Effect of weathering on fire retardant coatings

Weathering may be used to describe those changes developed by the action of weather that add to the aesthetics of a building and give character to its materials. It is preferable that the term weathering include all those changes, both desirable and undesirable. All of these elements including temperature, moisture, organic acids and dissolved carbon dioxide influence weathering rates but the major controlling factor of weathering rate is average rainfall [103].

Almeras et al. [104] reported, that many polymers undergo degradation caused by weathering in which photo chemical reactions involving ultraviolet (UV) solar exposition and atmospheric oxygen lead to chain scission. These changes of material

characteristics over time can cause problem in long term application of polymers and affect adversely the mechanical behaviour of polymers in many cases.

Weathering reactions also depend on temperature. Higher temperature will increase the rate of chemical reactions. Hence, such reactions are magnified more in the tropical areas than in colder temperature. It is estimated that the weathering rate due to solubilization and hydrolysis increases 1-1/2 to 2 times with each temperature increase of $10^{o}C$. In addition, it is estimated that the weathering rate can increase nearly 20 to 40 times in tropical areas [103].

Flame retardant coatings often become moisture sensitive and the ultraviolet rays during outdoor exposure will easily break the molecule structure of the coatings. Consequently, traditional flame retardant coatings are not durable in exterior applications [75, 105].

Most literature dealing with stability of polycarbonate carries the message that irradiation with UV light causes chemical changes in the structure of surface macromolecules. The chemical changes are limited to the top layer surface (0.5mm) and do not spread to the bulk. Fire spread, however, is a surface phenomena, therefore any changes in surface properties can affect the flammability behavior of the materials [106].

It is also understood that crosslink density and molecular weight eventually diminish, although both may increase early in the exposure. Normally, the glass transition temperature Tg increases gradually during exposure. During exposure, hydrogen bonding will increase as polymer binder becomes more oxidized. However, hydrogen bonds are usually regarded as being only 10-20% as strong as a covalent bond, so any increase in stiffness would require a large number of hydrogen bonds to be formed during weathering to counter the loss in covalent bonds [107, 108].

According to some published works, intumescent coatings intended for use within a structure need to be stimulated under several environmental conditions including accelerated aging and elevated humidity. Intumescent coatings intended for outside exposure stimulated under elevated humidity, carbon dioxide and sulfur dioxide air mixture, salt spray, ultraviolet light, freezing and stimulated rain. The evaluation of

degradation after aging often is made by visual check. Sometimes more precise and less subjective techniques are used in particular electrochemical techniques.

Deflorian F. et al. [109] described that during low humidity and high temperature environment, the evaporated water diffused in the coating. While in high humidity environment, no surface water condensation occurs but it is possible to have limited water vapour uptake. In a very high humidity environment, water will be condensed on the coating surface which leads to high water uptake. Electrochemical Impedance Spectroscopy studies show no significant differences in the coating resistance value in both lower and higher thickness coating after artificial UV radiation exposure. This result seems to indicate that physical modifications caused by photo-oxidation affecting the barrier properties are not very much influenced by the coating thickness.

Surface deterioration would be expected to have a substantive effect on the flammability of polycarbonate. Fire spread is a surface dependant phenomena and any changes in the surface will be reflected in fire properties e.g., fire release or heat release. Scission of macromolecules on the surface leads to monomers and to chains with lower molecular weight. The difference in bubble formation is a key difference between exposed and control samples. The exposed samples show more rapid smoke production compared to the control [106].

Micro bubble formation may result from UV induced changes in free volume over time from formation of microcrystallines which forms in increased sites for bubble nucleation, or most probably from migration of small molecules (phenolic) diffusing from the degraded surface through the sheet. The result is lower Tg, higher moisture uptake, and small bubble formation at lower temperatures for all sheet which also has more flammable degradation products coating the surface [106].

The ultimate goal of weathering studies is to provide a link between the composition of a coating or its constituents, and how well it performs its macroscopic function. It is common experience that coating becomes stiffer and more brittle during exposure.

2.15 Steel substrate used in fire retardant coatings

Steel is a non combustible material that is available in various product types: structural (hot-rolled), reinforcing, pre-stressing, or cold formed. As with any other material, exposure to elevated temperature leads to a temporary decrease in the strength and stiffness of steel. Such prolonged degradation adversely affects the resulting deformations and load-carrying capabilities of steel during fire exposure. Steel thermal properties are also affected, such as coefficient of thermal expansion, specific heat, and conductivity which affect the heat transfer and temperature profile calculations [110].

Unprotected steel will quite visibly deform, twist and buckle after exposures to temperatures in excess of about 600°C for more than 15 minutes. At and above such high temperatures, the crystalline/metallurgical changes are inconsequential during the fire itself relative to the significant decrease in strength at these elevated temperatures, but the significant heating effects of the fire could permanently alter the nature of the steel material. Usually, steel that has experienced a hot and prolonged fire will have such extensive damage that replacement, rather than its straightening and repair, will be prudent on cost considerations alone, so the long-term metallurgical [110].

Several researchers have used steel in their research, but the types of steel used was hardly mention. However, it is well known that the type of steel used for building and many structural uses is type A36, while carbon steel is chosen as a substrate due to its low cost and availability.

2.15.1 Structural Steel

Steel for structural uses may be classified by its chemical composition, tensile properties, and method of manufacture such as carbon steels, high-strength low-alloy (HSLA) steels, heat-treated carbon steels, and heat treated constructional alloy steels [111]. Figure 2.12 shows a typical stress-strain curve for steel in each classification to illustrate the increasing strength levels provided by the four classifications of steel.
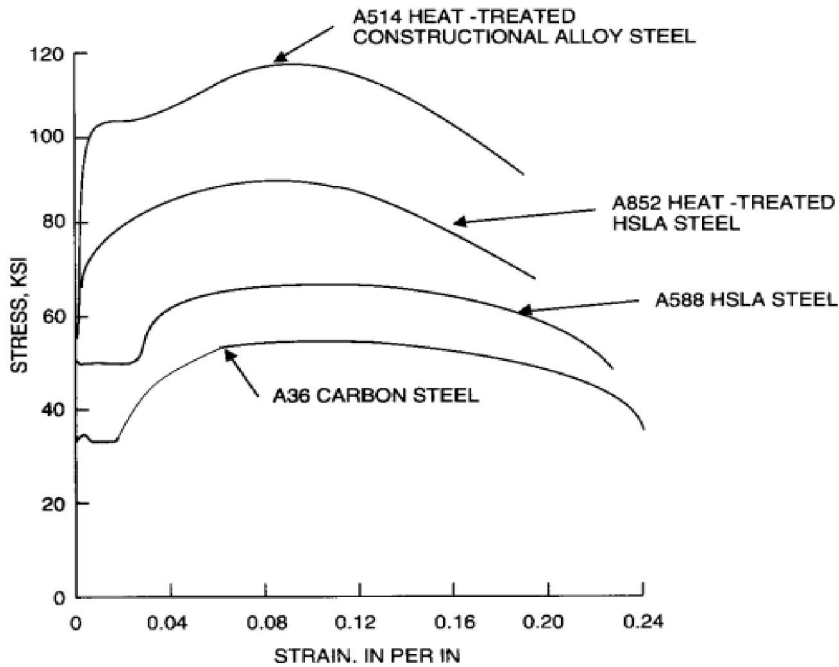
Figure 2.12: Typical stress-strain curves for structural steels [111]

2.15.1.1 Types of Carbon Steel

A steel may be classified as a carbon steel if the maximum content specified for alloying elements does not exceed the following [111], that is manganese (1.65%), silicon (0.60%), and copper(0.60%).

A36 steel - the principal carbon steel for bridges, buildings, and many other structural uses. This steel provides a minimum yield point of 36 ksi in all structural shapes and in plates up to 8 inch thick. In structural steel framing for building construction, A36 steel has been largely replaced by the higher strength A992 steel.

A529 - a carbon - manganese steel for structural purposes, available in shapes and plates of a limited size range. It can be furnished with a specified minimum yield point of either 50ksi or 55ksi.

A573 - another carbon steel which is available in three strength grades for plate application in which improved notch toughness is important.

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2.15.1.2 Effects of elevated temperature on tensile properties of steel

At elevated temperatures, the behaviour of structural steels subjected to short-time loadings is usually determined from short-time tension tests. Yield strength and tensile strength are reduced as temperatures are increased [111, 112]. Figure 2.13 shows the ratios of yield strength and tensile strength for structural steel at elevated temperatures to room temperature value.
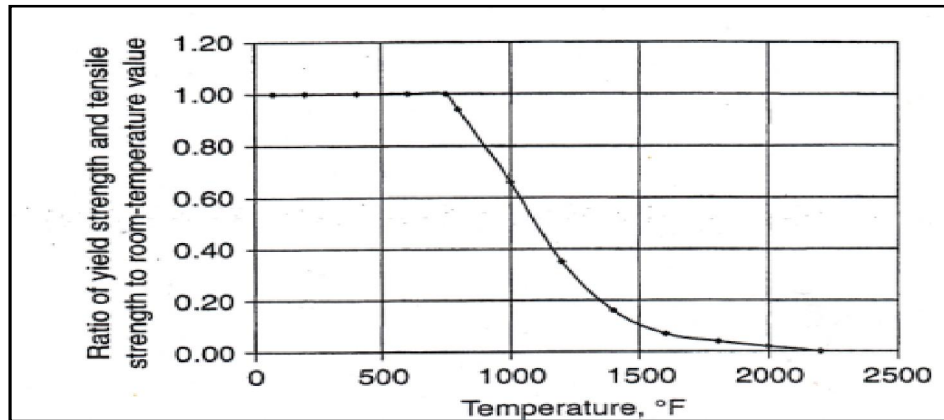
Figure 2.13: Effect of temperature on yield strength and tensile strength for structural steel [112]

Figure 2.14 shows the modulus elasticity decreasing with increasing temperatures. The relationship shown is typical for structural steel. The variation in shear modulus with temperature is similar to that shown for the modulus of elasticity. But Poisson's ratio does not vary over this temperature range.
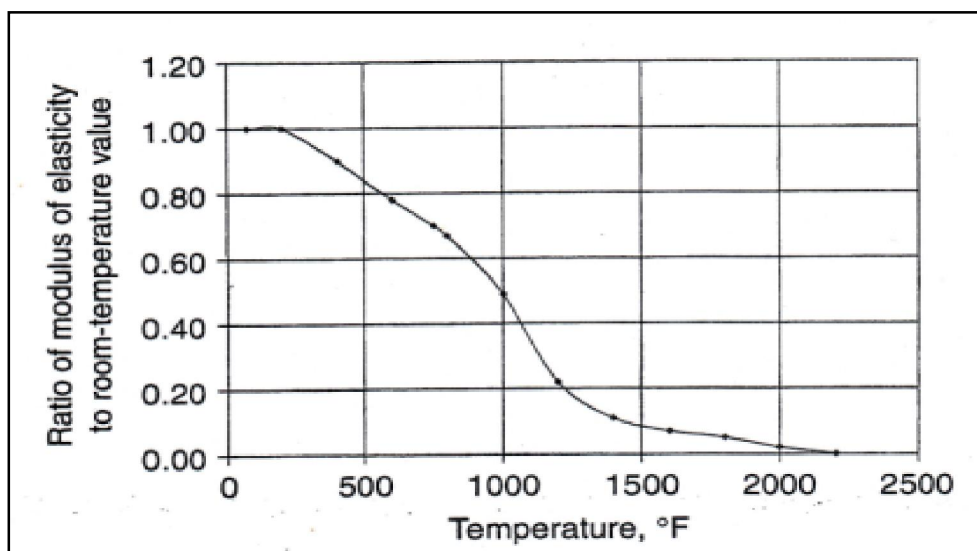
Figure 2.14: Effect of temperature on yield strength and tensile strength [112]

Ductility of structural steel as indicated by elongation and reduction of area values decreases with increasing temperature until a minimum value is reached. The initial decrease in ductility is caused by strain aging and is most pronounced in the temperature range of 300 to 700°F.

2.16 Thermal breakdown in intumescent coating by physical process

The various physical processes occurring during thermal decomposition depend on the nature of material. Thermosetting polymeric materials, which do not melt and are insoluble once they have been formed, do not undergo simple phase changes upon heating. Nelson and Wilkie [27] stated that the physical behaviour of thermoplastics following heating depends on the degree of crystallinity. Crystalline material has well-defined melting temperature, but amorphous materials do not.

Glass is an example of an amorphous material and it has given its name to "glass transition temperature". Amorphous material appears to have the structural properties of solid materials at low temperature. Then, at the glass transition temperature, the polymers start a transition toward a soft and rubbery state. This temperature is the lower use limit for elastomers, but for plastic materials requiring rigidity and compressive strength it is the upper use limit. Figure 2.15 shows an idealized view of the effect of increasing the temperature on deformability of thermoplastic [113].
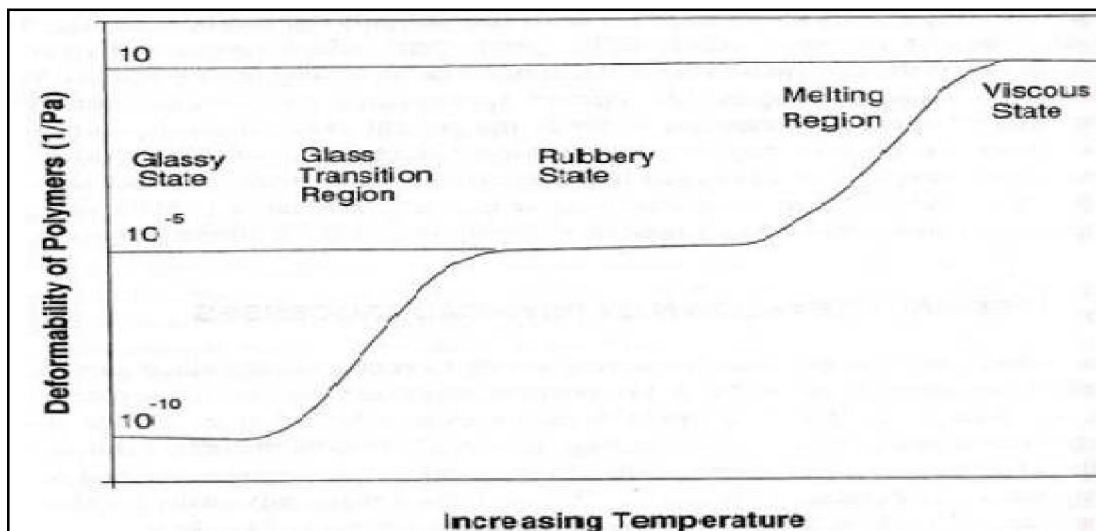
Figure 2.15: Nominal effects of increasing temperature on thermoplastic materials [113]

2.16.1 Thermal effects from filler in intumescent coating

Recently thermogravimetric analysis (TGA) have been widely used to study the thermal decomposition of hydrated mineral fillers [22]. The changes in thermal degradation profile often observed in thermoplastic in the presence of many types of filler can also be a significant factor affecting the action of fire-retardant fillers.

Almost all of the literatures that have been reviewed described thermal degradation of additives and fillers used in polymers. For example, Wei Gu et al. [68] prepared an intumescent flame-retardant coating by using unsaturated polyester resin and epoxy resin as two-component matrix resin, ammonium polyphosphate (APP) as acid source, melamine (MEL) as blowing agent and pentaerythritol (PER) as carbon agent, expandable graphite as synergistic agent, with the addition of titanium dioxide (TiO$_2$). Thermal decomposition of those additives used was analysed using TGA and DSC.

2.17 XRD analysis of intumescent coating

X-Ray diffraction (XRD) has been poorly used to characterize the carbon phase of intumescent structure. Previously, the carbon structure resulting from the development of the intumescent system is mainly disordered, whereas XRD characterizes ordered structure. However, this technique may be of interest to study the carbonization process in the case of flame retardant containing layered additives such as expandable graphite [84] or even more lamellar nanocomposite such as montmorilonite (MMT).

XRD analysis could provide interesting information regarding the inorganic materials formed during the carbonization process in complex formulation [85]. Previous study done by Wang et al. [85] found that the formation of titanium pyrophosphate resulted from the reaction of APP and titanium dioxide.

Another study done by Li et al. [84] on the effects of EG and MoSi$_2$ shows that several XRD peak of residue char were obtained at 0.3342 and 0.4255 which were assigned to silica (SiO$_2$), and those at 2.0265, 2.2663, 3.9684 and 3.9276 were

assigned to $MoSi_2$. The result also concluded that the reaction between $MoSi_2$ and O_2 can improve the performance of anti-oxidation of the APP-PER-MEL coating due to the presence of protective silica layer. Levchik and co-workers [82], from XRD result, found the reaction products of talc and APP; for the APP: talc ratio of 2:1, ammonium magnesium polyphosphate($MgNH_4(PO_3)_3$) and ammonium silicon tetrapolyphosphate ($Si(NH_4)_2P_4O_{13}$) were found to form at $300°C$, followed by the loss of all nitrogen compound and the formation of magnesium cyclotetrapolyphosphate ($Mg_2P_4O_{12}$), and silicon oxomonophosphate ($Si_5O(PO_4)_6$) at a higher temperature ($\sim 400°C$).

2.18 Adhesion in intumescent coating

Adhesion is about the physical and chemically intermolecular interactions in the interface or interface layer [114]. Adhesion promoters can be from a range of chemicals available including silicones, amides, phosphates or modified polymers. Besides that, there are binders and additives. This adhesion promoter is to ensure sufficient adhesive bonding between the coating and coated material, hence the coating is able to function effectively to protect the coated surfaces.

2.18.1 Coating substrate interaction

According to Reinhard [115], the surface of clean steel is not iron, rather hydrated iron oxides are present as a monolayer on the iron. Adhesion to this surface is promoted by developing hydrogen bonds between groups on the resin molecules, and the oxide and hydroxide groups on the surface of the steel.

Bisphenol-A (BPA) and their derivatives commonly provide excellent adhesion to steel. These resins have hydroxyl group and ethers group along the chain, which can provide interactions with both the steel surface and other molecules in the coating. It may also be important that the backbone consists of alternating flexible 1,3-glyceryl ether and rigid Bisphenol A group. According to literature [72], it seems logical that such a combination could provide the flexibility necessary to permit multiple adsorption of hydroxyl group on the surface of the steel, along with rigidity to prevent

adsorption of all hydroxyl groups. The remaining hydroxyl group can participate in crosslinking reactions or hydrogen bond with the rest of the coating.

A.C. Rouw [116] also stated that Bisphenol A containing many aromatic groups in its structure forms a good barrier to corrosion promoting compound like water, oxygen and ions. Moreover the presence of many secondary hydroxyl groups along the chain gives rise to a strong adhesion to metal. These hydroxyl groups are thought to bind strongly to the metal oxide surface because of hydrogen bonds interaction.

2.19 Standard testing of intumescent coating

Required levels of fire protection are normally specified in terms of time and temperature on the basis of one or more criteria, which may include statutory requirements, design considerations and insurance cost implications. The duration is established by a time rating which is determined by testing in accordance with an approved standard. Table 2.1 below shows the required standard that has been established by different countries [113].

Table 2.1: Usual test standard established by different countries [113]

Standard	Country	Description
ASTM E-119	United States of America	Cellulosic or wood fire, used since 1903
BS 476 Part 8 & Parts 20-22 (1987)	The United Kingdom	Cellulosic or wood fire
ISO 834 (standard time/temperature curve)	International	Cellulosic or wood fire
DIN 4102	Germany	Cellulosic or wood fire
BS 476 (Part 20,Appendix D)	The United Kingdom	Hydrocarbon fire
ISO 834(hydrocarbon time/temperature curve)	International	Hydrocarbon fire, developed early 1970
UL 1709	United States of America	Hydrocarbon fire, developed in the early 1970

2.19.1 Hydrocarbon and cellulosic fire characteristic

The hydrocarbon fire test curve developed by mobil oil company in the early 1970s has been adopted by a number of organizations, and in particular, Underwriter Laboratories (UL 1709 "rapid temperature rise"). U.K Department of Energy, BSI, ISO and the Norwegian Petroleum Directorate is now a common test method for high risk environment such as petrochemical complexes and offshore platforms.

Cellulosic fire curve (ASTM E119) simulates the rate of temperature increase observed in a residential or commercial building fire where the main sources of combustion fuel are cellulosic in nature, such as wood, paper, furniture and common building materials [117]. The fire curve is characterized by a relatively slow temperature rise to around 950°C after 60 minutes.

Figure 2.16demonstrates the different time temperature curves for this kind of 'hydrocarbon' fires and 'cellulosic' fires (as used for most Building Regulation standards on fire protection) [117]. The graph below interprets that the Hydrocarbon time temperature curve increases rapidly at the beginning of the graph and reaches higher temperature compared to the Cellulosic time temperature curve ('cellulosic' fires curve).
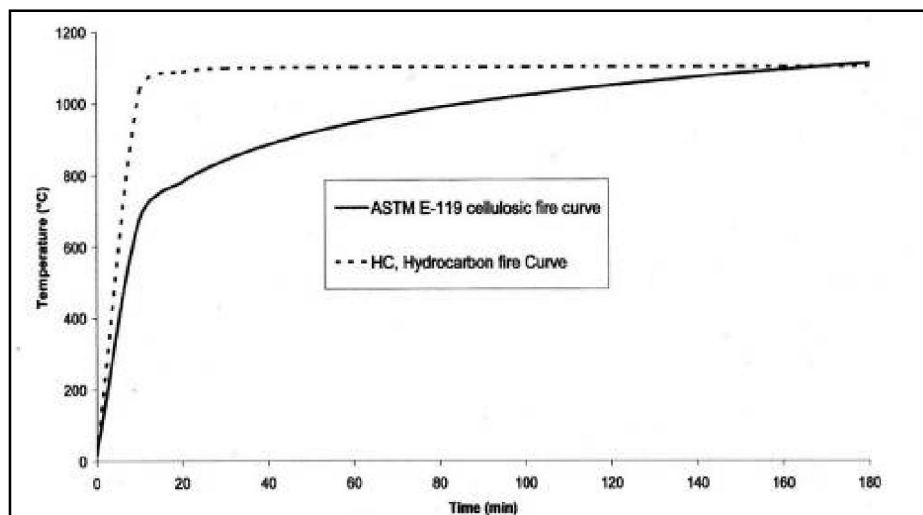
Figure 2.16: Time temperature curves for 'hydrocarbon' fire and 'cellulosic' fires [117]

Figure 2.17: Short literature summary on substrate temperature, char expansion and residual weight of intumescent fire retardant coating

No	Author	Title of research	Substrate Temp	Char expansion	Residual wt%
1	Duquesne et al., [65]	Thermoplastic resins for thin film intumescent coatings e towards a better understanding of their effect on intumescence efficiency	285°C after 23minutes	-----	32%
2	Wang et al., [118]	Influence of nano-LDHs on char formation and fire-resistant properties of flame-retardant coating	265°C after 60 minutes	17.1times	33%
3	Jimenez et al., [12]	Characterization of the performance of an intumescent fire protective coating	450°C after 60 minutes	-------	30%
4	Gu et al., [68]	Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings	--------	-------	20%
5	Li et al., [84]	Effects of EG and MoSi2 on thermal degradation of intumescent coating	400°C after 60 minutes	------	30%
6	Wang et al., [67]	Influence of expandable graphite on fire resistance and water resistance of flame-retardant coatings	320°C after 60 minutes	14.2 times	55%
7	Wang et al., [119]	Influences of binder on fire protection and anticorrosion properties of intumescent fire resistive coating for steel structure	245°C after 60 minutes	14 times	31%

2.20 Conclusion

From the literature review, the role of intumescent fire retardant coating has become clear. Due to its significant role in protecting lives and properties, extensive research has been conducted over the years to develop suitable materials. However,

despite the numerous efforts, there are still many gaps in past research such as the full understanding of what influences the type of char formed when polymeric materials burn. The application of phosphorus and nitrogen compounds and their related systems within intumescent systems need to be investigated. Why UV radiations affect the intumescent coating is need to further investigate. There is a need to improve the char expansion, char structure, heat shielding/insulation, thermal degradation and decomposition behaviors for polymer materials in order to improve the fire performance of intumescent coating. To understand char composition of intumescent fire retardant coating after burnt. To understand the weather ability of flame retardant coatings and development of flame retardants based on expandable graphite. There is need to develop a coating that has good char expansion, char morphology, keeps the minimum the temperature of the steel substrate as minimum possible, has high residual weight and environmental friendly.

CHAPTER 3

METHDOLOGY

3.1 Chapter overview

The first part of this chapter describes formulation design, as received material characterization, and preparation of expandable graphite used as carbon source in intumescent coating. The second part describes preparation of the structural steel substrate and a range of intumescent coating formulations. The third part describes the fire tests of intumescent coating formulations to evaluate the char expansion, insulation characteristic of the coating and their characterization before and after fire test. The forth part explains the weathering test of intumescent coating formulations i.e. the procedure adopted and test conducted in achieving the objectives of the current work.

3.2 Research procedure

The sequence of work and analyses involved in this project is summarised in the flow chart shown in Figure 3.1. Firstly, preparation of expandable graphite, design of formulation, preparation of EG formulation to study the effect of four different particle size (63μm, 150μm, 212μm and 300μm) on char expansion and char morphology were carried out. The effect of fillers was also investigated with optimized formulation of EG intumescent coating composition. A range of different formulations were prepared to determine the optimum formulation that was later used to study the effect of fillers. Inorganic fillers were then added to the optimized formulation; a total of 13 coating formulations were prepared using three types of fillers. The coated samples were cured at room temperature and their physical properties were measured. Thermal properties of the coated samples, heat flow by

differential thermal analysis (DTA) and residual weight were studied by thermogravimetric analysis (TGA). To investigate the effects of weather on the intumescent coating, weathering test was conducted using Q-Sun Xenon Test Chambers. The intumescent coating was then burned in the carbolite furnace at 800°C and the char physical properties were determined. Characterization of char was conducted using SEM, FESEM, XRD, FTIR, and XPS. The gaseous products produced during burning of the coating sample were analyzed by Pyrolysis Gas Chromatography. Finally, heat insulation test was performed using ASTM E119 test method. The results were analyzed and final conclusions of the research were drawn.

3.3 Materials for the intumscent coating

In the current research work epoxy resin Bisphenol A was used as a binder with polyamide amine as a hardener, APP is an acid source, melamine as a gas source, EG as a carbon, boric acid as additive, and three fillers (MWCNTs, kaolin clay and zirconium silicate) are selected to achieve the improve char expansion, char morphology, minimum temperature of steel substrate and high residual weight percentage of the char.

3.3.1 Epoxy resin and hardener as binder

In this study, epoxy resin Bisphenol A BE-188 (BPA) was selected as the binder and ACR Hardener H-2310 polyamide amine as the hardener. Bisphenol A is a precursor to the flame retardant tetrabromobisphenol A. The basic function of the binder is to bind fire retardant additives and to provide adhesion to the steel substrate. Epoxy and hardener were purchased from Mc-Growth chemical Sdn Bhd. The specification and typical properties of epoxy resin are shown in Table 3.1.
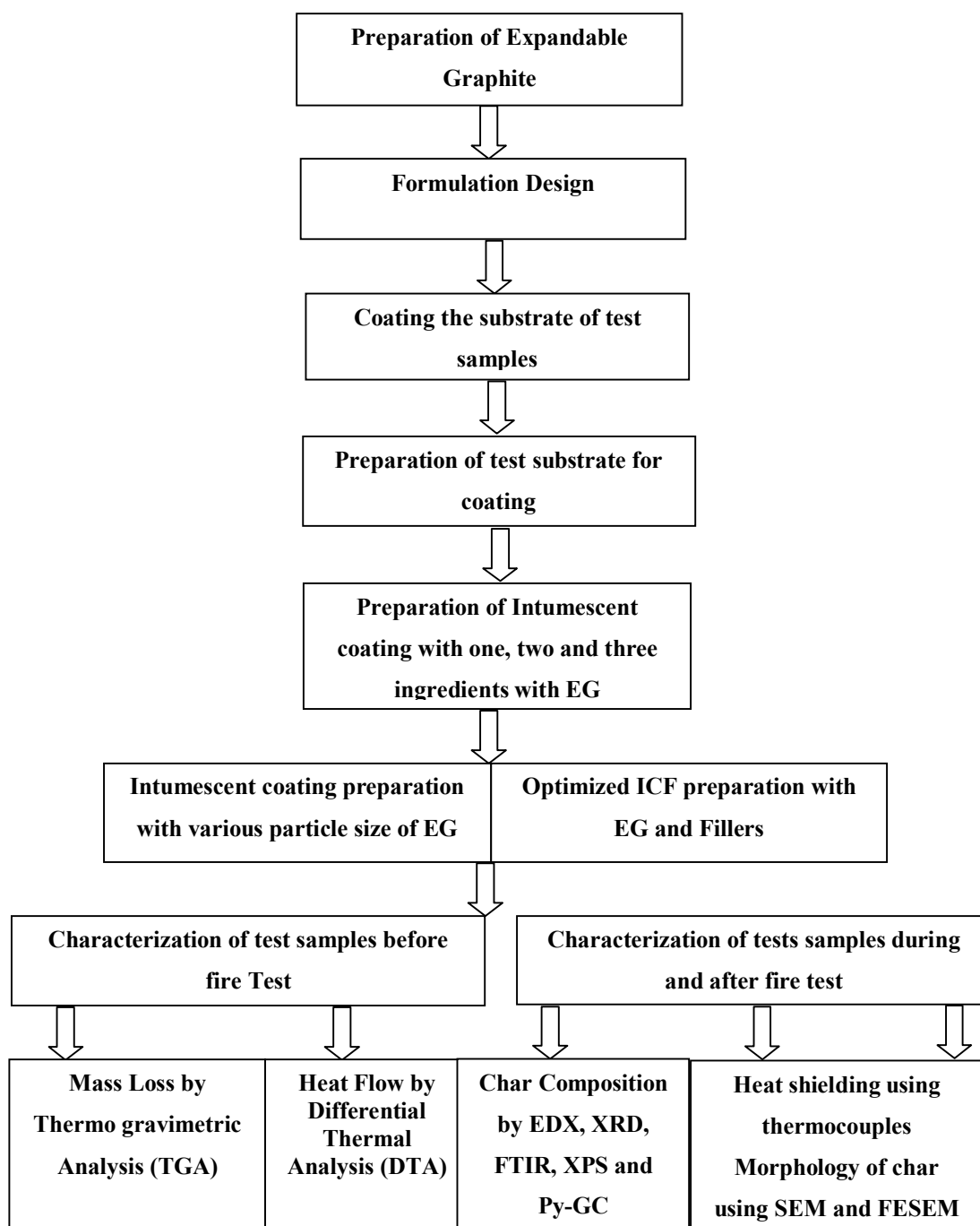
Figure 3.1: Process flow of the synthesis and characterization of ICFs

Table 3.1: Typical properties of epoxy resin

Physical Properties	Description
Physical state	Liquid
Viscosity (25°C g /cm^3)	11000 ~ 15000
Curing schedule	7 days at room temperature
Hardness (Shore D)	85
Bend strength (kg /cm^2)	820

3.3.2 Ammonium polyphosphate (APP)

In intumescent coating, APP acts as the acid source which reacts with carbon donor to form ester. It is an inorganic salt of polyphosphoric acid and ammonia. Ammonium polyphosphate was purchased from Clariant with product name Exolit AP 422. It is colourless, non-hygroscopic and non-flammable. Table 3.2 shows the properties of APP provided by Clariant (Malaysia) Sdn Bhd.

Table 3.2: Physical Properties of APP (Exolit AP 422)

Properties	Description
Physical appearance	Colourless solid
pH value	5.5-7.5
Solubility in water (10% suspension)	max 0.5% (w/w)
Average particle size	< 50μm
Viscosity (25°C, 10% suspension)	≤100 mPa
Decomposition temperature	>275°C

3.3.3 Melamine (MEL)

Melamine is used as a blowing agent source (gas source) in intumescent coating formulation, and decomposes to yield gaseous products such as nitrogen and ammonia to swell the carboneous char. The SEM image (Figure 3.2) shows the average particle size of melamine is 300 nm. Melamine was purchased from Sigma-Aldrich (M) Sdn. Bhd. Table-3.3 shows the properties of melamine used in the current work.
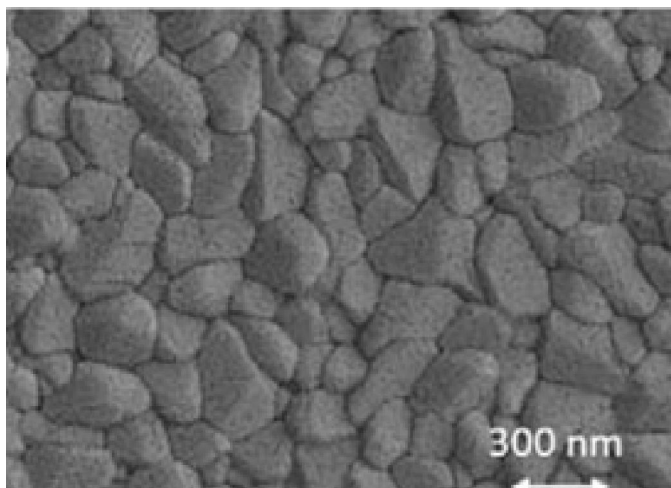
Figure 3.2: SEM image of Melamine used in coatings

Table 3.3: Properties of Melamine (MEL)

Properties	Description
Molecular formula	$C_3H_6N_6$
Appearance	White solid
Density	1574 kg/m^3
Melting point	345°C
Solubility in water	3.240 g/l

3.3.4 Preparation of expandable graphite

Natural graphite was grinded and four particle sizes are obtained by sieving analysis. Expandable graphite was prepared by reacting with mixtures of acetic acid sulphuric acid and potassium permanganate; EG was used as a source of both carbon and gas in the intumescent coating formulation. The natural flake graphite was reacted with the acids; 50g of natural graphite flake, 100g of glacial acetic acid, 25g of 98% H_2SO_4 and 3.5g of $KMnO_4$ were placed into a dry three necked round bottom flask equipped with a thermometer, a stirrer and a condenser. The mixture was stirred and reacted for two hours at a temperature of 25°C to form expandable graphite[120]. The graphite was then washed with water to remove any residual acid, dehydrated and dried at 50-60°C in an oven. The stages of EG preparation are shown in Figure 3.3 (a, b, c, d). The properties of expandable graphite are given in Table 3.4. The treated EG is shown in Figure 3.4(a, b, c, d).

(c) The graphite after grinded	(d) Reaction set up of graphite with acids
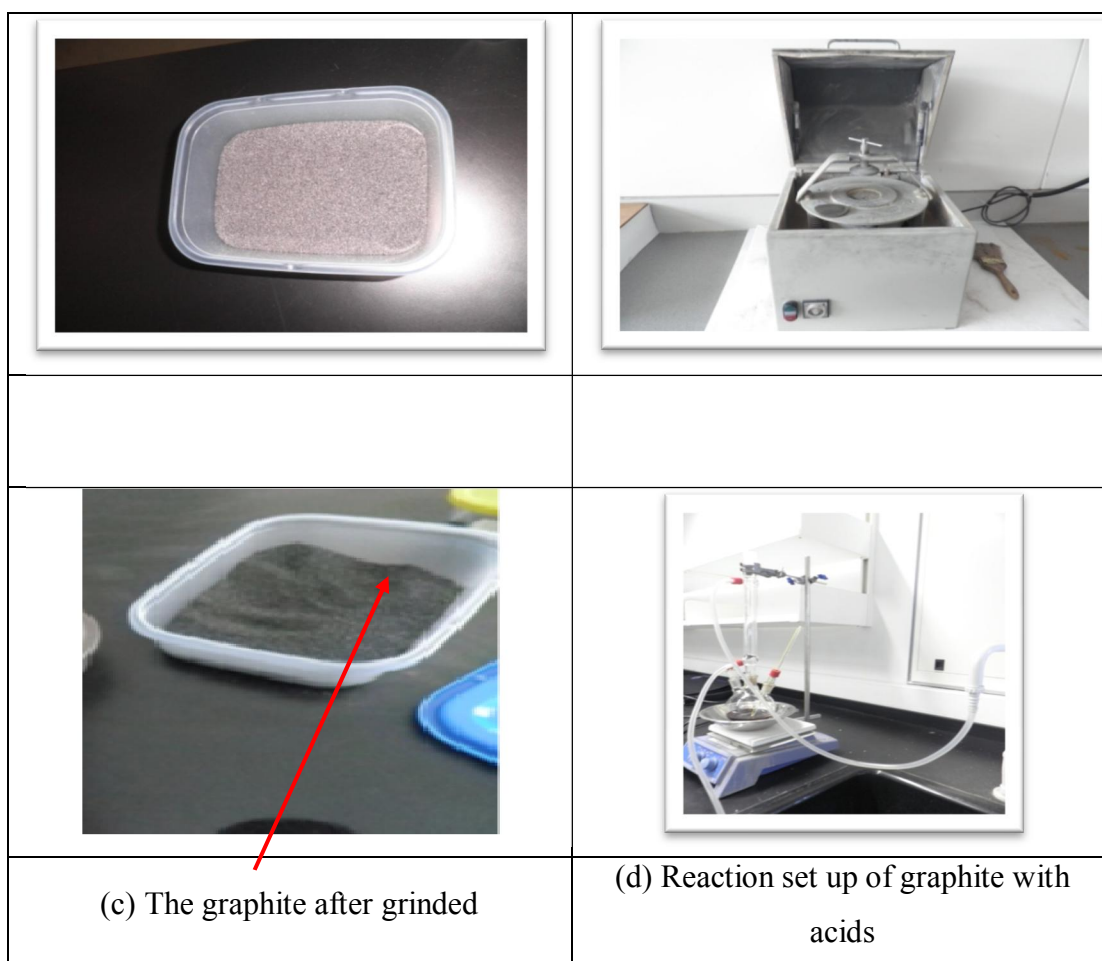
Figure 3.3: Steps in the preparation of expandable graphite

Table 3.4: Specifications of expandable graphite

Properties	Description
Purity	92-99%
Free water content	Max 1%
$_pH$-value	6-7.5
Particle Size	Average size, 63μm, 150μm, 212μm and 300μm
Expansion volume	Up to 100ml/g
Oxidation temperature	250-350°C
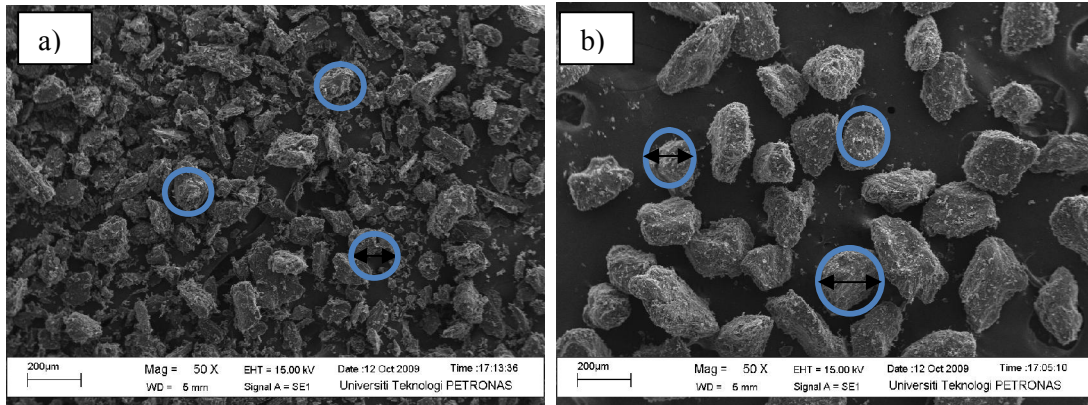
a) SEM of 63 µm of EG

b) 150 µm EG
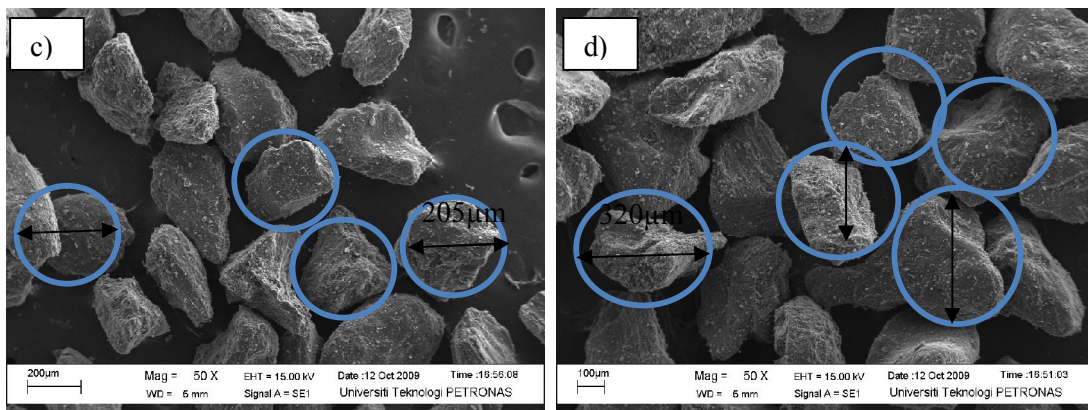
c) SEM of 212 µm of EG

d) 300 µm EG

Figure 3.4: SEM image of average particle sizes 63,150, 212 and 300 µm EG.

3.3.5 Boric acid

Boric acid inhibits the release of combustible gases from burning cellulosic materials, such as cotton, wood, and paper-based products. Boric acid also releases chemically bonded water to further reduce combustion. A carbon char is formed that further inhibits combustion [11]. It is used as a flame retardant in plastics, textiles, coatings, and there are also other industrial products that contain boric acid to strengthen their ability to withstand exposure to flames [121-123]. Boric acid, also known as boracic acid or orthoboric acid, is a naturally occurring compound containing the elements boron, oxygen, and hydrogen (H_3BO_3). In nature, the element boron does not exist by itself. Boron is combined with other common elements, such as sodium to make salts like borax and with oxygen to make boric acid. Boric acid crystals are white, odourless, and nearly tasteless. Borates (the general term associated with boron

containing minerals such as borax and boric acid) most commonly originate in dried salt lake beds of desert or arid areas.

Boric acid was purchased from Sigma-Aldrich (M) Sdn. Bhd. The specifications of boric acid are given in Table 3.5.

Table 3.5: Specifications of Boric acid

Properties	Descriptions
Molecular formula	H_3BO_3 or $B_2O_3.3H_2O$
Molecular weight	61.83
Physical state	White crystal
Melting point	170^oC
Boiling point	300^oC
Specific gravity	1.43-1.44
$_pH$-value	5.2 (1% Sol.)

3.3.6 Kaolin clay

Kaolin clay is selected as a reinforcement material of intumescent fire retardant coating as it has fire resistant properties of ceramic class. In the fire retardant coatings, it is used as an inorganic filler to enhance the fire protection performance [124]. Kaolin clay was supplied by Mc-Growth Chemical Sdn. Bhd. The physical properties are given in Table 3.6. The atomic structure and FESEM micrograph are presented in the Figures 3.5 and 3.6 respectively.
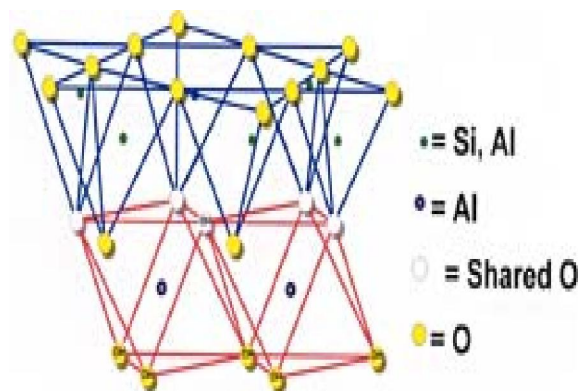
Figure 3.5: Structure of Kaolin clay [125]
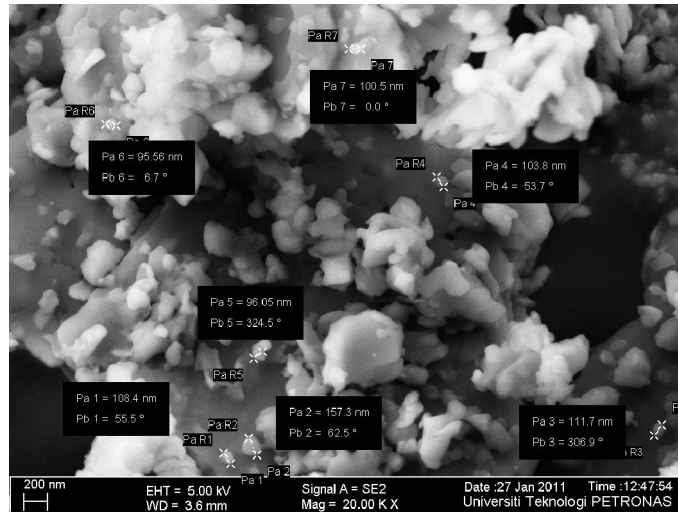
Figure 3.6: FESEM image of Kaolin Clay

Table 3.6: Properties of Kaolin Clay

Properties	Description
Molecular formula	$Al_2Si_2O_5(OH)_4$
Colour	white
Al_2O_3	39.0%
SiO_2	43.58%
Molecular Weight (g/mol.)	258.16
Bulk Density (lbs./ft.3)	25.3
Specific Gravity	2.6
pH	6-8
Melting Point (°C)	1350-1470

3.3.7 Zirconium silicate (ZrSiO$_4$)

Zirconium silicate is selected as a reinforcement material in intumescent coating formulation as it has high temperature resistance. Zirconium silicate is a fine white mineral powder that is chemically inert and stable to very high temperatures . It is insoluble in water, dilute acids and hot concentrated sulfuric acid. It is used as an abrasion-resistant resin filler and high temperature composite material. It has been widely used in various types of construction ceramics and sanitary ceramics, household ceramics and porcelain through the production of high-performance special stabilized zirconium silicate. It is one essential component in the preparation of high Glaze. The properties and FESEM micrograph of zirconium silicate are shown in

Table 3.7 and Figure 3.7 respectively. Zirconium silicate was bought from Mc-Growth Chemical Sdn. Bhd. Malaysia.
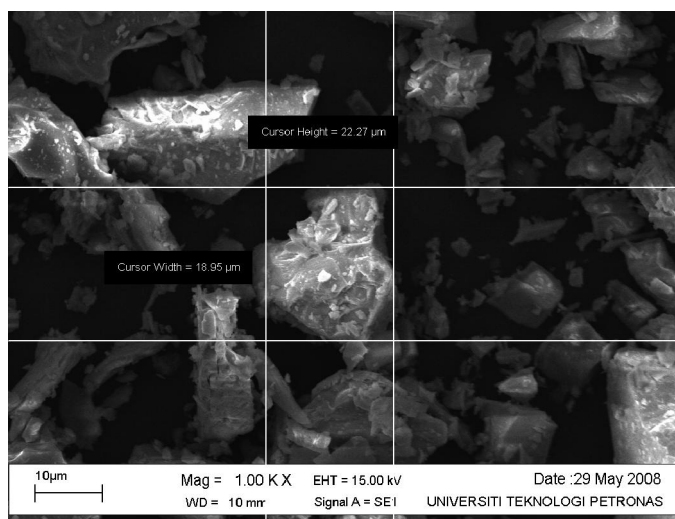
Figure 3.7: FESEM image of Zirconium Silicate

Table 3.7: Properties of Zirconium Silicate

Properties	Description
Color	off-white
ZrO_2	65.9%
SiO_2	32.0%
Molecular Weight (g/mol.)	183.1
Bulk Density (lbs./ft.3)	172-182
Specific Gravity	1.92-2.02 gm/cc
Solid Specific Heat	0.132
Melting Point (°C)	1538-1677
Dielectric Constant:	12.7
Thermal Expansion:	7.6×10^{-7} cm/cm/^{o}C

3.3.8 Multi-walled carbon nanotubes

Carbon nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Structurally, MWCNTs consist of multiple layers of graphite superimposed and rolled in on them to form a tubular shape. The MWCNTs are the most reasonable ones for commercialization as composite additives or coating elements. Carbon nanotubes are believed to be useful as flame retardant

nano additive because of their highly elongated shape, and balance between the effect of thermal conductivity and shielding performance of external radiant flux (and heat feedback from the flame) at certain amount in a structural material [95]. MWCNTs were supplied by Shenzhen Nano-Technologies Port Co., Ltd. Figure 3.8 shows the FESEM micrograph of MWCNTs.
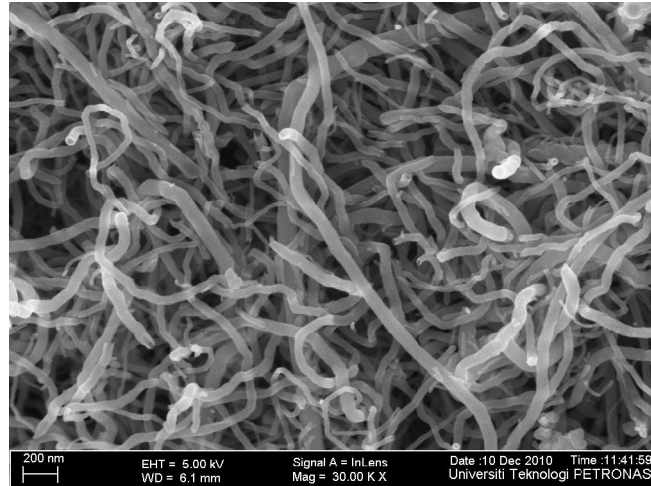
Figure 3.8: FESEM image of Multiwall-wall Carbon nanotubes

3.3.9 Steel substrate

Carbon steel plate with 1.5 mm thickness was prepared according to required standard NACE 2-SSPC-SP 10 [126]. Structural carbon steel was selected as substrate because of its low cost and it is used in vast application. Table 3.8 shows the composition of steel provided by the supplier.

Table 3.8: Chemical composition of structural steel as received

Element	Composition (wt %)
Carbon (C)	0.2-0.25
Silicon (Si)	0.15-0.40
Sulphur (S)	0.5
Phosphorus (P)	0.4
Manganese (Mn)	0.6-1.20

3.4 Preparation of the intumescent coating formulation (ICF)

This section describes the preparation of the steel substrate for coating and the intumescent coating preparation process.

3.4.1 Steel substrate preparation

Steel substrate was prepared according to the society of protecting coating standard (SSPC) [126] where the steel was cleaned to remove oil, grease, dirt, soil and other similar organic compounds. After cleaning, sand blasting was performed by using Air Compressor Airman 370 CFM. Garnet sand with particle size 30-60 mesh and 20-40 mesh were shot from a nozzle of size 3/8 to each steel surface. Two dimensions of steel cross section $25cm^2$ and $100cm^2$ were used to coat the intumescent coating formulation. Figure 3.9 shows the measurements obtained using MOHR Profilometer with three repetitions.

Ra is general surface roughness. This equipment measures average surface roughness by comparing all the peaks and valleys to the mean line, and then averaging them all over the entire cut-off length. Ten-point mean roughness (Rz). A section of standard length is sampled from the mean line on the roughness chart. The distance between the peaks and valleys of the sampled line is measured in the y direction. Then, the average peak is obtained among 5 tallest peaks (Yp) and (Yv) the average valley between 5 lowest valleys. The sum of these two values is expressed in micrometer (Om).

3.4.2 Intumescent coating preparation

All the weighed solid ingredients except EG were ground together using grinder. The ground mixture powder was then mixed with epoxy and hardener using shear mixer shown in Figure 3.10. The mixture was stirred at 40 rpm for 20 minutes to ensure uniform dispersion of intumescent ingredients in the binder [127]. Then the coating mixture was applied onto the steel substrates that have been cut in two sizes of 5cm×5cm and 10cm×10cm using a brush. The process of intumescent coating

preparation is shown in Figure 3.11. The coating was cured at room temperature for one week and then touched dry to ensure full curing. The thickness of the coating was measured using digital vernier caliper and the accuracy was within ± 0.05.
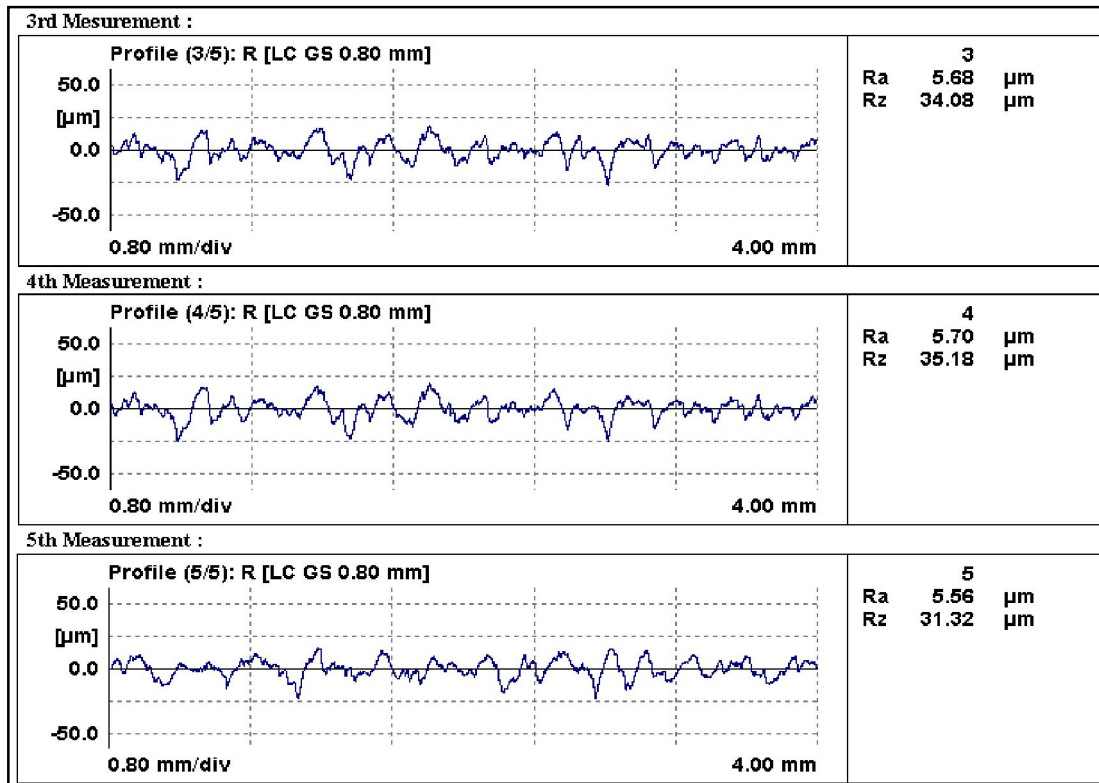
Figure 3.9: Surface roughness of sand blasted steel substrate measured using Profilometer.

Figure 3.10: Mixing process of intumescent coating using Shear Mixer
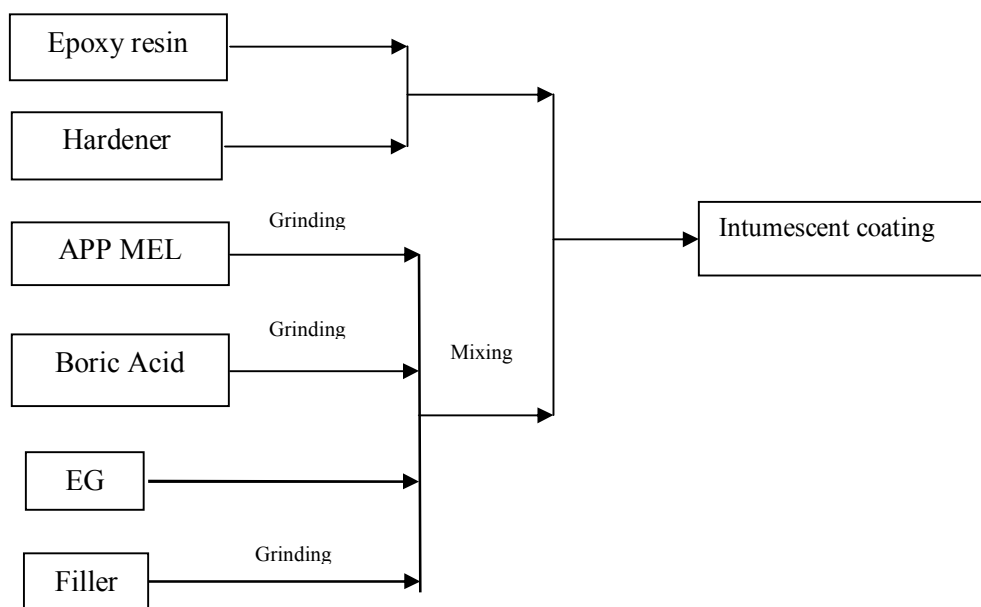
Figure 3.11: Process adopted for the preparation of intumescent coating

3.4.2.1 Intumescent coating based on one ingredient

The following four formulations were prepared to study the effects of one ingredient with epoxy and hardener on char expansion and char morphology of intumescent fire retardant coating. Each formulation was assigned a formulation number for example IF1-1, where the code "I" stand for intumescent, "F" stands for formulation, the first digit indicates how many ingredients are used in the formulation (1 indicates one ingredient) and the second digit indicates the formulation number (1 indicates that it is the first formulation). The formulations are listed in Table 3.9.

Table 3.9: The weight percentage of IF1 coating composition

Formulation No	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF1-1	14.28	0	0	0	57.14	28.57
IF1-2	0	14.28	0	0	57.14	28.57
IF1-3	0	0	14.28	0	57.14	28.57
IF1-4	0	0	0	14.28	57.14	28.57

3.4.2.2 Intumescent coating based on two ingredients

The following six formulations were prepared to study the effect of two ingredients with epoxy and hardener on char expansion and char morphology, and residual weight of intumescent fire retardant coating. Each formulation was assigned

a formulation number using the same coding process as for one ingredient. The formulations are listed in the Table 3.10.

Table 3.10: The weight percentage of IF2 coating composition

Formulation No	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF2-1	6.66	13.33	0	0	53.33	26.66
IF2-2	6.66	0	13.33	0	53.33	26.66
IF2-3	6.66	0	0	13.33	53.33	26.66
IF2-4	0	12.5	0	12.5	50	25
IF2-5	0	12.5	12.5	0	50	25
IF3-6	0	0	12.5	12.5	50	25

3.4.2.3 Intumescent coating based on three ingredients

Four formulations of intumescent coating with three ingredients were prepared to investigate the effect of three ingredients with epoxy and hardener on char morphology, composition of residual char, presence of functional groups in char residue and their thermal degradation behaviour. The compositions of the four formulations are given in Table 3.11. The formulations are coded using the same coding process as for one ingredient.

Table 3.11: The weight% of IF3 coating formulations

Formulation No	EG	APP	MEL	Boric A.	BPA	Hardener
IF3-1	0	11.11	11.11	11.11	44.44	22.22
IF3-2	5.88	0	11.76	11.76	47.05	23.52
IF3-3	5.88	11.76	0	11.76	47.05	23.52
IF3-4	5.88	11.76	11.76	0	47.05	23.52

3.5 Intumescent coating based on particle sizes of expandable graphite

The main objective of this particular investigation is to study the effect of particle size on char expansion and char morphology of intumescent coating, and select the one particle size out of 63 µm, 150 µm, 212 µm and 300 µm of expandable graphite which affects good char expansion and char morphology. A total of 36 formulations i.e. a set of 9 formulations of each particle size were prepared. The weight percent of

each particle size was increased to study the effect of amount of particle on char expansion and char morphology. Each formulation was assigned a code. For instance for the formulation No IF4-1-63µm, "I" stands for intumescent, "F" stands for formulation, "4" represents four ingredients, "1" is for first formulation and "63µm" stands for particle size of EG.

Table 3.12: The weight % of 63µm EG based intumescent coating formulations

Formula No.	WEIGHT PERCENTAGE					
	EG	APP	MEL	Boric.A	Epoxy	Hardener
IF4-1-63µm	5.8	11.76	11.76	5.88	43.2	21.60
IF4-2-63µm	6.8	11.76	11.76	5.88	42.53	21.26
IF4-3-63µm	7.8	11.76	11.76	5.88	41.86	20.93
IF4-4-63µm	8.8	11.76	11.76	5.88	41.20	20.6
IF4-5-63µm	9.8	11.76	11.76	5.88	40.53	20.26
IF4-6-63µm	10.8	11.76	11.76	5.88	39.86	19.93
IF4-7-63µm	11.8	11.76	11.76	5.88	39.16	19.63
IF4-8-63µm	12.8	11.76	11.76	5.88	38.53	19.26
IF4-9-63µm	13.8	11.76	11.76	5.88	37.86	18.93

Table 3.13: The weight % of 150µm EG based intumescent coating formulations

Formula No.	WEIGHT PERCENTAGE					
	EG	APP	MEL	Boric A.	Epoxy	Hardener
F4-1-150µm	5.8	11.76	11.76	5.88	43.2	21.60
IF4-2-150µm	6.8	11.76	11.76	5.88	42.53	21.26
IF4-3-150µm	7.8	11.76	11.76	5.88	41.86	20.93
IF4-4-150µm	8.8	11.76	11.76	5.88	41.20	20.6
IF4-5-150µm	9.8	11.76	11.76	5.88	40.53	20.26
IF4-6-150µm	10.8	11.76	11.76	5.88	39.86	19.93
IF4-7-150µm	11.8	11.76	11.76	5.88	39.16	19.63
IF4-8-150µm	12.8	11.76	11.76	5.88	38.53	19.26
IF4-9-150µm	13.8	11.76	11.76	5.88	37.86	18.93

Table 3.14: The weight % of 212µm EG based intumescent coating formulations

Formula No.	WEIGHT PERCENTAGE					
	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF4-1-212µm	5.8	11.76	11.76	5.88	43.2	21.60
IF4-2-212µm	6.8	11.76	11.76	5.88	42.53	21.26
IF4-3-212µm	7.8	11.76	11.76	5.88	41.86	20.93
IF4-4-212µm	8.8	11.76	11.76	5.88	41.20	20.6
IF4-5-212µm	9.8	11.76	11.76	5.88	40.53	20.26
IF4-6-212µm	10.8	11.76	11.76	5.88	39.86	19.93
IF4-7-212µm	11.8	11.76	11.76	5.88	39.16	19.63
IF4-8-212µm	12.8	11.76	11.76	5.88	38.53	19.26
IF4-9-212µm	13.8	11.76	11.76	5.88	37.86	18.93

Table 3.15: The weight % of 300μm EG based intumescent coating formulations

Formula No.	WEIGHT PERCENTAGE					
	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF4-1-300μm	5.8	11.76	11.76	5.88	43.2	21.60
IF4-2-300μm	6.8	11.76	11.76	5.88	42.53	21.26
IF4-3-300μm	7.8	11.76	11.76	5.88	41.86	20.93
IF4-4-300μm	8.8	11.76	11.76	5.88	41.20	20.6
IF4-5-300μm	9.8	11.76	11.76	5.88	40.53	20.26
IF4-6-300μm	10.8	11.76	11.76	5.88	39.86	19.93
IF4-7-300μm	11.8	11.76	11.76	5.88	39.16	19.63
IF4-8-300μm	12.8	11.76	11.76	5.88	38.53	19.26
IF4-9-300μm	13.8	11.76	11.76	5.88	37.86	18.93

3.5.1 Selected intumescent coating formulations with EG 300μm

From the analysis on char expansion and morphology of all of the above formulations, the following four formulations listed in Table 3.16 show the highest char expansion and improved char morphology. Therefore these optimized formulations of 300 μm EG were selected for further study on chemical composition of residual char, functional group of char residue and weight percentage of char residue.

Table 3.16: The weight % of selected intumescent coating of 300 μm EG

Formulation No	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF1	0	11.76	11.76	5.88	47.07	23.53
IF2	5.8	11.76	11.76	5.88	43.2	21.60
IF3	8.8	11.76	11.76	5.88	41.20	20.6
IF4	11.8	11.76	11.76	5.88	39.16	19.63

3.6 Effect of weight percentage of two ingredients on 300μm EG based ICF

This is the final laboratory investigation to determine the formulation that has the best fire performance properties. Five formulations were developed to study the individual effects of amount of two intumescent ingredients on char expansion, char morphology, chemical compositions, functional groups of residual char, char residual weight percentage and substrate rear temperature of the intumescent coating with

optimized EG particle size of 300μm. For each formulation, a set of three batches were prepared.

The following five formulations were prepared to study the effect of boric acid and melamine on the intumescent fire retardant coating formulations. The weight percentage of melamine was varied respective to boric acid in order to study the effects of melamine and boric acid on the parameters mentioned above.. Each formulation was assigned a formulation number using a similar coding system as the previous one. For example IF1-Mel where "I" stands for intumescent, "F" stands for formulation, "1" is for first formulation and the last two alphabets is an abbreviation of the IF3-BA-Mel used in the formulation; "BA" stands for boric acid and "Mel" stands for melamine.

Table 3.17: The weight % IF-BA-Mel of Intumescent Fire Retardant Coating

Formulation No	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF1-Mel	5.8	11.76	11.76	-	47.12	23.56
IF2-BA	5.8	11.76	-	11.76	47.12	23.56
IF3-BA-Mel	5.8	11.76	11.76	5.55	43.42	21.71
IF4-BA-Mel	5.8	11.76	8.76	8.55	43.42	21.71
IF5-BA-Mel	5.8	11.76	5.76	11.55	43.42	21.71

Next, another five formulations were prepared to study the effect of amount of boric acid with respect to APP on char expansion, char morphology, substrate rear temperature and char residual weight.

Table 3.18: The weight % of IF-BA-APP of Intumescent Fire Retardant Coating

Formulation No	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF1-BA	5.8	-	11.76	11.76	47.12	23.56
IF2-APP	5.8	11.76	11.76	-	47.12	23.56
IF3-BA-APP	5.8	11.76	11.76	5.55	43.42	21.71
IF4-BA-APP	5.8	8.76	11.76	8.55	43.42	21.71
IF5-BA-APP	5.8	5.76	11.76	11.55	43.42	21.71

Finally, five more formulations were prepared to study the effect of amount of EG with respect to APP on char expansion, char morphology, substrate rear temperature and char residual weight.

Table 3.19: The weight % of IF-APP-EG of Intumescent Fire Retardant Coating

Formulation No	EG	APP	MEL	Boric A.	Epoxy	Hardener
IF1-APP	-	11.76	11.76	5.88	47.05	23.52
IF2-EG	5.8	-	11.76	5.88	47.05	23.52
IF3-APP-EG	5.8	11.76	11.76	5.88	43.2	21.60
IF4-APP-EG	8.8	8.76	11.76	5.88	43.2	21.60
IF5-APP-EG	11.8	5.76	11.76	5.88	43.2	21.60

3.7 Intumescent coating reinforced with inorganic fillers

Fillers are non-polymeric materials. Fillers are helpful to reduce the quantity of smoke produced from a given mass of a polymer by sinking the amount of combustible material present in the coating or by absorbing heat to decrease the burning rate of the material. IF5-BA-Mel was selected due its better char structure, minimum temperature of the substrate, and high residual char weight compared to the above fourteen formulations. The optimized formulation was reinforced using three different inorganic fillers each. Based on the previous analysis, IF5-BA-Mel was selected for this investigation.

3.7.1 Intumescent coating reinforced with MWCNT

The optimized formulation from Table 3.17 i.e. IF5-BA-Mel was reinforced with MWCNTs to improve the char expansion, char morphology, substrate rear temperature and residual weight. . Three formulations were prepared, and one of them is a reference where MWCNTs was not added. The composition of the three formulations is given in Table 3.20.

Table 3.20: The weight % Intumescent Coating formulation based on MWCNTs

Formulation No	EG	APP	MEL	Boric A.	MWCNTs	Epoxy	Hardener
IF5-BA-Mel	5.8	11.76	5.76	11.5		43.42	21.71
IF1-MWCNTs	5.8	11.76	5.76	11.5	0.2	43.32	21.66

IF2-MWCNTs	5.8	11.76	5.76	11.5	0.3	43.25	21.62
IF3-MWCNTs	5.8	11.76	5.76	11.5	0.4	43.18	21.59

3.7.2 Intumescent coating reinforced with kaolin clay

The second inorganic filler is kaolin clay used to reinforce the optimized/reference coating formulation IF5-BA-Mel. The composition of the kaolin reinforced intumescent coating is given as follows.

Table 3.21: The weight % Intumescent Coating formulation based on Kaolin Clay

Formulation No	EG	APP	Mel	Boric A.	K.Clay	Epoxy	Hardener
IF5-BA-Mel	5.8	11.76	5.76	11.5	-	43.42	21.71
IF1-KC	5.8	11.76	5.76	11.5	1	42.76	21.38
IF2-KC	5.8	11.76	5.76	11.5	2	42.10	21.00
IF3-KC	5.8	11.76	5.76	11.5	3	41.42	20.71
IF4-KC	5.8	11.76	5.76	11.5	4	40.76	20.38
IF5-KC	5.8	11.76	5.76	11.5	5	40.1	20.00

3.7.3 Intumescent coating reinforced with zirconium silicate

The third inorganic filler used is zirconium silicate. The composition of the reinforced intumescent coating is given in Table 3.22 below.

Table 3.22: The weight % of Intumescent Coating based on Zirconium Silicate

Formulation No	EG	APP	Mel	Boric A.	Z. Silicate	Epoxy	Hardener
IF5-BA-Mel	5.8	11.76	5.5	11.1	-	43.8	21.9
IF1-ZS	5.8	11.76	5.76	11.5	1	42.76	21.38
IF2-ZS	5.8	11.76	5.76	11.5	2	42.10	21.00
IF3-ZS	5.8	11.76	5.76	11.5	3	41.42	20.71
IF4-ZS	5.8	11.76	5.76	11.5	4	40.76	20.38
IF5-ZS	5.5	11.76	5.5	11.1	5	41.1	20.6

3.8 Furnace test of intumescent coating formulations

To analyse the physical properties of char such as char expansion and char structure after fire test, the intumescent coating was burned in a Carbolite Furnace using the parameters shown in Figure 3.12 below. For the first 15 minutes, the furnace temperature was set at around 50°C, then the temperature was raised up to 800°C and this temperature was kept for 60 minutes to ensure the sample has burnt completely [11]. Ensuring complete burning, the sample was cooled in the furnace for approximately 60 minutes to avoid cracking of char.
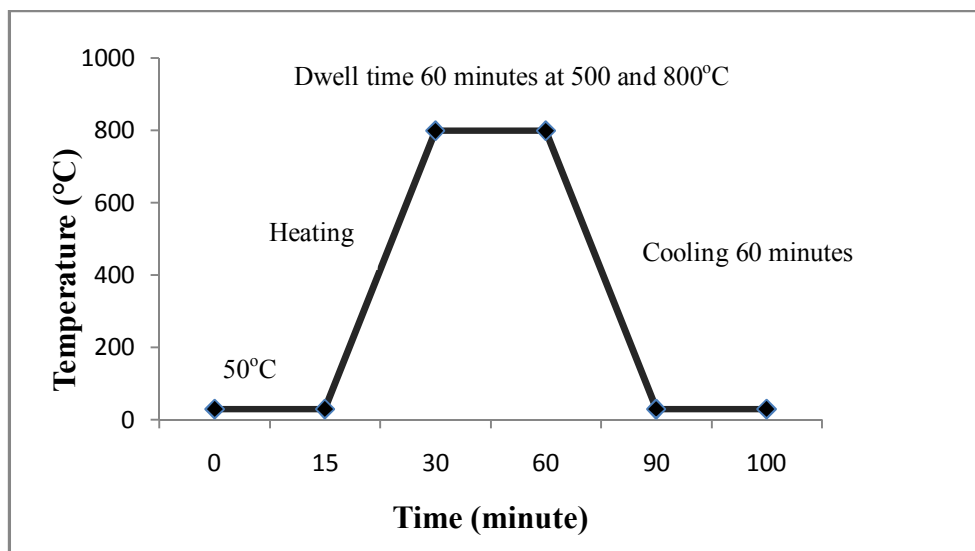
Figure 3.12: Temperature time plot for ICF sample burnt in furnace.

3.9 Heat shielding/insulation test of coating

Fire test was conducted on the intumescent formulations according to ASTM E119 standard to evaluate the penetration of fire to steel substrate [111]. Figure 3.13 shows the set up used for the fire test. The test was carried out for 60 minutes. Portable Bunsen burner was used to burn the coating, and the distance of the Bunsen from the coating was set at 7cm. Three thermocouples type K were connected to Anarittsu Data logger, Input Channel 6 Model AM-8000K with Anarittsu software, the other end of the three thermocouples were connected to the coated substrate. The temperature of the backside of the steel plate was measured for 60 minutes at an interval of 1 minute.

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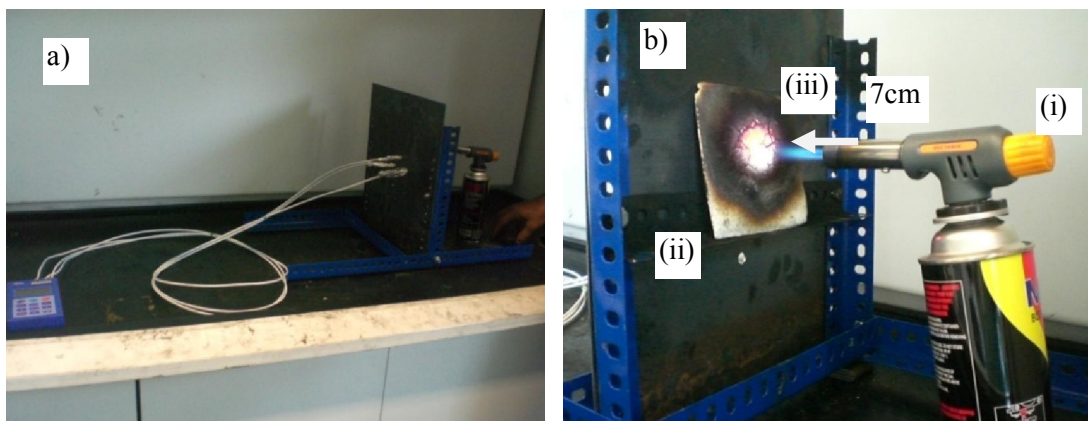
Figure 3.13: a) Fire test set up used for heat insulation test of intumescent formulation, b) (i) Portable Bunsen burner (ii) stand (iii) sample of ICF

3.10 Thermal properties of coating

For the intumescent coating ingredients that sustained their integrity for elevated temperature applications, it is important to investigate their decomposition with respect to temperature. To study the thermal properties of the intumescent coating, the following characterization techniques were used.

3.10.1 Thermo gravimetric analysis (TGA)

Thermo gravimetric Analysis (TGA) measures the amount and rate of change in the weight of an intumescent coating as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the decomposition of intumescent ingredients and to predict their thermal stability up to 800°C. This technique can characterize materials that exhibit residual weight (weight loss or gain) due to decomposition, oxidation, or dehydration. The thermo gravimetric analysis of intumescent coating sample (approx. 10mg) was carried out at a heating rate of 10°C/min in nitrogen gas, set at flow rate of 20ml/min over the whole temperature range of 50°C to 800 $^{\circ}$C. The data was recorded using Pyris Player Data Analyzer. The test was performed for a range of ICFs investigation.

3.10.2 Differential thermal analysis

Differential Thermal Analysis is a technique for observing the temperature of thermally induced transitions in a material by heating/cooling a sample, and comparing its temperature with that of an inert reference material under similar conditions. Differential thermal analysis is carried out by heating the sample together with a reference standard under identical thermal conditions in the same oven and measuring the temperature difference between the sample and reference substance during the period of heating. As soon as the sample changes state, crystal form, melts, *etc*. the latent heat of phase transition will be absorbed, and the temperature of the sample will lag behind that of the reference material. In this way, any change in state will be shown and the temperature at which it occurs will be recorded.

The DTA analysis of intumescent coating (approx. 10mg) was carried out at a heating rate of 10°C/min in nitrogen gas, set at the flow rate of 20ml/min over the whole temperature range of 50°C to $800 ^{\circ}$C. The data was recorded using Pyris Player Data Analyzer. The test was performed for the selected ICFs.

3.11 Char Characterization after Furnace Test

The following test was used to characterize char.

3.11.1 Char morphology characterization

The micro structure of the char was studied by Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM) to determine the effects of various intumescent ingredients on char morphology.

3.11.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to study the outer and inner char structures. Char samples for SEM observation were obtained after fire test of intumescent coatings in air at temperatures, 500°C and 800°C for 60 min in a

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Carbolite furnace. Morphologies of char samples were recorded with SEM operated at 25 kV. The SEM samples were prepared by sticking char to a double-coated tape fixed onto an aluminum specimen mount stub, and the samples were coated with an ultrathin gold film as an electrically conducting material which was deposited on the sample by using a low vacuum sputter coater.

3.11.3 Field Emission Scanning Electron Microscopy (FESEM)

Charring layer and their morphological structures were examined at higher magnification, 500x-30kx using AMARY 1000 FESEM.

3.12 X-Ray Diffraction (XRD) of Char

XRD was used to study the composition of residual char of ICFs produced at $500^{\circ}C$ and $800^{\circ}C$. XRD measurements were performed on a Bruker AXS D8 Advanced Diffractometer using Cu Kα radiation and a nickel filter (k = 0.150595 nm) in the range of $10 < 2\theta < 90$.

3.13 Fourier Transform Infrared Spectroscopy (FTIR) of Char

FTIR was used to detect the vibrational characteristics of chemical functional groups present in a char sample produced at $500^{\circ}C$ and $800^{\circ}C$. FTIR spectra were recorded using a Nicolet 400 D Shimadzu spectrometer in the range 4000–500cm^{-1}. Char samples were ground and mixed with KBr to make homogeneous mixture pellets. A 30 scans were necessary to attain spectra with fine signal to noise ratio. The residual char of ICFs were analyzed using spectroscopic tools to study the mechanism of interaction between EG, APP, melamine, boric acid, zirconium silicate, kaolin clay, MWCNTs in epoxy and hardener that contribute for their effectiveness in protecting the substrate from heat.

3.14 X-ray Photo Electron Spectroscopy (XPS)

XPS was used to analyze the elemental weight % of char residue, degree of char accumulation and anti-oxidation of intumescent coating formulation. The XPS instrument measures the kinetic energy of all collected electrons. The electron signal includes contributions from both photoelectron and Auger electron lines. The binding energy (BE) is characteristic of the core electrons for each element. The BE is determined by the attraction of the electrons to the nucleus. If an electron with energy x is pulled away from the nucleus, the attraction between the electron and the nucleus decreases which results in a reduction of BE. Eventually, there will be a point when the electron will be free of the nucleus. The samples were examined by XPS on a LEYBOLD spectrometer using Al Ka radiation (1486.6 eV). The spectrometer was run in fixed analyser transmission mode at a pass energy of 50eV with an X-ray power source of 300 W. Samples were mounted by pressing on to the indium holder and introduced in a pre-chamber to obtain a pressure of 10^{-5} Torr. All binding energies (BE) were referenced to C1s at 285eV. All the peaks (C 1s, N 1s, O 1s and P2p) were fitted into several components having the same full width at half maximum (FWHM).

3.15 Pyrolysis Gas Chromatography

The gaseous decomposition products from the pyrolyzed samples of intumescent coating were identified with Gas Chromatograph-Mass Spectroscopy (GC-MS). The Py-GC/MS analyses were carried out using a PYRO-CHEM WILKS pyrolyser, Hewlett Packard 5890 Series II gas chromatograph, and TRIO 1000 mass spectrometer. The gas chromatographic column (BPX 5, provided by SGE, nominal 25m, 0.25mm bore/0.25 mm thickness film) was heated from 40 to 220°C at 20°C/min in 10min, the initial temperature was held for 5min. The sample (10mg) was placed in the pyrolyser. The pyrolysis process was carried out at 25° to 800°C in 10 sec. Then the pyrolysis products in the gas phase were injected into the GC-MS by syringe to characterize the gaseous products. A mass spectrometric identification was carried out and the gaseous products were identified during burning of the intumescent coating.

3.16 Weathering chamber (Q-Sun Xenon Test Chambers)

Q-Sun Xenon Test Chambers was used for accelerated weathering test. It is designed to create a highly flexible mix of UV light, temperature and moisture conditions. In this research, ASTM D 6695-03 was used to study the effect of weathering on the optimized sample of ICFs. The tests are intended to reproduce the damage caused by sunlight, rain and condensed surface moisture or dew. In the test chamber, the test materials were subjected to alternating cycles of light and moisture at controlled elevated temperatures. The coated samples were tested for 3 months (90 days) under these conditions: the weather ability of specimens was assessed in an accelerated weathering chamber (Atras Ci4000) according to JIS K5600-7-7 (xenon lamp method) [128] for up to 2000 h. The accelerated weathering regime involved continuous exposure to xenon arc UV radiation ($0.35 \pm$ W/m2 at 340 nm = 41.5 W/m2 for 300–400 nm), 18min light and water spray 6h dark using 95% relative humidity (no water spray) with a black panel temperature of $65° \pm 2°C$ and a chamber temperature of $35° \pm 2°C$. The physical appearance, char expansion and char morphology of weathered intumescent coatings were conducted and compared to those not subjected to weathering conditions.

3.17 Chapter summary

In this chapter, the materials and methodology used in this research have been presented. This chapter begins with a simple process flow of the experimental work involved in this research. The characterization of materials used in this study, preparation of steel substrate and intumescent coating are briefly discussed. Details on the tests used and equipment involved for characterization of intumescent coatings have also been discussed.

In the next chapter, the results obtained from the laboratory tests are presented and discussed.