PALM OIL CLINKER AS A NOVEL BIO-FILLER IN INTUMESCENT FIRE PROTECTIVE COATINGS FOR STEEL

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PALM OIL CLINKER AS A NOVEL BIO-FILLER IN INTUMESCENT FIRE PROTECTIVE COATINGS FOR STEEL

ABSTRACT

Intumescent coatings are an effective method for fire protection of steel structures to ensure the fire safety and prevent the building from collapse in the fire incident. The search for more environmental friendly intumescent coatings has led to the utilization of palm oil clinker (POC) as a novel bio-filler in intumescent coatings in order to improve fire protection performance, mechanical strength and water resistance of steel structures. The purpose of this research is to develop the best composition of intumescent coatings using POC and hybrid fillers. In this research, three flame-retardant additives, i.e. ammonium polyphosphate, pentaerythritol and melamine were mixed with acrylic binder and flame-retardant fillers to produce the intumescent coatings. The first step of this research involved the investigation on the influence of different particle size of POC (micro and nano sizes) as a single filler to the intumescent coatings. The second part of the study attempted to investigate the effect of the optimum percentage of filler in the intumescent coatings formulation. For this part, four specimens using four different percentages of POC were prepared. After that, this research continued with the investigation on the effect of using different hybrid fillers to the intumescent coatings. Then, the last part of research was the investigation on the effect of binders (solvent-borne and water-borne) to the intumescent coatings performance. All specimens were investigated by using the Bunsen burner test, thermogravimetry analysis, field emission scanning electron microscope, static immersion test and adhesion strength test. The surface spread of flame test was carried out on the specimens with the best fire protection performance. It was found that the incorporation of micro size POC as a single filler gives better thermal stability and fire protection performance to the intumescent coatings due to its higher thermal stability. Meanwhile, the addition of 18 wt. % of micro size POC as a single filler in the intumescent coatings was found to be the optimal percentage of filler which resulted in significant improvement in thermal stability as well as the best fire protection performance. For hybrid fillers formulation, the addition of aluminium hydroxide gave better water resistance with the lowest rate of weight change in specimen C2/PTA, while the addition of magnesium hydroxide enhanced the bonding strength of specimen C1/PTM. Also, specimen C3/PTMA with the combination of POC and hybrid fillers showed an excellent fire protection performance with the highest thermal stability, water resistance and mechanical properties. The last part of research showed that the formulation of intumescent coatings with solvent-borne binder led to the best fire resistance performance due to the densest surface structure and greatest expansion. Moreover, the results of the surface spread of flame test showed that all specimens were classified as Class 1, which is the best classification except for specimen B3/20% which is classified as class 2. It can be concluded that the optimum combination of POC and hybrid fillers resulted in intumescent coating with the greatest fire protection performance.

Keywords: intumescent coating, fire protection performance, steel structures, palm oil clinker, hybrid filler

ARANG KELAPA SAWIT SEBAGAI NOVEL BIO-PENGISI DI DALAM LAPISAN PENAHAN API BAGI BESI

ABSTRAK

Lapisan penahan api merupakan kaedah yang efektif dalam perlindungan api bagi struktur keluli untuk memastikan keselamatan terhadap api dan mengelakkan bangunan dari runtuh apabila berlaku kebakaran. Pencarian lapisan penahan api yang lebih mesra alam telah membawa kepada penggunaan arang kelapa sawit (POC) sebagai bahan bio-pengisi novel di dalam lapisan penahan api bagi meningkatkan kadar kecekapan perlindungan api, kekuatan mekanikal, dan daya ketahanan terhadap air pada struktur keluli. Tujuan penyelidikan ini ialah untuk menghasilkan komposisi lapisan penahan api yang terbaik dengan menggunakan arang kelapa sawit dan bahan pengisi hibrid. Dalam kajian ini, tiga jenis aditif penahan api: ammonium polifosfat, pentaeritritol dan melamin digabungkan bersama bahan pengikat akrilik dan bahan pengisi penahan api untuk menghasilkan lapisan penahan api tersebut. Bahagian pertama penyelidikan ini meliputi penyiasatan tentang kesan penggunaan bahan pengisi POC yang berbeza saiz zarah (mikro dan nano) sebagai bahan pengisi tunggal terhadap lapisan penahan api. Bahagian kedua penyelidikan melibatkan penyiasatan tentang kesan penggunaan peratusan bahan pengisi didalam formulasi lapisan penahan api. Empat jenis spesimen telah disediakan menggunakan peratusan bahan pngisi POC yang berbeza. Selanjutnya, penyelidikan diteruskan dengan penyiasatan tentang kesan penggunaan campuran bahan pengisi hibrid terhadap lapisan penahan api. Diikuti dengan bahagian terakhir penyelidikan melibatkan penyiasatan tentang kesan bahan pengikat (berasaskan larutan dan berasaskan air) keatas kecekapan lapisan penahan api. Semua sampel diuji dengan menggunakan ujian penunu Bunsen, analisis termogravimetri, ‘field emission scanning electron microscope’, daya tahan air dan daya lekatan. Ujian penyebaran api dijalankan keatas spesimen dengan kecekapan perlindungan api yang terbaik. Didapati bahawa penggunaan POC bersaiz mikro sebagai bahan pengisi tunggal menunjukkan kestabilan haba dan kecekapan perlindungan api terbaik kerana mempunyai kestabilan haba yang tinggi. Manakala, penambahan 18 wt. % bahan pengisi POC bersaiz mikro sebagai pengisi tunggal dalam komposisi lapisan penahan api menunjukkan peratusan yang optimum kerana menghasilkan peningkatan yang mendadak terhadap kestabilan terma dan kecekapan perlindungan api. Untuk komposisi lapisan penahan api menggunakan bahan pengisi hibrid, penambahan aluminium hiroksida meningkatkan kadar ketahanan terhadap air dengan menunjukkan kadar perubahan berat yang paling rendah bagi spesimen C2/PTA, manakala penambahan magnesium hidroksida meningkatkan daya lekatan bagi spesimen C1/PTM. Selain itu, spesimen C3/PTMA yang mengandungi kombinasi POC dan bahan pengisi hibrid menunjukkan peningkatan yang terbaik terhadap kecekapan perlindungan api, kestabilan terma yang tinggi, daya ketahan terhadap air dan daya lekatan. Bahagian terakhir penyelidikan menunjukkan komposisi lapisan penahan api dengan bahan pengikat berasaskan pelarut menghasilkan kecekapan perlindungan api yang baik kerana kepadatan struktur permukaan dan pengembangan yang terbesar. Selain itu, keputusan penyebaran api menunjukkan semua spesimen diklasifikasikan sebagai kelas 1 iaitu kelas terbaik kecuali spesimen B3/20%. Kesimpulannya, komposisi optimum POC dan bahan pengisi hibrid memberikan kesan yang terbaik dalam kecekapan perlindungan api bagi lapisan penahan api.

Keywords: lapisan penahan api, kecekapan perlindungan api, struktur besi, arang kelapa sawit, pengisi hibrid

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wt % : Weight percentage
T_{m} : Maximum temperature
T_{a} : Ambient temperature
°C : Temperature
θ_{g} : Furnace temperature
t : Time
µm : Micrometer
mm : Millimeter
kV : Kilo volt
ΔW : Water intake ratio of the film
W_{e} : The weight of film after water immersion
W_o : The weight of film before water immersion

LIST OF ABBREVIATIONS

POC	:	Palm oil clinker
$Al(OH)_3$	:	Aluminium hydroxide
$Mg(OH)_2$	:	Magnesium hydroxide
TiO_2	:	Titanium oxide
CES	:	Chicken eggshells
APP	:	Ammonium polyphosphate
MEL	:	Melamine
PER	:	Pentaerythritol
H_2O	:	Water
IFR	:	Intumescent flame retardant
CO_2	:	Carbon dioxide
CaO	:	Carbon monoxide
MgO	:	Magnesium oxide
FRA	:	Flame retardant additives
e.g.	:	Exempli gratia (for example)
et al.	:	et alibi (and elsewhere)
Fe_2O_3	:	Iron (III) oxide
FESEM	:	Field emission scanning electron microscope
FTIR	:	Fourier transform infrared spectroscope
H_2O	:	Water
ISO	:	International Organization for Standardization
K_2O	:	Potassium oxide
NH_3	:	Ammonia
OMMT	:	Organically modified montmorillonite
PA	:	Polyamide
PP	:	Polypropylene
PDPs	:	Phosphorous degradation products
PEG	:	Polyethylene glycol
POCP	:	Palm oil clinker powder
rpm	:	Revolutions per minutes
SEM	:	Scanning electron microscope
SF	:	Silica fume
SiO_2	:	Silica dioxide
TGA	:	Thermogravimetric analysis
XRD	:	X-ray diffraction
XRF	:	X-ray fluorescence

CHAPTER 1: INTRODUCTION

1.1 Introduction and Problem Statement

Steel structure starts to lose its structural properties when temperature reached 550°C, leading to the rapid loss of its strength and stiffness, where collapse may occur (Dai et al., 2009; Norgaard et al., 2013). Fire protection systems for the building consist of active and passive fire protection. Active fire protection systems are installed inside the building to actively protect the building against fire at its onset, such as extinguishers, water sprinklers, and fire detectors. On the other hand, passive systems act as a form of second-line defense to lower the spread of fire which visibly look similar to ordinary paint finish. Usually, passive fire protection of steel members is achieved by using materials such as cement-based sprays, board, batt materials and intumescent coatings (Wang et al., 2006). Intumescent fire protective coatings is commonly used as passive fire protection materials to protect the steel against fire especially in industrial and commercial buildings due to its effectiveness (Liang et al., 2013). Intumescent coating is applied to the steel structure for fire protection to prevent the building from collapse in the event of fire, which can save a thousand of precious lives if the building can last for longer period and extending time for evacuation. When exposed to a sufficiently high temperature, the intumescent coating forms a porous char that thermally insulates the steel substrate from heat and prevents it from reaching critical temperature (Duquesne et al., 2004; Jimenez et al., 2006a). Intumescent coatings are designed to perform under severe fire conditions and to maintain the steel's integrity between 1 and 3 hours (Duquesne et al., 2004; Jimenez et al., 2006a). Three flame-retardant additives are employed in the formulation of intumescent coatings: (1) an acid source (ammonium polyphosphate, APP), (2) a carbon source (pentaerythritol, PER) and (3) a blowing agent (melamine, MEL), blended with flame-retardant fillers and binder.

The usage of intumescent coating as passive fire protection coating is one of the easiest way to block the penetration of heat to the steel substrate. However, due to the expensive synthetic fillers, it is not often use because this would increase the production cost. Several researches have been done in order to lower the production cost of intumescent coatings by using by-product waste as a bio-filler in intumescent coatings such as rice husk and chicken eggshells (CES) (Yew et al., 2013a). The use of chicken eggshells as bio-filler was studied by Yew et al. (2013a). It takes a lot of effort in processing CES to obtain required particle size before it can be used as filler, when compare to palm oil clinker (POC) which can be used directly from the sources without going through any process and its availability in bulk quantities. Hence, in this research, the usage of synthetic fillers in intumescent coating will be reduced by using POC as a bio-filler.

Malaysia is the second largest country in the world that produced palm oil and has to deal with a problem of by-product waste that is generated from palm oil processing. (Ahmmad et al., 2015). POC is a by-product produced from palm oil industry which is usually produced in large quantities and treated as disposal waste. POC is produced after the burning of oil palm shell and palm oil fibre with 30:70 ratio at high temperature of 850°C in generating energy to run the plants (Jumaat et al., 2015). Using POC as a bio-filler in intumescent coating is an alternative way to help in reducing the production cost as well as protecting the environment from the by-product waste. This research will focus on developing the best formulation of intumescent fire protective coating using hybrid fillers containing POC as a novel bio-filler and its performance on steel structure in the event of fire. This coating would be a high-demand fire protection materials in the future of construction because of its low cost while at the same time preserves the environment due to incorporation of by-product waste.

1.2 Research Objectives

The main objective of this research is to design the best composition of intumescent coating and investigate their effectiveness when using POC as a bio-filler. This is achieved by adopting the following specific objectives:

i. To examine the influence of particle size of POC filler in fire protection performance of solvent-borne intumescent fire protective coating.
ii. To determine the optimum percentage of POC fillers in solvent-borne intumescent fire protective coating.
iii. To evaluate the effect of hybrid fillers in solvent-borne intumescent fire protective coatings by means of fire protection performances, mechanical strength and water resistance.
iv. To investigate the influence of binder in intumescent fire protective coatings.

1.3 Scope of work

The work presented in this thesis involved a series of experimental work in order to investigate the intumescent coating performances with different compositions. In this research, APP phase II was used as an acid source, MEL as a blowing agent, PER as a carbon source, acrylic resin as a solvent-borne binder, vinyl acetate copolymer as a water-borne binder and four different hybrid fillers (POC as bio-filler). Four series of different formulations were prepared in order to characterize the intumescent coating performances in terms of fire protection performance, mechanical strength and water resistance. The first part of the research was to study the influence of particle size of POC filler as a single, followed by the optimum percentage of POC as a single filler, then the effect of hybrid fillers and lastly the influence of binder to the intumescent coating performance.

The coatings were characterized by thermogravimetry analysis (TGA), field emission scanning electron microscope (FESEM), Instron microtester, Bunsen burner test, surface spread of flame test and static immersion test. TGA curves were used to determine the thermal stability of each sample. From the TGA curves, the effect of different composition such as particle size of filler, percentage of filler, hybrid filler and binder in intumescent coating can be examined. The results of TGA can determine the thermal stability of the coatings as well as the loss of weight and decomposition of the materials as a function of temperature.

The fire protection performances of the intumescent coatings were studied using the Bunsen burner and surface spread of flame test. Bunsen burner is used to characterize the char formation and determine the temperature development on the single-side coated steel plate when exposed to high temperature. Meanwhile, the surface spread of flame test was performed in accordance with the BS 476: Part 7 standard (1997). The intumescent coating was classified according to the rate and extent of flame spread. Class 1 is the best classification whereas Class 4 is the worst classification. If the coating falls under Class 4, this means that the coating is at a high risk.

After the Bunsen burner test, a piece of char was cut from the centre of char layer for FESEM test in order to examine the surface morphology of the char layers. The physical structure of the char layer has a significant effect on the fire protection performance of intumescent coatings.

For the third and fourth part of the research study, the adhesion strength at the interface of the intumescent coating and steel substrate was determined using a pull-off adhesion tester for samples with different hybrid fillers and binders.

1.4 Thesis Outline

This thesis contains of five chapters. Chapter One explains the background and problem statement, the objectives of research, the scope and organization of the thesis. Chapter Two provides the previous studies on flame retardant materials and intumescent fire protective coatings for steel application. The mechanisms of intumescent coating when exposed to high temperature are discussed. Also, a review of existing standard fire curves from Eurocode and International Organization for Standardization (ISO) 834 specifications is presented.

Chapter Three describes the properties of materials used in the research, composition of intumescent coating, flow of research activity and characterization techniques to determine the intumescent coating performances.

Chapter Four discusses the results obtained from the characterization on intumescent coating performances in term of fire protection, surface morphology of char layer, mechanical strength and water resistance. The physical and chemical mechanisms of the samples are also studied. The overall discussion on the results of the present research work is given in this chapter as well.

Finally, conclusion of the research and recommendations for future research is given in Chapter Five. The conclusion explained on the results in each part of the research and the best intumescent coating formulation was briefly discussed. The recommendations for future research include the study on other available bio-filler and other test such as anti-corrosion and the toxicity test.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

According to Mount (1992), the word intumescence comes from Latin which can be translated as ‘begin to swell up’. The process of getting to a swollen state was known as tumid or tumescent. In other words, intumescence is defined as the swelling of certain substances when they are heated or exposed to fire (Camino et al., 1989; Camino et al., 1990). In flame retardant terms, exposure to fire or heat combustion initiates a series of chemical and physical processes, leading to an expanded multicellular layer, which acts as a thermal barrier that effectively protects the structural elements against a rapid increase of temperature, thereby prevent the building from the collapse under severe fire conditions (Duquesne et al., 2004).

Most structural steel buildings in Malaysia do not apply intumescent fire protective coatings due to usage of such coatings increase the building costs. The addition of flame-retardant fillers, such as aluminium hydroxide and magnesium hydroxide in intumescent coatings is an effective way to overcome fire propagation and surface spread of flame because of their high flame retarding efficiency (Huang et al., 2006; Yeh et al., 1995; Cross et al., 2003; Tai and Li, 2001). Unfortunately, current commercial intumescent coatings are very costly due to expensive flame-retardant fillers. Therefore, the usage of bio-filler in intumescent coatings such as palm oil clinker (POC) and chicken eggshells (CES) was recommended because of massive quantity of this by-product waste was produced in Malaysia and it is believed that by-product waste can creates a serious environmental pollution. As POC is abundant and have small commercial value in Malaysia, this industrial waste can be converted into potential construction materials due to its high thermal stability and its chemical composition. POC is a by-product from palm oil shell incineration which may be used as a filler in intumescent coating because it is thermally stable as it is produced under high temperature.

Different intumescent coating formulations can be improved to meet the specific fire protection requirements. The studies in this field are very wide and many parameters in the formulation can be developed. The purpose of this research is to study the intumescent coating that uses combinations of flame retardant additives, binder and palm oil clinker (POC) as a novel bio-filler with which enables significantly lowered production cost. The formulations will be mixed using a high-speed disperse mixer for several hours at room temperature until completely homogeneous. The coating will be characterized through a series of fire tests (e.g. Bunsen burner test and surface spread of flame), physical properties tests (e.g. thermogravimetric analysis, Field emission scanning electron microscopy, static immersion and adhesion strength). The effectiveness of intumescent coating formulations using POC as bio-filler will be obtained and evaluated. This low-cost intumescent coating will be able to protect the steel in the event of a fire as well as preserved the environment from by-product waste.

2.2 Fire Protection Methods on Steel Structures

Fire protection of structural steelwork plays an important role in ensuring that the buildings will not collapse when exposed to high temperature which will provide ample time for the occupants to escape. Building regulations require certain elements or all elements of a structure to have fire protection. Fire protection systems for the building consist of active and passive fire protection system. Active fire protection system is usually used inside the building such as fire extinguishers, water sprinklers, and fire detectors. While, passive systems act as a form of second-line defense to lower the spread of fire. Usually, passive fire protection of steel members is achieved by using materials such as cementitious/vermiculite sprays, non-combustible boards, intumescent coatings and mineral fibre casings which are applied to insulate the steel frame (Wang et al., 2006).

2.2.1 Gypsum Board

Boards are broadly used for fire protection of steel structure and can be classified into lightweight and heavyweight. Lightweight boards are usually used where aesthetics are not important. Meanwhile, heavyweight boards are usually in the range 700-950kg/m³ and generally used for decorative finishes. They protect the steel by providing a heatproof insulation and their mechanism depends on the formulation of the board. The boards can be made up from gypsum-based plasters or calcium silicate, fibre and specialist vermiculite containing materials. They have wide range of thicknesses and it is important to ensure that the correct board thickness is chosen to give the required period of protection. Kolaitis et al. (2012) studied the fire behavior of gypsum plasterboard wall assemblies. Gypsum plasterboards are used as an aesthetically pleasing, easily applied and mechanically enduring cladding material for walls, floors and ceilings for good thermal insulation and fire protection characteristics (Kolaitis et al., 2012). When gypsum is exposed to a high temperature environment, it released water molecules that bound in its crystal lattice and transferred through its mass. This gypsum dehydration process is highly endothermic, thus enhancing the fire resistance of the overall structure (Ang & Wang, 2004). Gypsum plasterboards based lightweight construction is gaining most attention in the market share due to its flexibility, lower construction time and cost as well as very good thermal and fire performance. According to Gypsum Association, gypsum board is an excellent fire-resistive building material. It is commonly used in North America for interior finish where fire resistance classifications are compulsory. It contains about 21% of chemically combined water where can slowly release as a steam when exposed to high heat which effectively delays the transfer of heat and spread of fire. Even after complete calcination, gypsum board continues to act as a heat-insulating barrier. The tests conducted in accordance with ASTM E 84 show that gypsum board has a low flame-spread index and a low smoke-density index. When installed in combination with other materials in laboratory-tested wall and ceiling assemblies, gypsum board serves to effectively protect building elements from fire for prescribed time periods (Gypsum Association).

2.2.2 Vermiculite Spray

Spray protection is used to cover complex shapes and details. It is probably the cheapest method of fire protection and can frequently be seen in places like multi-story car parks and basement areas of buildings, where a very rough and thick coating has visibly applied to the profile of the steel. It is made up of cement and exfoliated vermiculite. Exfoliated vermiculite spray was applied to commercial and industrial structural steel products to improve the application characteristics and increase the fire resistance. It is very efficient at retaining moisture, and when exposed to heat, this turns to steam which has a cooling effect on the steel substrate and thus delays its temperature rise.

2.2.3 Concrete

The use of concrete as fire protection for structural steelwork started to grow in the 1970’s. The advantage of concrete is durability and it tends to be used where resistance to impact damage, abrasion and weather exposure are important such as for external structures. Concrete is known to be non-combustible and do not emits toxic fumes. As temperature rises, concrete progressively loses moisture and gradually loses strength. The loss of strength is highest at temperatures above 450 to 600°C which depends on the type of aggregate. Concrete can spall off in a fire mostly when in moist or wet condition, due to the buildup of steam pressure within the concrete, leading to separation and loss of the surface layer. In most fire incident, concrete will retain its structural integrity and the structure can be successfully repaired. However, after the introduction of passive fire protection system into the construction industry such as boards, sprays and intumescent coatings, there has seen a dramatic reduction in its use.

2.2.4 Intumescent Coating

Recently, intumescent coating is widely used as structural fire protection due to its effectiveness and easily applied to the steelwork structures. They act as a fire protection by changing their nature from a decorative paint into a carbonaceous char, which forms when the coating is exposed to high temperature. This char layer can swell up to 50 times the thickness of the initial coat when it is heated. At these higher temperatures the resin system melts and allows the release of a mineral acid, which reacts with a carbon rich element in the paint to form a carbon char. At the same time a non-flammable gas is released, which expands the foam to form the thicker layer. The resin systems are used to bind other components together, either in a solvent-based or water-based. The coatings are applied up to 6mm for about 120 minute fire protection. The thick film intumescent is used mainly in the oil and gas industry. In particular, intumescent coatings present relevant benefits, like ease of processing and application on several materials without modifying their intrinsic properties (Duquesne et al., 2004). In the construction industry, intumescent coatings have been widely used, especially for retarding the collapse of steel and timber structures, acting as a passive protection to allow the necessary time for safe intervention of rescue teams and building evacuation (Jimenez et al., 2006b).

2.3 Intumescent Coating and Its Mechanism

Intumescent fire protective coating is one of the easiest and most economical ways that is recently used in many structural buildings as a structural fire protection which is one of the requirements of legislation to prevent failures of steel components when exposed to high temperature of heat. Fire protection material like intumescent coating is easily applied on the steel structures to maintain the structure element properties below the critical temperature of 550°C (Duquesne et al., 2004). Intumescent coatings provide fire protection by undergoing an endothermic decomposition reaction process at the elevated temperatures that causes the material to swell and foam into a highly porous, thick and thermally stable char layer (Vanderall, 1971; Kay et al., 1979; Camino et al., 1989; Kandola & Horrocks, 1997). Generally, three active ingredients are employed in the intumescent coatings, i.e. ammonium polyphosphate (act as an acid source), pentaerythritol (as a carbon source) and melamine as (a blowing agent) blended with flame-retardant fillers and binder (Jimenez et al., 2006). When intumescent coating is exposed to high temperature, three reaction processes will occurs (Jiang et al., 2012; Ma et al., 2012; Gomez-mares et al., 2012): (i) the acid source breaks down to yield a mineral acid; (ii) dehydration of the carbonization agent to yield a carbon char and (iii) expansion of the blowing agent to form a swollen multi-cellular char by releasing non-flammable gas. Figure 2.1 shows the images of intumescent coating after the Bunsen burner test.

Figure 2.1: Intumescent coating after the Bunsen burner test (Yew & Ramli Sulong, 2012)

A proper sequence of decomposition reactions and physical processes of all compounds in intumescent coating is needed for intumescence process to occur. The order of these processes is given in Figure 2.2. The intumescence process begins with the decomposition of the acid sources to produce a mineral acid which is catalyzed by organic amides or amines. The acid sources must decompose before any other compound in the coating in order for dehydration process of the carbonific compound to occur. Generally, the acid compounds used include zinc borate, linear high molecular-weight APP, melamine phosphate, organic esters, and salts of ammonium, amide or amine (Bourbigot et al., 1993; Castrovinci et al., 2005). The next stage is decomposition of the carbonific by a dehydration reaction that converts the carbonific into a carbonaceous char. The carbonific is a polycarbonate or phenol that yields a large amount of char. The char is then expanded with the decomposition of the blowing agent. The decomposition of the carbonific and blowing agent must occur at the same temperature for expansion of the char layer, otherwise the intumescence process might not take place. The decomposition of blowing agent will produces non-flammable gases that cause the char to swell. Blowing agents are usually nitrogen compounds such as urea, dicyandiamide, guanidine, melamine and glycine that yield ammonia (NH_3), carbon dioxide (CO_2) and water (H_2O) vapour (Banerjee & Chattopadhyay, 1993). The coating will produce char layer that acts as a physical barrier which slows down heat penetration to the substrate. The intumescent coating usually expands 50 to 200 times from their original thickness and forms a fine-scale multicellular network with a cell size of 20 to 50 µm and wall thickness of 6-8 µm (Cullis & Hirschler 1981; Anderson et al., 1985).

The chemical mechanism for intumescence was studied by Mount (1992), which is written in terms of simple acid-catalyzed and dehydration reactions (see Figure 2.3). The chemical reaction for the first two reactions show the depolymerisation catalyzed by an acid, followed by the dehydration of the carbonific when phosphoric acid is present. The -C=CH2 compound was produced at the chain ends for both reactions. These compounds condense to form carbon-rich char residues. The way the phosphorous compound work is that they phosphorylate carbonific such as PER to make polyol phosphates (Yew, 2011). These polyol phosphates can then break down to form the char layer (Weil, 1992).

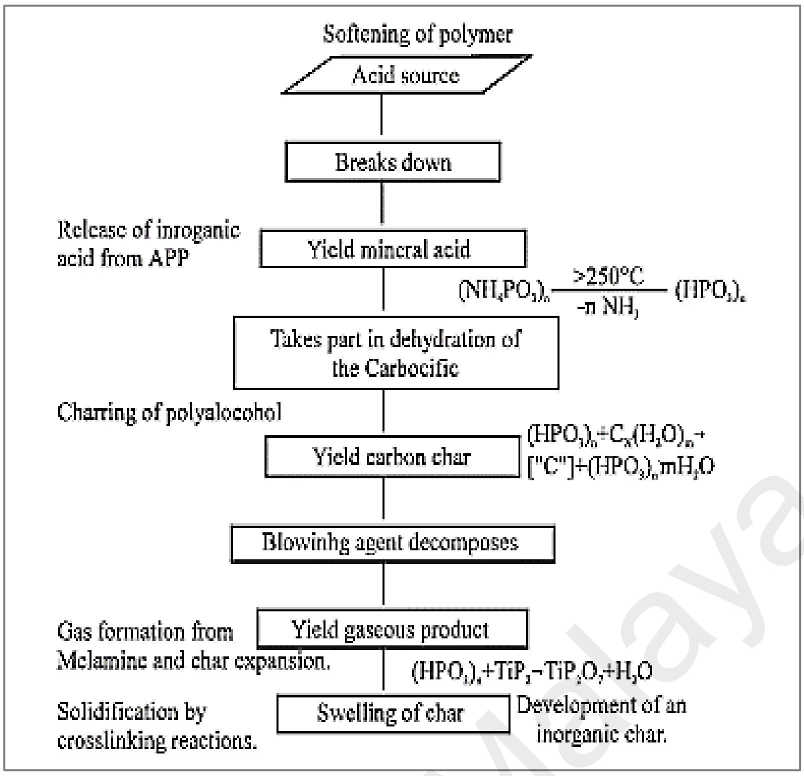


Figure 2.2: Intumescent coating mechanisms in a fire (Bourbigot et al., 2000)

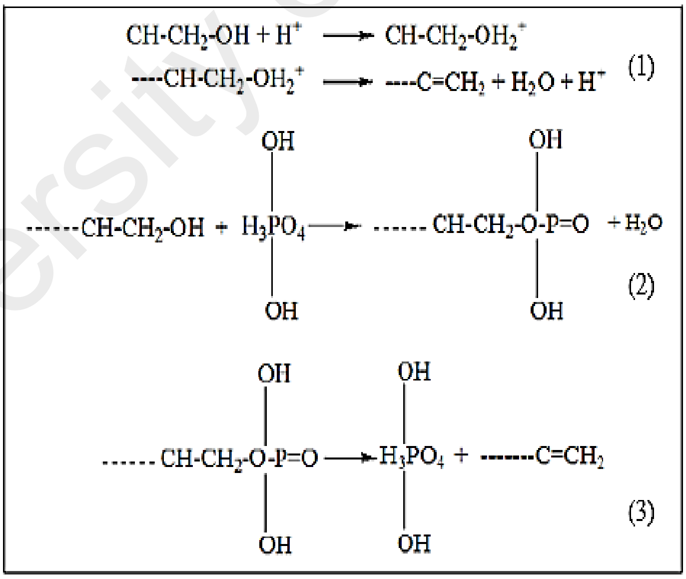


Figure 2.3: Chemical mechanism of intumescence (Yew, 2011)

2.4 Composition of Intumescent Coating

Generally, the intumescent coatings consist of three different flame-retardant additives mixed with flame-retardant fillers and binders. These compounds must undergo a series of decomposition reactions and physical processes within a proper sequence for intumescence process to occur. Intumescent coatings increase the fire resistance time of structural elements exposed to high temperatures, by swelling and forming a layer of carbonaceous char, which acts as a thermal barrier, to effectively insulate and thus protect structural elements against any temperature increases during a fire (Han, 2010). The formulation of the coating has been optimized in terms of physical and chemical process in order to form an effective protective char layer upon exposure to fire (Yew & Ramli Sulong, 2011; Bourbigot et al., 2004). Chemical interactions between the active ingredients in the formulation lead to the formation of the intumescent char. The acid source breaks down to yield a mineral acid, then it takes part in the dehydration of the carbonization source to yield the carbon char and finally the blowing agent decomposes to yield gaseous products. The latter causes 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 (Jimenez et al., 2006a).

Thermal protection is the main purpose of intumescent coating. Swelling is vital to the fire protective abilities and it is important to understand the fundamental of the mechanisms that cause expansion. Temperature gradients and heat transfer play a key role in intumescent behavior. To make the intumescent flame retardant efficient, a proper selection of components such as char formers, carbonizing, dehydrating substances and modifiers is essential in order to obtain a maximum degree of carbonization and thus the protective char layer. Furthermore, it is very important to select proper binder to bind all intumescent coatings components. The required components for intumescent coating production are shown in Table 2.1.

Table 2.1: The components of intumescent flame-retardant system (Rains, 1994)

Compounds	Function of components
Polyhydric alcohols (erythritol and its oligomers (pentaerythritol, pentaerythritol dimer and trimer, arabitol, sorbitol, inositol), saccharides (glucose, maltose, arabinose) and polysaccharides (starch dextrin, cellulose), polyhydric phenols (rezorcinol).	Carbonizing substance (With a considerable number of carbon atoms, thermal decomposition of which results in the formation of carbonaceous material having a large number of hydroxyl groups, able to be esterification with acids)
Phosphoric acid, its ammonium, aminic salt and esters (ammonium phosphate and polyphosphate, melamine and urea phosphate tributyl phosphate), boric acid and its derivatives (borax, ammonium borate).	Dehydrating agent (Substance releasing during its thermal decomposition an acid which esterifies hydroxyl groups)
Nitrogen or halogen compounds such as melamine and its phosphoric salts, urea, dicyandiamide, guanidine and its derivatives, glycine, chlorinated paraffins.	Foam forming substance (Releases large quantities of nonflammable gases during its thermal decomposition, thus forming foamed structure of carbonaceous layer)
Amino, epoxy, acrylic, polyacetic vinyl and polyurethane resins.	Binder resin
Specific, chemical compounds depending on the kind of resin	Solvents, stabilizers, etc.

Xia et al. (2014), studied the effect of the ammonium polyphosphate (APP) to pentaerythritol (PER) ratio on the flame retardancy, composition, the structural and thermophysical properties of carbonaceous foam. In this research, a classical system was used for intumescent flame retardant (IFR), consisting of ammonium polyphosphate (APP) and pentaerythritol (PER) and the effects of weight ratio of APP to PER on various aspects of carbonaceous foam deriving from polypropylene (PP)/IFR composites were investigated. The carbonaceous foam resulting from PP/IFR composites was a physical mixture of phosphorous degradation products (PDPs) and insoluble chars (Xia et al., 2014). The structural and thermophysical properties of the carbonaceous foam were affected by the APP-PER ratio, which include its expansion ratio, air tightness, thermal conductivity and thermal diffusivity (Xia et al., 2014), which subsequently affected the efficiency of both mass and heat transfer between the gas and the condensed phases. The content of PDPs in the mixed melt during the foaming stage and in the solidified carbonaceous foam was considered as the main regulator of these important properties of the carbonaceous foam (Xia et al., 2014). Wang and Wang (2014) studied the use of nano sized organically modified montmorillonite (OMMT) and reported that a ceramic-like layer of alumino phosphate formed from reactions between OMMT and APP during combustion, which improved the foam structure of the char. Dong & Wang (2014), found that nano-sized particles dispersed better in an intumescent coating that improved fire resistance time.

2.4.1 Flame Retardant Additives

In intumescent coating system, there are three flame-retardant additives, namely an acid source mostly ammonium polyphosphate (APP), a carbon source such as pentaerythritol (PER) and a blowing agent such as melamine (MEL). Theoretically, an acid source such as inorganic acid, acid salt or other acids elevates the dehydration of carbonizing agent while a carbonizing agent such as PER which is a carbohydrate that will be dehydrated by the acid source to become a char and also a blowing agent such as MEL will be decomposed to release gas resulting in the increase of polymer's volume and the formation of a swollen multi-cellular layer (Laoutid et al., 2009).

There are many different types of flame retardants available in the market. They can be classified into several classes which include organohalogen compounds (organochlorines and organobromines), organophosphorus compounds (organophosphates, phosphonates and phosphinates) and minerals (aluminium trihydrate and magnesium hydroxide) (Lim et al., 2016). Also, flame retardants can be classified into phosphorus-containing, halogen-containing, silicon-containing or any other chemical-containing flame retardants based on the chemical type in their structure. Currently, APP is getting the most attention among the industries. Two crystal forms of APP (APP-I and APP-II) are used as major ingredients in intumescent coatings. APP-I has a chain length of about 100, while APP-II has a chain length of more than 1000. Hence, APP-II catches more applications than APP-I, due to its lower water solubility and higher thermal stability in paints and coatings. It is known to be preferred over the other flame retardants due to its smaller loadings at lower cost and excellent process. Most importantly, APP is a halogen-free flame retardant and thus it does not generate additional amount of smokes, making it to be environmentally useful compared to other halogen-containing flame retardants (Levchik et al., 1996). During intumescence, a material start to swell when it is exposed to heat or fire to form a porous carbonaceous foam which acts as a barrier to prevent heat, air and pyrolysis product from entering the surface of the material (Camino et al., 1993; Le Bras et al., 1999). APP decomposed into polyphosphoric acid and ammonia when exposed to heat. The polyphosphoric acid would then reacts with hydroxyl group or other groups of synergists to form a non-stable phosphate ester (Cullis et al., 1991; Lewin, 1999). Charring would occur during dehydration of phosphate ester, which involves the formation of a carbon foam above the surface of the polymeric materials to against the heat source. Furthermore, a viscous molten layer or surface glass was also formed on the polymeric surface which protects the polymeric materials from heat and oxygen (Green, 1992). According to Jimenez et al., (2006c), in order to achieve an optimum performance, APP needs to be properly dispersed into the polymer system and compatible with the polymer matrix.

2.4.2 Flame Retardant Fillers

Flame retardant fillers can influence the combustion characteristics of intumescent coatings in terms of its resistance to ignition, the amount and nature of smoke and toxic gas emission products. According to Hornsby (2007), depending on the nature of the filler, the heat capacity, thermal conductivity and emissivity of the flame retardants composition may also change, giving rise to heat transfer and thermal reflectivity effects, which can also reduce the rate of burning. Any type of inorganic filler can influence the reaction of intumescent coatings to fire for several reasons such as it reduces the content of combustible products, modifies the thermophysical properties and thermal conductivity of the resulting material and removes a good deal of the heat evolved in a degradation and thus can prevent further degradation. Usually, fillers are used for specific applications, such as in improving the fire retardancy, anti-corrosion, density reduction, thermal conductivity, surface properties and thermal insulation. The most commonly used particulate fillers are industrial minerals, such as talc, calcium carbonate, mica, kaolin clay, wollastonite, feldspar, silica, wood flour, carbon black, titanium dioxide, and aluminum hydroxide (Mariappan, 2016). While, the most commonly used fibrous fillers are glass fiber, carbon fiber, aramid fiber, and natural fibers which are usually hydrophilic and rigid materials and are immiscible with the polymer matrix and form distinct dispersed morphologies (Mariappan, 2016).

2.4.2.1 Mineral fillers

The most commonly used mineral flame retardants are metal hydroxides, i.e. aluminum hydroxide and magnesium hydroxide, hydroxycarbonates and zinc borates. However, these inorganic fillers have a direct physical flame retardant action (Yew, 2011). As the temperature rises, these fillers decompose endothermically and therefore absorb energy. Then, they release non-flammable molecules (H_2O and/or CO_2), which dilute combustible gases, and can also promote the formation of a protective ceramic or vitreous layer. Zhang et al. (2009) investigated the effects of adding different combinations of nanoclay, magnesium hydroxide and aluminum trihydroxide into a polymer blend consisting of ethylene vinyl acetate and low-density polyethylene. From this research, cone calorimetry results indicated that the combination of polymer blend, nanoclay and aluminum trihydroxide exhibited the lowest peak heat release rate, therefore exhibiting superior fire retardancy in comparison to conventional formulations without nanoclays.

(a) ***Organo modified montmorillonite***

There are several researches that suggested incorporation of high aspect ratio nano-fillers into the intumescent formulations, including delaminated talc and organo modified montmorillonite clays, for example, poly(allylamine), methyl methacrylate and polypropylene (Laachachi et al., 2011; Wang et al., 2007; Dogan and Bayramlı, 2011). Other studies have also suggested the use of combinations of fire retardant additives and organo modified nanoclay for polyamide and propyl ester binders which have the potential of enhancing flame retardancy (Bourbigot et al., 2000; Sittisart & Farid, 2011). In another investigation, Wang et al. (2007) determined that the fire performance of the intumescent coating can be improved by the utilization of 1.5% by weight of organo-modified montmorillonite. In this study, the use of 3% by weight nanoclay in the nanocomposite coating, instead of 1.5% by weight, led to a decline in the fire performance of the coating. Chuang et al. (2011), also investigated the effects of adding organo-clays into acrylic-based intumescent coatings on their fire-retardancy performance. They reported cone calorimetry results showed that coatings containing 3%C30B type of organo-modified (methyl-tallow-bis-2-hydroxyethyl, quaternary ammonium) montmorillonite exhibited superior fire retardance when compared to similar formulations containing a higher concentration, i.e., 5% of C10A type of organo-modified (dimethyl-benzyl-hydrogenated-tallow, quaternary ammonium) montmorillonite.

(b) *Titanium oxide*

According to Beheshti & Heris (2016), the char structure formed after exposing the intumescent coatings to fire is easily damaged at high temperature. Therefore, it is necessary to improve the fire retardancy and durability of these systems. Other research has focused on introducing synergistic flame retardant nano-fillers as a simple method into intumescent systems (Alongi et al., 2015). In polymer nanocomposites it is believed that nano-filler are more effective in reducing flammability and improving thermal stability of polymers (Liang et al., 2013; Wang et al., 2014; Wang et al., 2014; Hong et al., 2014). Beheshti & Heris (2016) had studied on the incorporation of a combination of titanium oxide (TiO_2) nano particles and micro particles of chicken eggshell into traditional intumescent coating. Results indicated that performance of coating is improved as the weight fraction of nano particles is increased. Accurately, the best result in the term of char layer expansion and anti-oxidation property is achieved by incorporation of 20 wt. % nano-TiO_2 and 15 wt. % chicken eggshell.

Meanwhile, Aziz & Ahmad (2016), studied the effects of nano-titanium oxide on the thermal resistance of an intumescent fire retardant coating for structural applications. This research developed an epoxy based intumescent flame retardant coating containing phosphate, nitrogen, barium and boron. The coating was reinforced with nano-titanium oxide and then characterized using a lab scale hydrocarbon fire test. The characterization studies included FESEM, EDS, FTIR, XRD and XRF to determine effects from nano titanium oxide on char's performance. The results obtained indicated that a coating reinforced with 4.5 wt% of nano-TiO_2 increased the residual weight to the coating and provided longer thermal protection time compared to conventional fire retardant coatings.

2.4.2.2 Fillers from renewable resources

(a) ***Chicken eggshells***

The usage of bio-filler in intumescent coatings like chicken eggshells (CES) was recommended because of massive quantity of this by-product waste and it has created a serious environmental pollution (Yew et al., 2015a). It is known that CES waste consists of about 95% calcium carbonate in the form of calcite and 5% organic materials such as type X collagen, sulphated polysaccharides, and other proteins (Arias et al., 1993; Arias et al., 2003). Although there have been several attempts to use CES components for various applications (Ishikawa et al., 2004; Tsai et al., 2006; Yi et al., 2004; Yew et al., 2013a; Yoo et al., 2009), its chemical composition and availability makes CES a potential source for bio-filler reinforced bio-polymer composites, improving their mechanical properties (Yew et al., 2013a). From the previous study, Yew et al. (2015a) studied the influence of chicken eggshells (CES) as a novel bio-filler for intumescent flame-retardant coatings and showed that the addition of 5.0 wt% and 2.5 wt% CES bio-filler into intumescent coating formulation improved fire protection due to char formation, with better morphology, height and structure of the protecting shield. From this research, the different filler compositions of samples applied at a thickness of 1.5 ± 0.2 mm achieved the lowest fire propagation index with a value of 4.5 and 5.0, respectively (BS 476 Part 6, Class 0 materials) which indicates excellent fire-stopping properties. The results showed that the coatings were effective in fire protection, with good qualities of water resistance, thermal stability, and adhesion strength. It proved that, utilization of by-products materials into other application is a partial solution to environmental problems and it may help in reducing the cost of manufacturing. Unfortunately, there are limitations of preparing eggshell particle size unless the eggshell is ground to very fine particle size, it will exhibit high aspect ratio due to the thin plate like nature of a shell (Yew et al., 2013a). Depending on the particle sizing technique, this aspect ratio property will strongly influence the assumed particle size, particularly if sedimentation or air classification is used, or certainly if the wrong form factor is applied in light scattering methods (Yew et al., 2013a).

(b) ***Palm oil clinker***

Malaysia is the second largest palm oil-producing country in the world, producing about 3.13 million tons of palm shell as waste, which has been projected to grow because of the ongoing global consumption demand for palm oil (Basri et al., 1999). However, the palm oil industry is also a major contributor to the pollution problem occurring in the country, with an estimated 2.6 million tons of solid waste produced annually which is mostly composed of palm oil clinker (POC) and palm oil shell (Basri et al., 1999). POC is abundant and have small commercial value in Malaysia, hence, this industrial waste can be converted into potential construction materials. Due to its high thermal stability and its chemical composition, there are several attempts to use POC in different applications. POC as shown in Figure 2.4, is a by-product from palm oil shell incineration. It is a light, solid, and fibrous material, which may be used as filler in intumescent coating because of its thermally stable as it is produced under high temperature. POC was produced at high temperature of 850°C in generating energy to run the plants (Jumaat et al., 2015). Using POC as a bio-filler in intumescent coating is an alternative way to help in reducing the production cost as well as protecting the environment from the by-product waste.

Malaysia has to facing a problem of waste by-product generated from the processing of palm oil. Palm oil clinker was collected inside the boiler after being heated under high temperature in order to generate steam engine for extracting palm oil. Also, this waste was used as materials of heaping up to cover puddle, muddy yards or roads in rural roads but mostly this waste being dumped near the palm oil plant. According to

Siddique (2008), solid waste management contributes one of the major environmental in the world. With the increasing awareness about the environment and lack of land-fill space, waste materials and by-products utilization has become an attractive alternative to disposal (Siddique, 2008). No doubt the way of POC being disposed all this while will create an environmental problem in the future too. Therefore, several researches have been done to solve this problem by substituting this waste as raw material in other application. The physical properties and chemical composition of POC was shown in Table 2.2 and Table 2.3, respectively.

Table 2.2: Physical properties of fine and coarse POC (Mohammed et al., 2014)

Physical properties	Fine	Crushed stone
Aggregate size (mm)	<5	5–14
Bulk density (kg/m^3)	1118.86	781.08
Specific gravity (SSD)	2.01	1.82
Moisture content	0.11	0.07
Water absorption (24 h)	26.45	4.35
Fineness modulus	3.31	6.75

Table 2.3: Chemical composition of POC (Ahmmad et al., 2014)

Oxides	SiO_2	K_2O	CaO	P_2O_5	MgO	Fe_2O_3	Al_2O_3	SO_3	Na_2O	TiO_2	Cr_2O_3	Others
POC	59.63	11.66	8.16	5.37	5.01	4.62	3.7	0.73	0.32	0.22	-	0.58

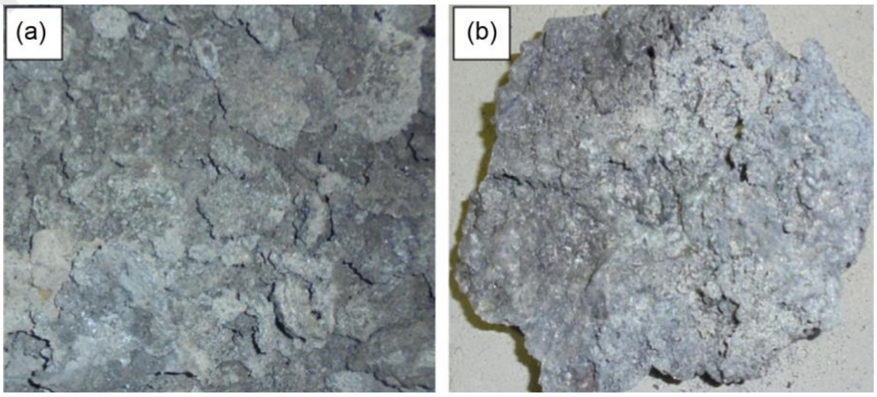


Figure 2.4: Photographs of (a) bulk quantity and (b) a big chunk of POC (Karim et al., 2017)

Karim et al. (2017) studied the characterization of POC powder for utilization in cement based applications. This research presented the results of a study on the physical properties (particle size, specific surface, specific gravity, loss of ignition, morphology), chemical composition, organic carbon, thermal stability and mineralogical composition of palm oil clinker powder (POCP). The characterization was carried out using particle size analyzer, scanning electron microcopy (SEM), X-ray fluorescence (XRF), field emission scanning electron microcopy and energy-dispersive X-ray analysis (FESEM-EDX), thermogravimetric analysis (TGA), total organic carbon (TOC) analysis, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. The chemical composition of POCP was a mixture of inorganic oxides and it was considered stable under normal environmental condition. The XRF spectrophotometer observation revealed that low calcium content in POCP, which contains a mixture of SiO_2, Al_2O_3, and Fe_2O_3, as well as low concentrations of several transition metal and alkali oxides. The main component in POCP was SiO_2. Microstructure analysis confirmed that the particle of POCP is irregular in shape, contain small pores and blackish in color while fibrous materials are also present. From the TGA result, it was found that the main weight loss of 1.44 occurred in the temperature range 45.20 °C to 328.45 °C. In addition, another minor peak was observed at temperature range 573.11 °C to 698.14 °C. The weight loss in POCP is mainly due to the presence of organic carbon (Karim et al., 2017). SEM image obtained from POCP as shown in Figure 2.5.

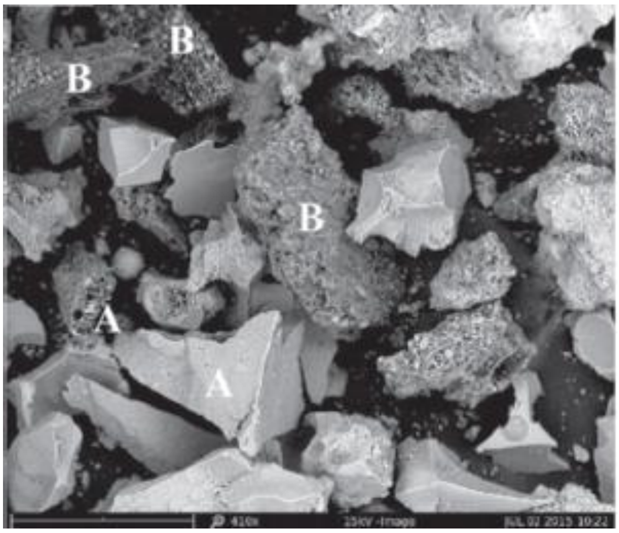


Figure 2.5: SEM image obtained from POC powder (Karim et al., 2017)

2.4.3 Binders

Several research have been conducted to investigate the influence of binder to the intumescent coating performance. The influence of the binder in water-borne coatings was recently studied by Wang & Yang (2010). The binder in the intumescent coating plays an important role as it contributes to the char layer expansion and ensured the formation of uniform foam structure (Wu et al., 2008; Jimenez et al., 2006b; Wang & Yang, 2010). The hydrophilic fire retardant additives such as APP and PER, in the intumescent coatings were very sensitive to corrosive substances like water, acid and alkali. They could easily migrate to the surface of the coatings in corrosive environment. This would significantly depress the expected effect of intumescent coatings. The binder as a film-forming component could prevent or remarkably reduce migration of fire retardant additives and access of the corrosive substances (Wang &Yang, 2010).

Binder is the main ingredient of paints and known as resin that will form a continuous film on the substrate surface. Binders are responsible for good adhesion of the coating to the substrate. In most coating systems, binder may consist of up to two and more resins or polymers. The binder provides durability, hardness and adhesiveness to the substrate. Thus, binder is the most crucial part to produce acceptable film coating systems. Yew et al. (2013a) studied on the effect of different types of fillers and particle sizes on the thermal stability and mechanical properties of acrylic coating. Acrylic resin has high heat and impact resistance, as well as good clarity and UV resistance. This polymeric coating system is widely used to provide protective and decorative functions to substrates due to its low cost, good adhesion and more durable resin (Boxall & Von Fraunhofer, 1980; Carretti & Dei, 2004).

The performance of an intumescent coating is also affected by the type of polymeric binder (Wang & Yang, 2010; Duquesne et al., 2005). When the blowing agent decomposition starts, the rheological characteristics of the film will determine the effectiveness of the foam expansion process (Blasi et al., 2001). In addition, the polymeric binder may also contribute to char formation, increasing the amount of thermally stable material in the insulating foam (Duquesne et al., 2005). The use of binder can be an important matter in developing the intumescent coating formulation. They were incorporated in an intumescent paint formulation, and characterized extensively in terms of thermal degradation behavior, intumescence thickness and thermal insulation.

2.5 Standard Time-temperature Fire Tests on Steel

The temperature of steel increases once it is exposed to fire resulting in the reduction of the strength and stiffness of the steel, which can lead to deformations and failure, depending on the applied loads, temperature profile, and support conditions. The increase in steel temperature depends on the severity of the fire, the area of exposed steel and the amount and type of applied fire protection materials (Yew, 2011). In addition, unprotected steel structures perform poorly in fires compared to other structural materials. This poor performance can be partly attributed to the thinner elements used, the higher thermal conductivity of steel and high thermal expansion (Buchanan, 2002). Fire resistance tests were used to determine the performance of building materials and structural elements during a fire. The time temperature curve used in fire-resistance tests is called the standard fire (Yew, 2011). Fire resistance tests are carried out in order to determine the numeric values of the fire resistance of building structures with appropriate coating. Fire resistance is understood as ability of building structures to resist high temperature for a certain time under simulated fire environment. Where structural steel members are required to have enhanced fire resistance, they can be protected by applying insulating materials (Yellow book, 2007). The most important factor in determining the efficiency of fire protective coating of structure is its resistance to the effect of standard fire temperature for a certain period of time. When exposed to intense fire even incombustible materials such as steel can be weakened, so that building constructions may be damaged and finally destroyed (Bartholmai et al., 2003). Determination of fire resistance of building structures in the European Union is regulated by a number of standards. This standard contains a description of the test equipment and main conditions of testing with permitted tolerances However, the differences in test results are conditioned by different test equipment and skills (Lukošius, 2004). The standard for fire testing that is most widely used is ASTM E-119 (ASTM, 1988), ISO 834 (ISO, 1975) and Eurocode.

2.5.1 The Eurocode Time-temperature Curve

This standard is more rational indication of compartment temperatures than other nominal fire curves. Parametric fire curves are described in Eurocode 1 part 1-2 (EC1, 2002). The Eurocode gives an equation for ‘parametric’ fires, allowing a time-temperature relationship to be produced for any combination of fuel load, ventilation openings and wall lining materials. The equation for the heating phase of the Eurocode parametric time-temperature curve is as follows.

$$T_m = 1325(1 - 0.324exp^{-0.2t} - 0.204exp^{-1.7t} - 0.472exp^{-19t}) + T_a{}^{\circ}\mathrm{C} \quad (2.1)$$

Where T_m, maximum temperature and T_a, ambient temperature (°C).

The most common Eurocode parametric time-temperature curve that is used for fire testing is shown in Figure 2.6.

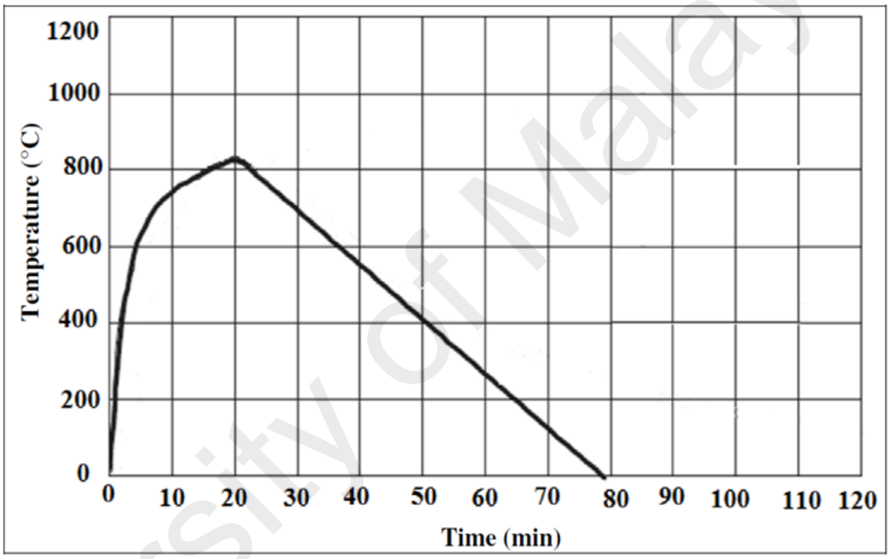


Figure 2.6: Eurocode parametric time-temperature curve (EC1, 2002)

2.5.2 ASTM E-119 Time-temperature Curve

ASTM E-119 is a guideline for fire safe design of buildings and does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products or assemblies under actual fire conditions (ASTM, 1988). Real fires are a function of many variables, such as fuel load, thermal radiation, heat flux, ventilation factor, and area of openings, which are related to the type of construction, building occupancy, and design (Yew, 2011). The time-temperature profile for ASTM E-119 is shown in Figure 2.7. The main purpose of using the ASTM E-119 protocol is to establish and document the fire rating of different elements of a building.

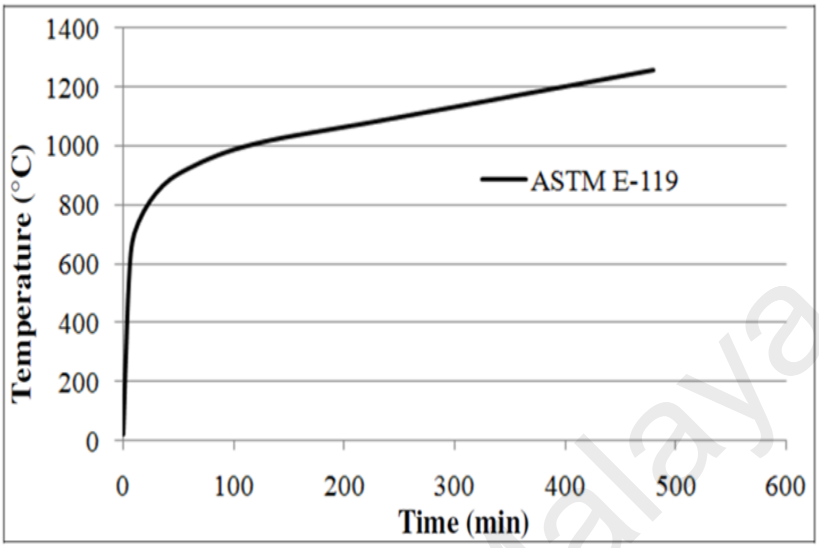


Figure 2.7: ASTM E-119 time-temperature curve (ASTM, 1988)

The ASTM E-119 fire curve is not described as an equation, but rather by a series of data points as shown in Table 2.4, which give temperature values at different times (Buchanan, 2002).

Table 2.4: Time-temperature curve as specified by the ASTM E-119 (1988), (Buchanan 2002)

Time (min)	ASTM E-119 Temperature (ºC)
0	20
5	538
10	704
30	843
60	927
120	1010
240	1093

2.5.3 ISO 834 Standard Time-temperature Curve

The corresponding standard curve prescribed by the International Standards Organization, ISO 834 is produced by the equation below and is displayed in Figure 2.8.

$$\theta_g = 20 + 345 \log(8t + 1) \tag{2.2}$$

Where, θ_g= furnace temperature (ºC), t = time (minutes)

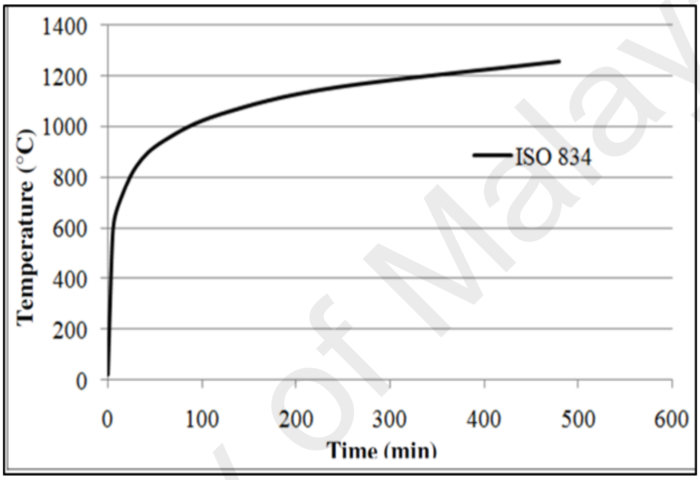


Figure 2.8: ISO 834 time-temperature curve (ISO, 1975)

ASTM E-119 is operated at a negative pressure and IS0 834 at a positive pressure as listed in Table 2.5.

Table 2.5: Time-temperature curves as specified by the ISO 834 standards (1975), reported by Buchanan (2002)

Time (min)	ISO 834 Temperature (ºC)
0	20
5	576
10	678
30	842
60	945
120	1049
240	1153

2.6 Research Gaps and Concluding Remarks

This chapter has presented an extensive review of the previous studies on intumescent coating formulations. It has shown that the intumescent coating has received attention from construction industries due to its effectiveness and convenience. There are many studies conducted to understand their mechanism and improve their performance in terms of many aspects. Different intumescent coating formulations can be improved to meet the specific fire protection requirements. Study in this field is very wide and many parameters in the formulation can be developed. However, very little research is available on the use of bio-filler in intumescent coating formulation. Current research is more focused on other inorganic materials as a filler. The purpose of this research is to develop a novel intumescent fire protective coating using POC waste, which could significantly reduce the production cost and at the same time has excellent fire protection performance.

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Introduction

This chapter consists of three sections which include the materials, sample preparation methods and characterization of sample. In this study, the first step involves the processing of POC to get the appropriate particle size using lab bead mills in specific time interval. The investigation on their thermal stability is conducted using thermogravimetric analysis (TGA). POC with different particle size was used in this research to study their influences in fire protection performance.

The second part is to characterize and optimize the intumescent coatings formulation which consists of flame retardant additives, fillers and binder. Different series of specimens were prepared to investigate the influence of coating composition towards the fire protection performance, mechanical properties and water resistance of intumescent coatings. Four different hybrid fillers was used in this study: (1) palm oil clinker (POC), (2) magnesium hydroxide [$Mg(OH)_2$], (3) aluminium hydroxide [$Al(OH)_3$] and (4) titanium oxide (TiO_2).

The last part of this research explained the overall research methodology and characterization techniques that have been used to investigate the fire protection performance, adhesion strength, surface morphology, static immersion and thermal stability of each intumescent coating composition. The flow of research methodology is shown in Figure 3.1.

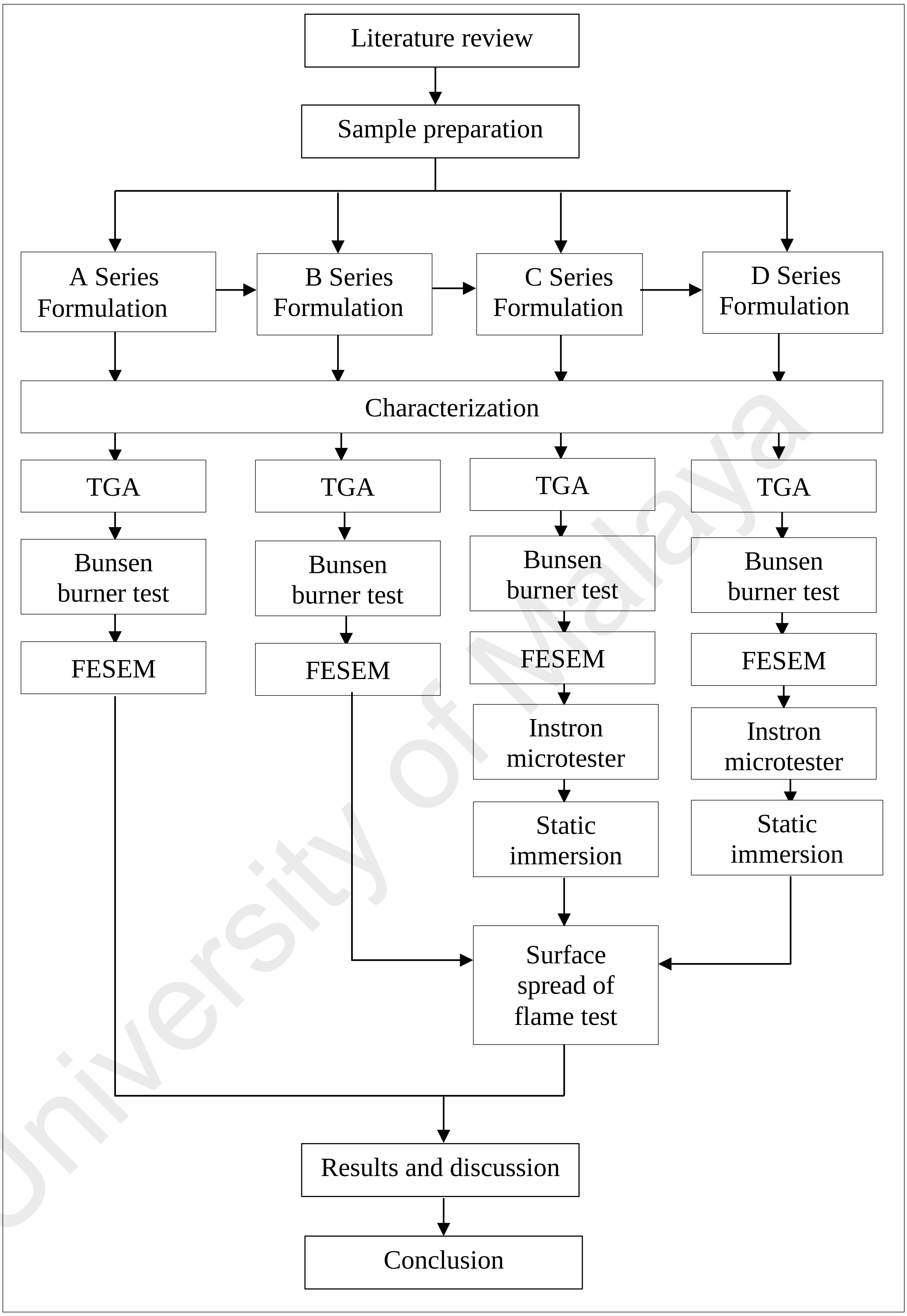


Figure 3.1: Flow chart of the research methodology

3.2 Materials

The intumescent coatings are composed of three main halogen-free flame retardant additives (FRA): (i) commercial crystal phase II ammonium polyphosphate (APP II) as an acid source, (ii) melamine (MEL) as a blowing agent and (iii) pentaerythritol (PER) as a carbon source at a ratio of 2:1:1. Many coatings containing halogen flame retardant additives have been developed and commercialized which was believed will release toxic gasses to the environment when exposed to fire. In this study, the three halogen-free flame retardant additives with low smoke density and do not emit corrosive gases in a fire were used. Commercial crystal phase II ammonium polyphosphate (APP II) (n>1000) derivative acts as an acid source. The molecular weight of APP II is much higher than APP I with "n" value higher than 1000. APP II has a higher thermal stability where the decomposition starts at temperature more than 270°C and lower water solubility than APP I. The physical and chemical properties of APP II are presented in Table 3.1.

Table 3.1: Physical and chemical properties of APP II

Phosphorus % (w/w)	>31
Nitrogen %(w/w)	>14
PH value (10% suspension)	5.5-7.0
Water content %(w/w)	<0.25
Thermal decomposition	°C > 275
Density at 25°C kg/L	1.9
Apparent density kg/L	0.7
Viscosity (25°C in 10% suspension) mPa.s	<100
Solubility in water (g/100cm3) %(w/w)	<0.5
Average particle size (µm)	<15

Melamine (MEL) was used as a blowing agent. The physical and chemical properties of MEL are presented in Table 3.2.

Table 3.2: Physical and chemical properties of MEL

Purity %	99.8min
Moisture %	0.1max
pH	7.5-9.5
Formaldehyde dissolve test	All dissolved in 10 minutes
Ash	0.03max
Colority (platinum-cobalt color)	20max
Particle size (µm)	40max
Turbidity (kaolin turbidity)	20max

Pentaerythritol (PER) was used as a carbon source in intumescent coating. The physical and chemical properties of PER are presented in Table 3.3.

Table 3.3: Physical and chemical properties of PER

Monopentaerythritol content %	98min
Hydroxyl group content %	48.5min
Water content %	0.2max
Ash content %	0.05max
Pthalic color	2max
Particle size (µm)	40max
Melting point (°C)	240min

Four different hybrid fillers was used in this study: (1) palm oil clinker (POC), (2) magnesium hydroxide [$Mg(OH)_2$], (3) aluminium hydroxide [$Al(OH)_3$] and (4) titanium oxide (TiO_2). POC) was taken from Sri Ulu Langat Palm Oil Mill factory. This by-product waste was collected inside the boiler. The appearance of POC looks like a gray porous stone with flaky and irregular shaped. The physical and chemical properties of $Mg(OH)_2$, $Al(OH)_3$ and TiO_2 are shown in Table 3.4, Table 3.5 and Table 3.6, respectively.

Table 3.4: The physical and chemical properties of $Mg(OH)_2$

Properties	Content
Chloride (Cl)	≤ 0.05 %
Sulphate (SO_4)	≤ 0.1 %
Calcium (Ca)	≤ 0.5 %
Lead (Pb)	< 0.001 %
Iron (Fe)	< 0.05 %
Loss on ignition (900 °C)	30.0 – 32.5 %
Bulk density	About 50 g/100ml
Loss on drying (105 °C)	< 2 %

Table 3.5: The physical and chemical properties of $Al(OH)_3$

Properties	Content
Chloride (Cl)	≤ 0.01 %
Sulphate (SO_4)	≤ 0.05 %
Fe (Iron)	0.2max
Na (Sodium)	0.05max
Loss on ignition (700 °C)	30.0 – 35.0 %
Bulk density	About 90 g/100ml
Particle size (< 150 µm)	About 90 %

Table 3.6: The physical and chemical properties of TiO_2

Properties	Content
Arsenic (As)	≤ 0.0005 %
Lead (Pb)	< 0.002 %
Iron (Fe)	< 0.005 %
Antimony (Sb)	≤ 0.01 %
Loss on ignition (900 °C)	30.0 – 32.5 %
Bulk density	About 50 g/100ml
Loss on drying (105 °C)	< 0.5 %
Substance soluble in water	≤ 0.5 %

Acrylic resin was used as solvent-borne binder in this study. Acrylic resins are polymers of acrylic or methacrylic esters which are sometimes modified with monomers such as acrylonitrile and styrene. Acrylic resin has high heat and impact resistance, as well as good clarity and UV resistance. This polymeric coating system is widely used to provide protective and decorative functions to substrates due to its low cost, good adhesion and more durable resin (Boxall & Von Fraunhofer, 1980; Carretti & Dei, 2004). The acrylic resin binder was supplied by Shinko Chemical Sdn. Bhd. POC was used as a bio-filler because of its high thermal stability. POC is a by-product produced from palm oil industry which is usually produced in large quantities. The high thermal stability of this filler was attributed to the process of burning of oil palm shell and palm oil fibre with 30:70 ratios at high temperature of 850ºC during energy generating process. Moreover, in order to investigate the effectiveness of intumescent coating in terms of mechanical strength and water resistance, hybrid fillers such as aluminium hydroxide, titanium oxide and magnesium hydroxide was used in intumescent coatings composition.

3.2.1 POC preparation

(POC) was taken from Sri Ulu Langat Palm Oil Mill factory. Initially the large size chunks of POC (Figure 3.3) were crushed using a jaw crusher (Karim et al., 2017). The smaller pieces after crushing were then ground using lab bead mills machine (Figure 3.2) at a milling speed of 280 rpm for 5 h, 10 h, 15h and 20h to obtain nano particle size of POC as discussed by Yew et al. (2013a). The POC was tested using particle size distribution for particle size confirmation.

The compositions of intumescent coatings were prepared based on:

(i) A series: specimens with incorporation of different particle size of POC,
(ii) B series: specimens with incorporation of different percentage of POC,
(iii) C series: specimens with incorporation of different hybrid fillers,
(iv) D series: specimens with incorporation of different binders.

The next section will describe the detail composition for each sample, their preparation method and characterization method that has been conducted.

Figure 3.2: Lab bead mills machine

Figure 3.3: Palm oil clinker

3.2.2 Preparation of A series composition

Two different particle sizes (i.e. micro and nano) of POC were prepared for A series. For each particle size, the testing was repeated three times to ensure the consistency of the results. Acrylic resin was used as solvent-borne binder. The composition of intumescent coatings is shown in Table 3.7, based on the formulation developed by Yew et al. (2015a). The flame retardant additive (FRA), binder and filler at a weight ratio of 37 : 53 : 10 were blended in container using a high-speed disperse mixer (Figure 3.4) for 2-3 hours at room temperature until completely homogeneous. Specimen for A series was characterized by means of thermal stability and fire performance test using thermogravimetric analysis and Bunsen burner test, respectively. The details of sample characterization were explained in the next section. The A series specimen with the highest thermal stability and the best fire protection performance was selected for the next step of research investigation.

Table 3.7: A series composition

Specimen	**POC size**	**Composition (wt. %)**		
		Binder	FRA	POC
A1/PM-1	Micro	53	37	10
A1/PM-2	Micro	53	37	10
A1/PM-3	Micro	53	37	10
A2/PN-1	Nano	53	37	10
A2/PN-2	Nano	53	37	10
A2/PN-3	Nano	53	37	10

*FRA- flame retardant additive, POC- palm oil clinker

Figure 3.4: High-speed disperse mixer

3.2.3 Preparation of B series composition

The A series specimen with the highest thermal stability and fire protection performance was extended with different percentage of POC as a single filler, i.e. 10%, 15%, 18% and 20%, in order to investigate the optimum percentage of fillers in intumescent coating composition. The composition of intumescent coatings is shown in Table 3.8. Similar with the previous part of research, B series compositions were mixed using high-speed disperse mixer for about 2-3 hours until completely homogenous. Specimen for B series was characterized using TGA, Bunsen burner test and surface spread of flame test. The details of sample characterization techniques were explained in the next section. The B series specimen with the highest thermal stability and the best fire protection performance was selected for the next steps of research investigation.

Table 3.8: B series composition

Specimen	Percentage of POC (%)	Composition (wt. %)	
		Binder	FRA
A1/PM	10	53	37
B1/15%	15	48	37
B2/18%	18	45	37
B3/20%	20	43	37

*FRA- flame retardant additive, POC- palm oil clinker

3.2.4 Preparation of C series composition

The B series specimen with the highest thermal stability and fire performance test was selected for formulating C series compositions which consist of different hybrid fillers in order to investigate their effectiveness on fire performance, mechanical properties and water resistance. The composition of intumescent coatings is shown in Table 3.9. The flame retardant additives were mixed with binder at a weight ratio of 37:45, then the mixture was added to 18% of three different hybrid fillers compositions. The mixture were blended using high-speed disperse mixer for about 2-3 hours until completely homogenous. Specimen for C series was characterized based on thermal stability and fire performance test using TGA test, Bunsen burner test and surface spread of flame test. Moreover, the specimens were tested on water resistance and mechanical strength using static immersion test and Instron microtester, respectively. The C series specimen with the highest thermal stability and the best fire protection performance was selected for the next steps of research investigation.

Table 3.9: C series composition

Specimen	Composition (wt. %)					
	Binder	FRA	POC	TiO_2	$Al(OH)_3$	$Mg(OH)_2$
B2/18%	45	37	/	-	-	-
C1/PTM	45	37	/	/	-	/
C2/PTA	45	37	/	/	/	
C3/PTMA	45	37	/	/	/	/

*FRA- flame retardant additive, POC- palm oil clinker, TiO_2- titanium oxide, $Al(OH)_3$- aluminium hydroxide, $Mg(OH)_2$- magnesium hydroxide

3.2.5 Preparation of D series composition

The last step of research investigation was to study the effect of binder to the intumescent coatings performance. Three specimens using acrylic resin as solvent-borne binder (B2/18%) and three specimens using vinyl acetate copolymer as water-borne binder (D1/WBP) were prepared to ensure the consistency of the results. The composition of intumescent coatings is shown in Table 3.10. D series composition were mixed using high-speed disperse mixer for about 2-3 hours until completely homogenous. Specimen for D series was characterized by means of thermal stability and fire performance test using TGA test, Bunsen burner test, surface spread of flame test, static immersion test and Instron microtester. The details of characterization techniques were explained in the next section.

Table 3.10: D series composition

Specimen	Binder	FRA: Binder (wt. %)	POC
B2/18%-1	Solvent-borne	37 : 45	/
B2/18%-2	Solvent-borne	37 : 45	/
B2/18%-3	Solvent-borne	37 : 45	/
D1/WBP-1	Water-borne	37 : 45	/
D1/WBP-2	Water-borne	37 : 45	/
D1/WBP-3	Water-borne	37 : 45	/

3.3 Characterization and measurement techniques

Several tests were carried out in order to characterize and determine the properties of the intumescent coatings. The techniques include Thermogravimetric analysis (TGA), Instron microtester, Field Emission Scanning Electron Microscope (FESEM), Bunsen burner test, static immersion test and surface spread of flame test.

3.3.1 Bunsen burner test

Bunsen burner test was carried out to characterize the char formation and determine the temperature development on the single-side coated steel plate for each specimen. The mixture was coated on one-side of steel plate (100 x 100 x 2.6 mm) using a gun sprayer and this step was repeated until dry film thickness of 1.5±0.2 mm was achieved (see Figure 3.5). The thickness of intumescent coating was measured using Elcometer model A456. The specimens were considered ready for characterization when it is fully dried after cured for 3 days. The specimen was mounted vertically and exposed to high temperature of ~1000°C for 1 h using the Bunsen burner. A thermocouple wire was attached to the back side of the steel plate to measure the temperature during the Bunsen burner test. The thermocouple was connected to a digital thermometer in order to record the temperature measurements. The arrangement of equipment for Bunsen burner test was shown in Figure 3.6. The temperature was recorded in 1-min intervals until the steel plate reached its critical temperature. A temperature of 400°C was chosen as the failure temperature for the steel structure to ensure a higher level of safety and protection (Yew and Ramli, 2009).

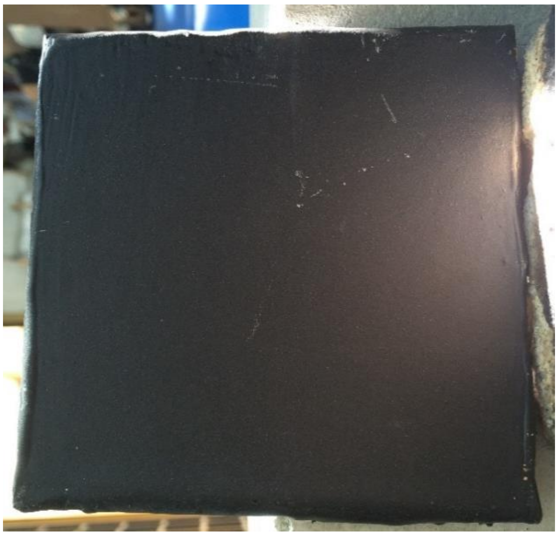


Figure 3.5: The intumescent coating was coated on one-side of steel plate

Figure 3.6: Bunsen burner test set up

3.3.2 Thermogravimetric analysis (TGA)

The mixture of intumescent coating was cast into Petri dishes and left to dry at room temperature until films were formed. The films were then dried at 60°C in the oven to produce completely dry films for TGA test. The TGA was carried out in the temperature range of 30-1000°C at the heating rate of 20°C/min under air flow using a TGA/SDTA851e model. This test was used to measure the weight change of the coating as a function of temperature while being heated at a constant rate. Figure 3.7 shows the thermogravimetry analysis equipment.

Figure 3.7: Thermogravimetry analysis

3.3.3 Field emission scanning electron microscopy (FESEM)

After the Bunsen burner test, a piece of char was cut from the centre of char layer for FESEM test in order to examine the surface morphology of the char layers. Field emission scanning electron microscope (Model: GEMINI®, Carl Zeiss AG, Germany), with a low beam energy of 1 kV was used to observe the morphology of the char layer (see Figure 3.8).

Figure 3.8: Field emission scanning electron microscopy

3.3.4 Static immersion test

Static immersion test was used to evaluate the water resistance of thin films. The intumescent coatings were immersed in distilled water at 25°C (see Figure 3.9) and then dried with a piece of paper towel to remove excess water. The weight change of the specimen was recorded for 7 days and this step was repeated at a specific time interval. The weight change of the specimen was calculated using Equation (3.1) and expressed as a function of time (Yew et al., 2013a).

$$\Delta W = (W_e - W_o)/W_o \times 100\% \tag{3.1}$$

where ΔW is the water intake ratio of the film, W_e is the weight of the film after water immersion, and W_o is the weight of the film before water immersion.

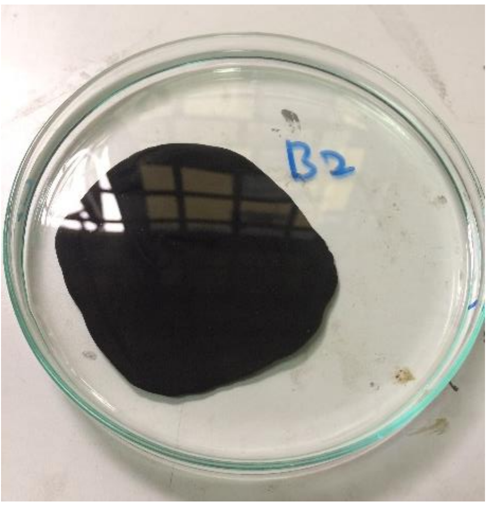


Figure 3.9: Static immersion test

3.3.5 Adhesion strength test

The adhesion strength at the interface of the intumescent coating and steel substrate was determined using a pull-off adhesion tester (PosiTest-AT-A Automatic, DeFelsko) as shown in Figure 3.10. The coating was applied onto one side of a steel plate (dimensions: 50 mm × 50 mm × 2.6 mm) to obtain a film thickness of 0.5 ± 0.05 mm. The flat face of a pull stub (20 mm dolly) was adhered to the coating using epoxy glue (thickness: 0.5 ± 0.05 mm) (see Figure 3.11). The force of peeled-off area of the samples were classified according to ASTM D4541 standard classification.

Figure 3.10: The pull-off adhesion tester

Figure 3.11: The dolly was adhered to the coating using epoxy glue

3.3.6 Surface spread of flame test

The surface spread of flame test was performed in accordance with the BS 476: Part 7 standard (BS 476 Part 7, 1997). The test was carried out on the specimens with the best fire protection performance. The test specimen was oriented in a vertical position and the lateral spread of flame over the surface was measured. The sample was then classified based on the rate and extent of flame spread. The steel plate (885 mm × 270 mm × 2.3 mm) coated with the best formulation of intumescent coating (film thickness: 1.5 ± 0.2 mm) was exposed to specific heating conditions during the test. The test specimen was mounted vertically and placed at an angle of 90° from the radiation panel and was exposed to the radiation panel for 10 min. The pilot flame was applied to the bottom corner of the specimen during the first minute of the test. The time required for the flame front to reach the reference marks on the specimen and the extent of flame spread were recorded over a period of 1.5 min as well as at the end of the test. The intumescent coating was classified according to the rate and extent of flame spread, as shown in Table 3.11. Class 1 is the best classification whereas Class 4 is the worst classification. If the coating falls under Class 4, this means that the coating is at a high risk.

Table 3.11: Flame spread classification (BS 476 Part 7, 1997)

Classification	Spread of flame at 1.5 min		Final spread of flame (10 min)	
	Limit (mm)	Limit for one specimen in the sample (mm)	Limit (mm)	Limit for one specimen in the sample (mm)
Class 1	165	165 + 25	165	165 + 25
Class 2	215	215 + 25	455	455 + 45
Class 3	265	265 + 25	710	710 + 75
Class 4	Exceeding the limits for class 3			

3.4 Concluding Remarks

This chapter includes the experimental work that was conducted to investigate the performance of intumescent coating in terms of fire protection performance, mechanical strength and water resistance. The compositions of intumescent coatings were prepared based on; i) A series: specimens with incorporation of different particle size of POC, ii) B series: specimens with incorporation of different percentage of POC, iii) C series: specimens with incorporation of different hybrid fillers and iv) D series: specimens with incorporation of different binders. Several tests were conducted for fire protection performance such as Bunsen burner test, TGA and surface spread of flame test. The adhesion strength was determined using a pull-off adhesion tester, while the water resistance was conducted using static immersion test. The results obtained will be discussed in the next section.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter explained the test results of thermal stability, surface morphology, fire protection performance, adhesion strength and water resistance of the intumescent coating by Bunsen burner test, thermogravimetry analysis (TGA), field emission scanning electron microscope (FESEM), static immersion test and adhesion strength test. The surface spread of flame test was carried out on the specimens with the best fire protection performance in accordance with the BS 476: Part 7. The first part of this research was to investigate thermal stability of different particle size of POC as a single filler in intumescent coatings. The best formulation was used for the second part of the research which is on the investigation of intumescent coatings with different percentage of POC as a single filler. Then, the next part of this research was to investigate different formulation of intumescent coating using hybrid fillers followed by comparison of the intumescent coatings performance in different binders.

4.2 Investigation on the Different Particle Size of POC as a Single Filler

In order to investigate the effects of different particle size of POC in intumescent coatings, POC was milled at a milling speed of 280 rpm for 5 h, 10 h, 15h and 20h to get appropriate particles size using lab bead mills. The Mastersizer Micro Particle Size Analyzer was used to measure the particle sizes and the particle size distribution profiles of the fillers are shown in Figure 4.1. From the results, it shows that the time at 5h, 10h, 15h and 20h of milling process, resulting with the mean particle size of 396.10 nm, 68.06 nm, 57.8 nm and 50.75 nm for POC, respectively. Hence, the mean particle sizes of POC used in this study was 56.22 µm for POC before milling process and 50.75 nm for POC after 20h of milling process.

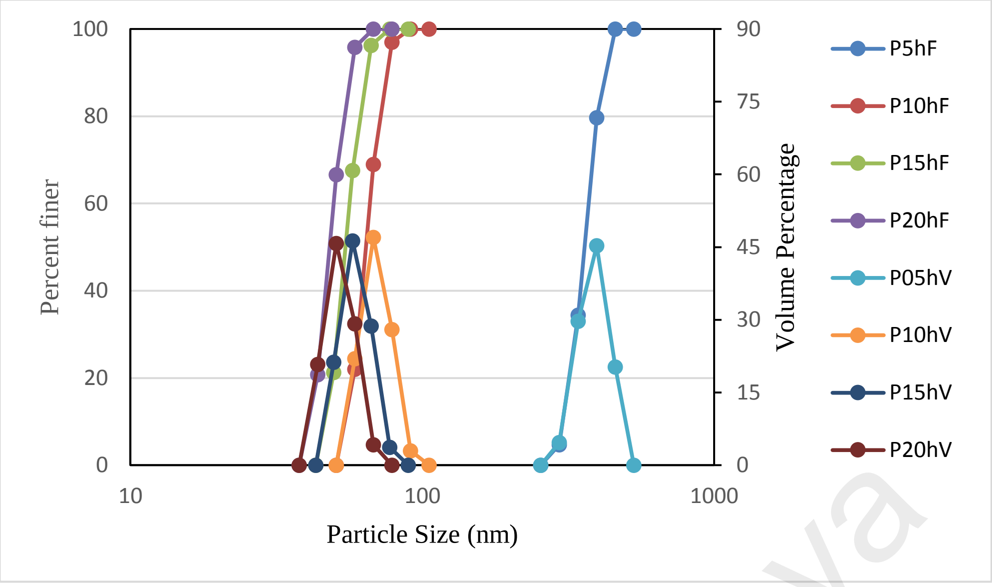


Figure 4.1: Particle size distribution profiles of the POC after milling

4.2.1 Thermal stability of intumescent coatings with different particles size of POC

TGA analysis was done to obtain the residual weight for each of formulations as the residual weight play an important role in intumescent coating (Amir et al., 2011). When the residual weight is high, resulting in improvement of the anti-oxidation and thermal stability of char layer. Hence, it is good for intumescent coating to have this characteristic (Ahmad et al., 2012). Moreover, TGA was done in order to know the degradation time and temperature for each formulation. It can be concluded that, a good intumescent coating must have a high residual weight as reported by Ahmad et al., (2012). Three repeating samples were prepared using micro and nano particles size of POC to ensure the consistency of the results. The TGA curves were presented in Figure 4.2. All specimens show almost similar curve between temperatures of 100°C to 250°C. At temperature of 400°C, the curve of each coating became slightly different from each other. The residual weight of all specimens is presented in Table 4.1. The average residual weight was calculated for each specimen. Overall, it shows that specimen A1/PM has better thermal stability with the higher residual weight compared to A2/PN.

This situation can be explained based on the TGA curves of POC filler. After the temperature reached 750ºC, the weight loss for micro size POC is only about 4 wt. %. The residual weight for micro and nano size of POC at 750°C was 96.70 wt. % and 20.84 wt. %, respectively as shown in Figure 4.3. Due to smaller particle size after a milling process, thermal stability of nano size of POC decrease rapidly with the total weight loss of about 80% between 100 to 200ºC. Previous study reported that the oil palm shell used as boiler feed composed of hemicelluloses (1.2 wt. %), cellulose (38.6 wt. %) and lignin (39.0 wt. %), and also contained some extractives (Ninduangdee & Kuprianov, 2013). Lignin is moderately stable at elevated temperatures due to its highly aromatic backbone (Karim et al., 2017). A major mass loss (about 40%) of kraft lignin observes between 200 to 600ºC (Sen et al., 2015). According to Karim et al. (2017), the first major weight loss of POC in the temperature range of 45.20 to 328.45ºC due to degradation of lower molecular weight cellulose and moisture presence in POC. Second highest weight loss was observed in the subsequent step of temperature range from 328.45 to 573.11ºC due to the degradation of lignin and cellulose presence in POC and minimal contribution through the decomposition of $CaCO_3$. Further minor weight loss was observed within the range of 573.11 to 698.14ºC due to the degradation of high molecular weight lignin (Karim et al., 2017). Hence, it proves that POC powder with lower particle size had a lower thermal stability which led to reduce in thermal stability of specimen A2/PN. For the next part of research, POC with micro particle size was selected as a single filler in order to investigate the optimum percentage of filler in intumescent coatings.

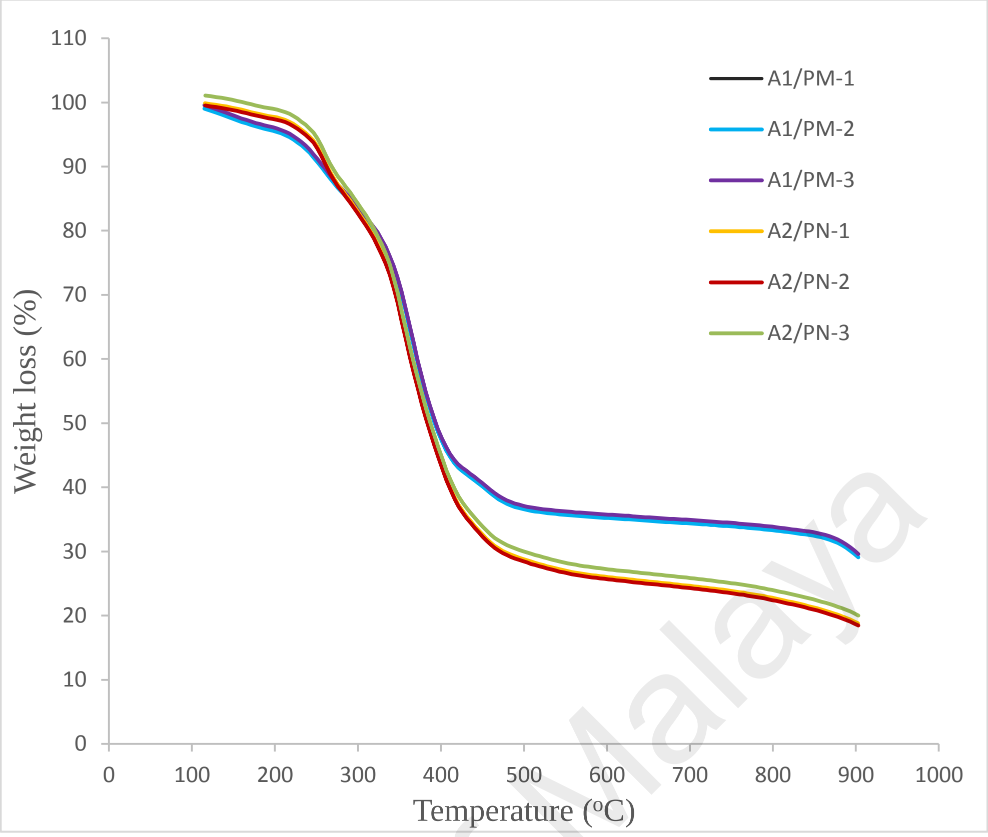


Figure 4.2: TGA curves of A series specimens

Table 4.1: The residual weight for A series specimens

Specimen	Residual weight (wt. %)	Average residual weight (wt. %)
A1/PM-1	34.41	33.92
A1/PM-2	33.10	
A1/PM-3	34.24	
A2/PN-1	23.15	23.30
A2/PN-2	22.91	
A2/PN-3	23.85	

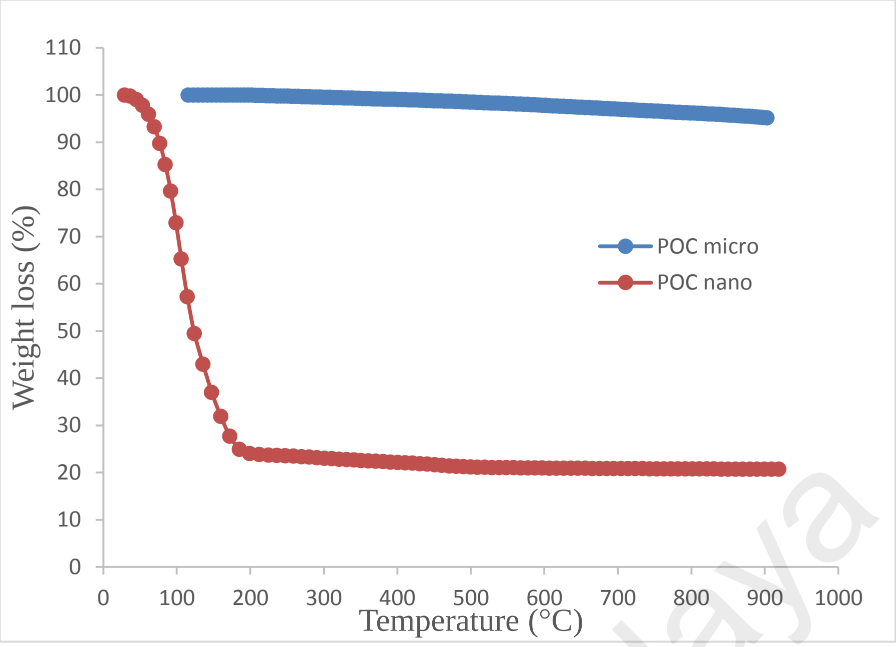


Figure 4.3: TGA curves of micro and nano size POC

4.2.2 Fire performance test of intumescent coatings with different particles size of POC

Fire performance test of intumescent coatings is conducted using Bunsen burner test. During this test, the evolution of temperature on back of the coated steel plated was measured in a specific time using digital thermometer which was connected to a thermocouple and the time-temperature curves were plotted. The temperature curves for all specimens are presented in Figure 4.4. The result shows that the temperature of the coatings increased rapidly during the first 5 to 10 minutes. After about 30 minutes, the temperature reached an equilibrium value and almost unchanged. The equilibrium temperature and the thickness of char layer for all specimens is presented in Table 4.2. From the results, the average for three repeating samples of each formulation is calculated. Overall, specimen A1/PM shows significantly increased in fire protection performance with higher thickness of char layer compared to specimen A2/PN. Hence, it proves that micro particles size of POC with higher thermal stability as reported in section 4.2.1, gives a better fire protection to the steel substrate. An increase in the residual weight of the char layer shows that the coating was hardly damaged by oxidation when exposed to a fire, which demonstrates the enhancement of anti-oxidation of the intumescent flame retardant coating as reported by Almeras et al. (2003).

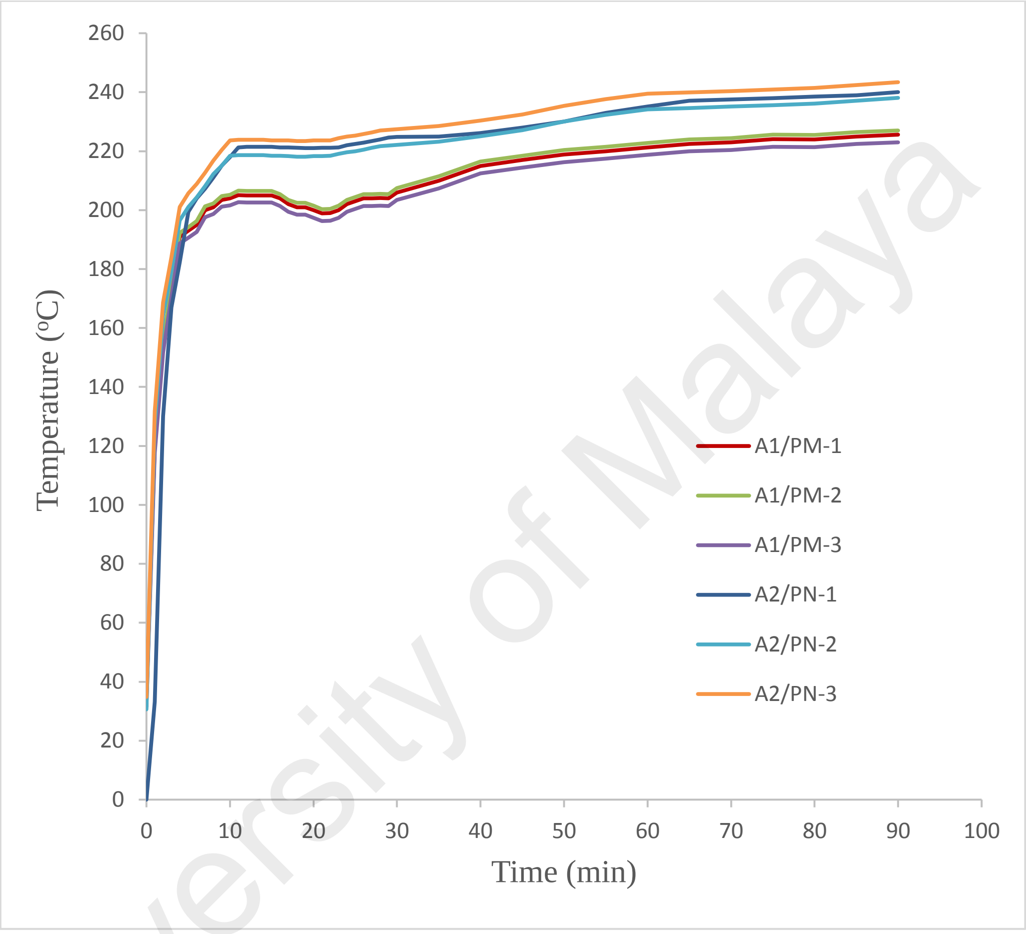


Figure 4.4: The time-temperature curves for A series specimens

Table 4.2: The equilibrium temperature and the thickness of char layer for A series specimen

Specimen	Equilibrium temperature (°C)	Average of equilibrium temperature (°C)	Thickness of char layer (mm)	Average thickness of char layer (mm)
A1/PM-1	205.0	204.7	15.12	15.27
A1/PM-2	206.5		15.23	
A1/PM-3	202.7		15.47	
A2/PN-1	221.5	221.3	14.72	14.71
A2/PN-2	218.4		14.90	
A2/PN-3	223.9		14.51	

4.2.3 Morphology of intumescent char layers with different particles size of POC

Figure 4.5 shows the surface morphology of the char layer for specimens A1/PM-1 and A2/PN-1 after the Bunsen burner test. It can be observed that specimen A2/PN-1 have a highly porous surface structure, which reduces the fire protection capability of the coatings. This is indeed expected since the heat penetrates to the steel substrate through the char layer since the char layer is highly porous and non-uniform. The fire protection performance indicated that the efficiency in fire resistance depended strongly on its physical structure of the char layer (Wang et al., 2006). The char layer for specimen A1/PM-1 is more uniform with a dense foam structure which prevents heat from penetrating through the steel substrate. This enhances the fire protection performance of the coatings as supported by Yew & Ramli Sulong (2012).

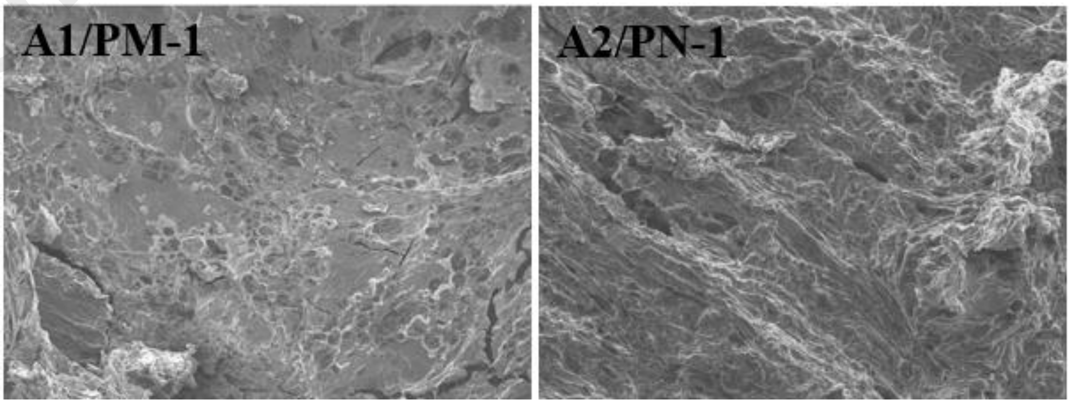


Figure 4.5: Structure of the char layer for A series specimens

4.3 Investigation on the optimum percentage of POC as a single filler

To study the optimum percentage of filler in intumescent coatings, four specimens with different percentage of POC were prepared. Specimen A1/PM, B1/15%, B2/18% and B3/20% consist of 10 wt. %, 15 wt. %, 18 wt. % and 20 wt. % of POC as a single filler, respectively. All specimens were characterized based on thermal stability and fire performance test. In this part of research, the surface spread of flame test was carried out on the specimens with the best fire protection performance and thermal stability.

4.3.1 Thermal stability of intumescent coatings with different percentage of POC

The TGA curves were presented in Figure 4.6. The residual weight for specimen A1/PM, B1/15%, B2/18% and B3/20% at 750°C was 34.41 wt. %, 41.57 wt. %, 42.17 wt. % and 41.74 wt. %, respectively. The result indicates that the increase in POC content led to the increase in the thermal stability of the intumescent coatings. But, when it comes to 20 wt. % of POC content, there is slightly decrease of the residual weight. The addition of 20 wt. % of POC exceeded the optimal content of filler in intumescent coating and reduced the thermal stability of specimen B3/20%. Specimen B2/18% was found to be the optimal percentage of filler in intumescent coatings due to the highest thermal stability. Hence, specimen B2/18% was selected as new composition in the next step of research investigation in determination of the influence of different hybrid fillers to the intumescent coating.

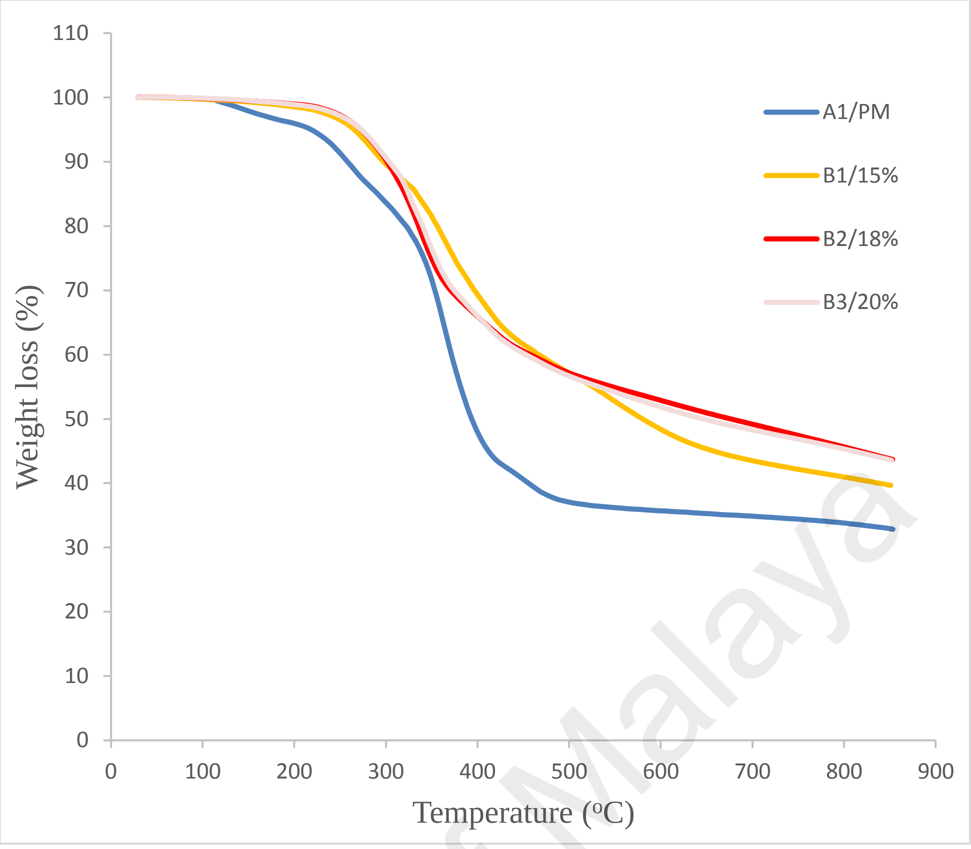


Figure 4.6: TGA curves for B series specimens

4.3.2 Fire performance test of intumescent coatings with different percentage of POC filler

The fire protection performance of intumescent coatings was conducted by using Bunsen burner test and surface spread of flame test. The results obtained for fire performance test was discussed in the next section.

4.3.2.1 Bunsen burner test for B series specimens

The equilibrium temperature and thickness of char layer was shown in Table 4.3. The images of specimen before and after Bunsen burner test was shown in Figure 4.7. The curves for each coating during the first 5 to 10 minutes had increased rapidly after exposed to fire. Similar with the previous part of research, after about 30 minutes, the temperature reached an equilibrium value and almost unchanged. From the results, when the percentage of filler increase, the fire protection performance for intumescent coating is significantly increased but started to reduced when reached 20 wt. % of filler. That means, the addition of 20 wt. % of POC exceeded the optimal content of POC for effective fire protection. This disturbed the mechanism of intumescence which led to reduced fire protection ability of the coating (Yew, 2011). Hence, addition of 18 wt. % of POC was found to be the optimal content of POC in intumescent coatings which resulted in the highest thickness of char layer and lowest equilibrium temperature. The thicker the char layer, the lower the equilibrium temperature. The tendency for char expansion to reduce with increasing of filler contents have also been reported by Ahmad et al. (2012). The temperature curves for intumescent coatings are presented in Figure 4.8.

Table 4.3: The equilibrium temperature and thickness of char layer for specimen A1/PM, B1/15%, B2/18% and B3/20%

Specimen	Equilibrium temperature (°C)	Thickness of char layer (mm)
A1/PM	205.0	15.12
B1/15%	191.1	15.35
B2/18%	187.7	17.21
B3/20%	201.1	16.94

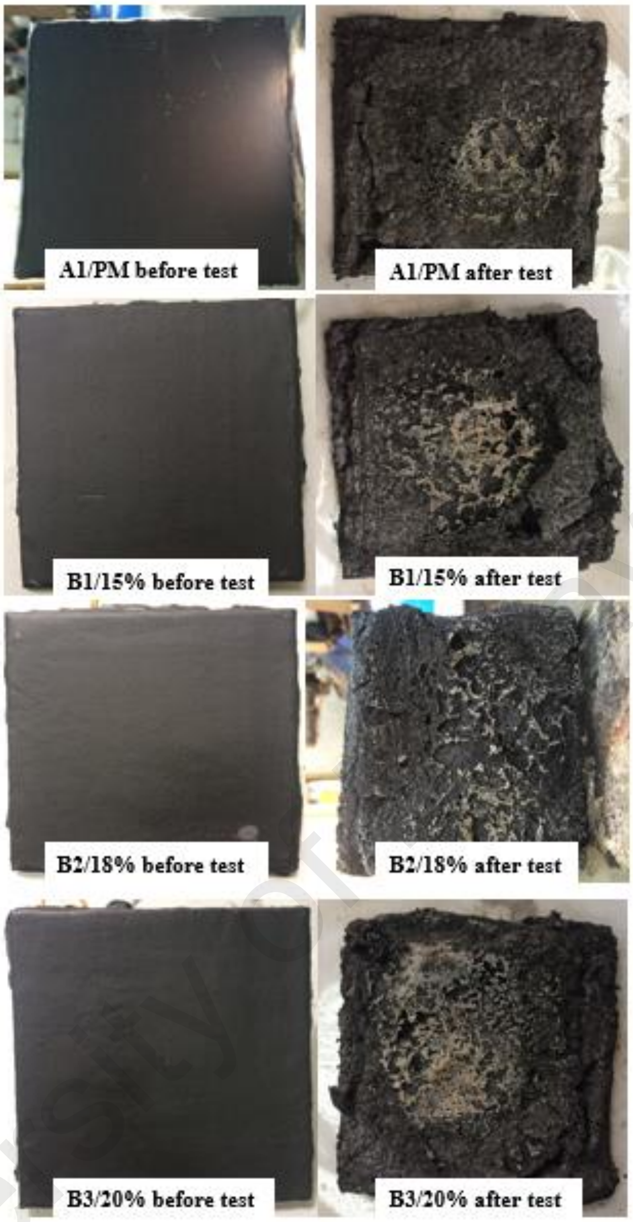


Figure 4.7: B series specimens before and after Bunsen burner test

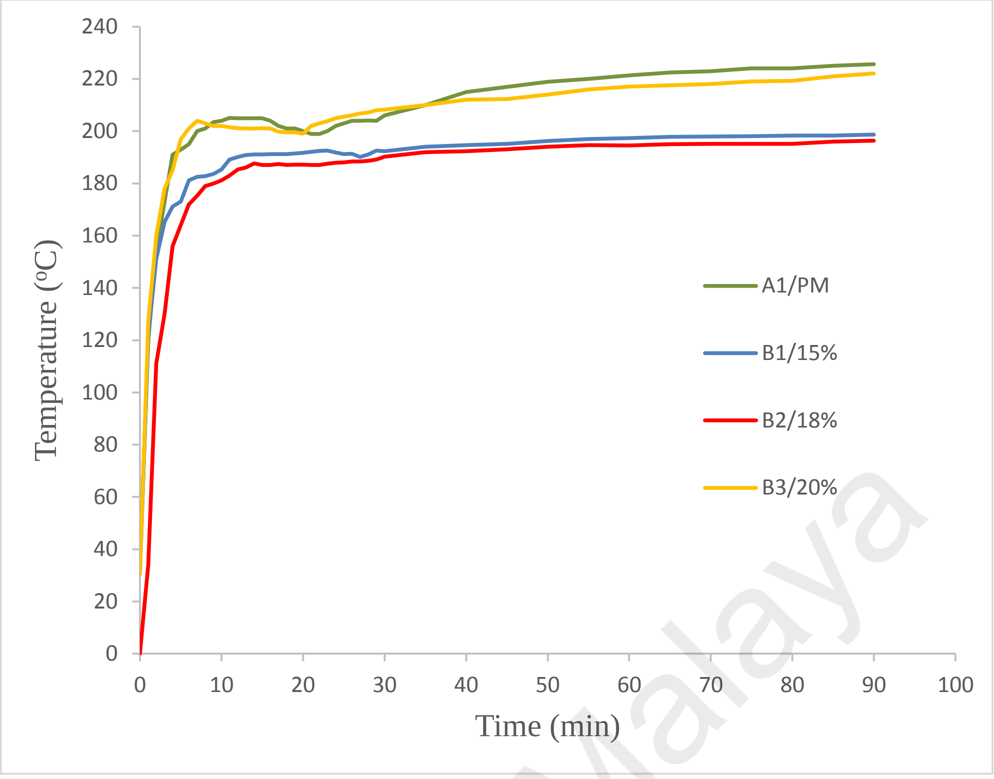


Figure 4.8: The time-temperature curves for B series specimens

4.3.2.2 Surface spread of flame test for B series specimens

The surface spread of flame test was performed according to the procedure specified in the 'BS 476: Part 7' standard (BS 476 Part 7, 1997). The test involves measuring the lateral spread of flame over the surface of a specimen oriented in a vertical position and classifying the system based on the rate and extent of flame spread. The results for the test specimens are shown in Table 4.4. From the flame spread classification, Class 1 is the best classification while Class 4 is the worst classification and is considered high risk. From the results, all specimens was classified as Class 1 except for specimen B3/20% which is classified as Class 2. Specimen A1/PM and B1/15% had 190 mm and 165 mm surface spread of flame at 53 s and 59 s, respectively. Meanwhile, specimen B2/18% with 18% of POC had 75 mm surface spread of flame, proved that this optimum percentage of POC resulting in a significant improvement in lowering the rate and extend of flame spread. Unfortunately, specimen B3/20% had 215 mm surface spread of flame at 0.57 s was classified as Class 2 due to addition of 20% of POC in intumescent coating exceeded the optimal content of POC for effective fire protection which increased the rate and extend of flame spread. The char formation after the test is shown in Figure 4.9.

Table 4.4: The surface spread of flame test for B series specimens

Specimen No.	A1/PM	B1/15%	B2/18%	B3/20%
Spread of flame at 1 1/2 minutes (mm)	190	165	75	215
Distance (mm)	Time of spread of flame to indicated distance (min.s)			
75	0.29	0.56	0.53	0.31
165	0.43	0.59		0.40
190	0.53			0.49
215				0.57
240				
Time of maximum spread of flame (min.s)	0.53	0.59	0.53	0.57
Distance of maximum spread of flame (mm)	190	165	75	215
Classification	Class-1	Class-1	Class-1	Class-2

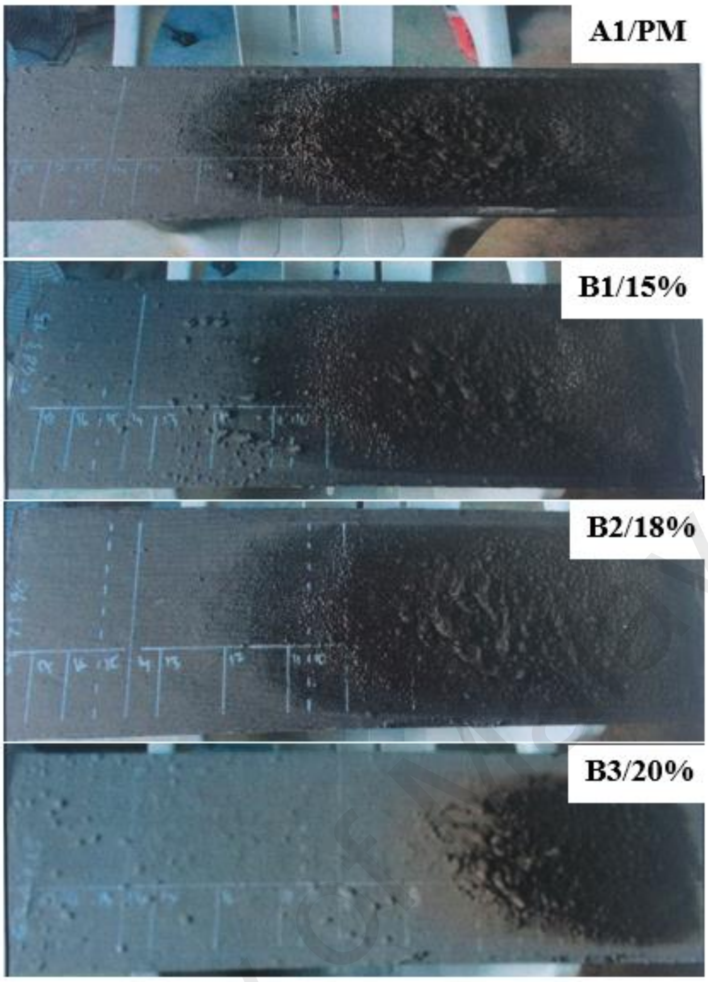


Figure 4.9: The char formation after test for B series specimens

4.3.3 Morphology of intumescent char layers with different percentage of POC

Figure 4.10 shows the surface morphology of the char layer for all specimens. It can be observed that specimen B3/20% have a highly porous surface structure, which reduces the fire protection capability of the coatings. The char layer for specimen B2/18% is more uniform with a dense foam structure which prevents heat from penetrating through the steel substrate. This enhances the fire protection performance of the coatings. As reported by Yew et al. (2015b), the char layer with more uniform and denser foam structure, could isolate the steel substrate from fire and provide better fire protection.

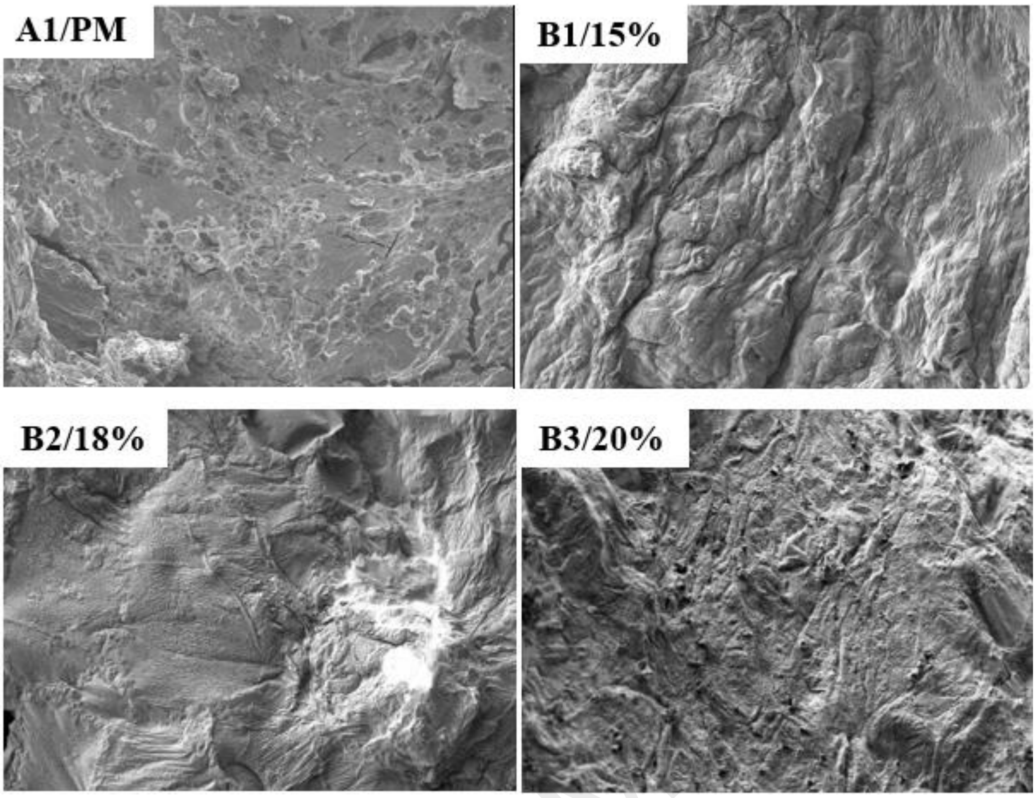


Figure 4.10: Structure of the char layer for B series specimens

4.4 Investigate on the effect of hybrid fillers to the intumescent coatings

To study the effect of hybrid fillers on thermal stability of intumescent coating, four specimens was prepared, i.e. specimen B2/18% consist of single POC, and specimen C1/PTM, C2/PTA and C3/PTMA consist of different composition of hybrid fillers (refer Table 3.9). All specimens were characterized based on thermal stability, fire performance test, adhesion strength and water resistance.

4.4.1 Thermal stability of intumescent coating with different hybrid fillers

The TGA curves are presented in Figure 4.11. The curves of the coatings were similar between 100°C to 250°C. After temperature higher than 250°C, the curves became slightly different from each other. The residual weight for specimen B2/18%, C1/PTM, C2/PTA and C3/PTMA at 750°C was 42.17 wt. %, 46.84 wt. %, 41.98 wt. % and 47.42 wt. %, respectively. The results show that the percentage different of POC as a single filler with specimens contain hybrid fillers is less than 6%, indicate that POC alone significantly enhanced thermal stability of the intumescent coatings due to the higher decomposition temperature of POC, as described in Section 4.2.1. Specimen C1/PTM containing POC/$Mg(OH)_2$ had 5% increase in residual weight which contribute to a better thermal stability compared to specimen C2/PTA containing POC/$Al(OH)_3$, which specifies that incorporation of $Mg(OH)_2$ significantly increase thermal stability of the intumescent coating. This situation happened due to the higher thermal stability of $Mg(OH)_2$ than $Al(OH)_3$ filler. More importantly, it can be seen that the addition of all hybrid fillers increases the thermal stability of the intumescent coating up to 47.42 wt. %, as evidenced from specimen C3/PTMA. Incorporation of combinations of flame retardant fillers could slow down the rate of burning by reducing the flammability and changing the melt rheology of the coatings as reported by Ostman et al. (2001). Specimen C3/PTMA has the highest thermal stability, which clearly indicates that the combination of POC and suitable amount of hybrid fillers improves anti-oxidation, thermal stability and fire protection performance of the intumescent coatings (Yew et al., 2015a). It can be deduced that the intumescent coating has superior fire protection performance with the incorporation of hybrid fillers, whereby POC is one of the key components.

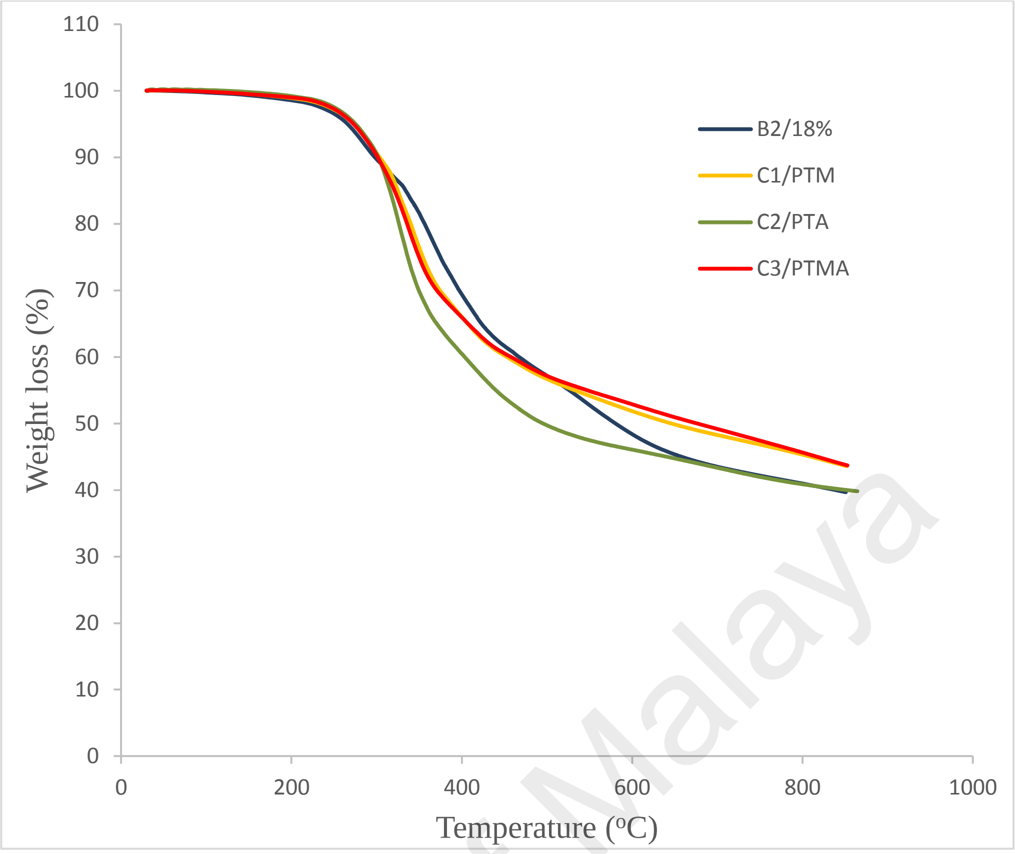


Figure 4.11: TGA curves for C series specimens

4.4.2 Fire performance test of intumescent coatings with different hybrid fillers

The fire protection performance of intumescent coatings was conducted by using Bunsen burner test and surface spread of flame test. The results obtained for fire performance test are discussed in the next section.

4.4.2.1 Bunsen burner test for C series specimens

The temperature curves for specimens B2/18%, C1/PTM, C2/PTA and C3/PTMA are presented in Figure 4.12. The curves for each coating during first 5 to 10 minutes had increase rapidly after exposed to fire which is similar to the previous series of specimen. After 30 min, the temperature of all coatings reaches an equilibrium value, whereby the temperature is almost invariant with respect to time. The equilibrium temperature and thickness of char layer is shown in Table 4.5. The equilibrium temperature of specimen C1/PTM (175.3°C) is significantly lower than specimen B2/18% and C2/PTA due to the addition of $Mg(OH)_2$. This is due to the higher thermal stability of $Mg(OH)_2$ compare to $Al(OH)_3$ filler. Specimen C3/PTMA offers the best fire protection with the lowest equilibrium temperature (172.0°C) and the highest char layer thickness (20.02 mm). The results indicate that the optimum combination of POC and hybrid fillers is highly effective to enhance the fire protection performance of intumescent coatings. . Incorporation of combinations of flame retardant fillers could slow down the rate of burning by reducing the flammability and changing the melt rheology of the coatings as reported by Ostman et al. (2001). There was a correlation between the thickness of char layer and the equilibrium temperature. The thicker the char layer, the lower the equilibrium temperature. The images of specimen before and after Bunsen burner test are shown in Figure 4.13.

Table 4.5: Equilibrium temperature and thickness of char layer of C series specimens

Specimen	Equilibrium temperature (°C)	Thickness of char layer (mm)
B2/18%	187.7	17.21
C1/PTM	175.3	19.17
C2/PTA	183.1	17.53
C3/PTMA	172.0	20.02

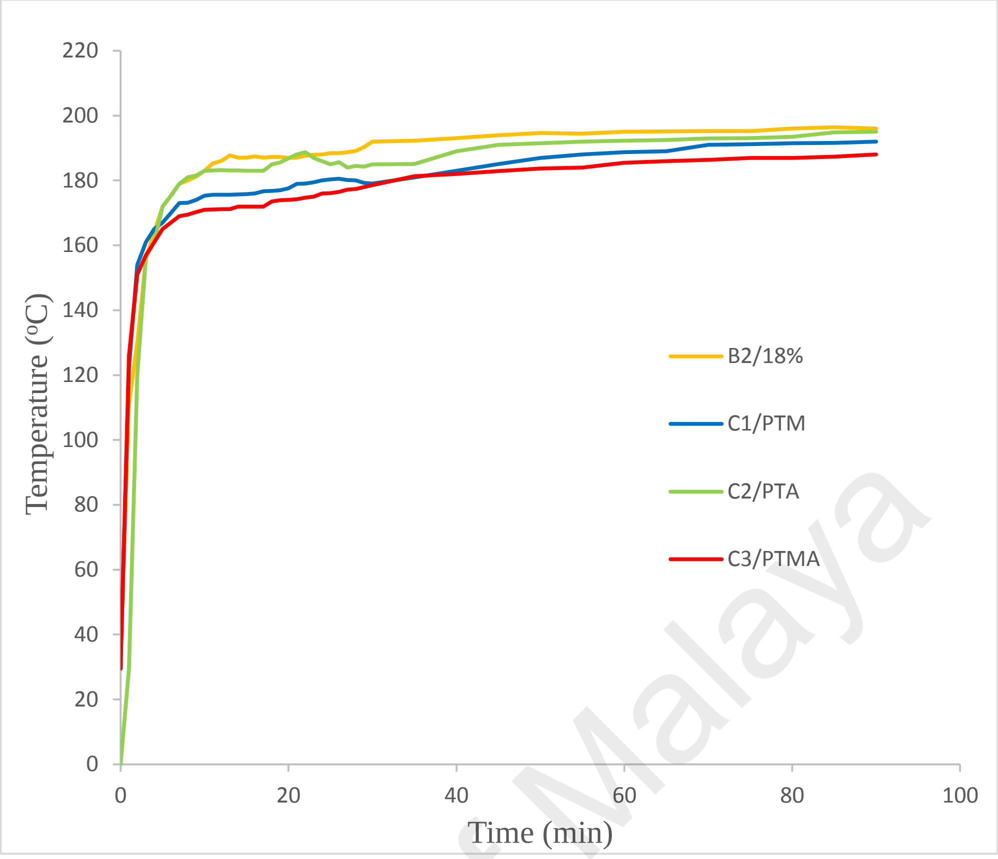


Figure 4.12: The time-temperature curves for C series specimens

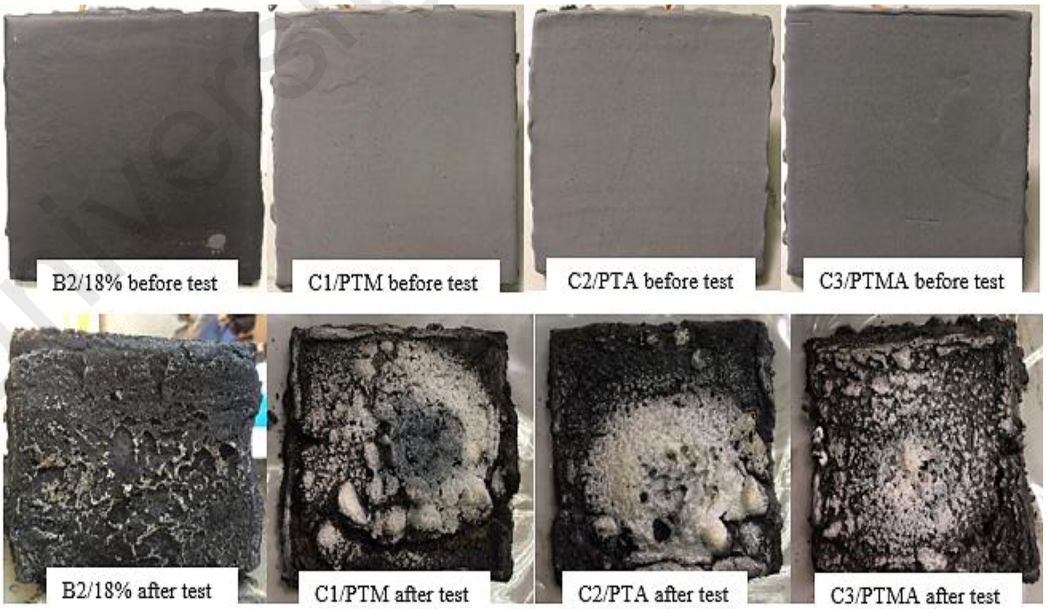


Figure 4.13: C series specimens before and after Bunsen burner test

4.4.2.2 Surface spread of flame test for C series specimens

The surface spread of flame test was performed according to the procedure specified in the ‘BS 476: Part 7’ standard (BS 476 Part 7, 1997). The results for the test specimens are shown in Table 4.6. From the results, all specimens are classified as Class 1 which is the best classification as described in BS 476 Part 7 standard. Specimen B2/18%, C1/PTM and C2/PTA had 75 mm, 165 mm and 190 mm surface spread of flame at 53 s, 55 s and 52 s, respectively. In contrast, the surface spread of flame is 0 mm for specimen C3/PTMA, which attests that the optimum composition of POC and hybrid filler significantly lowers the rate and extent of flame spread which have similarly been reported by Yew et al. (2015a). The char formations after the test are shown in Figure 4.14.

Table 4.6: The surface spread of flame test for C series specimens

Specimen No.	B2/18%	C1/PTM	C2/PTA	C3/PTMA
Spread of flame at 1 1/2 minutes (mm)	75	165	190	0
Distance (mm)	Time of spread of flame to indicated distance (min.s)			
75	0.53	0.34	0.30	
165		0.55	0.45	
190			0.52	
215				
240				
Time of maximum spread of flame (min.s)	0.53	0.55	0.52	-
Distance of maximum spread of flame (mm)	75	165	190	0
Classification	Class-1	Class-1	Class-1	Class-1

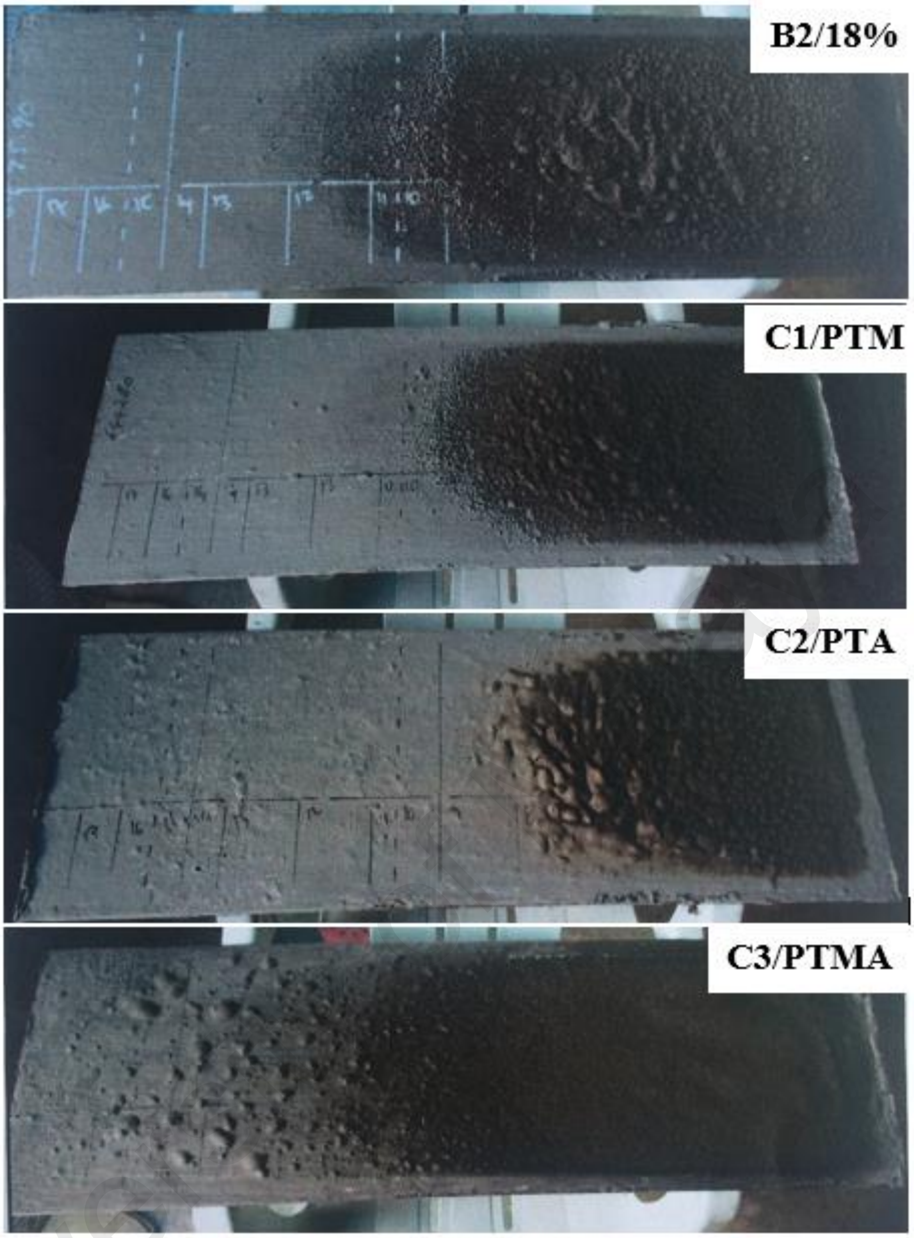


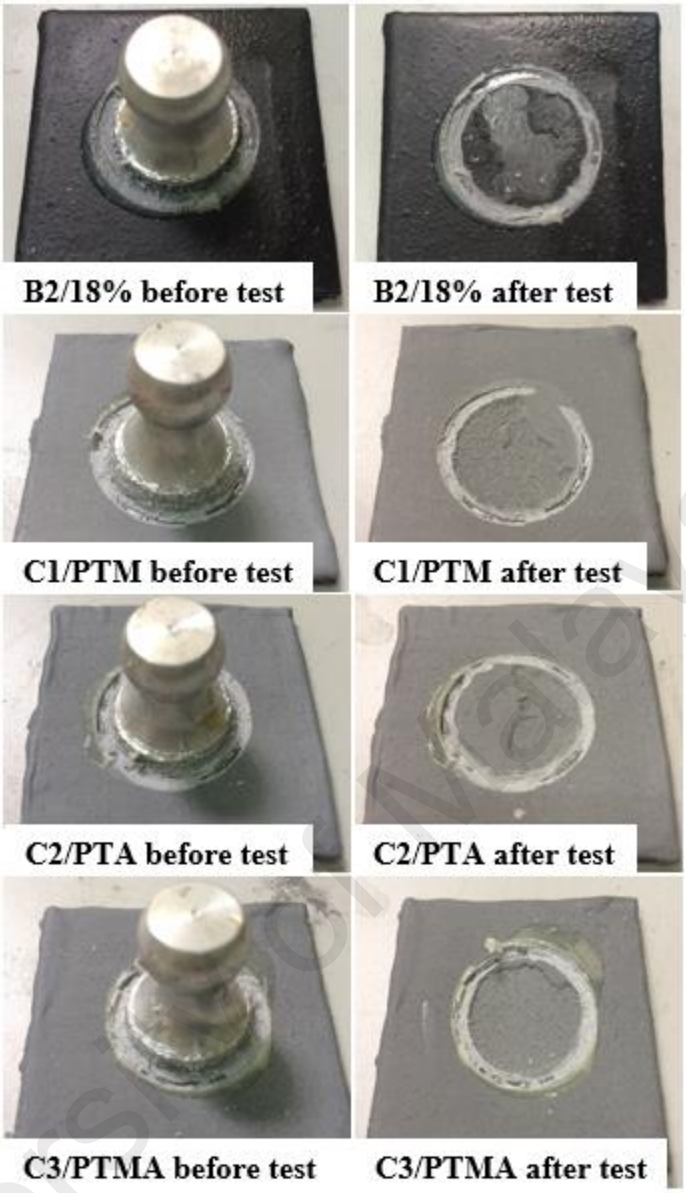
Figure 4.14: The char formation after test for C series specimens

4.4.3 The effect of hybrid fillers on the adhesion strength

The bonding strength of intumescent coating was investigated using the Instron microtester. The result for adhesion strength is shown in Table 4.7. This test was done on specimen containing hybrid fillers in order to investigate the effect of hybrid fillers to the intumescent coatings performance. Specimen B2/18% (with POC), shows better adhesion strength compared to specimen C2/PTA. However, there is a significant enhancement in the adhesion strength for hybrid filler formulations, which is evident for specimen C1/PTM and C3/PTMA. The increased in adhesion strength of specimen C1/PTM with $Mg(OH)_2$ filler up to 0.65 MPa is due to the strong bonding strength between the metal surface and acrylic binder/$Mg(OH)_2$ filler, which distributes stresses effectively as supported by Devendra & Rangaswamy (2012). Specimen C3/PTMA had increased the adhesion strength up to 5.21 MPa since this coating has the optimum combination of POC, $Mg(OH)_2$, TiO_2, and $Al(OH)_3$ fillers, as expected. In general, the addition of POC and $Mg(OH)_2$ fillers enhances the adhesion strength of the intumescent coating, while the optimum combination of hybrid fillers will significantly boost the adhesion strength of the intumescent coating. Figure 4.15 show the image of specimen before and after test.

Table 4.7: The adhesion strength of C series specimens

Specimen	Adhesion strength, f_b (MPa)
B2/18%	4.39
C1/PTM	4.68
C2/PTA	4.03
C3/PTMA	5.21



B2/18% before test

B2/18% after test

C1/PTM before test

C1/PTM after test

C2/PTA before test

C2/PTA after test

C3/PTMA before test

C3/PTMA after test

Figure 4.15: C series specimens before and after adhesion strength test

4.4.4 The effect of hybrid fillers on the water resistance of intumescent coatings

The weight change rate curves for specimens B2/18%, C1/PTM, C2/PTA and C3/PTMA are shown in Figure 4.16. The experimental results show that the weight of specimen B2/18% is gradually increased due to the permeation process which means water could infiltrate into high porosity structure of the coating which led to the weight gain of the sample. The weight gain is also due to the solubility of POC in water. This indicates that intumescent coatings with POC can be used for internal use since it can absorb water. In contrast, there is a weight loss for coatings C3/PTMA and C1/PTM due to the migration process. As reported from previous study, the migration process may occur when some hydrophilic fire retardant additives dissolved in water, hence reduce the weight of the coating (Yeh et al., 2006). Meanwhile, it seems that both migration and permeation processes occur for specimen C2/PTA which contains $Al(OH)_3$ filler. The permeation of water and dissolution of the fire-retardant components can be slowed down by the addition of $Al(OH)_3$ filler due to its low solubility in water, which improves the water resistance of the intumescent coating (Harlan Laboratories, 2010). In general, the rate of weight change is less than 0.3% for all specimens, indicating that the specimens have excellent water resistance.

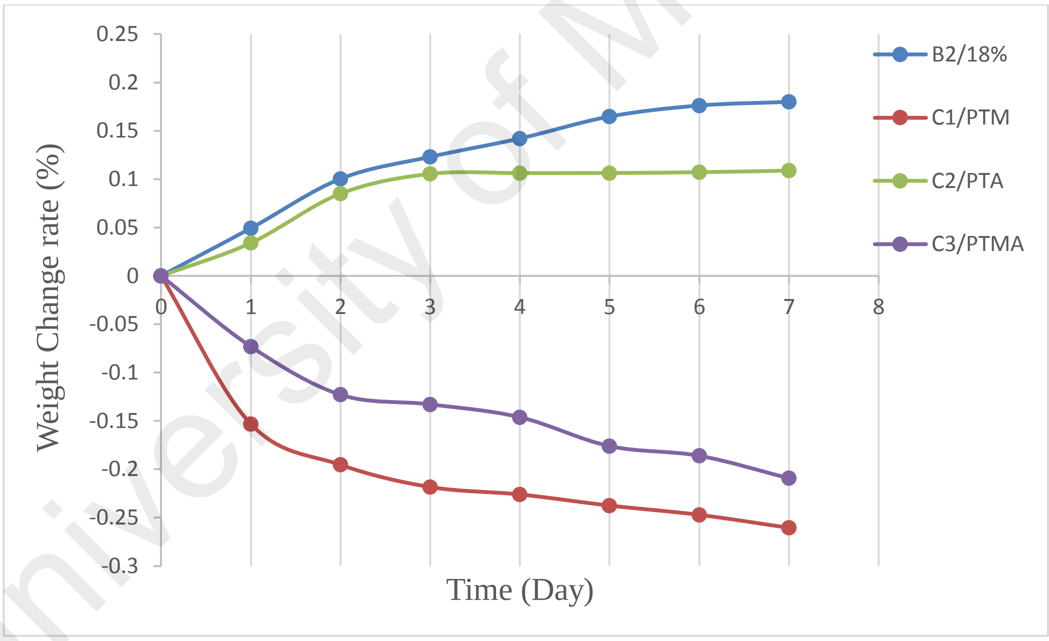


Figure 4.16: The weight change rate curves of C series specimens

4.4.5 Morphology of intumescent char layers with different hybrid fillers

Figure 4.17 shows the surface morphology of the char layer for all specimens. It can be observed that specimen C2/PTA shows loose char structure with low strength, which reduces the fire protection capability of the coatings. This is indeed expected since the heat penetrates to the steel substrate through the char layer due to highly porous and non-uniform char layer as reported by Yew et al. (2015a). The char layer for specimen C3/PTMA is more uniform with a dense foam structure which prevents heat from penetrating through the steel substrate. This enhances the fire protection performance of the coatings. This shows that the incorporation of POC and hybrid fillers allow the binder to mix well, resulting in a more homogeneous coating with better interfacial bonding of the filler/matrix components.

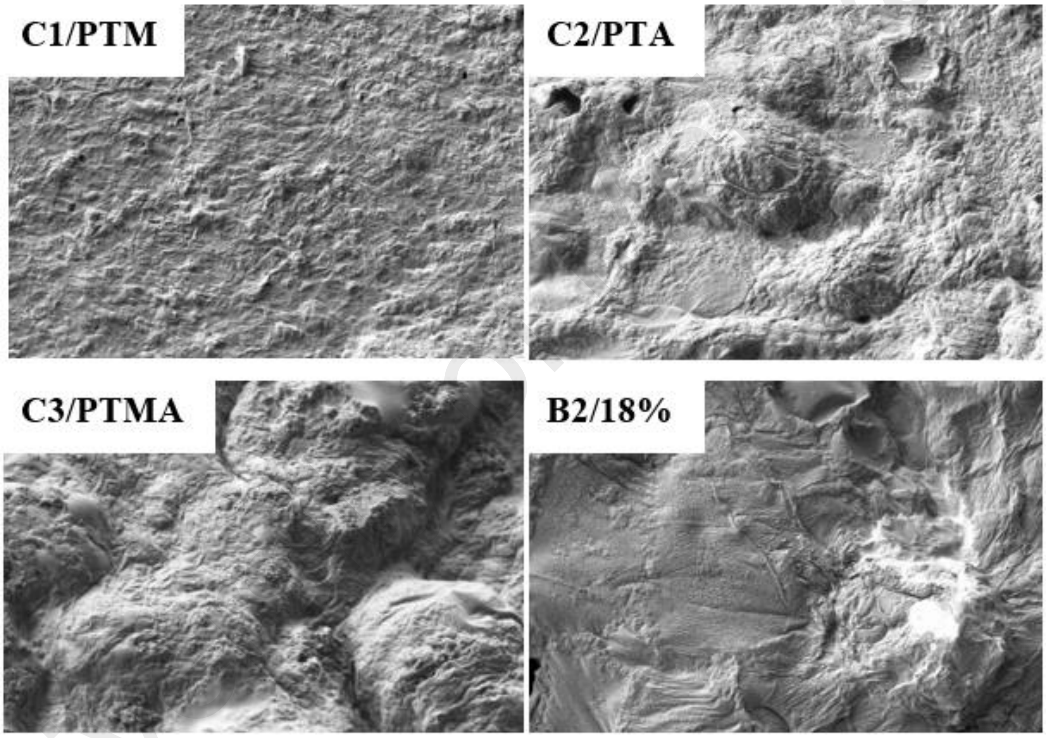


Figure 4.17: Structure of the char layer for C series specimens

4.5 Investigation on the effect of different binders to the intumescent coatings

Two specimens in solvent-borne and water-borne binders were prepared in order to investigate the effect of binder to the intumescent coatings performance. Both specimens were characterized based on thermal stability, fire performance test, adhesion strength and water resistance. Three specimens using acrylic resin as solvent-borne binder (B2/18%-1, B2/18%-2, and B2/18%-3) and three specimens using vinyl acetate copolymer as water-borne binder (D1/WBP-1, D1/WBP-2, and D1/WBP-3) were prepared to ensure the consistency of the results.

4.5.1 Thermal stability of intumescent coatings with different binders

The residual weight for all specimens is shown in Table 4.8. The TGA curves for intumescent coating are presented in Figure 4.18. The curves of each specimen are similar between 100°C to 250°C. The weight loss of each coating was less than 30 wt. % at 280◦C, where softening of the binder occurred. When the temperature is higher than 280°C, the curves became slightly different. The degradation of coatings happened due to chemical reactions between the active ingredients, fillers and acrylic binder when exposed to heat. The acid source breaks down to yield a mineral acid, which then takes part in the dehydration of the carbon source to yield the carbon char while the blowing agent decomposes to yield gaseous products. The latter causes the char to swell and produce the insulating multi-cellular protective layer (Jimenez et al., 2006). The average residual weight for both specimens B2/18% and D1/WBP at 750°C is 41.95 wt. % and 37.32 wt. %, respectively. Coating B2/18% with the highest average residual weight indicates that the combination of acrylic binder and POC significantly enhanced the thermal stability and anti-oxidation of the coating. An increase in the residual weight of the char layer shows that the coating was hardly damaged by oxidation when exposed to a fire, which demonstrates the enhancement of anti-oxidation of the intumescent flame-retardant coating (Almeras et al., 2003; Qu & Xie, 2003). It can be concluded that acrylic binder mixed all intumescent coating components very well, which increased the thermal stability of the intumescent coating.

Table 4.8: The residual weight for D series specimens

Specimen	Residual weight (wt. %)	Average residual weight (wt. %)
B2/18%-1	42.17	41.95
B2/18%-2	40.94	
B2/18%-3	42.75	
D1/WBP-1	37.78	37.32
D1/WBP -2	36.90	
D1/WBP -3	37.28	

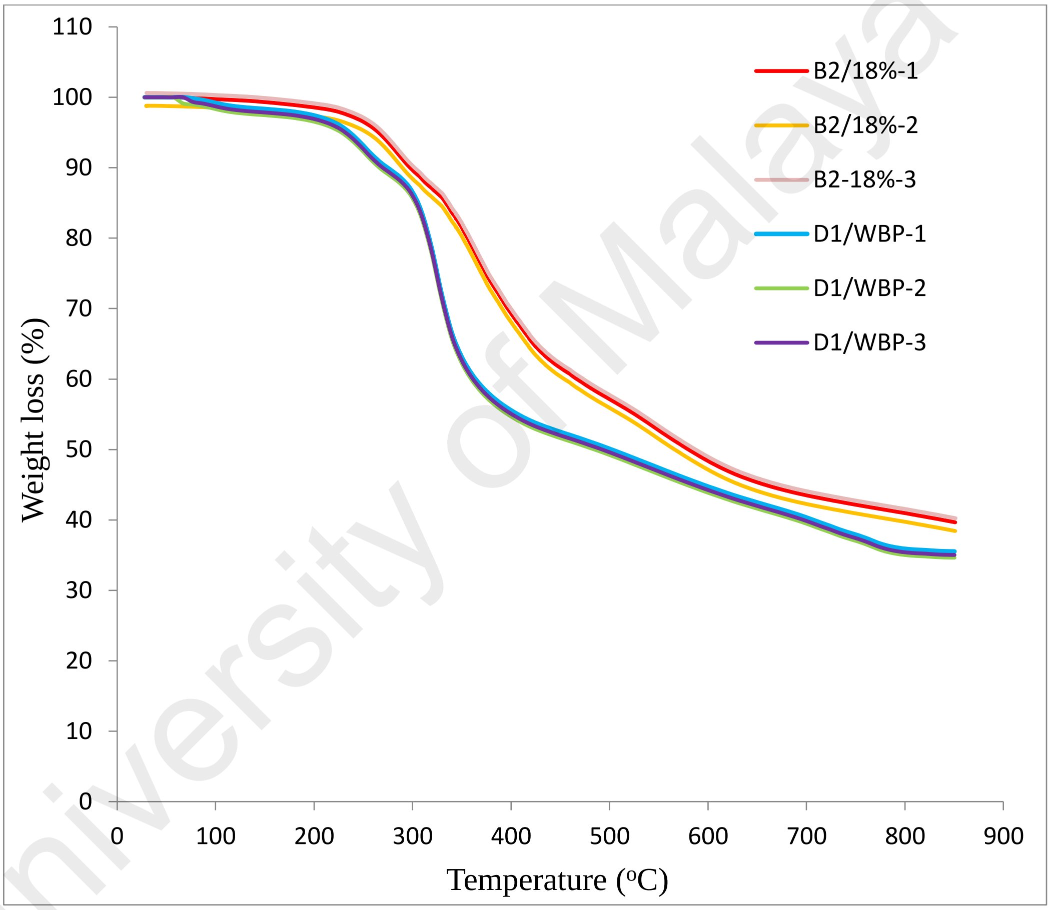


Figure 4.18: TGA curves for specimen D series specimens

4.5.2 Fire performance test of intumescent coatings with different binders

For Bunsen burner test, one sample for each specimen with the highest residual weight was prepared. The temperature curves for specimens B2/18%-3 and D1/WBP-1 are presented in Figure 4.19. The curves for each coating during first 5 to 10 minutes had increase rapidly after exposed to fire. The temperature for specimen B2/18%-3 reached an equilibrium value and almost unchanged at about 187.7°C after 25 minutes and remained almost unchanged afterwards. The high melting temperature and decomposition temperature of acrylic resin are attributed to high molecular weight and a great number of benzene rings in its molecular structure as reported by Wang et al. (2006). However, specimen D1/WBP-1 reached an equilibrium temperature at about 265.1°C, and continuously increased. The char formation for specimen D1/WBP-1 is very fragile (see Figure 4.20). From the images of char layer, it shows that the char were porous with non-uniform structure. The heat might transfer to the steel substrate through the porous foam structure, which could reduce the fire protection performance. The thickness of char layer for specimen B2/18%-3 and D1/WBP-1 is 17.21 mm and 16.54 mm, respectively. There is a correlation between thickness of the char layer and equilibrium temperature. The higher the char layer led to the lower equilibrium temperature. This shows that the thickness of the char layer affects the fire protection performance of the coating. Specimen B2/18%-3 shows the best fire protection performance due to good combination of flame retardant additives and filler in the acrylic binder. The protective char limits the heat transfer from the heat source to the substrate, resulting in conservation of the underlying material, subsequently protecting steel in a fire (Yew & Ramli Sulong, 2012).

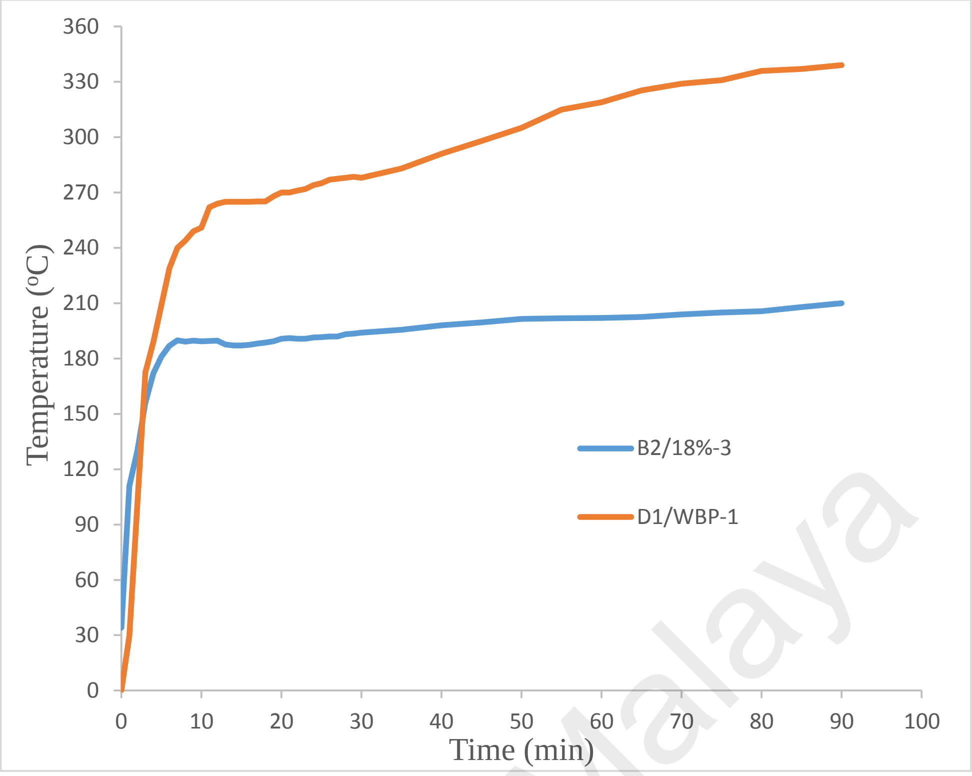


Figure 4.19: The time-temperature curves for specimens B2/18%-3 and D1/WBP-1

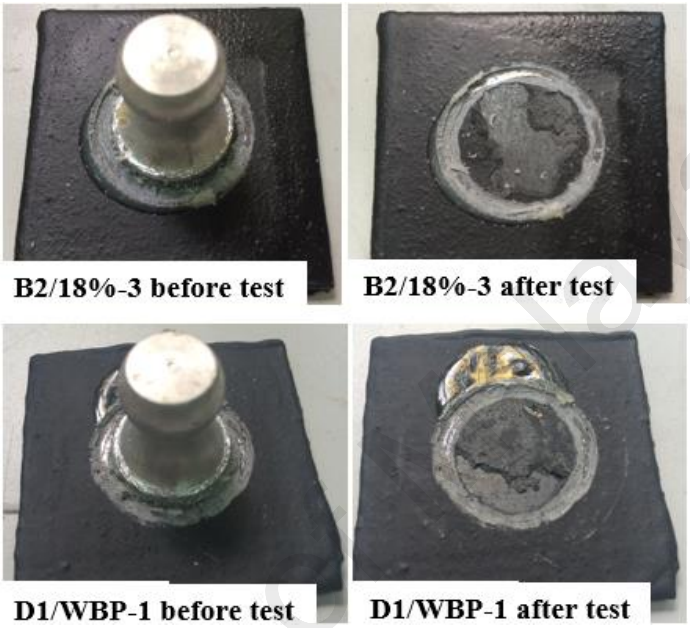
Figure 4.20: Specimen D1/WBP before and after Bunsen burner test

4.5.3 The effect of binder on the adhesion strength

The adhesion strength for specimen B2/18%-3 and D1/WBP-1 are tabulated in Table 4.9. The addition of acrylic binder to the specimen B2/18%-3 results in a strong bonding strength between the steel surface and coating layer. The results showed that the bonding strength of B2/18%-3 achieved 4.39 MPa which is slightly higher than specimen D1/WBP-1. The increase in adhesion strength of coating B2/18%-3 is due to the strong bonding strength between the metal surface and acrylic binder/POC filler, which distributes stresses effectively (Devendra & Rangaswamy, 2012). Hence, it can be concluded that intumescent coatings with acrylic binder gives better adhesion strength to the intumescent coatings. The images of specimen before and after adhesion strength test are shown in Figure 4.21.

Table 4.9: The adhesion strength of specimen B2/18% and D1/WBP

Specimen	Adhesion strength, fb (MPa)
B2/18%-3	4.39
D1/WBP-1	4.08



B2/18%-3 before test

B2/18%-3 after test

D1/WBP-1 before test

D1/WBP-1 after test

Figure 4.21: Specimen B2/18%-3 and D1/WBP-1 before and after adhesion strength test

4.5.4 The effect of binder on the water resistance

The weight change rate curves for specimens B2/18%-3 and D1/WBP-1 is shown in Figure 4.22. It can be observed that the weight of both specimens increases gradually due to the permeation process. This means that water can infiltrate into the porous structure of the coatings, which leads to weight gain of these specimens. This situation has also aroused due to high solubility of POC in water as it can absorb water. However, it was found that specimen B2/18%-3 with solvent-borne binder had a lower weight change rate compared to specimen D1/WBP-1. It proves that specimen B2/18%-3 had a better water resistance than specimen D1/WBP-1 due to the incorporation of acrylic binder. The even distribution of the POC filler in acrylic binder resulted in a uniform and smoother surface structure, thereby improving impermeability and enhancing the water resistance of the specimen B2/18%-3. The weight change rate of all the thin films increased less than 0.25% after the water immersion test, which indicates that the overall water resistance of the coating formulations was very good as supported by Yew et al. (2013a). Figure 4.23 show the images of both specimens after 7 days of static immersion test.

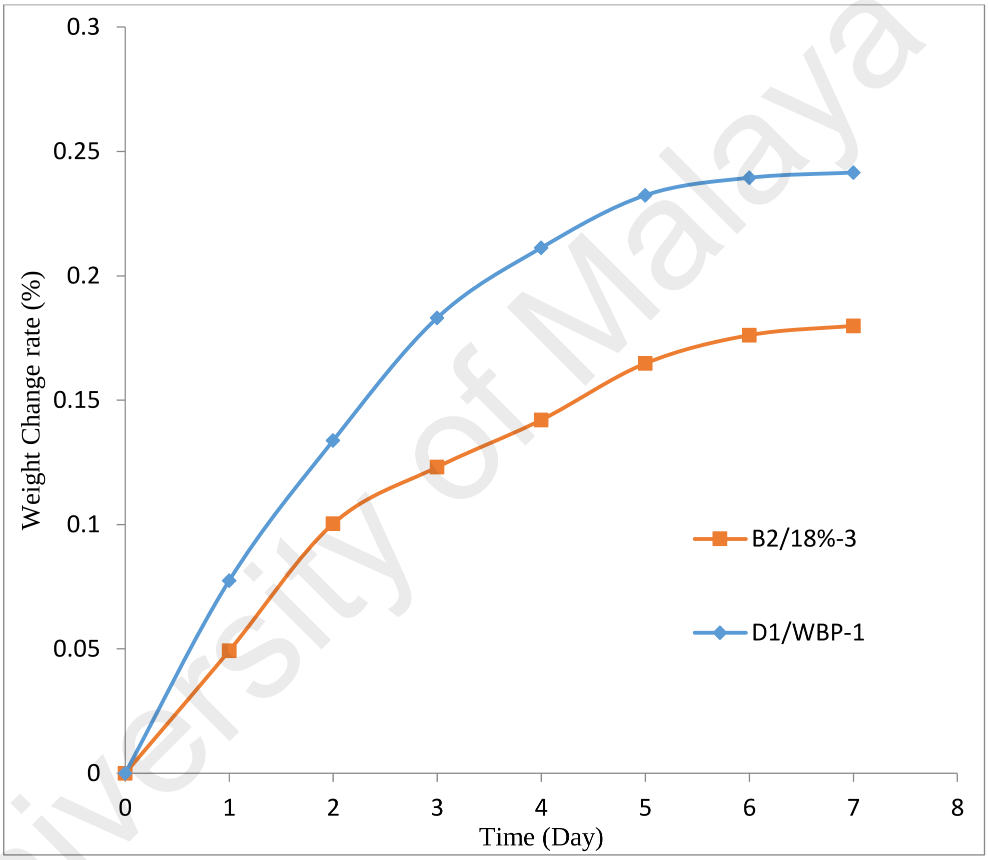


Figure 4.22: The weight change rate curves of specimens B2/18%-3 and D1/WBP-1

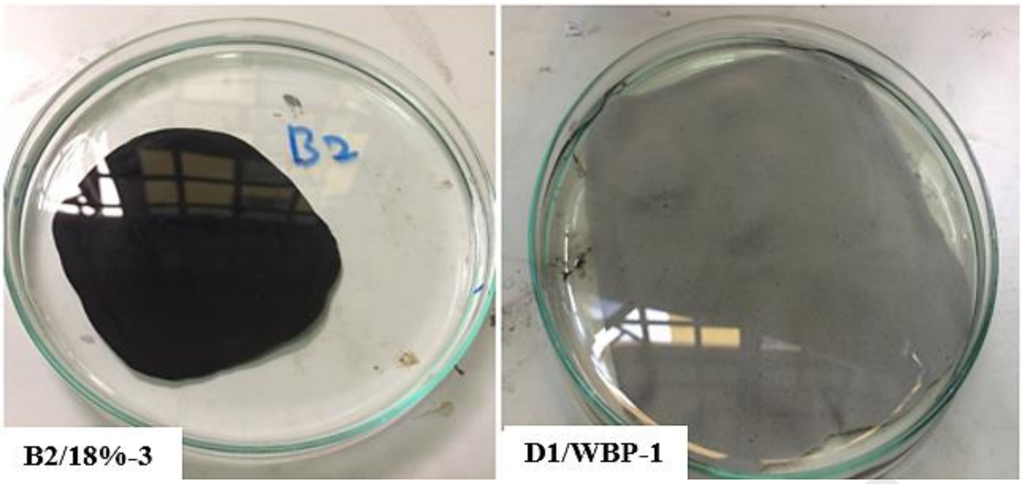


Figure 4.23: The images of specimens B2/18%-3 and D1/WBP-1 after static immersion test

4.5.5 Morphology of intumescent char layers with different binders

Figure 4.24 shows the surface morphology of the char layer for specimens B2/18%-3 and D1/WBP-1. It can be observed that specimen D1/WBP-1 have a porous surface structure, which reduces the fire protection capability of the coatings due to the penetration of heat to the steel substrate through the highly porous and non-uniform char layer. In contrast, the char layer for specimen B2/18%-3 is more uniform with a dense foam structure which prevents heat from penetrating through the steel substrate resulting to the best fire protection performance of the coatings. This happened due to good interaction between acrylic resin and other intumescent coating components. The intumescent char layer acting as an insulating barrier that prevent the heat transfer between the flame zone and the underlying substrate, and thus protects the substrate from heat and fire as supported by Wang et al. (2006).

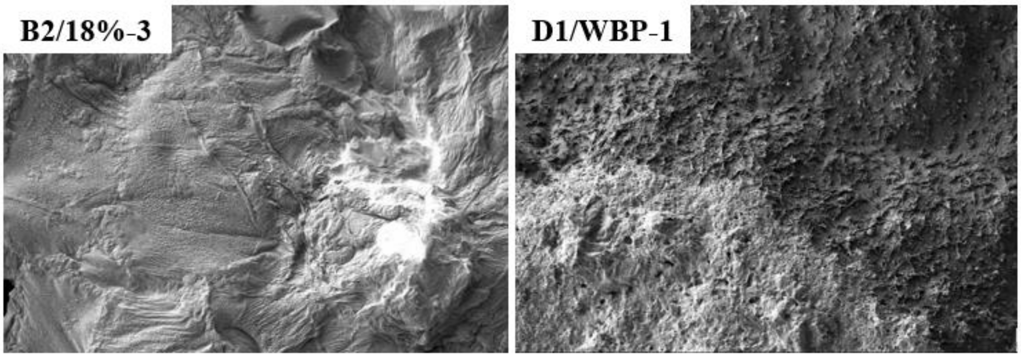


Figure 4.24: Structure of the char layer for D series specimens

4.6 Concluding Remarks

Based on the results of the present investigation, the following conclusions can be drawn:

- The addition of POC with micro particle size to the intumescent coating formulation results in higher thermal stability as well as better fire protection performance. This happen due to higher thermal stability of POC filler in micro particle size compared to in nano particle size.
- The result shows that the increase in POC content led to the increase in the thermal stability of the intumescent coatings. Addition of 18% POC as a filler in specimen B2/18% was found to be the optimal percentage of filler in intumescent coatings due to the highest thermal stability obtained.
- The addition of hybrid fillers in intumescent coating has significant effect on the intumescent coating performance. The incorporation of POC and $Mg(OH)_2$ fillers enhances the adhesion strength of the intumescent coating, while the optimum combination of hybrid fillers will significantly boost the adhesion strength of the intumescent coating. Meanwhile, the permeation of water and dissolution of the fire-retardant components can be slowed down by the addition of $Al(OH)_3$ filler

due to its low solubility in water, which improves the water resistance of the intumescent coating.

- The acrylic binder mixed all the components in intumescent coating very well resulting in more homogeneous coating with better interfacial bonding of the filler/matrix components, hence increased the thermal stability and fire protection performance, as well as better mechanical strength and water resistance.

CHAPTER 5: CONCLUSIONS

5.1 General

This research is focused on investigating the fire protection performance of different formulations of intumescent coatings, incorporating POC as a bio-filler and hybrid fillers. The effects of flame retardant components on the performance of intumescent coatings were investigated by using the Bunsen burner test, thermogravimetry analysis, field emission scanning electron microscope, static immersion test and adhesion strength test. The surface spread of flame test was carried out on the specimens with the best fire protection performance. The following section concludes the studies carried out in this research.

5.2 Conclusions

This research involves the investigation on influence of different particle size of POC (micro and nano sizes) as a single filler to the intumescent coatings formulations. It shows that specimen A1/PM, with micro POC particle has better thermal stability with higher residual weight compared to A2/PN. This situation happened due to higher thermal stability of micro POC compared to nano POC. The weight loss for micro size POC is only about 4 wt. % and due to smaller particle size after a milling process, thermal stability of nano size of POC decrease rapidly with the total weight loss of about 80 wt. % at 750ºC. Hence, it proves that POC with micro particle size had an excellent thermal stability which led to a better thermal stability of specimen A1/PM. Furthermore, specimen A1/PM shows significantly increased in fire protection performance with higher thickness of char layer due to higher thermal stability that gives a better fire protection to the steel substrate. From this results, it shows that the first objectives of this research has been achieved, which concluded that POC with micro particle size gives better thermal stability to the intumescent coating, and was selected as a single filler in the next part of research.

In the investigation of the optimum percentage of POC filler in the intumescent coatings, the formulation shows that the increase in POC content led to the increase in the thermal stability of the intumescent coatings. But, when it comes to 20 wt. % of POC content, there is slightly decrease of the residual weight. Specimen B2/18% was found to be the optimal percentage of filler in intumescent coatings due to the highest thermal stability, which resulted in the highest thickness of char layer and lowest equilibrium temperature. From the surface spread of flame test, all specimens was classified as class 1 since the final spread of flame was less than 165 + 25 mm except for specimen B3/20% which is classified as class 2.

Furthermore, on the investigation of the effect of using different hybrid fillers to the intumescent coatings, the addition of all hybrid fillers increases the thermal stability of the intumescent coating up to 47.42 wt. %, as evidenced from specimen C3/PTMA. Specimen C3/PTMA has the highest thermal stability, which clearly indicates that the combination of POC and suitable amount of hybrid fillers improves anti-oxidation, thermal stability and fire protection performance of the intumescent coatings. Also, the surface spread of flame is 0 mm for specimen C3/PTMA, which shows that the optimum composition of POC and hybrid filler significantly lowers the rate and extent of flame spread. Meanwhile, in adhesion strength test, the addition of $Mg(OH)_2$ filler into specimen C1/PTM results in a strong bonding strength between the steel surface and coating layer. Specimen C3/PTMA has the highest adhesion strength since this coating has the optimum combination of POC, $Mg(OH)_2$, TiO_2, and $Al(OH)_3$ fillers, as expected. The permeation of water and dissolution of the fire-retardant components can be slowed down by the addition of $Al(OH)_3$ filler due to its low solubility in water, which improves the water resistance of the intumescent coating as evidence in specimen C2/PTA and C3/PTMA. In general, the rate of weight change is less than 0.3% for all specimens, indicating that the specimens have excellent water resistance.

Lastly, the highest residual weight as evidence in specimen B2/18% (42.17 wt. %) indicated that the formulation of intumescent coatings with solvent-borne as a binder had the best anti-oxidation and highest thermal stability, resulting in the best fire protection performance. The char formation for water-borne specimen D1/WBP was very fragile with non-uniform structure, which could reduce the fire protection performance of the intumescent coatings. Specimen B2/18% showed the best fire protection performance due to good combination of flame retardant additives and filler in the solvent-borne binder. Moreover, specimen B2/18% results in a strong bonding strength (4.39 MPa) and lower weight change rate compared to specimen D1/WBP due to the incorporation of acrylic binder.

In general, it can be concluded that the optimum composition of hybrid fillers (with POC as one of the key components) results in the best fire protection performance, high water resistance, and excellent adhesion strength for the intumescent coatings.

5.3 Recommendations and future work

- Further work can be carried out by adding other by-waste products into existing intumescent coating formulation to characterize its performance in terms of fire protection performance, sticking ability, water resistance, and surface morphology as well as bonding strength.
- Further work can be carried out using water-based intumescent coatings to characterize its performance in terms of fire protection performance, sticking ability, water resistance, and surface morphology as well as bonding strength.

- Further research can be done to determine the heat release and ignitability of the intumescent coatings by using the cone calorimeter.
- The anti-corrosion and toxicity level of solvent-based and water-based intumescent coatings should be studied in the future work.
- A standard intermediate-scale fire resistance test furnace should be used to comply with the time-temperature curves specified by the ASTM E119 and ISO 834 standards or a custom designed time-temperature curve.

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