

# **Improving the thermal stability and fire safety of PVC formworks**

A Thesis submitted in fulfilment of the degree of  
**Doctoral of Philosophy**

By  
**Zahra Nouri Emamzadeh**

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia

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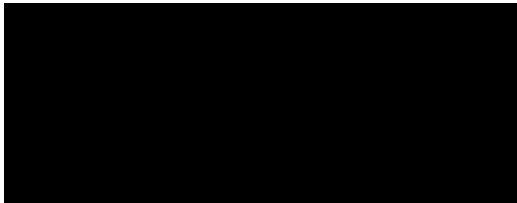
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Signature of candidate

**Zahra Nouri Emamzadeh**



## **Dedication**

To my beloved Parents,

To my amazing brother, sister and niece,

You have given me the best feelings in life: love, support, and encouragement.

You are wonderful.

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# 1. LIST OF ACRONYMS

ABS: Acrylonitrile Butadiene Styrene  
ADP: Alkyl Di aryl Phosphates  
AFm: Alumina, Ferric Oxide, monosulfate or  $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$   
AFM: Atomic Force Microscopy  
AFM-IR: Atomic Force Microscopy-Infrared Spectroscopy  
AS/NZS: Australian/New Zealand Standards  
ASTM: The American Society for Testing and Materials  
ATH: Aluminium Trihydrate  
ATR: Attenuated Total Reflectance  
CMB: Calcium metaborate  
DOP: Diiso octyl Phthalate  
Dipentaerythritol: DPE  
DSC: Differential Scanning Calorimetry  
DTG: Derivative Thermogravimetry  
EDS: Energy-Dispersive X-ray Spectroscopy  
FT-IR: Fourier-Transform Infrared  
GGBFS(GGBS): Ground Granulated Blast-furnace Slag  
HAC: High alumina cement  
HAPS: Hindered Amine Photo stabiliser  
HCAC: Hydrated Calcium Aluminate Cement  
HGGBS: Hydrated Ground Granulated Blast-furnace Slag  
HRR: Heat Release Rate  
ISO: International Organization for Standardisation  
MASN: Melamine Hydroxystannate  
MLR: Mass Loss Rate  
OI: Oxygen Index  
PENZINC: Pentaerythritol-Zinc complex  
Phr: part per hundred ratio  
PVC: Poly Vinyl Chloride  
PVC-C: Chlorinated PVC  
PVC-P: Plasticised PVC, also named soft or flexible PVC

PVC-U: Un plasticised PVC, also named rigid PV

rpm: revolution per minute

SEM: Scanning Electron Microscope

SHMP: Sodium hexametaphosphate

SIP: Stay In Place

SRR: Smoke Release Rate

TAP: Tri Aryl Phosphate

TGA: Thermo Gravimetric Analysis

TGA-FTIR: TGA combined with FTIR

THF: Tetrahydrofuran

THR: Total Heat Release Rate

TTI: Time to Ignition

UV: Ultra Violet

XRD: X-ray powder diffraction

W: Weight

WD: Working Distance

ZINCDPE: Zinc-Dipentaerythritol complex

ZnSt: Zinc stearate

## Abstract

This study examines the impact of materials and compositions on the fire design considerations of plastic formworks, focusing on the influence of building materials on the fire resistance of buildings, the safety of occupants, and the environment. The study investigates the chemical properties of formworks, including heat resistance, UV resistance, and smoke suppressant properties, which are essential for developing and optimizing formwork products. The research covers three key areas for improving thermal behaviour of PVC: (a) the development and evaluation of new metal complexes with dipentaerythritol, (b) cementitious compositions as a novel class of thermal stabilizers, and (c) the development and evaluation of a new synergistic thermo stabilizer based on sodium hexametaphosphate.

To investigate the thermal degradation procedures of each additive for fire retardancy workability, the study utilizes advanced techniques such as thermal gravimetric analysis (TGA), fourier transform infrared spectroscopy (FT-IR), X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), and Energy Dispersive Spectroscopy (EDS). The results demonstrate that hydrated cementitious materials are more effective in stabilizing PVC than metal chelates of dipentaerythritol or synergistic stabilizers based on sodium hexametaphosphate. Moreover, the study found that zinc, as a metal complex with dipentaerythritol, is more effective than traditional stabilizers. The research on cementitious compositions also revealed their highly economical, environmentally friendly, and compatible nature, making them an attractive option for use in the PVC formwork construction industry. The study also highlights the positive impact of calcium metaborate and sodium hexametaphosphate in improving the thermal behaviour of PVC.

The study emphasizes the significance of fire-resistant materials in ensuring the safety of occupants and the environment, and the need for innovative solutions to enhance their effectiveness.

In conclusion, this research underscores the importance of materials and compositions in the fire design considerations of plastic formworks. The study's findings can imply the development of more effective and sustainable fire-resistant materials and promote safer buildings.

**Key words:** PVC, plastic formworks, fire retardancy, thermal stability, smoke suppression, UV resistance.

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# CHAPTER 1

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia



# 1. Introduction

## 1.1 Introduction to formworks

Formwork in construction is defined as a temporary or permanent mould into which fresh concrete or a similar mixture is poured. Its main function is confining and supporting the fresh concrete until the concrete has completely cured and hardened. Consequently, it allows concrete to be shaped into structural elements such as columns, walls, beams, slabs, shells and other non-conventional shapes [1, 2].

Formworks are very important to support the building medium and the final appearance of structures. Moreover, for safety assurance and the number of formworks required, formworks are a major cost component within the total cost of a concrete structure, particularly for formworks that are assembled on site [3]. Therefore, proper formwork system design can lead to a considerable reduction in cost and potential accidents.

Temporary formworks are removed or stripped after the concrete has gained adequate strength, while permanent or stay-in-place formworks are considered to be a part of the final structure. As permanent formworks are not dismantled, they save time, labour and cost. However, some defects and voids of concrete in form of a honeycomb might be present and not seen or easily detected in such permanent formworks [4, 5].

In general, formworks have a great influence on the cost, speed, quality and success of structural projects. Generally, a suitable formwork system should be designed to fulfil market requirements so that (a) it should be light but strong enough to tolerate all loads, (b) the joints of formworks should be tight and firm to avoid leak and permeation of cement and fresh concrete pressure, (c) the material of formwork should be available and cost effective[6, 7].

Formworks can be made of different materials such as timber, steel, aluminium and plastic[8, 9]. Formworks made of wood are some of the most traditional and available formworks but they are associated with some disadvantages, such as deforestation, huge waste, limited recycling potential and high labour cost [2, 10]. Although aluminium and steel formworks are more expensive than timber, they are often preferred over timber formworks due to their higher speed of dismantling, more reusability, and less required material because of their better strength [5, 11-13]. There are some other benefits associated with steel and aluminium form

works compared with timber formwork. For example, more durability and longer life, easier installation and dismantling, not absorbing moisture from concrete, and not shrinking, warping or swelling [5, 14]. Timber formworks are still being used, but for smaller structures. They are not suitable for reuse because of their tendency to deformation and swelling when they are exposed to humidity and moisture. It should also be noted that between steel formworks and aluminium formworks, aluminium is corrosion resistant, cheaper and lighter but its compromised durability reduces its ability for reuse [15-17].

Plastic formworks are other type of formworks which have been favoured in recent years due to their advantageous properties such as durability, flexibility, cost-efficiency and labour friendly, as well as prefabrication [18, 19]. For example, (a) plastic formwork can be applied several times, while timber doesn't have this possibility. (b) Although plastic is somewhat more expensive than timber or steel, it is still more economical because of its repeatability property. (c) The flexibility of plastic causes these formworks to be easily made in various shapes. (d) Lightweight plastic saves a lot of time and labour in handling, fixing, installing and dismantling of formworks and consequently results in money savings and a safer working environment. (e) They also have insulating and corrosion-resistance properties (f) as there is no need to apply oil to the plastic formwork before casting concrete, dismantling would be more comfortable. Moreover, as plastic does not stick to concrete final cleaning is easier and can be achieved by just spraying water [20-24]. Plastic formworks are mainly made of poly vinyl chloride (PVC)[25]. PVC is categorized as a polymer material. Polymer refers to a substance which is made of macromolecules and its structure is characterized by the repetition of a large number of units called monomer [26].

Direct use of polymer right after polymerization is almost impractical and adding some other ingredients to polymer is necessary and the process is known by compounding. The art of formulation is the addition of proper additives and fillers to the polymer to convert it to a useable product. Thus, any plastics or polymeric materials such as formworks can have a wide competitive range of formulations regarding its functionality and user's requirements [27, 28].

PVC is one of the most commercially used plastics because of its low-maintenance, low cost, and especially its better properties compared to other plastics [29, 30]. Its advantages include high resistance to abrasion, high durability, high mechanical and physical stability, good electrical insulation, low diffusion for humidity, and excellent resistance to acids, bases, alcohols, oils and water [31]. The thermal conductivity of PVC is only 0.45%–0.6% of a steel

tube, therefore, it leads to a stable curing condition and hence the high performance and durability of the core concrete [32, 33].

In comparing PVC to timber, as a structural formwork, it is evident that the required temperature to inflame PVC is 150°C which is higher than wood, correspondingly, once the flame occurs, the PVC has self-extinguishing behaviour and does not ignite spontaneously[34]. The heat release of PVC is lower than other compounds such as wood, and obviously, the amount of heat release is a key factor for the intensity and speed of fire propagation[35]. Thus, the usage of PVC (with a coefficient of thermal conductivity lower than wood: 0.17 W/m<sup>2</sup> °C, compared to 0.23 W/m<sup>2</sup> °C) [36], is advantageous with respect to fire risk reduction, and at the same time reduction of the speed of fire propagation in case of an incident [37]. PVC molecules are made up of 57% chlorine and only contain 43% ethylene (derived from petroleum) [38]. Without considering the consumed energy in its production process, with respect to other materials such as aluminium and steel are lower, it is also a generally recyclable material. It can be incinerated, or re-used for the manufacturing of plastics. Additionally, PVC is easier to assemble and has also a lower price compared to other formwork materials and even other polymers such as fibre-reinforced polymers. All of these advantages, make PVC an ideal polymer for the secure, fast and convenient design of stay in place (SIP) formwork systems [34, 39]. The PVC formwork contains interconnected panels that act as permanent formwork for the concrete walls and columns and also encase the wall or column surface. This system can be used to construct retaining walls, foundations, walls in water such as walls for swimming pools, etc [40]. Generally, PVC stay in place formworks are left in place permanently as a construction element (wall, column, slab, roof, pool, etc.), becoming a component of the final structure and providing a protective shell to concrete in comparison to conventional formworks. PVC SIP formwork also provides some additional advantages to its embedded concrete by confining it [41]. For example, improvement of structural strength, improvement of structural resistance to corrosion and protection of concrete against thermal loads by confining it. Furthermore, PVC avoids moisture loss which is essential for the hydration and setting of fresh concrete. Thus, it reduces the cost and time of the curing process of concrete [40-45]. PVC formwork systems seal the concrete, providing a water-resistant shield that protects concrete from the environment. Also, connectors in the newest version of PVC formworks lead to rapid installation and better core filling which consequently eliminates the need to settle the concrete by vibration. Industrially developed PVC formworks play an important role in the reduction of health risks and environmental impacts on building sites. The latest systems need reduced steel

reinforcement, less materials consumption and less building carbon footprint. Moreover, no requirement for stripping PVC formwork along with its ease of installation and lightweight lead to less injury risk with increased safety and health on site. Figure 1-1 shows panels of PVC permanent formworks, known as Rediwall manufactured by AFS and Figure 1-2 shows its smooth finished substrate. The clean and bright surface of these PVC permanent formwork systems provide a low maintenance finish which doesn't need further treatment for majority of applications.



Figure 1-1 AFS Rediwall



Figure 1-2 Smooth finish of AFS formwork system

PVC formworks are manufactured on a mass scale by plastic extruders. Plastic compounding extrusion is a high-volume and continuous manufacturing process method in which plastic materials in raw form such as powder, pellets, or granules are mixed with different additives and fed into the hopper of the machine. In the next stage, the mixture moves into a large heated and barrel-shaped chamber. It goes over this chamber by either one or two rotating screws[46]. As all materials (different polymers and additives) do not have similar properties, a heating temperature should be well-defined for the type of compound being processed (type of polymer, filler, viscosity). In the final stage, the molten plastic flows through an opening termed a die to make the shape of the final product. When the polymer is extruded from the die, it is loaded into a cooling conveyor. Cooling can be done by water or air [47, 48]. Additionally, co-extrusion is achievable when two or more extrusion machines are operating to supply one die head. This is functional and helpful when combined layers of various substances are required for the final product. Co-extrusion can also be utilized to add up a top coating layer to boost the product's aesthetic appearance whilst minimizing costs by using a cheaper substance at the inner layers of the product. The extrusion compounding process is like injection moulding except that in the extrusion method the melted polymer makes its way through a die and not into a mould. The die of the extruder is designed so that the polymer flows evenly and smoothly from the cylindrical part into the final desired shape. Obviously, consistency and uniformity in this passage (from cylindrical part to die and final desired shape) is important in obtaining a final product with integrity [49-51]. In general, the extrusion machine provides an economical, efficient and practical process for the factories to manufacture the polymeric product. For polymeric formwork systems, the extrusion method is efficient and fast for manufacturing constant shapes in different lengths. It also offers production on large scale with minimal wastage. Moreover, a wide range of additives can be fed into plastic wall extrusion machines to improve the fire resistance and durability of formworks whilst minimizing friction.

## **1.2 Research motivation**

Due to new progress in building materials, strong requirements are needed to specify their fire behaviour under different scenarios. As new and modern materials pose new challenges, their performance in fire incidents should be specified before their usage in buildings. Many of the

current studies are focused on the degradation of the new materials under fire, however, there are limited research works on assessing the combustibility and toxicity of new materials. High combustibility accelerates fire intensity by making quick fire spread, whereas, high toxicity may enhance risk level to life safety. Therefore, research and thorough studies should determine all fire aspects (combustibility, toxicity, strength degradation,) in the usage of new materials in the buildings

### **1.3 Aims, objectives and scope of the research**

Formwork systems play an important role in the construction industry. Choosing an appropriate formwork system could lead to faster, more economical and more sustainable construction practices. In recent years, the application of plastic formworks in structures has been on the increase and research on plastic formworks has shown great success. However, several challenges still remain. In this project, we aim to take a closer look at this issue by overcoming the formulation barrier and tackling the remaining problems. This study, therefore, aims to present a new formulation for heat stabilisation of PVC used in the formwork industry used in building and infrastructure engineering and to overcome the health hazards related to the formation of toxic chlorinated fumes and smoke in case of fire accidents plus improving its UV resistance while maintaining its mechanical properties.

### **1.4 Structure of the thesis (Thesis outline)**

This thesis consists of six chapters including the background, research motivation, objectives and scope of the study included in Chapter 1 (Introduction).

Chapter 2 Presents a comprehensive literature review of the subject matter.

Chapter 3, Details explain the materials and methods common to all chapters, while the experimental description of specific studies can be found in the respective chapters.

Chapter 4 Contains the synthesis and evaluation of a new series of metal chelate complexes with Dipentaerythritol as a thermal stabiliser for PVC

Chapter 5 Presents a novel cementitious composition as an effective thermal stabiliser and HCl-suppressing additive for PVC.

Chapter 6 Compares the synergistic effect and char morphology of sodium hexametaborate with other additives during the increasing temperature of PVC.

Conclusions and recommendations for future work are presented in Chapter 7.

# CHAPTER 2

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia



## 2. Literature Review

### 2.1 Review of the formulation of PVC for Thermal resistance

This chapter provides an up to date overview of the heat resistance, flame retardants, smoke suppressants and thermo-oxidative degradation of PVC. It presents different properties of additives and their working mechanism in either the solid phase or the vapour phase of the thermal degraded PVC. Different additives with varied properties, individually and in collectively, are introduced in order to investigate their synergistic effects.

PVC is a thermoplastic polymer which has a wide range of applications, especially in the building industry. PVC is also a halogen-containing polymer that contains a considerable amount of chlorine (about 56%). Chlorine is classified as a halogen element in the chemical group that gives good fire-retardant properties to a polymer and is known as a self-extinguishing polymer. In other words, chlorinated radicals react with extremely reactive OH and H and other alkyl free radicals and reduce the combustion kinetics [70]. Moreover, released hydrogen chloride during the combustion of PVC acts as an inert diluent in the fire. Therefore, PVC tends to be a good fire retardant material inherently [71], but like other organic polymers, PVC undergoes thermal degradation at elevated temperatures and is still considered as a combustible substance at high temperatures due to its carbon-carbon backbone [72].

PVC is compatible which is formulated with many additives and fillers. Such additives might alter the polymer's flammability properties including, resistance to combustion, thermal stability, and the amount of char, gases and smoke generated from the polymer [73]. For example, DOP [di (2-ethylhexyl) phthalate] is a type of phthalate plasticizer added to rigid PVC in order to make it flexible and easy to use. The plasticizer (DOP) negatively influences the fire properties of PVC and makes it more flammable than rigid PVC [74, 75]. Phosphate Esters can be alternative to phthalate plasticizers. After Pyrolysis, Plasticizers based on Phosphate esters form pyro or polyphosphoric compounds which are thermally stable and act as a protective barrier. This property causes phosphate esters to have better flame retardancy in comparison with phthalates [70].

As PVC has a growing market in many industries from construction and electrical to packaging and clothing, accordingly improving and controlling the fire hazardous properties of PVC has become a widespread concern. Additionally, the improvements and further developments of

fire standards during recent decades have led to a significant increase in the study and use of different fire retardants and smoke suppressants in plastics. This chapter aims to summarize some of the relevant literature and publications in this area.

Selecting efficient thermo stabilisers and smoke suppressants for PVC is not a simple matter and many factors such as compatibility with other additives, not negatively changing mechanical and physical properties of the polymer and not leading to harmful compounds should be considered when choosing thermo stabilisers for the best formulation. Moreover, the rate of flame spread and released heat and the amount of smoke, toxic fumes and acidic gases should be looked into in determining the performance of the stabilisers. Overall, the best formulation should be a balance between the performance and the cost to meet market requirements and fire standards.

The main products of PVC degradation are HCl, char, and very little alkyl aromatic or condensed ring aromatic hydrocarbons. In other words, the thermal decomposition of PVC initiates with dehydrochlorination through a zipper mechanism that leads to conjugated bonds in different lengths of polyene sequences. Although the produced HCl is a toxic and corrosive gas, it contributes to the reduction of flammability due to its chlorine content. In the secondary reactions, polyene sequences undergo other reactions, one of them being radical elimination that leads to cyclization and generation of benzene and intermolecular crosslink of macromolecules which cause the production of char on continued heating [76-78]. The weight of char is inversely proportional to the molecular weight of PVC because of the concentration of chain ends. When the molecular weight of the polymer decreases, it acts as a crosslinking site. This is also the reason for the reduced amount of benzene in the pyrolysis of PVC with low molecular weight [79]. A char layer positively influences the flame retardancy of PVC, because it acts as a barrier and insulates the interior layers of polymer against oxygen and thermal degradation and protects the polymer during combustion. It should be considered that the effectiveness of enhancing the fire resistance of the polymer by creating a char layer is contingent on the properties of the char. Porous carbon-based chars are generally susceptible to oxidation and may release a considerable amount of heat. However, certain chars derived from an intumescent layer may be impermeable to oxygen and can provide insulation to the underlying material.

Char yield values are calculated by Equation 2.1, where  $W_1$  is the weight of PVC before combustion and  $W_2$  is the weight of the residue of PVC after combustion.

$$\text{Char Yield (\%)} = W_2/W_1 \times 100 \quad (\text{Equation 2.1})$$

Another way of producing a protective layer for the polymer is forming an intumescent coating. At high temperatures, the coating starts swelling and decomposing to form an insulated foamed barrier. An intumescent system contains three components; a carbonisation agent, an acid source, and a blowing agent. The drawbacks of this method are the high cost of formulation, processability and high loading require [72].

## 2.2 Combustion Principles

The combustion process of polymers mainly contains four stages: heating, degradation, ignition, and propagation [80] which are defined below

- Heating: exposure of an external source of heat to polymeric materials causes an increase in the temperature of the polymer. In this stage, thermoplastics such as PVC will tend to soften or melt.
- Degradation: This stage occurs at a particular temperature at which thermally weaker bonds start breaking. The degradation step will cause the formation of radicals which will result in the formation of lower molecular weight organic compounds, which are mainly volatile flammable products. The composition of products made at this stage is dependant on the chemical structure of the polymer and the oxygenic environment.
- Ignition: The ignition stage depends on many factors, such as the chemical and physical properties of the polymer, oxygen concentration and temperature. When the volatile products reach a suitable concentration for the production of the gas mixture – air is flammable, and then ignition starts. Combustion will be continued so long as there is enough energy transferred to the surface and interior mass of the polymer to keep its decomposition, which leads to the production of combustible gases.
- Propagation: Fire spread is obtained by heat transfers that could be convective, conductive or radiative.

## **2.3 Fire protection of polymers**

Thermo stabilisers, fire retardants and smoke suppressants aim to interfere with the combustion process by reducing the flame and smoke spread. Such fillers can improve fire properties in several ways, such as diluting combustible content of organic polymers, reducing the amount of released heat to below sufficient heat needed for combustion, reducing the amount of evolved smoke and flammable volatiles, and isolating a major content of polymer from flame, heat and oxygen. In other words, the mechanism of the action takes place chemically or physically in different phases. For example, in the gas phase, flame retardants act by the chemical mechanism through scavenging free radicals or by the physical mechanism through producing huge amounts of non-flammable gases which dilute combustible environment, and sometimes reduce the temperature by dissociating endothermically and absorbing the heat. In the condensed phase, charring is the main cause of flame retardancy which can be promoted chemically by catalysis and chemical interaction of additive with polymer or physically by retention of the polymer in the solid phase. Generally, char is a carbonaceous substance generated during pyrolysis. A desirable char layer should be difficult to burn, provide good insulation, have integrity and coherence, and be able to stay in place.

Synergistic refers to combinations of different mechanisms or several additives in order to improve the performance of the mixture compared to the single additive. In the following paragraphs, an explanation of different types of additives having different mechanisms will be discussed in more detail.

## **2.4 Fillers as fire retardants and smoke suppressants**

Fillers are commonly used in the formulation of polymers for improving their physical, mechanical, thermal and fire retardancy properties such as calcium carbonate, clays, silica and carbon black, carbon fibres, carbon nanotubes and others. Several of these fillers are considered to be fire retardants. Regarding fire retardancy, there are two types of fillers: inert fillers and reactive fillers, both classes improve fire retardancy and smoke suppressant properties by diluting the flammable organic content of the polymer with non-combustible material. Fillers may not be inert in all polymers. For example,  $\text{CaCO}_3$  is considered a multi-functional reactive filler for PVC, it reacts with HCl produced from PVC degradation, forming calcium chloride

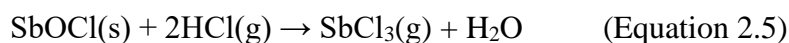
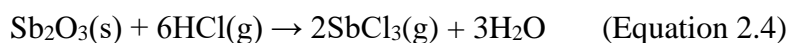
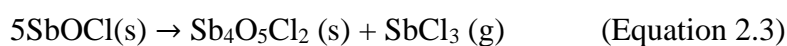
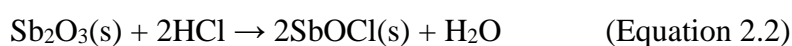
and carbon dioxide which is considered a strong fire retardant and thermo stabiliser because the produced HCl acts as an auto catalyst for thermal degradation of PVC [encyclopaedia of PVC Ref] while it doesn't involve in any reaction in polypropylene combustion [81] we observe its decomposition at about 500°C to CO<sub>2</sub> and CaO. Calcium carbonate converts hydrogen chloride of PVC into the chloride salt CaCl<sub>2</sub> thus reducing the escape of corrosive and hazardous HCl gas into the atmosphere by binding the acid into the residual char.

The addition of nanoclays based on hectoritec (Na<sub>0.3</sub>(Mg,Li)<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>) or bentonite Al<sub>2</sub>O<sub>3</sub> • 2SiO<sub>2</sub>•H<sub>2</sub>O in PVC formulation decreases the total smoke and increases the time over which smoke is produced [82]. This might be due to the interference of clay with the cyclization of the conjugated system. Nano clays can also show synergism in combination with aluminium trihydrate or magnesium hydroxide. The nanoclay leads reduction in the amount of ATH or magnesium hydroxide used to achieve a given flame retardancy rating [83]. Silica (SiO<sub>2</sub>) has reinforcing properties, while clay and CaCO<sub>3</sub> are non or semi reinforcing fillers that can be used in applications where cost is the primary concern [84]. A study has shown that increase in CaCO<sub>3</sub> content causes a decrease in elongation values and an increase in the tensile strength of PVC[85]. On the other hand, thorough dispersion of nanoclay in PVC increases modulus and mechanical properties of PVC with no considerable change of elongation and tensile strength [86]. Microzeolites with general formula Me<sub>2/m</sub>.Al<sub>2</sub>O<sub>3</sub>.nSiO<sub>2</sub>.pH<sub>2</sub>O (where Me=Fe<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>) have both fire retardant and smoke suppressant effects in PVC compositions. Modifying microzeolite with 3.5-4% zinc can improve these effects [87]. Several mechanisms are believed to contribute to their efficiency; a) water available in chemical formula of zeolite can evaporate during burning and lead to dilution of burning gases and cooling down of temperature. b) Al<sub>2</sub>O<sub>3</sub> in combination with Fe<sub>2</sub>O<sub>3</sub> and MgO, which are all available in the chemical formula of zeolites, promote the formation of the char. C) SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> formed on the surface of burning polymer protect inside the polymer from burning, and d) zeolite is a porous compound which can absorb the evolved HCl from burning PVC[88]. Moreover, zeolite can increase mechanical strength of the char and make it stable by forming Al-O-P-C and Si-O-P-C bonds[89]. Combinations of the finely-divided zeolite with antimony trioxide cause an excellent flame retardancy but increase smoke evolution [88].

## 2.5 Antimony compounds

Antimony compounds such as antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) and antimony pentoxide ( $\text{Sb}_2\text{O}_5$ ) are cost-effective but toxic fire retardants. The efficiency of Antimony trioxide is at low loadings, so it doesn't have a considerable effect on the mechanical properties of the PVC. Using antimony trioxide can enhance smoke evolution so it is used only as a flame retardant, while colloidal antimony pentoxide can be used as both flame retardant and smoke suppressant [72].

The existence of antimony trioxide can cause two separate reaction schemes in the thermal decomposition of PVC. A) reaction of  $\text{Sb}_2\text{O}_3$  with the released HCl from PVC, resulting in an intermediate substance named antimony oxychloride ( $\text{SbOCl}$ ), which is then transferred to  $\text{SbCl}_3$  and  $\text{SbCl}_5$  (Equations 2.2 and 2.3).  $\text{SbCl}_5$  is volatile and acts in the gas phase by interfering with fire reactions through the scavenging of free radicals. B)  $\text{Sb}_2\text{O}_3$  and  $\text{SbOCl}$  can also directly react with HCl to form  $\text{SbCl}_3$  and  $\text{SbCl}_5$  (Equations of 2.4, 2.5) [90].



Nowadays, there are increasing global concerns about the toxicity and the environment which have forced the industry to use other fire retardant additives that could be used as alternatives to antimony compounds that are categorised as hazardous and carcinogenic materials.

## 2.6 Metal Hydroxides

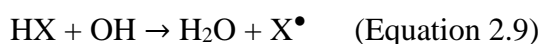
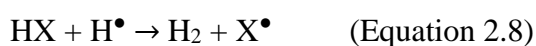
Aluminium trihydrate,  $\text{Al}(\text{OH})_3$  (ATH) and magnesium hydroxide,  $\text{Mg}(\text{OH})_2$  are non-toxic flame retardants that can play both roles of flame retardancy and reinforcing. Their act is based on the dilution of the volatile products by releasing water at high temperatures in the gaseous phase. In other words, releasing water is an endothermic process which lowers the temperature and dissipates heat. Consequently, it stops further degradation and combustion. Aluminium

trihydrate is cheaper than magnesium hydroxide, while magnesium hydroxide is more thermally stable. Both fillers are associated with the disadvantage of high loadings in order to apply a reasonable level of fire retardancy [72]. Similar to other fillers, the metal hydroxides can change the elongation and tensile strength of PVC at the break point. This is due to the decrease of the interactions among the polymer molecules and the limitation of movements of the polymer chains when the flame retardants reach 30 parts [91].

The metal oxides and metal hydroxides also react with the produced HCl from the degradation of PVC, forming metal chlorides such as  $AlCl_3$  and  $MgCl_2$ .

## 2.7 Halogen-based flame retardants

Halogenated flame retardants act in the vapour phase. These compounds are based on hydrocarbon halides: bromide, chloride or fluoride. The bond between carbon and halogen is weak and thermally unstable so they release halogen radicals which terminate the free radical chain reactions involved in the decomposition of polymers and accordingly retard combustion decomposition reactions. These are not used with PVC since PVC is a halogen containing polymer. As radicals have one unpaired electron, they are highly reactive to get an electron from other substances. Therefore, they react easily with polymer free radicals, OH and H free radicals are released during combustion and finally form hydrogen ( $H_2$ ) and water ( $H_2O$ ) (Equation 2.1-2.6 to 2.1-2.9). As a result halogen radicals scavenge OH and H radicals which are key substances in fire spreading reactions from the combustion zone and reduce the heat of combustion and slow down the spreading of the fire [89, 92].



X = Cl or Br

Halogens are released from either the polymer itself, like PVC, or the additives containing halogen atoms. Apart from the effect of radical scavenging imparted by halogenated flame retardants, other physical factors such as the mass and density of halogen have a considerable effect on the performance of the fire retardants[93].

The performance of halogenated flame retardants can be increased by the addition of particular inorganic filler which has the fire retardant properties, known as synergists. The main synergist is antimony trioxide, which acts by producing volatile antimony halides and consequently interferes with the gas phase. Other possible synergists are borates, stannates and molybdates. These additives act both in gas phase, similar to antimony trioxide, and in solid phase by increased char formation. Significant amounts of metal remains in the condensed phase and halide salts play an important role on the effects of solid state [73].

Chlorinated paraffin and olefines are examples of inexpensive halogenated flame retardants for polymers, generally. They can also give polymer flexibility, so they are also recognized as secondary plasticizers. The term secondary is given to them because of their low solubility and compatibility with polymers, while primary plasticizers such as phthalate esters and phosphate esters have better compatibility with PVC. The compatibility of chlorinated paraffin with polymers and other plasticizers can be improved by increasing the number of chlorine in their structure. The cost of the formulation can be improved by the combination of inexpensive chlorinated paraffinic plasticisers with some portion of more expensive primary plasticizers such as phosphate esters [94]. It should be noted that phosphate esters due to phosphorous content can act as flame retardant and plasticisers.

## **2.8 Phosphorus-containing additives**

Fire retardants containing phosphor element, organophosphorus compounds and phosphates act in the condensed phase by forming polyphosphoric acid. This acid causes a char layer around the polymer and acts as a barrier and protective coating. Alkyl di aryl phosphates (ADP) and tri aryl phosphates (TAP) are examples of important plasticisers for PVC that can act as flame retardants as well. These plasticizers can be combined with other flame retardants. For example, a combination of phosphate ester plasticizer with a mixture containing the other three fire retardant additives (antimony trioxide, zinc borate and aluminium tri hydroxide) causes an increase in LOI value (index which shows the minimum concentration of oxygen, that will

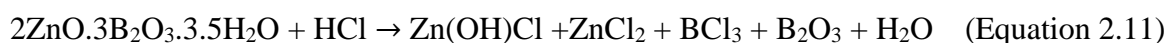
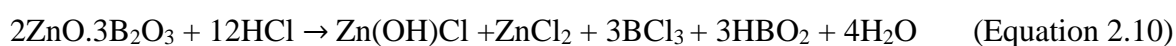


support combustion of a polymer) and makes a final product more stable with high resistance to burning [95].

Another study has used inorganic hypophosphite as a flame retardant for PVC. U.S. Patent Application 14/409,359 to Zucchelli discloses that inorganic hypophosphite also named hypophosphorus acid, metal salt or inorganic phosphinate with formula  $\text{Me}(\text{H}_2\text{PO}_2)_n$  where Me is a metal from groups I, II, III and IV of the periodic table and n is an integer number from 1 to 4, as flame retardant agent in a plasticized PVC composition [96]. Inorganic hypophosphites, especially calcium hypophosphite and aluminium hypophosphite when used in PVC formulations together with already existing primary and secondary plasticizers and conventional additives, like stabilizers, colourants and lubricants can cause very good flame retardancy so that they can even totally replace antimony trioxide in the same formulation, still keeping the same flame retardant properties.

## 2.9 Boron compounds

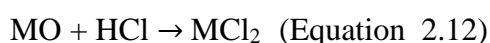
Anhydrous zinc borate or hydrated zinc borate are generally used from boron category as flame retardants. The hydrogen chloride produced from burning PVC reacts with zinc borate and yields water, non-volatile zinc chloride and volatile boron trichloride (Equation 2.10 and 2.11)



Released water cools down the combustion zone while boron trichloride acts as a gas phase flame retardant, but the main function is due to zinc chloride ( $\text{ZnCl}_2$ ) which acts in the solid phase, promoting cross-linking and char formation, but accelerates dehydro-chlorination reaction in PVC which is one of the drawbacks of this fire retardants when used for PVC [89, 97]. In this situation,  $\text{ZnCl}_2$ , which is a Lewis acid, accepts a chloride from PVC forming carbonium ion which consequently decomposes into alkene and  $\text{ZnCl}_3^- \text{H}^+$ . The ionic adduct  $\text{ZnCl}_3^- \text{H}^+$  is a more stable ionic structure of HCl and  $\text{ZnCl}_2$ . In the next stage, the unsaturated groups in PVC react with carbonium ions and ultimately promote cross linking reactions in the same way which is then resulting in char formation.

Another study has investigated the synergistic effect of zinc borate and aluminium trihydrate on PVC. It concludes that a mixture of both zinc borate and aluminium trihydrate in PVC can

greatly increase char formation, inhibit smoke production, decrease aromatic and hazardous gases such as benzene and toluene, decrease the activation energy for dehydrochlorination and thus accelerates the dehydrochlorination reaction. It has also shown that the heat stability of zinc borate-filled PVC improves in the presence of aluminium trihydrate [98]. The combination of zinc borate and antimony trioxide shows another synergistic scheme [72]. The synergism of antimony trioxide and zinc sulphide has been investigated in another study [99]. The advantage of zinc sulphide over zinc borate is its cheaper cost, but unlike zinc borate, zinc sulphide cannot be used as a complete replacement for  $\text{Sb}_2\text{O}_3$ . Synergism allows the feasibility of replacing half of antimony trioxide with zinc sulphide to show equivalent fire retardancy in PVC. Other compounds such as  $\text{ZnO}$ ,  $\text{MgO}$  and  $\text{CaO}$  have the same mechanism in reaction with PVC. They react with  $\text{HCl}$  and form Lewis acid (Equation 2.12).



M= Zn, Mg, Ca, ...

In general, many metal compounds with the highest oxidation state of metal such as Molybdenum trioxide  $\text{MoO}_3$  and Tin oxide  $\text{SnO}_2$  are good Lewis acid and smoke suppressants. The problem of molybdenum trioxide is its colour (blue-green) and abrasion effect, so for this reason Ammonium octamolybdate with whiter colour and less abrasion effect has a better commercial usage [100]. Tin and zinc content in zinc stannate ( $\text{ZnSnO}_3$ ) and Zinc hydroxyl stannate ( $\text{ZnSn}(\text{OH})_6$ ) lead these compounds as both are flame retardants and smoke suppressants [101]. They have low health hazards and are effective at low loadings.  $\text{Zn}^{2+}$  in these compounds reacts with produced  $\text{HCl}$  of PVC to form  $\text{ZnCl}_2$  which is a strong Lewis acid and accelerates the dehydrochlorination reaction and consequently promotes early crosslinking and rapid charring to PVC. Furthermore,  $\text{SnO}_3^{2-}$  in these compounds reacts with  $\text{HCl}$  to form  $\text{SnCl}_2$  and  $\text{H}_2\text{O}$ .  $\text{SnCl}_2$  it also acts as a Lewis acid and like  $\text{ZnCl}_2$  enhances fire retardancy by rapid char formation in the solid phase. In the gas phase, there is a small amount of tin compound which volatilizes oxyhalide which acts according to the radical scavenging mechanism. There is only one more extra process in the mechanism of zinc hydroxyl stannate over zinc stannate. Zinc hydroxyl stannate undergoes endothermic decomposition when heated and produces water which transfers heat away from the combustion environment. This particular mechanism in this compound is not as important as previous mechanisms and that is

why zinc hydroxyl stannate, unlike aluminium or magnesium hydroxide, can be effective at low loadings.

Another study has investigated other metal hydroxyl stannates as flame retardants and smoke suppressants for PVC. It shows adding  $M\text{Sn}(\text{OH})_6$  where  $M = \text{Co}, \text{Cu}, \text{Ni}, \text{Mn}, \text{Mg}, \text{Sr}$  to PVC cause an increase in LOI and a decrease SDR for PVC [102].

## 2.10 Copper compounds

Low-valent metals, such as  $\text{Cu}(0)$ , can improve crosslinking through another mechanism named reductive coupling mechanism and, consequently, resulting in smoke suppression (Figure 2-1) [103].

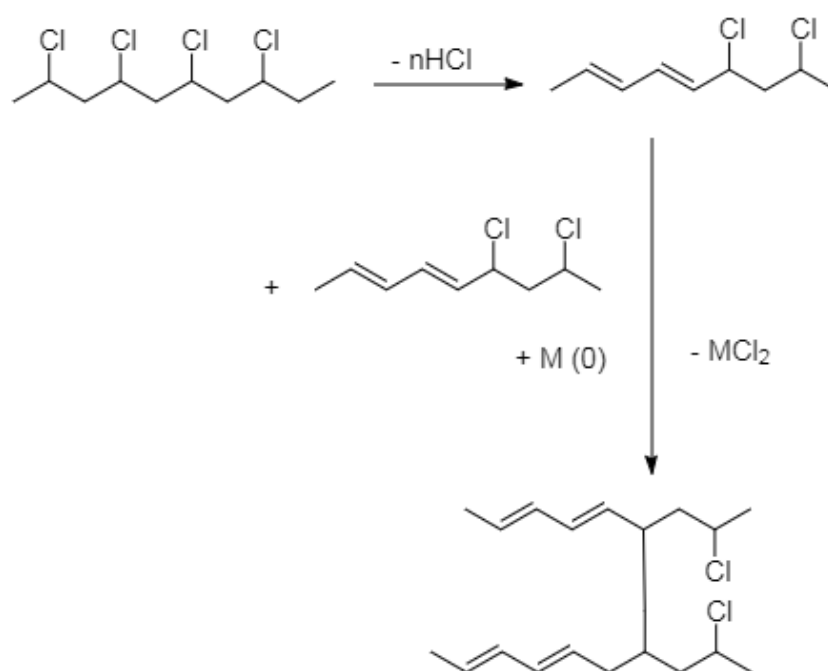


Figure 2-1 reductive coupling mechanism by low-valent metals

Copper compounds are inexpensive and non-toxic, which makes them good smoke suppressants. As copper is easily reduced thermally, the original filler may be a compound of  $\text{Cu}(\text{I})$  or  $\text{Cu}(\text{II})$ . Copper (I) compounds are colourless and tend to be disproportionate to  $\text{Cu}(0)$ .

and Cu (II).  $\text{Cu}_2\text{O}$ ,  $\text{CuC}_2\text{O}_4$ ,  $\text{CuCl}$  and  $\text{CuBr}$  are examples of copper compounds that show smoke suppression. The study has investigated synergism of mixed-metal oxides of copper in smoke suppression. It has shown that combination of  $\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$  and  $\text{CuSnO}_3$  has strong synergism in the reduction of smoke [103]. This synergism might result from the action of different mechanisms: one is Lewis-acid-promoted crosslinking caused by acids such as  $\text{CuCl}_2$ ,  $\text{SnCl}_4$ , and  $\text{MoO}_2\text{Cl}_2$ , while another is a reductive crosslinking caused by Cu (0).

## 2.11 Other metal compounds

Iron oxides including ferric oxide ( $\text{Fe}_2\text{O}_3$ ), yellow iron oxide ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), and black iron oxide ( $\text{Fe}_3\text{O}_4$ ) are considered smoke suppressants. They also show fire retardancy effects in halogenated polymers. The main barrier to using these compounds is their colour [72]. It has been shown that a very small amount of an organometallic compound of iron named Ferrocene with the chemical formula  $\text{Fe}(\text{C}_5\text{H}_5)_2$  can noticeably decrease the smoke and aromatics in the combustion of PVC [104]; However, its colour and high volatility (boiling point:  $249^\circ\text{C}$ ) made this compound an unsuitable additive. Other studies have shown that incorporating iron oxides in PVC/ ABS blends cause a linear correlation between smoke suppression and char formation [105].

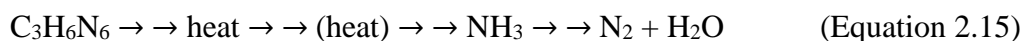
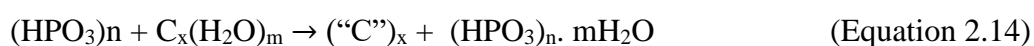
Metal chelates are also used as flame retardants and smoke suppressants for thermoplastic polymers and their effectiveness can synergistically be increased by halogen compounds [106]. Another study has been conducted on the synergistic behaviour of metal chelates containing Cu, Fe, Ni, Co and Zn in combination with  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  [91]. It has been proven that metal chelates, such as bis (acetylacetonate) copper (II) [ $\text{Cu}(\text{acac})_2$ ], tris (acetylacetonate) iron(III) [ $\text{Fe}(\text{acac})_3$ ], bis (acetylacetonate) nickel(II) [ $\text{Ni}(\text{acac})_2$ ], bis (acetylacetonate) cobalt(II) [ $\text{Co}(\text{acac})_2$ ] show improved fire retardancy and smoke suppression properties in conjunction with  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ . According to another study, low-melting point sulfate glasses were prepared by combining:  $\text{K}_2\text{SO}_4$ ,  $\text{NaSO}_4$ ,  $\text{CaSO}_4$  with  $\text{MSO}_4$  ( $\text{M} = \text{Cu}, \text{Zn}, \text{Ni}, \text{Mn}$ ) and investigated their smoke suppression and flame retardancy effects [85]. The role of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  sulfates lead PVC to crosslink to generate char and, additionally, the molten sulfate glasses can glue the char together and enhance its integrity and as a result, it acts as a heat barrier for both char and undecomposed PVC.

## 2.12 Melamine compounds

Melamine contains 67 wt% nitrogen and it is recognized as an inexpensive and thermally stable compound. It easily disperses in many thermoplastics and it is also commercially available in a wide range of particle sizes. Melamine is a blowing agent used in intumescent systems in combination with pentaerythritol and ammonium polyphosphate [107]. Generally, an intumescent formulation consists of three materials:

1. Carbon rich polyhydric compound (e.g., pentaerythritol, polyalcohols, starch, pentaerythrite)
2. An organic acid donor compound (e.g., ammonium polyphosphate)
3. A blowing agent (a nitrogen containing compound) (e.g., melamin)

At high temperatures, an acid donor compound, such as ammonium polyphosphate release polyphosphoric acid (Equation 2.13) which reacts with carbon-donor compound (e.g., polyalcohol) to form charring and C-P residue (Equation 2.14). Additionally, melamine decomposition at high temperatures leads to the gas formation (Equation 2.15). Gases and water released from the reactions cause blowing of the carbonizing mass and finally a charred solid foam which acts as an intumescent fire retardant [108].



Besides the application of melamine as one of the components in intumescent fire retardant systems, it should be noted that melamine alone can also retard fire by its own role in several ways [109]. Firstly, melamine sublimes at about 350° C. During sublimation, a considerable amount of energy is absorbed, which causes an enormous cooling effect and sublimated melamine also dilutes the gaseous combustibles. Secondly, Nitrogen which is a combustion product of melamine is an inert diluent. Thirdly, in the vapour phase, melamine may dissociate into cyanamide which is an endothermic reaction and lead to more cooling. Furthermore,

released ammonia from the further decomposition of melamine and cyanimide has a flame retarding effect.

A study has proven two about inorganic melamine salts as fire retardants and smoke suppressants for PVC. It showed that melamine molybdate and melamine tungstate can form a char layer and consequently decrease fire parameters, such as heat release rate (HRR) and smoke density rate (SDR) [110].

Another study has shown that melamine hydroxystannate (MASN) or a composite of melamine hydroxystannate and zinc hydroxystannate (MAZSN) can be used as effective flame retardants and smoke suppressants for PVC. MASN or MAZSN and PVC form a novel intumescent system in which PVC acts as a carbonization agent while zinc hydroxystannate  $[\text{Zn}^{2+} \text{Sn}(\text{OH})_6^{2-}]$  acts as the acid source. As explained before,  $\text{Zn}^{2+}$  accelerates dehydrochlorination reactions and promotes early crosslinking in the solid phase. Released melamine and hydrogen chloride act as the blowing agent. Additionally, metal ions left in char residues improve the stability of the char [111].

## 2.13 Expandable graphite

An oxidized form of graphite comprising intercalated guest species (e.g., sulfuric acid anions) between the graphene layers is called expandable graphite and it has good intumescent flame retardant and antistatic properties for many polymers. It is referred to as expandable because when it is exposed to high temperatures, it starts exfoliating and during exfoliation, it expands quickly in a worm-like way to produce vermicular graphite with a low density. Expandable graphite is commercially produced by liquid-phase graphite-sulfuric acid reactions with the presence of strong oxidants such as  $\text{KMnO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  [112, 113]. A study has investigated expandable graphite as a fire retardant additive for flexible PVC. It has shown that even adding only 5 wt. % expandable graphite reduces the peak heat release rate and the total heat release of flexible PVC. It reported that the effectiveness of samples with expandable graphite on fire retardancy is due to two general parameters. Firstly, the massive expansion of the expandable graphite at the exposed surface causes a heat barrier to heat transfer to the interior substrate. This reduces the rate of pyrolysis and slows down the rate at which combustible fuel is generated. Secondly, inert gases ( $\text{CO}_2$  and  $\text{SO}_2$ ) from the exfoliation of the expandable graphite and HCl emitted by the degradation of the PVC are released at the same

time. These gases dilute the flammable air-fuel mixture and lead to early flame out and inhibit further pyrolysis. This study has also shown that the expandable graphite, unlike many other flame retardant additives, did not decrease the degradation temperature of the matrix polymer [114]. This is while many fire retardants decrease the decomposition temperature of PVC because of their effects on changing the pattern of heat degradation by promoting early dehydrochlorination and crosslinking and early char formation[85].

## **2.14 Flame retardant coating**

One approach to providing fire retardancy to polymer is the surface modification of polymer by a fireproof coating. In a fire retardant coating system, fireproof properties are concentrated at the surface of the polymer as a coat. Thus, the bulk properties of the polymer, such as mechanical properties, may remain unchanged. Fire retardant coatings can be categorized as either intumescent or non-intumescent systems according to their mechanism of action. As discussed in the previous section, intumescent formulations contain a mixture that is able to expand and generates a porous carbonaceous residue on the surface of the material in exposure to fire, and finally protects the underlying polymer from heat, oxygen and fire propagation. While non-intumescent coating contains fire retardant additives and inhibits fire spread without the formation of remarkable foaming residue and voluminous char.

Coatings can be applied to the polymer by brush, spray, roller methods, or immersing of the polymer into the coating solutions with subsequent drying of solvent. These techniques are associated with some disadvantages including limited adhesion and high consumption of chemicals and energy. Recently, advanced methods such as UV-curing technology, Plasma technology, sol-gel process, layer-by-layer assembly approach, and physical and chemical vapour deposition, [115].

## **2.15 Compounding PVC with fire-retardants and other additives.**

Fire retardants are not the only additives that are added to the PVC because PVC itself has fire retardant characteristics due to its high halogen contents. several other additives are

incorporated into the PVC resin to improve its processing and impart required characteristics such as plasticizers, thermo-stabilizers, UV stabilisers, antioxidants, lubricants, colourants and fillers. The decomposition temperature of pure PVC is lower than its melting point, and additives must be added to retard the heat of decomposition and lower melting point. Those additives that retard heat decomposition are heat stabilizers and those that lower melting point and T<sub>g</sub> are known as plasticizers. PVC is not stable when exposed to light and heat. Heating PVC to above 100 °C causes the release of gaseous HCl which acts as an autocatalyst for the degradation, liberating an extra amount of HCl. As this autocatalytic reaction initiates at around 100 °C, during the process of PVC as pure polymer without the heat stabilizer, PVC would decompose at the required temperature for extrusion or moulding (150 °C– 200 °C). Plasticizers are other necessary additives for commercially used PVC. They make PVC more flexible, softer, and easier to handle. As mentioned earlier, primary plasticizers are a group of plasticizers which have good compatibility with PVC resin and can be loaded in large quantities, while secondary plasticizers have low compatibility with PVC. As a result, for price and compatibility optimization of PVC formulation, secondary plasticizers are usually used together with a primary plasticizer. It is notable that the primary plasticizer available in flexible PVC can somehow act as a lubricant because of its properties in decreasing melting viscosity and increasing the flow rate of PVC. Accordingly, flexible PVC compounds have the ability to be processed at lower temperatures and need less heat stabiliser in comparison with rigid PVC compounds [116].

## **2.16 Heat stabilisers**

As the heat degradation mechanism of PVC is the same in the presence of fire, an ideal and strong stabiliser can also play a role as a fire retardant additive.

As mentioned before, degradation (Figure 2-2) starts with a zipper elimination mechanism which is an autocatalytic dehydrochlorination reaction that finally causes the formation of a conjugated double bond (polyene).



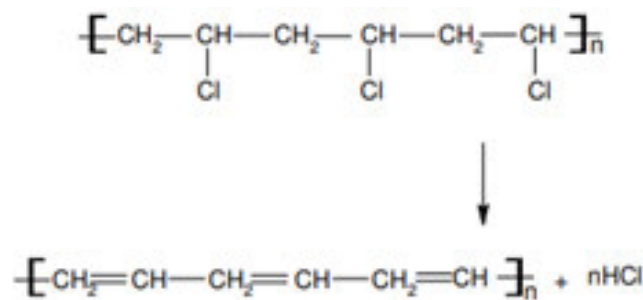


Figure 2-2 thermal degradation of PVC

Actually, allylic chlorine compound (Figure 2-3) which is a structure formed after the loss of the first HCl, motivates the next release of HCl and repeats the process to the consequent formation of conjugated double bonds. Therefore, the release of HCl initiates at 70°C (the glass transition temperature) and continues to be the main volatile compound up to 330°C [117].

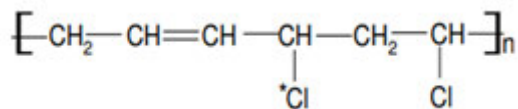


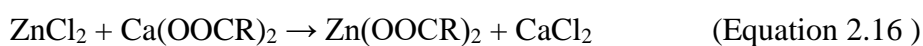
Figure 2-3 Allylic chlorine atom

Another volatile formed during the heat degradation of PVC is Benzene, which is the result of the intramolecular cyclization of polyene. It has been reported that between temperatures of 200-360 °C, almost 15% of polyene transforms to benzene, while at lower temperatures (150 to 160°C) only small traces of benzene have been reported.

Thermal stabilizers are very essential additives in PVC compounding and cause the processing of PVC to commercial materials to be accomplished above 160 °C which is higher than 70 °C (glass transition temperature) [117].

Generally, the thermal stabilizers act by absorbing the produced HCl and/or replacement of labile and active groups such as allylic chlorine atoms in the PVC [118]. Lead salts and metal soaps such as Pb, Cd, Ba, Ca are the common types of thermal stabilizers used in industry. Metal soaps are safer than lead salts but their efficiency is not as good as lead salts. In general, PVC thermal stabilizers based on their mechanism of action can be categorized as primary stabilizers and secondary plasticizers [117]. Primary stabilizers are able to react with labile

chlorine atoms (e.g. allylic or tertiary chlorine atoms), so they inhibit further dehydrochlorination and stop long polyenes formation. As a result, short-time discoloration of PVC is prevented by this type of stabilizer. Secondary stabilizers don't protect resin against early discoloration but delay degradation of the resin by reacting with generated HCl. As HCl is the key factor in catalysing and accelerating thermal degradation, scavenging this gas by secondary stabilizers delay degradation [119]. For example, strongly basic carboxylates that have weak or no Lewis acidity (e.g. Ca, K or Ba) are only HCl scavengers and are categorized as secondary stabilizers. On the other hand, Cd and Zn carboxylates, which have stronger Lewis acidity properties, are able not only to scavenge HCl but also to react with labile chlorine atoms [119]. The disadvantage of Zinc stearate as a thermal stabilizer for PVC is the ZnCl<sub>2</sub> formation, which can enhance and accelerate the dehydrochlorination of PVC, while, CaCl<sub>2</sub> cannot enhance dehydrochlorination. However, it has been investigated that such sudden dehydrochlorination occurs only after ZnCl<sub>2</sub> concentrations reach a suitable level [119-121]. As an alternative, synergism and combination effects of calcium and zinc soap have been studied [121]. In this case, coordination sites of zinc may be filled with carboxylate anions from calcium soap (reaction Equation 2.16).



## 2.17 Phenolic Structures

Compounds containing phenolic structures can act as an antioxidant and thermal stabiliser. Phenolic antioxidants act as a radical scavenger. In other words, peroxy radicals formed during oxidation are converted to hydroperoxides by reaction with phenolic compounds. Phenolic compounds themselves change to phenoxy radicals. The phenoxy radicals can again scavenge another peroxy radical in different ways (Figure 2-4) [122].

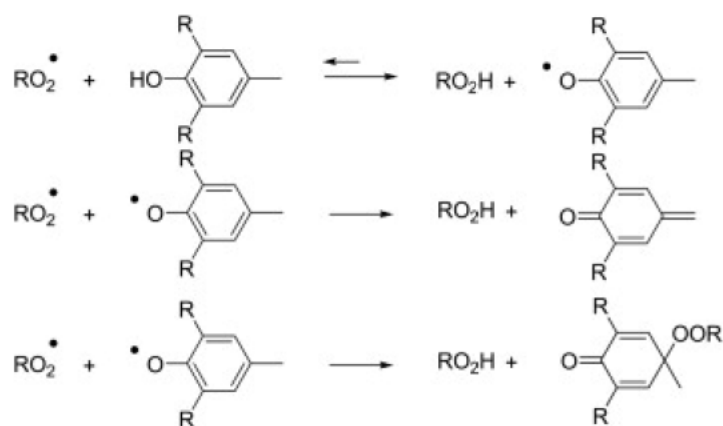


Figure 2-4 Mechanism of phenolic compounds as an antioxidant

Compounds containing phenolic structures can also act as a thermal stabilizer by reaction and scavenging released HCl. Especially in the presence of metal ions, the chelated metal structure of such compounds is highly able to react with HCl and absorb this gas to retard thermal degradation. For example, Humic substances, such as humin, humic acid and fulvic acid, showed great efficiency in improving the thermal stability of the PVC [123]. Another example of such a thermal stabilizer is Pentaerythritol-Zinc (Penzinc), which can be obtained by reacting with pentaerythritol and ZnO. This structure can absorb released HCl with high reactivity ([124]. Table 2-1 demonstrates TGA data obtained by this work.

Type	First decomposition temperature/ °C	Rate of mass loss/ % min <sup>-1</sup>
Pure PVC	269.5	15
PVC/ 2 phr Penzinc	275.8	14
PVC/ 4 phr Penzinc	270.3	15.5
PVC/ 6 phr Penzinc	264.3	13

Table 2-1 TGA results of different compositions of Penzinc as the thermal stabilizer for PVC

Another study has investigated the influence of calcium on tannin structure as an HCl scavenger and thermal stabiliser [125]. Tannin is a natural compound and can make chelated complexes with a lot of metal ions including calcium. This study has also shown that the mechanical properties of PVC are improved by this type of stabilizer. Another study also

investigated tannin-Ca complex as the stabilizer for PVC and compared this type of stabiliser to commercial stabilizers [126]. This study prepared variable compositions: (1, 2, and 3) part per hundred ratio (phr) of tannin-Ca complex in the presence of 10 phr Di iso octyl phthalate (DOP) as plasticizer in all PVC formulations by melt mixing using internal mixer at 165°C and gained the following results (Table 2-2).

Type	First decomposition temperature/ °C	Rate of mass loss/ % min <sup>-1</sup>
PVC/Commercial stabilizer	255	15.7
PVC/ 1 phr tannin.Ca complex	285	8.88
PVC/ 2 phr tannin.Ca complex	280	7.77
PVC/ 3 phr tannin.Ca complex	280	7

Table 2-2 Comparison of TGA results of different compositions of tannin-Ca as the heat stabiliser for PVC

Another study used Cd (Cadmium) as a metal ion for making a complex with tannin [127]. The study investigated this type of thermal stabilizer in different ratios on the heat stability of PVC and also compared the obtained results with commercial stabilizers. Table 2-3 shows the TGA results of this work.

Type	First decomposition temperature/ °C	Rate of mass loss/ % min <sup>-1</sup>
PVC/ 2 phr commercial stabilizer	279	14.47
PVC/ 1 phr tannin.Cd complex	282	12.8
PVC/ 2 phr tannin.Cd complex	281	12.77
PVC/ 3 phr tannin.Cd complex	280	12

Table 2-3 comparisons of TGA results of different compositions of tannin-Ca as the heat stabiliser for PVC

According to TGA data of these studies, pentaerythritol-zinc and tannin-cadmium do not show a noticeable difference in decomposition temperature and mass loss of PVC. Whereas, tannin-calcium shows a better heat stabilising effect for PVC not only by increasing decomposition temperature but also by decreasing mass loss of PVC.

## **2.18 Evaluation of fire retardants, thermo stabilisers and smoke suppressants**

The flammability and smoke emission properties of PVC formulations are determined and measured by different small and large-scale tests including cone calorimetry, LOI and TGA apparatuses.

A cone calorimeter is a benchtop-scale test that measures the response of a material to a constant heat flux. This device mainly consists of an ignition source, an electric heater, and a gas collection system. The cone calorimeter quantitatively investigates parameters such as heat release rate (HRR), total heat release (THR), time to ignition, and mass loss [128, 129]. If it is added to a gas analyser, it is also able to measure the production of smoke and toxic gases.

LOI device stands for 'limiting oxygen index' device in which a small part of the specimen is clamped vertically and the minimum concentration of oxygen that will support the burning of a polymer is measured [70]. Thermal gravimetric analysis (TGA) is another method which is commonly used for interpreting PVC degradation. In this test, the mass of a sample is evaluated by the temperature increases in a controlled atmosphere. The weight of the PVC samples decreases due to material decomposition or the production of volatile gases, but in other materials, the weight could be gained due to chemical reactions or gas absorption. The TGA curve of PVC usually contains two stages: the first stage is mainly because of the releasing HCl and the decomposition of plasticiser and the second stage is mainly because of the cyclisation of conjugated polyethylene to form and emit aromatic compounds such as benzene[130].

## **2.19 Ultraviolet radiation and weathering effects on PVC**

Natural weathering leads PVC to become brittle, coloured and causes a decline in its mechanical properties such as elasticity, tensile strength, and impact resistance. Ultraviolet radiation is one of the natural weathering factors which negatively affects PVC.

## **2.20 Ultraviolet (UV) radiation**

The Sun emits ultraviolet radiation with a wide range of wavelengths from 10 nm to 400 nm. As the earth's atmosphere absorbs and scatters (filters) UV wavelength shorter than 290 nm, the UV part of terrestrial sunlight is between 290 nm – 400 nm. When UV light interacts with a substance, the energy of UV photon is transferred to the electron of a molecule, causing an excited state. For a molecule in order to be able to absorb photons of a certain wavelength, it must have electrons in suitable energy levels so that the difference in energy between the states before and after absorption (excited state of the molecule) equals the amount of energy of incoming radiation and a particular photon. Based on quantum theory, a photon of electromagnetic waves carries a discrete quantity of energy which depends on its frequency ( $\nu$ ). According to Planck's Law, the energy of radiation of a particular wavelength can be calculated by (Equation 2.17) and consequently, the excitation energy per mole of the molecule can be obtained by (Equation 2.18)

$$E = h * \nu \quad (\text{Equation 2.17})$$

$$E = N h \nu = N h c / \lambda = 119627 / \lambda \text{ [KJ/mol]} \quad (\text{Equation 2.18})$$

where:

E= energy of radiation

$\nu$ = frequency of radiation

h= Planck's constant =  $6.63 \times 10^{-34}$  in J s

$\lambda$ = wavelength of radiation in nm

c= velocity of light =  $2.998 \times 10^8$  in m /sec

N= Avogadro's number =  $6.022 \times 10^{23}$  in  $\text{mol}^{-1}$

Thus, the amount of photon energy is specific and cannot be divided such that the energy of a photon is either absorbed or rejected. This property restricts which particular wavelength of radiation is able to be absorbed by a particular molecule. As a result, it can be concluded that all molecules are not able to absorb all UV wavelengths. A molecule which is able to absorb a given UV wavelength is termed a chromophore for that wavelength. It should be also noted that energy of UV radiation must be first absorbed by a substance in order to cause degradation or any other changes in molecular structure.

Surprisingly, PVC doesn't have any chromophores for the wavelength range of terrestrial solar radiation and, therefore, it is not capable to absorb UV radiation of any terrestrial solar radiation. As a result, Photodegradation and poor light stability of PVC are related to photosensitive structures such as aromatic plasticisers, polymerisation initiator residues, and other impurities that act as absorbing chromophores at these wavelengths which have been formed during the polymerisation or processing. The common reactive functional groups are alkene linkages, ketones, hydroperoxides, aromatic structures and others.

Among the mentioned impurities, conjugated alkene linkages play the most important role as the light-absorbing chromophore to initiate the photodegradation of PVC. Available heat during the Processing and storage of PVC causes some dehydrochlorination and consequently, dienes, trienes or longer polyenes might be formed in the chemical structure of PVC. Therefore, a good heat stabilizer can somewhat play as a UV stabilizer as well due to its ability to prevent the formation of polyene chromophoric groups.

The conjugated bonds are considered initially as primer absorbing chromophores even if their concentration in the total structure of the polymer is very low. Absorbed UV radiation by polymer causes it to move from the ground state to a higher energy level (excited state). Substances in their excited states have very short-life which release their energy and disappear by different routes. In this case, the most probable reaction is photocleavage of allylic C-Cl bond, due to its low dissociation energy as seen in Figure 2-5 [131].

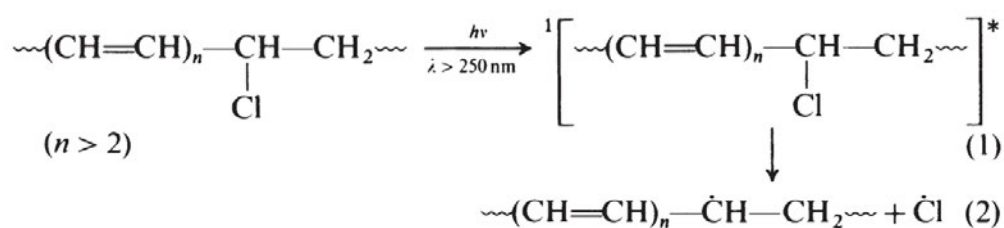


Figure 2-5 cleavage of allylic C-Cl bond of PVC by UV radiation

The radical substance formed in Figure 2-5 is very active and can undergo the following reactions:

Chlorine radical is very active toward the abstraction of hydrogen, so dehydrochlorination occurs and conjugated polyene sequences expand as the primary degradative product.

Secondary photochemical reactions of these polyene radicals are chain scission, cross-linking and oxidation. These free alkyl radicals can react with oxygen available in the air (photo-oxidation), or chain reaction in the polymer (chain scission or crosslinking) and generally lead to polymer degradation.

Overall, it can be concluded that the photo ageing mechanism of PVC proceeds with the radical mechanism. UV light breaks the chemical bonds in PVC and makes free radicals which are the main factor for the activation of chemical reactions such as the elimination of HCl to form polyene, crosslinking and chain scissions. These chemical reactions cause several changes in the microstructure and properties of PVC.

All these photochemical reactions lead to colour changes, brittleness, and loss of physical properties such as elongation, tensile strength, and others. Thus, photo-stabilization of PVC against the damaging effects of sunlight is very necessary. The photo-stabilization means elimination or at least retardation of photochemical or photo-physical reactions that occur in polymer by solar radiation. This can be obtained in various ways, depending on the type of stabilizer. There are four different types of UV stabilizing systems depending on their mechanism of action including, an ultraviolet absorber, an ultraviolet screener, an excited-state quencher, and a free radical scavenger. Some stabilizers can impart more than one of these routes in the inhibiting photo-degradation of polymer. Some UV stabilizers are introduced below:

### **2.20.1 UV Screening Pigments**

UV screening can be achieved by reflective coating or by pigments. Some pigments can reflect sunlight from the surface of the polymer. These pigments can be applied to the polymer by coating or incorporation. For example, Titanium dioxide which is used as the white pigment can impart UV stability to the polymers as well. The main disadvantage of Titanium dioxide is its high cost which restricts its usage as a UV stabilizer in big industries such as structural projects which contain large and multiple surfaces to be modified. Generally, white pigments have better reflectance than coloured pigments in the 300-400 nm wavelength range [132].

The maximum amount of TiO<sub>2</sub> used in PVC is 5%, higher contents might lead to surface permeation of titanium dioxide particles and increase the risk of chalking. In order to impart



UV protective effects of TiO<sub>2</sub> without chalking or developing bright colours in the mass, 1% is recommended [80]. The increasing amount of Titanium dioxide is sometimes used for aesthetic reasons (improving whiteness).

### 2.20.2 UV Absorbers

The chemical structure of these compounds is so that they have high absorption at wavelength 290-400 nm regions. For example, benzophenones and benzotriazoles are good UV absorbers that absorb UV radiation and dissipate it as heat. The advantage of benzotriazole is that it can be used in low amounts, eg, below 0.5% [133]. The UV absorber compounds can compete with all chromophores in the polymer and avoid photo-initiation as the first step of photo-degradation. UV absorbers can be combined with other kinds of UV stabilizers which are able to avoid other steps of the photo-degradation.

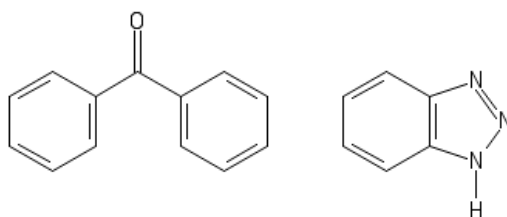


Figure 2-6 UV absorber chemical structures

### 2.20.3 Hindered amine photo-stabiliser (HAPS)

These compounds avoid degradation of the polymer by scavenging free radicals generated by photo-oxidation of the polymer. Hindered amine photo stabilizers inhibit further radical oxidation by reaction with polymer peroxy radical (ROO•) and alkyl polymer radicals (R•) (Figure 2-7).

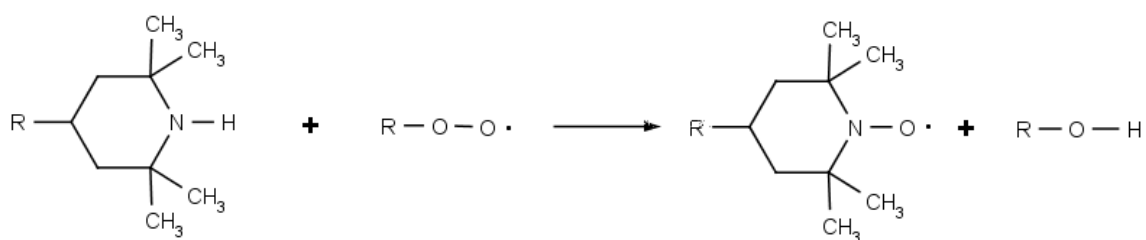


Figure 2-7 Mechanism of action of HAPS

Although HAPS can cause very good light stability, co-additive interactions should be considered during formulation. It is known that phenolic antioxidants, some fire retardants and even pollutants might interact with HAPS under particular conditions. For example, the acid generated by the brominated flame retardants can reduce the effectiveness of HAPS [72].

#### 2.20.4 Coating PVC

Coating polymer with a substance which is resistant to UV is another way to protect PVC against weathering. The coating based on highly cross-linked epoxy-acrylates has a good light-screening effect which ensures the protection of PVC against UV. This coating also provides a very good surface hardness. The disadvantage of this type of coating is its poor adhesion on PVC [134]. In the present research, this issue will be considered and addressed, offering several suggestions to enhance the adhesion of the coating to PVC.

#### 2.20.5 Composite and nanocomposite materials

Inorganic fillers have the ability to shield sunlight and improve the UV ageing properties of PVC. Other advantages of using inorganic fillers in PVC are due to their role in enhancing mechanical properties and decreasing the cost of PVC. However, good and uniform dispersion of inorganic fillers in PVC matrix is not easy because of their different interfacial properties [135]. Inorganic fillers such as  $\text{TiO}_2$ ,  $\text{CaCO}_3$ , and  $\text{ZnO}$  can act as UV screening agents by absorbing or reflecting UV light. Moreover, their efficiency is enhanced when they are

uniformly and homogeneously dispersed in PVC [135]. For good dispersion, inorganic fillers should be modified by coating (surface treatment). The most common coating for this purpose is fatty acids and their salts. For example, coating  $\text{CaCO}_3$  with stearic acid is commercially available and commonly used due to its low cost and efficiency in PVC processing .. Generally, coatings cause a hydrophobic surface on the inorganic fillers which inherently are hydrophilic. Since PVC and other polymers are hydrophobic and non-polar, such coatings modify the degree of interfacial adhesion between polymer and filler, thus consequently, leading to better dispersion of fillers [72].

According to a study, PVC/ $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{O}$  nanocomposites have high UV shielding efficiency when compared with standard PVC films [136]. This composite has also shown improved thermal stability.

## **2.21 Fire safety of formworks in buildings**

PVC SIP formworks like other building elements must be designed to last for so many decades. During this long period, all building parts including SIP formworks are subjected to several manmade and natural hazards. Fire hazard is one of the severe hazards in buildings that can lead to the partial or complete collapse of the structures and causes a serious threat to the life of inhabitants and property. Thus, to reduce the impact of fire incidents, it is necessary to assign fire safety criteria in buildings. Fire safety includes the set of practices to avert, stop, or prevent fire incidents and manage the spread and consequences of intentional or accidental fires by keeping the losses to the minimum level [52]. Fire safety in buildings is based on building standards and codes of practice which issue guidelines and regulations for the assessment and design of structural elements for fire resistance. Although strategies and specifications are different in these codes, all are derived from strict and established principles to assure fire safety in buildings. Building standards and codes apply three main criteria based on the function of building assemblies. These criteria include a) stability and inability to tolerate applied loads in fire incidents; b) integrity and inability to avoid fire development; and c) insulation and inability to isolate the unexposed surfaces in fire exposure. Most of the standards, according to which the performance of buildings formworks in fire is examined, have been studied in detail and summarized in Table 2-4.

Test	Description	Exposure Condition	Outputs and results	Findings
<p style="text-align: center;"><b>AS ISO 9705-2003</b></p>	<p>-full-scale room test for surface products which involves combustion process from ignition to a fully developed room fire.</p> <p>-it simulates a fire that under well ventilated conditions begins in a corner of a small room with a single open doorway.</p>	<p>-in contact with a propane gas burner which produces a heat release rate of 100 KW in 10 min, and then 300 KW for the following 10 min</p> <p>- the burner shall also be in contact with corner wall and be placed on the floor in an opposite corner to the doorway wall.</p> <p>- Natural grade propane (95% purity) shall be supplied to the burner.</p> <p>- A standard ignition source is specified, but other alternatives are allowed</p>	<p>- evaluation of fire growth and surface flame spread</p> <p>- measurement of total rate of heat release</p> <p>- time to flashover.</p> <p>- measurement of production of smoke and gases including carbon monoxide(CO) Carbon dioxide (CO<sub>2</sub>), Hydrogen Cyanide (HCN), Nitrogen oxides NO<sub>x</sub>, Hydrocarbons (CH<sub>n</sub>).</p> <p>-Additional information such as mass flow in and out the doorway.</p>	<p>-contribution to fire growth because of surface product.</p> <p>-the method is <b>not</b> intended to evaluate the fire resistance of a product.</p>
<p style="text-align: center;"><b>AS/NZS 3837:1998</b></p>	<p>- cone calorimeter test based on usage of</p>	<p>0-100 KW/m<sup>2</sup> either with or without a spark ignition</p>	<p>-Heat Release Rate (HRR)</p>	<p>The less ignition time of the material, the faster the material is</p>

	<p>oxygen consumption calorimeter</p> <p>-it works based on the relationship that is approximately <math>13.1 \times 10^3</math> kJ of heat is released per 1kg of oxygen consumed</p> <p>-Cone calorimetry Is applicable for essentially flat homogenous products</p>	Normally 50 KW/m <sup>2</sup>	<p>-Smoke Release Rate (SRR)</p> <p>- mass loss rate</p> <p>-ignitability</p> <p>-time to sustained flaming</p> <p>- effective heat of combustion</p>	capable to ignite and the risk of fire is higher.
<b>AS 5637.1:2015</b>	<p>-Test Certificates</p> <p>-the NCC stipulated that test certificates quoting a group number must be compliant in accordance with AS5637.1:2015.</p> <p>test certificates must also state the test method used, e.g. “tested in accordance with ISO9705:2003 (R2016) and AS5637.1:2015” or AS5637.1</p>	-	<p>-determination of group number</p> <p>-Average Specific Extinction Area (ASEA)</p> <p>-time to 50 KW/m<sup>2</sup></p> <p>-the time in seconds when heat release rate reaches 50KW/m<sup>2</sup></p> <p>-Smoke growth rate index</p>	<p>-determining the suitability of wall and ceiling</p> <p>linings in different building classes based on the group number expressed from 1 to 4</p> <p>-material tested in accordance with AS5637.1 determines the Material Group number.</p>

<p><b>AS/NZS 1530.3:1999</b></p>	<p>Methods for fire tests on building materials, components and structures</p>	<p>near a pilot flame that doesn't touch the specimen which</p> <p>increasing radiation intensity recorded by radiometer by 1.4 KW/m<sup>2</sup></p> <p>- specimen moved towards the heater, in steps over a period of 20 min or until ignition</p>	<p>-ignitability</p> <p>-flame propagation</p> <p>-heat release</p> <p>-smoke Release</p> <p>- ignition time</p>	<p>-classification for ignitability (ignitability index)</p> <p>-classification for spread of flame (if the ignitability index is zero, the spread of flame index and heat evolved index shall be deemed to be zero</p> <p>- heat evolved index and smoke developed index</p>
<p><b>AS 1530.1 -1994</b></p>	<p>combustibility test</p>	<p>750°C</p>	<p>-specimen centre temperature rise</p> <p>-specimen surface temperature rise</p> <p>-duration of sustained flaming</p> <p>-weight loss</p>	<p>combustible or not</p>
<p><b>AS 5113:2016</b></p>	<p>test method for classification of external walls of buildings</p>	<p>specimen should be exposed to the required heat flux for a minimum of 30 min</p>	<p>-total mass of debris and number of fragments</p> <p>-specimen temperatures</p>	<p>- categorization for external walls of buildings in accordance with their capability to limit the spread of fire via:</p>

			-duration and extent of flaming on the side of specimen exposed to the radiant heat	i) the external wall ii) between adjacent buildings  -tendency of external walls to limit falling debris  -building-to-building fire spread classification.
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Table 2-4 some relevant standards for examination of fire safety in the buildings

According to table 2-4, one of the most known fire testing apparatuses is the cone calorimeter. Several parameters can be determined through this instrument, such as carbon monoxide production, time to ignition (TTI), mass loss rate (MLR), heat release rate (HRR), total heat release (THR), and so on. The flammability of the membranes and the flue gas properties of the materials can also be evaluated by the experimental data obtained from the cone calorimeter [53]. According to the standard, specimens to be tested are burned in ambient air conditions, while being subjected to a predetermined initial test of external heat flux, which can be set from 0 to 100 KW/m<sup>2</sup>. It is obviously more desirable to have a formulation, which is more resistant to ignition under lower radiation flux.

Ignition time is one of the principal parameters to analyse the burning property of materials. The risk of fire can be determined by ignition time: the faster a material is capable to ignite, the higher the risk. In other words, by applying different external heat fluxes, the minimum heat flux for ignition can be a factor for analysing the resistance of materials to combustion. Figure 2-8 shows a cone calorimeter instrument.



Figure 2-8 A photo of a cone calorimeter (source: Suzhou Yangyi Vouch Testing Technology Co., Ltd)

Full-scale room fire test (AS ISO 9705-2003) is another important standard test for evaluating the fire performance of plastic ceilings and PVC room walls which is mentioned in Table 1-1. In this test, PVC formworks are placed in a corner of a room with an open door, under ventilated conditions. For this test, adequate precautions must be taken to protect health against risks associated with the combustion procedure and extreme temperatures from the ignition stage to a fully grown room fire. It is mandatory for all operators to wear protective clothing and a face shield. Additionally, equipment for extinguishing a fully grown fire must be accessible when doing this test. Figure 2-9 shows a room-scale fire test.



Figure 2-9 Room-scale fire test (source: IXL FR Panel)



## **2.22 Sources of fire hazard**

Fire hazard is related to all factors existing in a building that can lead to ignition, fire initiation and growth, and inability to escape or obstruction to firefighting equipment [52, 54]. All live flames, electrical faults, fireworks, hot surfaces, heaters, and arson are included as ignition sources of flame in a building. Moreover, wildfires coming from forests and bushfires are considered another source of fire in Australia and any other populated areas adjacent to dense vegetation [55]. After initial ignition occurs, fire intensity may be increased by some factors including a high amount of combustible household items, rubbish, unsuitable storage of items, volatile flammables (paints, petroleum etc) and flammable building elements such as timber and composite panels [56]. Also, the existence of glass partitions, large windows and false ceilings in a building can lead to rapid fire development by supplying constant oxygen and fuel to fire [52, 57].

## **2.23 Fire performance of PVC materials used in building formworks**

Fire safety is one of the most important factors in building design. The science and art of designing structures for life safety require many measures based on national codes and regulations to prevent or at least reduce the likelihood of unwanted fire, which results in property damage, injuries or fatalities. Thus, the construction industry allocates large budgets on fire safety measures to protect people and properties from the tragic consequences of fire. The allocated budgets due to additional measures are even greater in sensitive and public structures such as shopping centres, schools and theatres [58-61]. The role of plastic products in the fire safety of buildings should be carefully considered in order to reduce their contribution to fire propagation. Some types of plastics like PVC, have inherently good fire performance because of the halogen element in their chemical formulation [42].

Fire hazard in the building industry depends on the structural elements of the buildings, installation of building products and buildings contents. It means, PVC like other building materials, should be utilized for the right applications and conditions. Development and spread of structural fire are also dependent on the ignition source, meteorological factors, location of the building and quantity of substances [62]. A structural fire contains combustible and non-combustible materials. Organic compounds such as wood, plastics, and polymeric formworks

are combustible in a fire because of their carbon source. In fire incidents, these organic compounds release a significant amount of heat in addition to gaseous products which cause fire smoke hazards [63].

Fire incidents in structures start with an external ignition source. Polymers and other combustible materials start to burn and generate heat. The fire development is propagated further by the elevated heat release and high temperature of the surrounding areas [64]. When the fire has developed in an enclosed environment, to the point that a particular amount of organic substances is thermally decomposed and produces flammable gases (flash point). Then, the gas ignition leads to high fire propagation over the enclosed area, termed flashover which finally results in a fully developed fire. At this stage, the fire passes through walls, windows, ceilings and doors and extends to the adjacent areas until the entire building is engulfed. When the fire reaches its peak the room temperature can exceed 1000 °C [63, 65, 66].

## **2.24 Material fire properties related to PVC SIP formworks**

According to ISO/TR 20118:2019, typical combustible compounds have carbon and hydrogen in their chemical composition. The combustion product of hydrogen is water (H<sub>2</sub>O) and the combustion formation of carbon is carbon dioxide (CO<sub>2</sub>). These two elements have high heat of combustion, 32.8 kJ/g for carbon and 141.8 kJ/g for hydrogen [67]. As a result, compounds containing only hydrogen and carbon, known as hydrocarbons, produce the highest heat of combustion among almost all combustible compounds. On the other hand, the presence of any other elements, except hydrogen and carbon, in the chemical composition of a compound reduces the heat of combustion. For example, PVC has a chlorine atom and that is why it has a lower heat of combustion in comparison with Polystyrene, polypropylene, Paraffin wax, and Polyethylene. Additionally, PVC will not ignite easily and the exposure temperature to ignite PVC is generally higher than many other polymers. Another factor related to fire performance is the Oxygen Index (OI), which is generally high in PVC compounds. According to ISO 4589-2:2017, the Oxygen index is the minimum amount of oxygen needed for the combustion of a material in an oxygen/nitrogen environment. This is a factor, that indicates ease of extinction related to the combustion of a substance and the lower the oxygen index the more likely it is that the substance will continue burning. Substances with an oxygen index of more than 30 will burn only when the source of heat and flame is available, otherwise, they tend to extinguish.

The oxygen index factor is good for quality control and R&D purposes and it is not being used as a main factor for fire hazard prediction. PVC compounds show higher oxygen index values in comparison with many other polymeric compounds. Thus, PVC compounds are less likely to continue burning if the heat source is removed. Table 2-5 compares the fire properties of PVC with some other materials used in the construction industry [67-69].

<b>Substance</b>	<b>Gross heat of combustion (kJ/g)</b>	<b>Flash ignition temperature (°C)</b>	<b>Spontaneous ignition temperature (°C)</b>	<b>OI</b>
Polyethylene	47.7	343	349	17
Polypropylene	45.8	320	350	17.1
Polystyrene	43.7	352	492	17.7
PVC-P	11-27	330	>330	21-36
PVC-U	10-15	391	454	47

Table 2-5 Comparison of fire properties of PVC with some other materials used in construction industry

## 2.25 Logic behind the study

Formwork systems play an important role in the construction industry. Choosing an appropriate formwork system could lead to faster, more economical and more sustainable construction practices. In recent years, the application of plastic formworks in structures has been on the increase and research on plastic formworks has shown great success. However, several challenges still remain. In this project, we aim to take a closer look at this issue by overcoming the formulation barrier and tackling the remaining problems related to plastic formworks used in building and Infrastructure Engineering.

Actually, this study investigates how ingredients in building materials formulations may influence the fire resistance of buildings, and the safety of the occupants and the environment. This work also shows the importance of chemical properties of formworks such as heat

resistance, UV resistance and smoke suppressant properties in the future development and performance of formwork products.

This study, therefore, aims to present a new chemical formulation in order to achieve improved formworks aiming at overcoming the health hazards associated with fire accidents via retarding the heat decomposition of polyvinyl chloride PVC which leads to the formation of hazardous hydrogen chloride toxic fumes by reducing the speed of fire spread, UV resistance, and maintaining its mechanical strength.

# CHAPTER 3

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UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia

## 3. Materials, Instrumentation and Methods

### 3.1 Materials

In this PhD project, Ordinary Portland Cement and Ground Granulated Blast Furnace Slag were supplied from Cement Australia Pty Limited. Calcium aluminate cement and dipentaerythritol and other samples were provided by Parchem for construction Co/Dulux group of Australia. Pure PVC powder was provided by CSR Limited of Australia. Calcium Oxide, Magnesium Oxide, and Tetrahydrofuran were purchased from Sigma Aldrich Australia. Zinc Oxide was supplied by Merck.

### 3.2 Instrumentation:

#### 3.2.1 UV Weathering test chamber

Temperature, Humidity and UV Test Chamber belonging to Western Sydney University (AISI Li product, XU-1000 model with Internal Dimension: 1000 x 1000 x 1000 mm (W x H x D) and External Dimension of 1550 x 2150 x 1500 mm (W x H x D) was used for investigation of UV resistance of the samples. This chamber uses QUV fluorescent tube as a source (Figure 3-1). This device contains a total of 6 UV lamps located on the top of the trays. It simulates the influence of the sun by the fluorescent ultraviolet (UV) lamps, while dew and rain are simulated by the condensation of water and humidity.



Figure 3-1 UV test chamber , Western Sydney University

### 3.2.2 Vacuum Oven

A vacuum oven is generally used for drying or testing materials that are heat sensitive, oxidizing or easy to decompose in vacuum conditions. Vacuum environment decreases the boiling point of the material, so the vacuum oven can be simply applied to heat-sensitive materials. For instance, the vacuum drying method is able to reduce the drying time of the powdery or when granular samples are difficult to dry. In this project, samples were completely dried in a vacuum oven with vacuum pumps housed at Western Sydney University. The 26L vacuum oven is supplied by International Australia Supplier and is Manufactured in accordance with ISO 9001:2000 and ISO 12100-1:200 (Figure 3-2).



Figure 3-2 Vacuum Oven, at Western Sydney University

### 3.2.3 Thermo-gravimetric analyser (TGA instrument)

TGA measures the variation in the mass of a sample as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of air, nitrogen, helium, other gases, or in vacuum. A TGA consists of a sample pan supported by a precision balance that resides in a furnace to heat up or cool during the experiment. The mass of the sample is monitored during the experiment. A purge gas controls the sample environment that may be inert or a reactive gas that flows over the sample and exits through an exhaust. This device can analyse inorganic materials, polymers, metals, glasses, ceramics, and composite materials.

In this project, thermal analysis including TGA, differential thermogravimetry analysis (DTG) and Differential Scanning Calorimetry (DSC) were conducted with a NETZSCH STA 449F3 STA449F3B-0022-M instrument at Western Sydney university (Figure 3-3). In a heat flow DSC, the exothermic reactions release energy and the instrument must supply lower power to

the sample to keep the reference furnace and the sample at the same temperature. These exothermic reactions lead the sample to release heat and be hotter than the furnace, thus they point up. The reverse logic applies to endothermic reactions where energy is absorbed, thus, they point down in the DSC graph.

For TGA sample preparation, about 7 mg of the specimens were heated from 30-590°C at a linear heating rate of 10 Kmin<sup>-1</sup>. All runs were done in air atmosphere (N<sub>2</sub>/O<sub>2</sub>) at a flow rate of 25 ml min<sup>-1</sup>. Each test was carried out twice to ensure the results are repeatable and a mean value was reported. Table 3-1 summarizes TGA test conditions for all the runs of this project.



Figure 3-3 TGA instrument, Western Sydney University



Instrument	NETZSCH STA 449F3 STA449F3B-0022-M
Method used	30-590°C 10Kmin Al-pan P2=Air25mL Pro=Air25mL.ngb-d-sta
Mode	DSC-TG
Measurement Type	sample with correction
Correction	Correction for method 30-590°C 10Kmin Al-pan P2=Air25mL Pro=Air25mL
Crucible	Standard Al 25 µl, pierced lid 0.05 mm
Reference crucible	Standard Al 25 µl, pierced lid 0.05 mm
Reference Mass	0 mg
Sample determination mode	Manual
Atmosphere	N2/O2

Table 3-1 TGA test condition

### 3.2.4 FT-IR (Fourier transform Infrared)

FTIR is a vibration spectroscopy used to provide an infrared spectrum of emission or absorption of the material. This technology is able to characterize the molecular structure of a sample based on different stretching or bending vibrations of the different molecular bonds. In this project, Bruker Vertex 70 FTIR (Figure 3-4) of Western Sydney University is used to characterize and confirm the formation of new bonds in a complex product. This modern spectrometer (Bruker Vertex 70) has an attenuated total reflectance (ATR) accessory. ATR causes samples to be tested directly without extra sample preparation. In the FTIR-ATR method, samples were pressed towards an ATR diamond crystal. Thus there is no need to prepare KBr. FTIR-ATR unlike the normal FTIR peaks points upward. To ensure the results are reproducible, the FTIR analysis was repeated three times. The conditions of the method used in the experiment are summarized in Table 3-2.

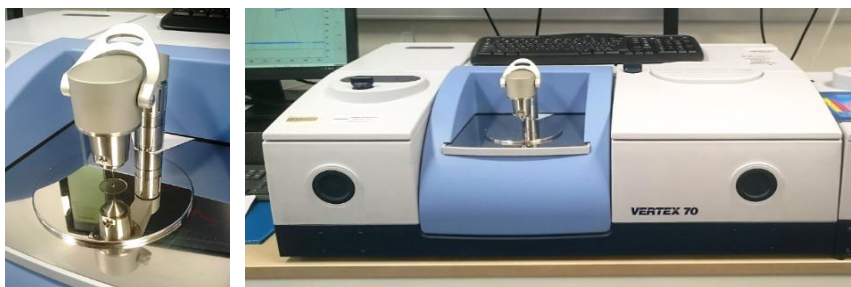


Figure 3-4 FT-IR instrument, Western Sydney University

Instrument	Bruker Vertex 70 FTIR
Scan Range	400 - 4000cm <sup>-1</sup>
Sample scans	32
Resolution	4cm <sup>-1</sup>
Aperture	6 mm
Stage used	Diamond ATR
Spectrum type	Absorbance
Background correction	Background correction is completed before each new sample set to correct for the environment in the laboratory.

Table 3-2 FT-IR condition

### 3.2.5 TGA-FTIR

Thermal gravimetric analysis can be interfaced with FT-IR to identify and measure the evolved vapours and gases. In this project, another model of TGA device of Western Sydney University (NETZSCH 449C Jupiter STA) attached to FT-IR device (Bruker Vertex 70 FTIR) of Western Sydney University (Figure 3-5) was used for gas characterization of the substances during thermal degradation.

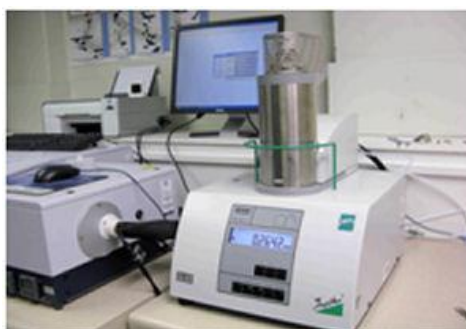


Figure 3-5 TGA coupled with FT-R, Western Sydney University

### **3.2.6 SEM (Scanning Electron Microscope) with EDS detector**

A scanning electron microscope (SEM) is an electron microscope that generates images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, generating various signals holding information about the surface topography and the sample composition. A scanning electron microscope typically contains the sample chamber at the base, the electron gun at the top, and the column, down which the electron beam travels.

In this project, SEM was used to examine and analyse the structure of plastics exposed to fire as a function of time in order to understand different additives effects on barring heat transfer and penetration of evolved gases. The aim of this part was to examine concrete structures cast in PVC formwork after subjecting them to fire tests to check if any positive or negative effect can be noticed because this type of structure has not been investigated to the best of our knowledge. Thus, the morphology of the ashes obtained from the TGA tests was investigated by JEOL 6510 LV SEM (Figure 3-6) at Western Sydney University. In each analysis, quite a few images and several EDS elemental analyses were taken and only a few were represented in the discussion chapters.

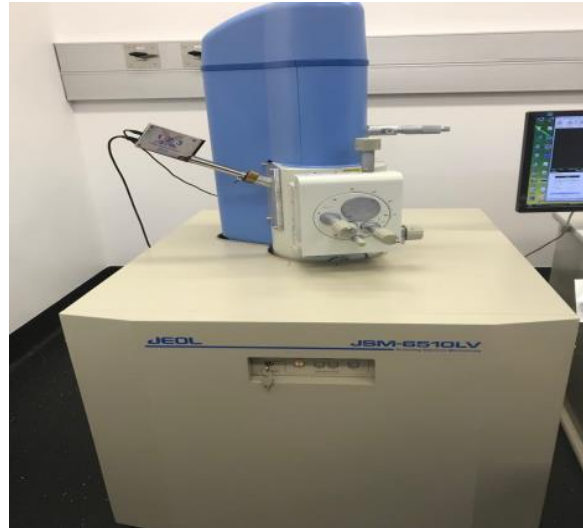


Figure 3-6 SEM instrument, Western Sydney University

For SEM-EDS sample preparation, samples were mounted on aluminium holders using double-sided conductive carbon adhesive tapes. Carbon tape is useful for holding the samples during the test in an uncoated situation. The double-sided adhesive also causes rapid mounting of the samples without using colloidal or liquid adhesives (Figure 3-7). Then, Nitrogen gas is used to blow away the unstuck powder which might contaminate the detector of the SEM. As the samples are uncoated, all the analyses are done on low vacuum mode. The pressure is set at 30 Pa or lower and working distance (WD) is fixed at around 15 mm for all samples.



Figure 3-7 Sample preparation for SEM-EDS analysis (left: copper standard, right: ash related to one of the samples)

### 3.2.7 Energy-Dispersive X-Ray Spectroscopy (EDS)

Energy-Dispersive X-Ray Spectroscopy (EDS) integrated with the SEM devices is used to characterise the available elements of the sample and estimate their relative abundance based on the strengths of the signal. Although EDS is a very useful technique, there are some difficulties that limit its accuracy and sensitivity. For example, light elements cannot be detected by EDS and some elements show overlapping peaks. Generally, an EDS detector has a crystal that absorbs the incoming energy of X-rays by ionization, causing free electrons to become conductive and finally leading to an electrical charge bias. Thus, the energy of x-rays is converted to electrical voltages of relative size and finally, the obtained electrical pulses can correlate to the elemental characterization. In this project, confirmation of the available elements and their approximate quantity is measured by an EDS detector attached to JEOL 6510 LV SEM of Western Sydney University.

EDS calibration was done by putting the standard copper stub into the SEM chamber before conducting each EDS test of this project. The voltage is set to 25 or 30 kV (it should be consistent with SEM accelerating voltage), and the count rates were set to 10,000-20,000. Figure 3-8 demonstrates the obtained EDS spectrum for the copper standard.

Ashes of the samples were recovered from the TGA crucible following thermal decomposition in air and prepared for EDS elemental analysis.

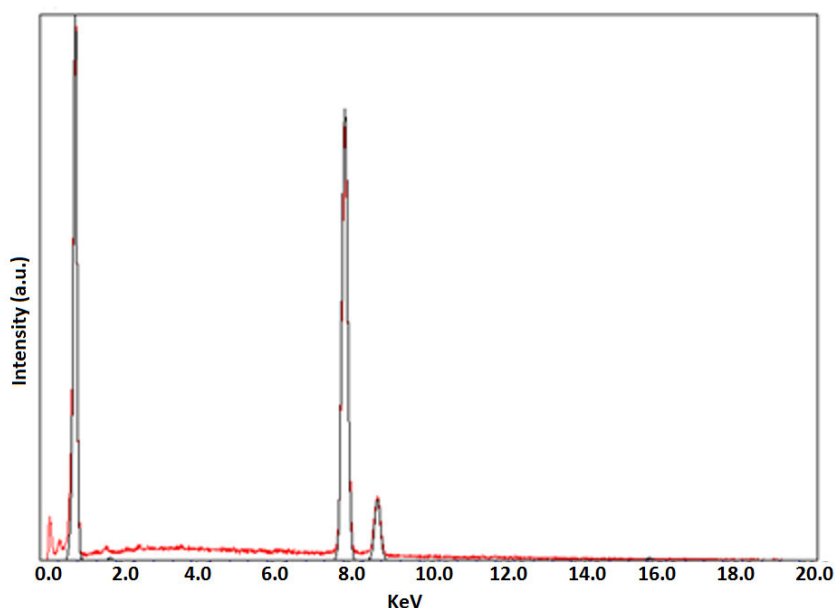


Figure 3-8 EDS spectrum obtained from the copper standard during calibration

### 3.2.8 X-ray diffraction (XRD)

Powder x-ray diffraction (XRD) utilizes x-rays to quantify and explore the crystalline content of a substance by evaluating X-ray diffraction from the planes of the atoms that make up the substance. XRD is sensitive to both atom positions and the length scale of the crystalline order. Thus, it can measure the crystalline phases and determine the atomic and molecular structure of a material. In this project, XRD tests were performed on a Bruker D8 Advance (Figure 3-9) at Western Sydney University with  $\lambda = 1.54060$  and a scan range of  $0-90^\circ 2\theta$ . To ensure the accuracy of the result, a considerable amount of the sample was taken for each analysis.



Figure 3-9 XRD instrument, Western Sydney University

## 3.3 Experimental Preparation Phase

### 3.3.1 Preparation of Metal Chelate complexes with Dipentaerythritol (ZINCDPE)

The new metal chelates were prepared to adopt the same procedure reported to be successfully used in the preparation of Zinc pentaerythritol metal chelate [137]. The powder of Dipentaerythritol and each of the metal oxides, zinc oxide, magnesium oxide and calcium oxide were mixed in a molar ratio of 1.4:1 in a grinder for 5 minutes to get homogenous mixed powder. The powder was placed into a reaction vessel immersed in a thermostatic oil bath at  $200-210^\circ\text{C}$ . The reaction was continued for two hours, samples were taken at several heating intervals and examined by thermal analysis and IR techniques as detailed in Chapter 4. The efficiency of each of the prepared metal chelates was evaluated as a thermostabiliser for PVC [Ch. 4].

### **3.3.2 Preparation of PVC films containing -Metal Chelate complexes of Dipentaerythritol**

A 5 grams sample of PVC homogenous ground powder containing (10 phr) of the metal chelate prepared in section 3.2.1, was dissolved in 100 ml of Tetrahydrofuran solvent (THF). The solution was agitated at room temperature until a homogenous viscous solution was obtained. The homogenous mixture was poured into a Teflon mould in order to obtain 0.4 mm thickness of Polymer films. The films were obtained by evaporating the solvent at room temperature for 24 h and then drying for 3 h in a vacuum oven [0.1 mm Hg] at room temperature to make sure that all the solvent was removed. Vacuum drying was continued until a constant weight was obtained. The samples were used in the thermal stability evaluation.

### **3.3.3 preparation of PVC- HCAC samples**

10 g of cold water (4 °C) was added to 5 g of calcium aluminate cement (W/C=2) in order to fulfil the hydration. The mixture was then left in a cold environment at 10 °C for 2 days to delay the formation of conversion reaction products. The paste was completely dried in a vacuum oven at room temperature. The samples of stabilised PVC with different weight contents of HCAC (phr) of PVC powder were mixed and pressed into discs and used in this study.

### **3.3.4 Preparation of PVC- GGBFS Samples**

GGBS (Ground granulated blast-furnace slag) was hydrated with boiled water in the presence of 0.1% calcium hydroxide so that the ratio of water/mix (mixture of slag and calcium hydroxide) was 2. The mixture was left for two weeks in a closed container at 50 °C in an oven to complete the hydration reaction. The product was ground to a fine powder and mixed with PVC powder in a grinder with different phr. The final samples were pressed to discs and used in this study.

### 3.3.5 Preparing PVC compounded sheets by compression moulding

Some of the PVC - compounded samples consisting of the new stabilisers prepared in this study were also produced in sheets for the final study. In this project, the homogenous sheet forms of PVC composites were prepared at “APN compounding Pty Ltd” facilities under the budget of CSR limited company. APN compounding is the largest PVC manufacturer in Australia with a capacity of over 15,000 tpa with six production lines.

The first stage involved PVC compounding with all the additives at predetermined constituents (phr). The ingredients were mixed in the lab mixer of APN compounding for 10 minutes (Figure 3-10) in order to be completely homogenized. The mixing temperature was fixed at 82 °C with a speed motor of 2000 rpm.



Figure 3-10 Lab mixer of APN compounding pty Ltd

In the next stage, the homogenous mixture was transferred to Mill heaters at APN compounding. (Figure 3-11). The mill is fitted with a safety pedal which, heater and calendaring roles as shown in Figure3.11





Figure 3-11 Mill heaters of APN compounding

The mill heater was turned on, for 60 minutes to reach a temperature of 87 dial units for both front and back rolls. Approximately, half (50 g) of the sample was poured into the nip of the rollers. The material was allowed to soften and homogenize. A boot knife was used where necessary to guide the material or minimise any sticking (Figure 3-12).

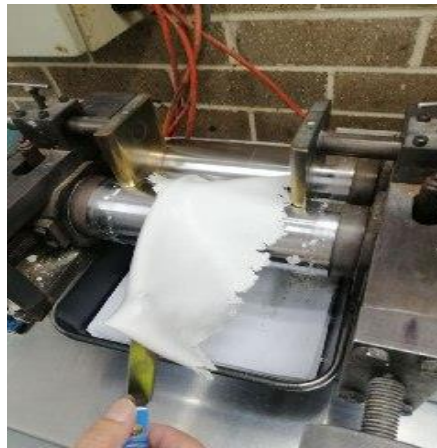


Figure 3-12 Using knife for guiding the material and minimize sticking

When the PVC compounded product was fused, the sample was pulled off the rollers and allowed to cool to room temperature. The formed calendared sheet sample was cut out into small pieces of 50mm squares and transferred to the stainless steel mould with the size of 150\*150\*2.3 mm (Figure 3-13).



Figure 3-13 Stainless steel mould

The mould containing the material was transferred to a plastic heat press machine, and compression moulding machine at APN compounding unit. The pressing temperature was set at 195 °C and the pressure was adjusted to 10,000 psi (Figure 3-14) with a holding time of 1 minute and a cooling time of 2 minutes.



Figure 3-14 Plastic heat press machine of APN compounding

Finally, the identical, flawless and smooth plastic sheets were removed from the moulds (Figure 3- 15).



Figure 3-15 smooth and flawless appearance of PVC film

### **3.3.6 Oven discolouration method**

The PVC films were cut into small strips (10 mm x 10 mm). These strips were heated in the oven at 180 °C in air mode. The colour of the samples with different additives was visually observed and determined every 10 min.

### **3.3.7 Test scope of Ultra Violet (UV) weathering and accelerated UV method**

PVC samples were cut into the same sizes and exposed to Accelerated UV exposure in accordance with the Australian Standard method (ASTM G154), in which the test was repeated twice to increase the accuracy. The aim of the test is to determine an estimated UV exposure resistance of the samples. Temperature Humidity & UV Test Chamber at Western Sydney University was used for a continuous period of UV exposure to the samples for up to 300 hours. Samples were distinguished by unique numbers which were written on the underside (not directly exposed to UV) of each sample with a permanent marker. Then, samples were placed in the machine in such a manner that the samples were not subject to any unnecessary applied stress. Test conditions included cycles of UV exposure for 8 hours at 60 °C then 4 hours at 50 °C with UV lamps of UVA -340 and the Irradiance of 0.89 W/m<sup>2</sup>. During the repetitive cycles, the samples were exposed to extremely humid conditions by the action of water vapour with condensation. Evaluation of appearance, colour and other property changes of exposed samples were made based on comparisons to unexposed samples of the same material that had been

stored in the dark. For each inspection, Samples were photographed and inspected to determine whether any changes to colour or texture have occurred. After inspection, the samples were returned to the UV chamber with their test surface in the same direction as previously exposed. Periodic repositioning of the Samples during exposure was not necessary as the irradiance at the positions farthest from the centre of the specimen area was at least 90 % of that measured at the centre of the exposure area [138].

# CHAPTER 4

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia

## 4. Evaluation of Dipentaerythritol Metal Chelate complexes as a new series stabilisers for PVC

### 4.1 Introduction

This chapter will cover the evaluation of the new family of metal-dipentaerythritol complexes prepared in Chapter 3 as new stabilisers for PVC. Introducing these new Zinc chelate stabilisers aims at the improvement of the mechanism related to absorbing HCl released from thermally degraded PVC and overcoming the catalytic effect of dehydrochlorination based on Lewis acid characteristics of  $ZnCl_2$  as explained in detail in Chapter 2. This contributes to the further formation of oxidisable and coloured conjugated polyene structures and, accordingly, to the deterioration of mechanical properties [139]. In order to produce thermally stable PVC products, Zinc compounds are usually used as stabilizing additives [140-142] because of their low cost, non-toxicity, and environmentally friendly properties [143]. Among the great variety of zinc-containing stabilizers, Zinc Carboxylates such as zinc stearate are well-known. These types of stabilizers are based on Frye–Horst mechanism. This mechanism includes the substitution of labile chlorine atoms for more stable carboxylate groups. Metal soaps are the most common stabilizers for PVC composites. The metal soaps most commonly used to stabilize PVC compositions are likely to cause dust formation, thus, they are not safe from the point of view of industrial hygiene. Furthermore, Fire retardants containing Zinc such as Zinc Borate and Zinc stannate or thermal stabilizers like Zinc soap form strong Lewis acid ( $ZnCl_2$ ) in reaction with evolved HCl of PVC. This strong Lewis acid is able to catalyse the decomposition of PVC and causes sudden black colouration [144]. Thus, a new type of zinc-based compound that has no catalytic effects on PVC degradation is a key element of this research.

Other than that, transition metal oxide fillers such as Zinc Oxide have been reported to be suitable smoke suppressants for PVC.  $ZnO$  is also low-cost, and non-toxic and it is largely used in the Ceramic industry because of its high heat capacity and high-temperature stability [145]. Moreover, Zinc Oxide has a wide ultraviolet protective spectrum and is a good sunscreen filler for PVC [146, 147].

Thus, this chapter provides a much-needed study on the Zinc oxide-dipentaerythritol complex which not only has all the advantages of Zinc oxide but also Zinc of this complex is coordinated

to the ligand of complex and won't be free as  $Zn^{2+}$  and make Lewis acid and won't catalyse dehydrochlorination. In the second part of this chapter, some other transition metal oxide-dipentaerythritol complexes will be investigated. When a central metal ion or atom (Lewis acid) surrounds an anion or neutral molecules (termed ligands) by covalent bonds, a Lewis acid-base reaction occurs and finally, a coordination complex will be produced. Most metal-containing compounds, remarkably those with a transition metal, are named coordination complexes [148]. Zinc shows considerable coordination chemistry and it readily forms complexes with a wide range of ligands, especially Oxygen donor ligands [148].

In this study, Dipentaerythritol  $(CH_2OH)_3CCH_2OCH_2C(CH_2OH)_3$ , is used as an oxygen donor ligand for Zinc and other metal ions. Dipentaerythritol is a polyhydric alcohol compound (polyol) as it has multiple hydroxyl groups in its structure. In general, polyhydric alcohols (polyols) are white solid compounds, ranging from crystalline forms including pentaerythritols of waxy forms such as trimethylol alkyls. Polyols has multiple hydroxyl groups which can be potential coordination sites for metal cations or atoms. At the time of reaction, the electron pairs available in multiple hydroxyl groups of dipentaerythritol can get involved in the sphere around the metal atom. Consequently, the reactants bond together by sharing two electrons and making a covalent bond. although, both electrons are donated by one reactant itself (dipentaerythritol). Additionally, Zinc is flexible with the number of ligands it can surround. Complexes of Zinc are also kinetically labile [149]. For example, bonds with Zinc and its ligands exchange with other ligands rapidly. The most probable structure of zinc complexes is tetrahedral. However, octahedral complexes can also be made [150].

This chapter aims to provide a process for producing a novel complex of metal oxide-dipentaerythritol. The process includes heating a mixture of dipentaerythritol and metal oxide to 200 °C to react dipentaerythritol and metal oxide in that way to produce at least one mole of water for each mole of metal oxide used and releasing at least one mole of water.

## **4.2 Analysis and structure confirmation of Zinc- Dipentaerythritol chelates (ZINCDPE)**

Samples synthesised as detailed in Chapter -3 were analysed by several techniques as detailed in the following sections.

#### 4.2.1 TGA analysis of ZINCDPE

The composition of DPENTZINC was confirmed by TGA analysis. Samples of ZnO, DPE, the mixture of ZnO and DPE before reaction, and ZnO and DPE reaction product (ZINCDPE) were examined by TGA, adopting a standard analysis procedure. Figure 4-1 shows the TGA curve of the mixture dipentaerythritol and ZnO in an air atmosphere. Accordingly, when the temperature goes above 200 °C, weight loss due to dehydration takes place. The weight % loss due to dehydration in Figure 4-1 is 64.57% based on the residual mass of the complex (dipentaerythritol + ZnO). This huge amount of dehydration has a significant role in cooling down the combustion environment.

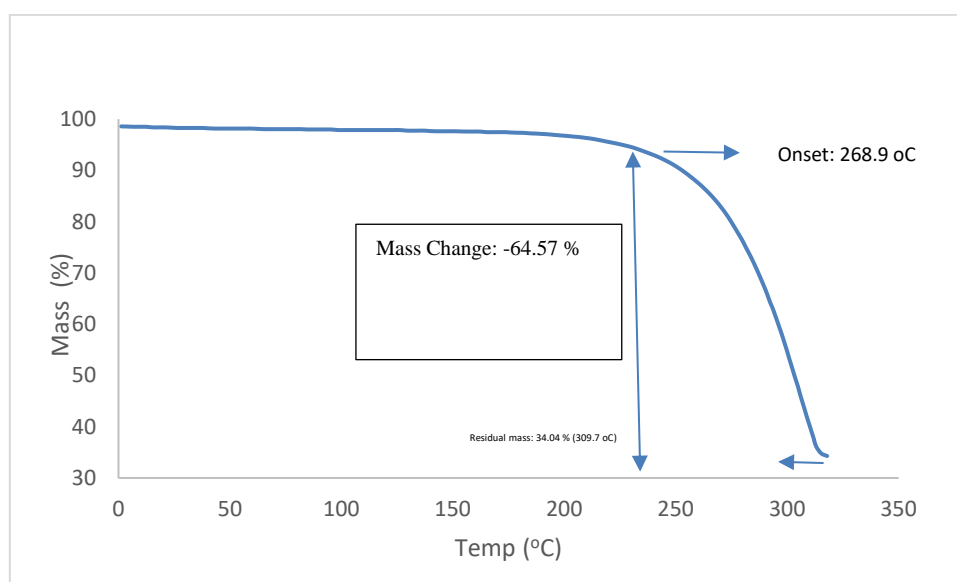


Figure 4-1 TGA curve of mixture (Dipentaerythritol + ZnO)

Figures 4-2 and 4-3 show the TGA curve of Dipentaerythritol and Zinc oxide. It should be noted that the melting point of Dipentaerythritol is: 215-218 °C and melting point of ZnO is: 1,975 °C. It can be seen that the complex (ZINCDPE) is formed as it has TGA thermograms different from each of dipentaerythritol and ZnO.



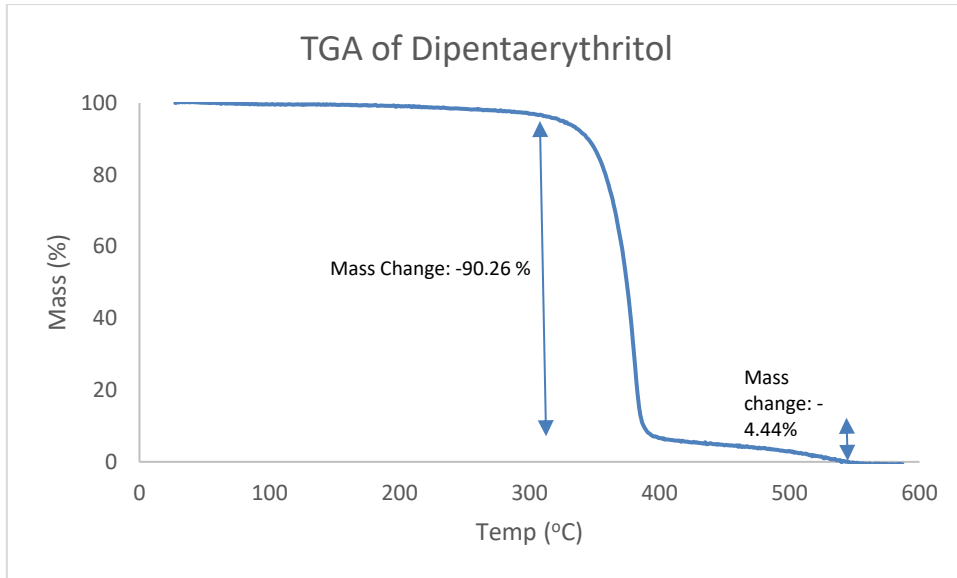


Figure 4-2 TGA curve of Dipentaerythritol

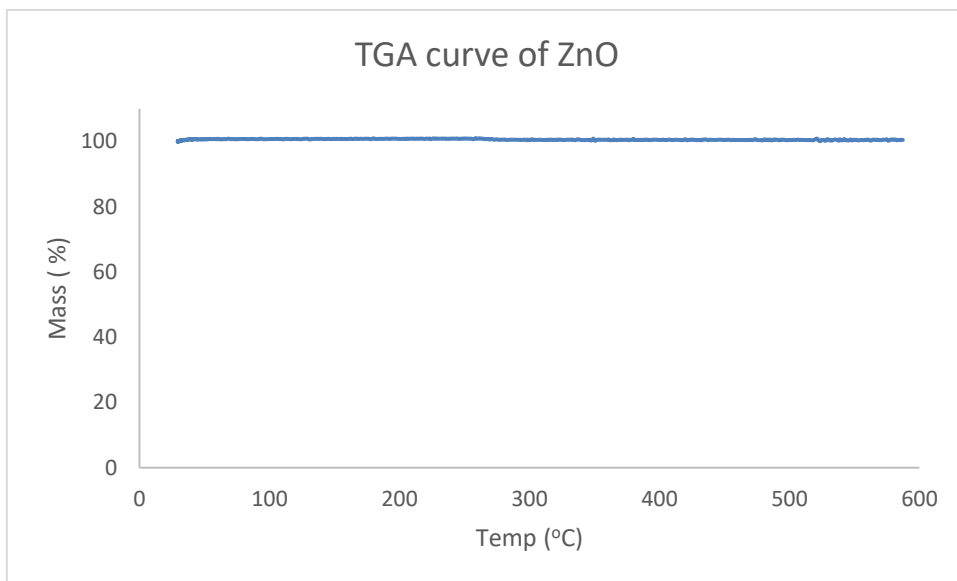
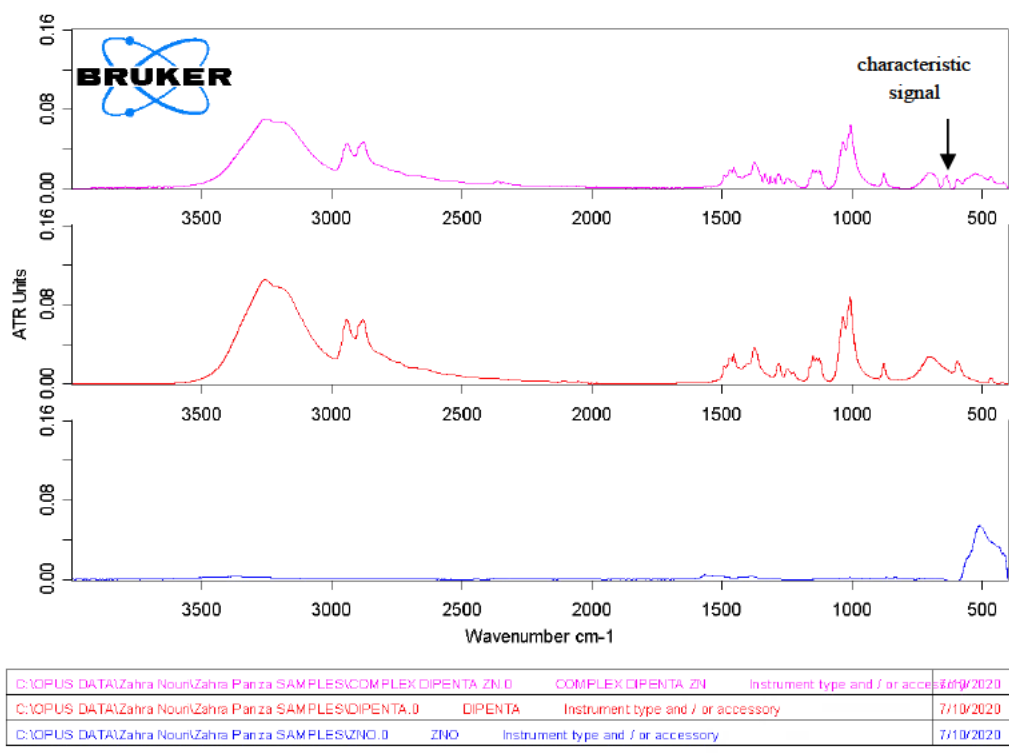


Figure 4-3 TGA curve of ZnO

#### 4.2.2 Characterisation of the novel complex (ZINCDPE) by FT-IR spectroscopy:

Further confirmation for the complex formation was carried out by FT-IR analysis FT-IR spectra of the starting materials separately and the reaction products were recorded.

Figure 4-4 shows the FT-IR spectra of Zinc oxide, dipentaerythritol and Zn-dipentaerythritol complex (DPENTZINC). The spectrum of raw reactant of Zinc oxide shows a single peak around  $500\text{ cm}^{-1}$ . According to dipentaerythritol spectrum, a peak at  $3000\text{-}3500\text{ cm}^{-1}$  is attributed to the stretching vibration of hydroxyl groups. The peaks around  $2900\text{ cm}^{-1}$  are assigned to the C-H stretching vibrations, and the peaks between  $1200\text{-}1400\text{ cm}^{-1}$  are related to the C-H bending vibrations. Also, the peaks at  $1000\text{ cm}^{-1}$  are ascribed to the bending vibrations of hydroxyl groups. In Figure 4-4 (purple spectrum) there is a new peak around  $700\text{ cm}^{-1}$  which is not observed in the spectra of both reactants. This new peak corresponds to the characteristic signal of the Zn-O bond in the complex in a chelation form [151]. The product spectrum (purple spectrum), shows also similar peaks to raw reactants which indicates the presence of unreacted raw materials in the complex product. This is due to the solid phase reaction and limits the reaction to reach the end. The smaller peak OH stretching vibration in the complex product rather than the reactant is due to the reaction of ZnO with hydroxyl groups and the destruction of hydrogen bonds in dipentaerythritol. Additionally, the complex product has also some small extra peaks from  $1200\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$  that could be attributed to the CH. The spectroscopy results are in good agreement with the TGA analysis data confirming the composition of ZINCDPE complex; the thermal reaction product of Dipentaerythritol with ZnO.



Page 1/1

Figure 4-4 The FT-IR spectra related to the product ZINCDPE(purple graph) and reactants(blue graph :ZnO, red graph: dipentaerythritol)

### 4.3 Optimization of the amount of complex additive for PVC

The different amounts of 5, 10 and 15 phr of this complex additive were added to PVC to optimize the suitable amount of this additive. TGA curves are illustrated and compared in Figure 4-5 and the results are summarized in Table 4-1. Accordingly, 5 phr of the complex did not show improvement to the thermal behaviour of pure PVC, While the improvement related to 15 phr is very close to the amount of 10 phr. As a result, the smaller amount (10 phr) is chosen as an optimized amount of the complex additive for PVC. Adding 10 phr of complex additive to PVC can increase the temperature of the first stage of degradation from 268.2 to 272°C which is a good improvement. This additive also decreases the mass loss of PVC at the first stage from 66.05% to 49.43%.

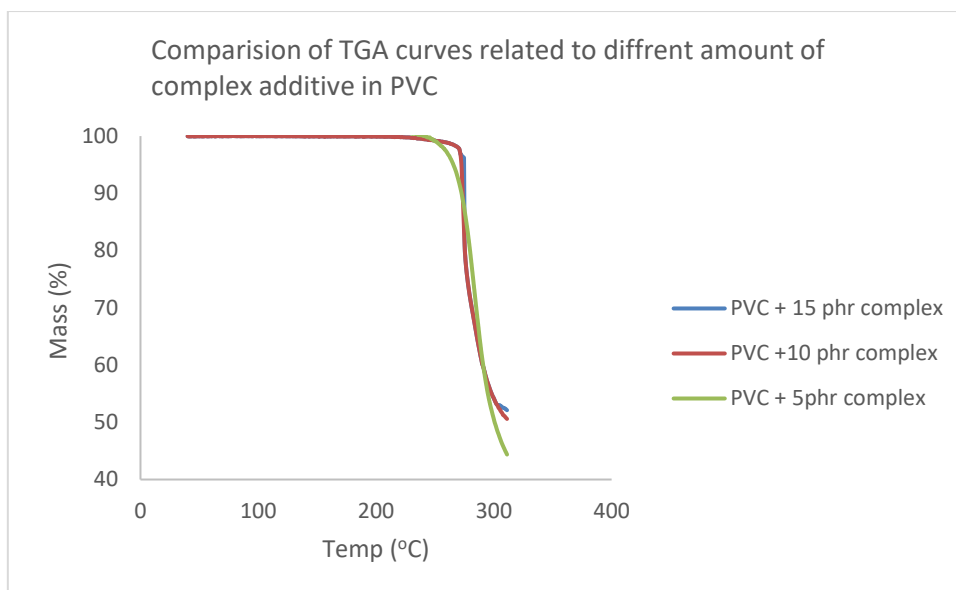


Figure 4-5 TGA curves of different amounts of complex additive (ZINCDPE) in PVC

Material	T <sub>1</sub> °C	Mass loss (first stage)
Dipentaerythritol (alone)	319.3	-90.26 %
ZnO (alone)	-	-
Complex (ZnO + Dipentaerythritol)	268.9	-64.57 %
PVC +complex 5 phr	259.8	-55.63 %
PVC + complex 10 phr	272	-49.43 %
PVC+ complex 15 phr	272.5	47.90 %
PVC (alone)	268.2	-66.05 %

Table 4-1 Comparison of thermal gravimetric data of the materials

#### **4.4 Investigation of the effect of a novel complex (ZINCDPE) on cooling down and diluting the corrosive and toxic atmosphere of combusted PVC by coupled TGA-IR Analysis and monitoring released gasses**

Thermal analysis is a commonly used analytical technique for materials study. However, the thermal procedure can be described more completely and precisely by utilizing simultaneously released gas analysis. Among many different gas analytical methods, FT-IR has several advantages. It is one of the most effective and reliable methods for emissions recording because of its high sensitivity to detect gases even in extremely low levels of concentration. FT-IR works based on detecting gaseous products by their different absorption of infrared radiation. The FT-IR spectrum of a substance is like a fingerprint. It means each component has a distinctive combination of the atom or molecular structure. When exposed to IR radiation they make a unique and distinctive IR spectrum based on which they can be identified.

Figure 4-6 shows a graph extracted from a TGA-IR experiment on the PVC with 10phr of the complex additive (ZINCDPE) along with its 3D FTIR spectrum. It shows two signals of FT-IR (green and purple curves) that appeared at the same time as the first stage of decomposition in the TGA test (blue curve). It means that weight loss of PVC in the first stage is not only related to the release of HCl, but also to water.

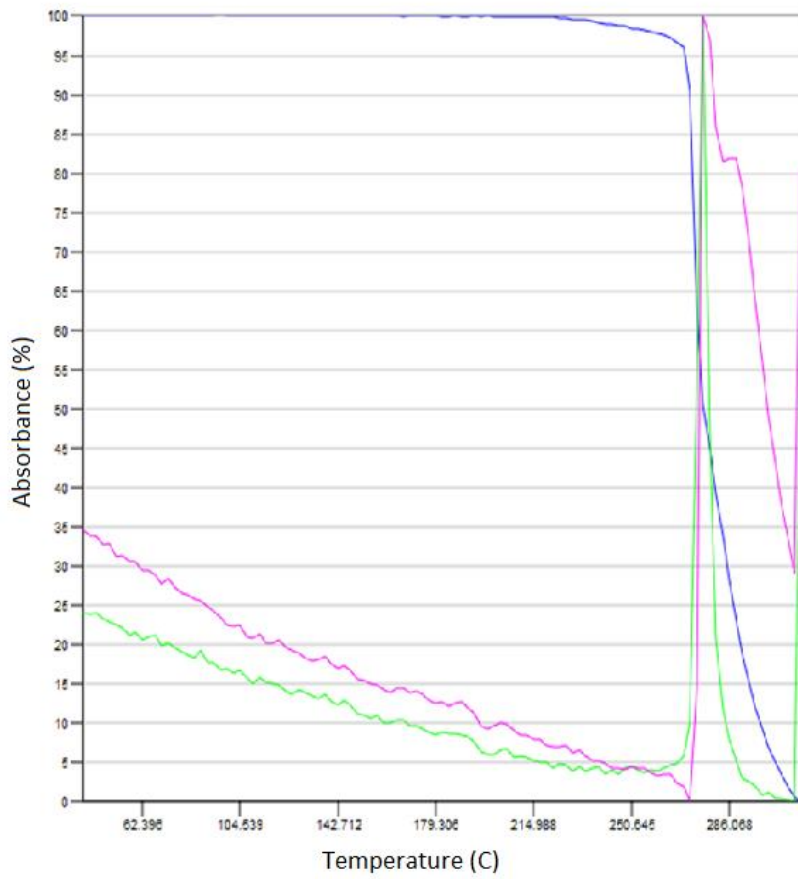
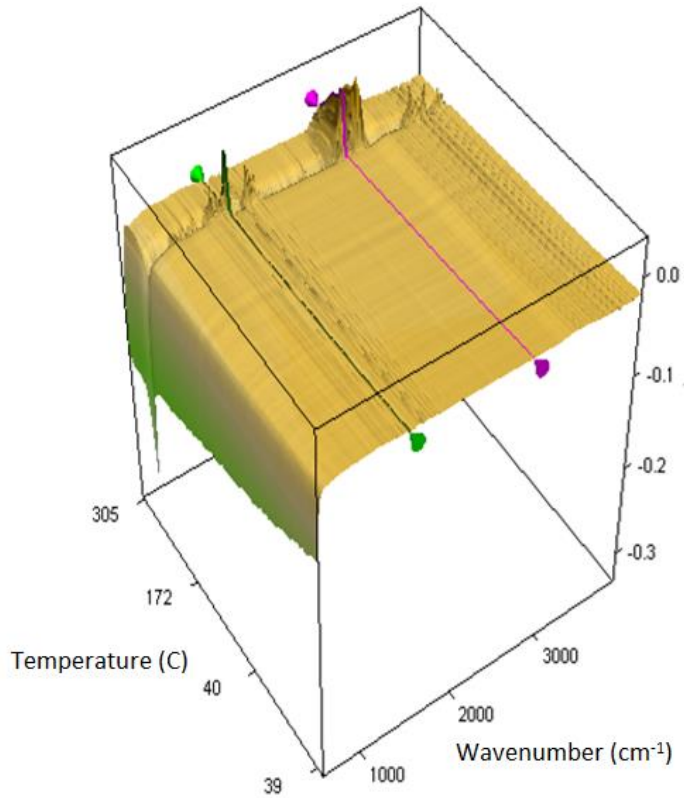


Figure 4-6 A graph extracted from a TGA-IR experiment on the PVC with 10 phr of the complex additive (ZINCDPE) along with its 3D FT-IR spectrum

According to the lower image in Figure 4-6, there are two gases evolved (green and purple curves) in the range of 277-288 °C. Figures 4-7 and 4-8 show FT-IR for the released gases at 277.31 and 288 °C, respectively, where two sharp peaks were observed. HCl signals in FT-IR are obvious as a set series of doublet peaks between 2650  $\text{cm}^{-1}$  and 3100  $\text{cm}^{-1}$ . HCl Peaks are risen and fallen to zero continuously and each peak is split to doublet in the comparative ratio of 3:1 which corresponds to the proportion of  $^{35}\text{Cl}$ :  $^{37}\text{Cl}$  isotopes. FT-IR of the evolved  $\text{H}_2\text{O}$  peaked in the range of 3900-3500  $\text{cm}^{-1}$ . Thus, the investigation of gas products and the degradation mechanism of PVC at the first stage shows main gases released at this stage are HCl and Water. Simultaneous release of water with toxic and corrosive HCl gas helps to dilute the acidic and toxic environment with the additional cooling down benefit.

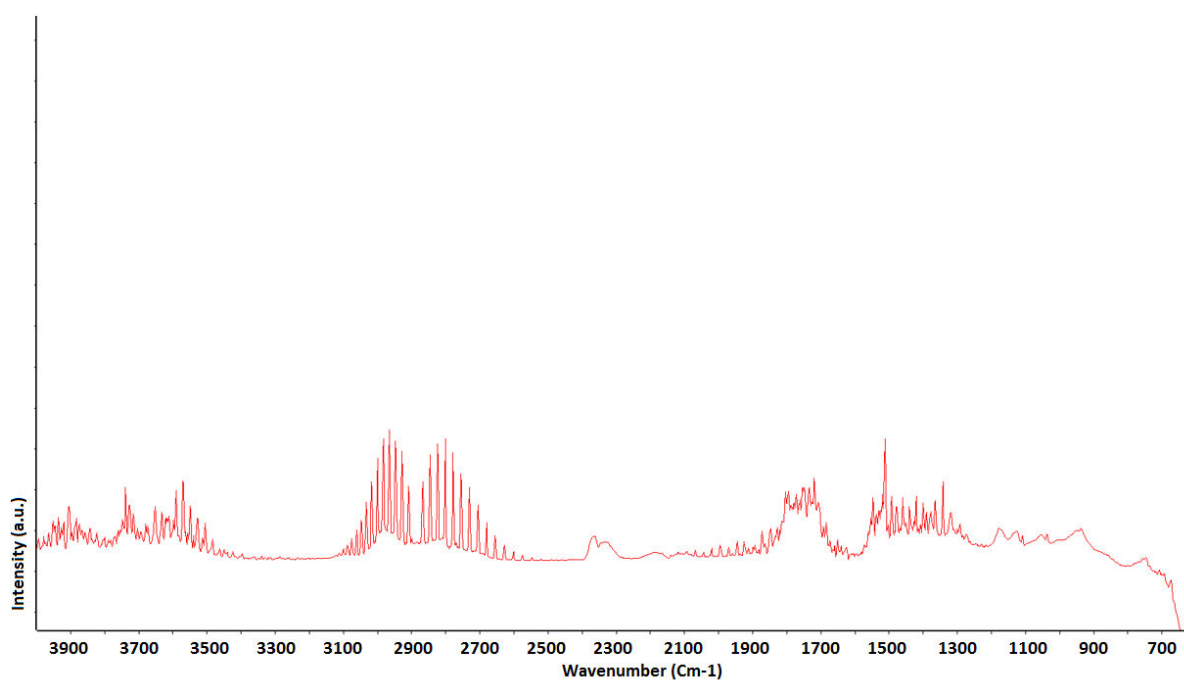


Figure 4-7 FT-IR of released gases at 277.3 °C

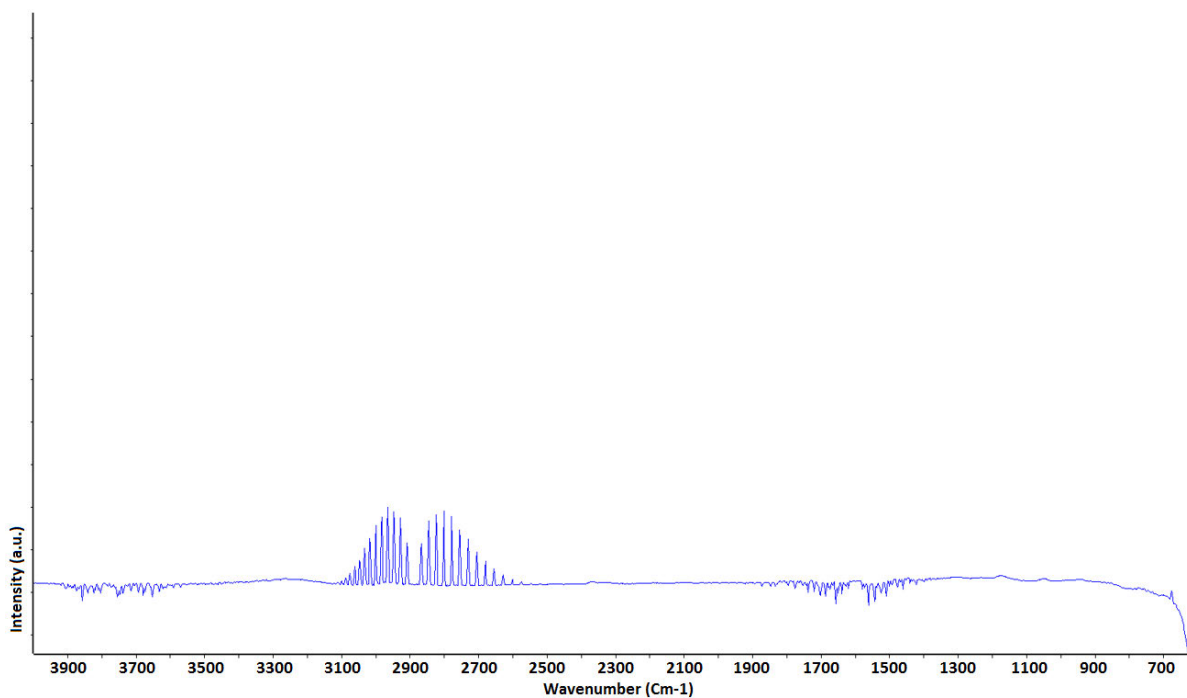


Figure 4-8 FT-IR of released gas at 288 °C

#### 4.5 Evaluation of the efficiency of the new ZINCDPE complex by EDS analysis

In the previous section (part 4.4), monitoring released gasses by TGA-FTIR showed that HCl gas from the decomposition of PVC is partially released into the atmosphere. To understand Cl captured in the solid phase, EDS analysis was done on the ash of PVC stabilised with complex additive (Figure 4-9), the ash of pure PVC (Figure 4-10) and the complex additive (Figure 4-11). Ashes of the samples were recovered from the TGA crucible following thermal decomposition in the air.

The Cl signal in the ash of PVC with complex additive was present, while the Cl signal was neither observed in the ash of pure PVC nor the ash content of the complex additive. It means, part of HCl has been captured in the solid phase (ash) and is not released into the atmosphere. Overall, it can be concluded that although this formulation is not effective enough to capture all of HCl gas, it is still able to capture a significant part of this gas in the solid phase based on



the strong chlorine signal seen in the EDS spectrum of the ash related to this formulation (Figure 4-9).

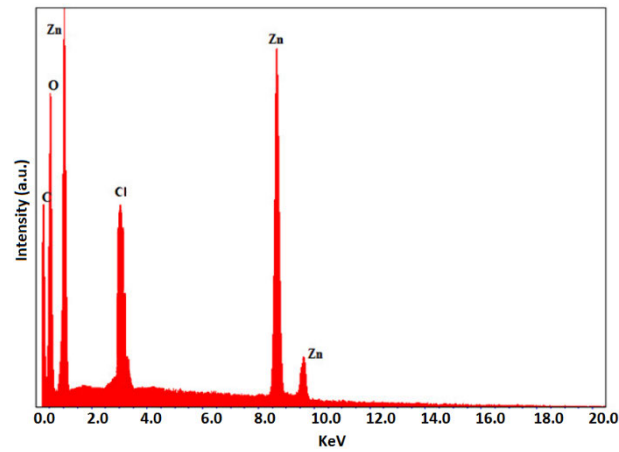


Figure 4-9 EDS spectrum of ash residue of the decomposed PVC stabilised with complex additive

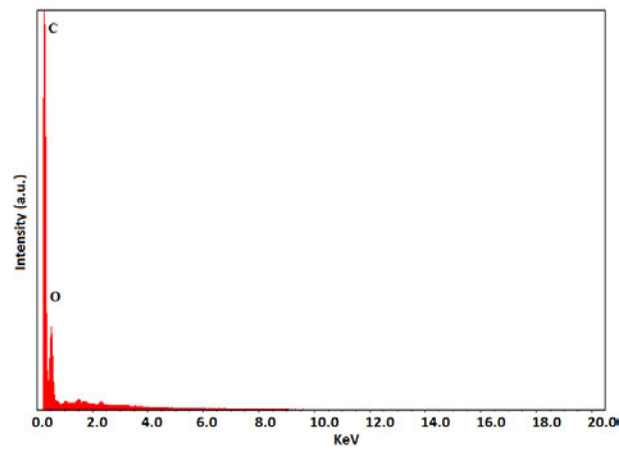


Figure 4-10 EDS peaks related to ash of pure PVC

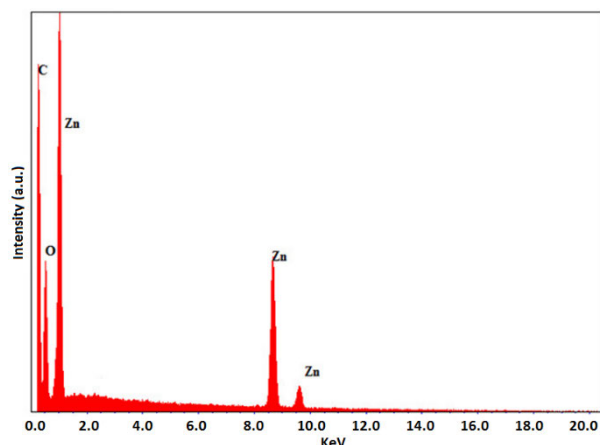


Figure 4-11 EDS peaks related to complex additive

#### 4.6 Complexes of Dipentaerithritol with other metal oxides

Complexes of Dipentaerithritol with 10 phr of the other metal oxides CaO and MgO, were synthesised and evaluated in this study by the TGA method. The obtained thermograms are shown in Figures 4-12 and a summary of the results is listed in Table 4-2. The results showed that the complex of dipentaerythritol with calcium is the most effective one for enhancing the thermal stability of PVC composite (green curve in Figure 4-12). In other words, the calcium dipentaerythritol complex additive showed the highest thermal degradation temperature, the lowest rate of degradation and the highest residual mass (ash residue) in the TGA tests. It should be noted that this test was repeated three times. Although each time the curve corresponding to PVC+10 phr complex CaO and PVC+complex MgO showed approximately the same in TGA, the results related to PVC+10 phr complex CaO showed slightly better in all repeated tests.

The greater efficiency of the Calcium –DPE complex may be related to the more stable complexes than other metal complexes of Zn and Mg. Figure 4-13 shows EDS analysis done on the ash residue of PVC stabilised with 10 phr Calcium –DPE complex after the TGA test. The existence of chlorine signal in the solid phase proves the capture of some amount of HCl gas in the solid phase of this sample, like ZINCDPE sample which was fully disused in section 4.5

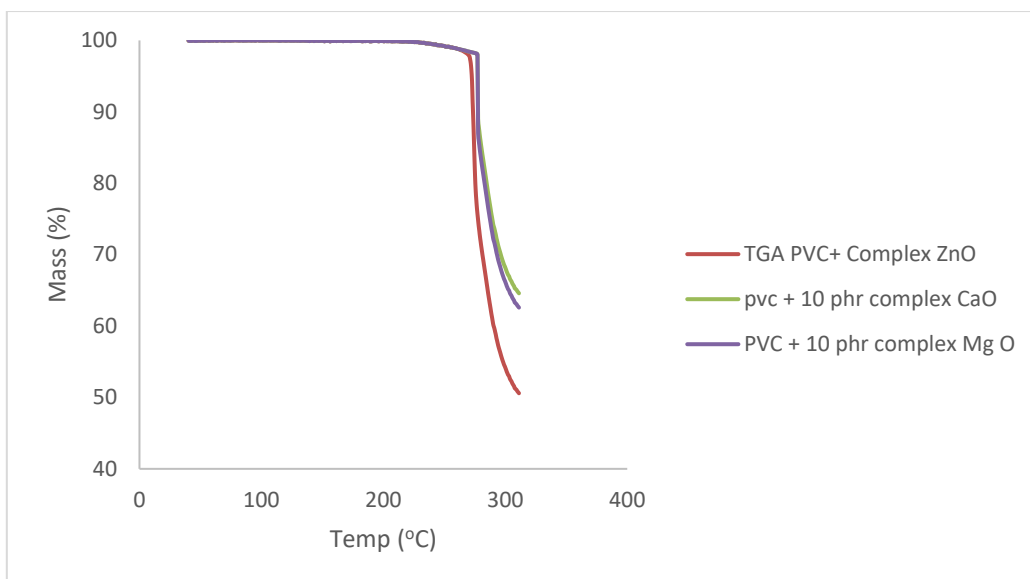


Figure 4-12 TGA curves of PVC stabilised with other complexes

Samples	T1 (°C)	% residual mass at 310 °C
Pure PVC	268.2	44.82
PVC+10 Phr complex dipentaerythritol and calcium	277.7	64.70
PVC+10 phr complex dipentaerythritol and magnesium	276.2	62.70
PVC+10 phr complex dipentaerythritol and zinc	272	50.70

Table 4-2 Summary of the thermal characteristics of PVC with different complexes

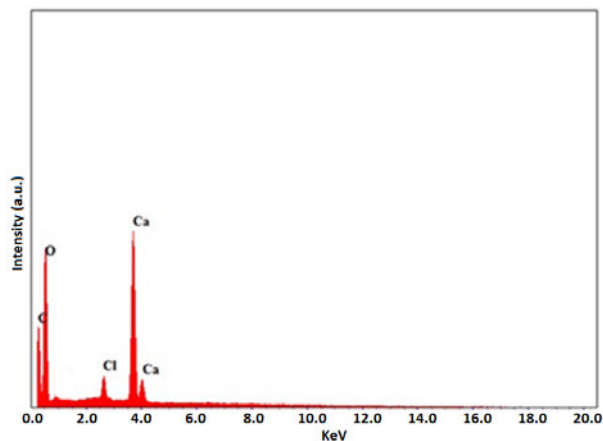


Figure 4-13 EDS spectrum of PVC stabilised with the other complex additive (DPE + CaO)

#### 4.7 Evaluation of the thermal stability of PVC- DPE complexes of Zn and Ca (Thermal degradation) by Oven Discoloration method

The samples were placed in the thermostated oven  $\pm 0.1^\circ\text{C}$  with a transparent glass window for observing the oven discoloration effect.

When the temperature goes further than  $120^\circ\text{C}$ , PVC starts thermal ageing and degradation. In this condition, the unstable chlorine in tert-butyl chloride and allyl chloride link to adjacent hydrogens to produce hydrogen chloride. As a result, the  $-\text{C}=\text{C}-$  starts to form and develop in PVC structure and causes the conjugated system [152]. When the conjugated system increases to a specific length, the colour of PVC starts turning darker (changes are from light brown to dark brown, and eventually to black colour).

Table 4-3 shows the comparison of the thermal ageing tests related to pure PVC and PVC with 10 phr of commercially used ZnSt<sub>2</sub>, and PVC with 10 phr of Zinc-Dipentaerythritol complex (novel complex). The initial colour of all samples was white as all ingredients in the samples were also white and no thermal degradation occurred during preparing and drying of the PVC film samples.

According to images in Table 4-3, increasing the heating time causes the colour change of pure PVC gradually into a yellowish brown (10 min), brown (30 min) and dark brown (50 min).

PVC samples with 10 phr ZnS showed very good initial colour (initial 10 min), indicating that ZnSt<sub>2</sub> additive is able to stabilize the initial colour of PVC. However, increasing the heating time to 20 min caused quick dark spots on this sample which is ascribed to the zinc burning effect and the low long-term stability of this formulation. In this formulation, zinc stearate and HCl released from heated PVC react together and produce ZnCl<sub>2</sub>. ZnCl<sub>2</sub> is recognized as a strong Lewis acid in catalysing the decomposition stage of PVC. When the amount of produced ZnCl<sub>2</sub> reached a particular level, it would accelerate the ageing and degradation rate of PVC all of the sudden. This phenomenon is termed Zinc-burning.

PVC stabilized by 10 phr of new and novel complex presented in this study (PVC +10 phr complex of Zinc-dipentaerythritol) showed better short-term and even long-term colour stability among pure PVC and PVC stabilised with commercially used ZnSt<sub>2</sub>. The colour gradually turned yellow and did not turn wholly black within the inspection time (50 min). Therefore, complex of Zinc-dipentaerythritol showed higher thermal stabilization. Although there is Zinc in this complex, there are no quick black spots in the sample of this formulation. This is based on the chemical structure of Zinc-dipentaerythritol. This structure has several hydroxyl groups that are able to form a complex with the ZnCl<sub>2</sub> and consequently avoid the catalytic degradation of PVC. For long-term colour stabilization, the discolouration of PVC with the complex additive showed slower changes than pure PVC. This is due to the good capability of this complex in absorbing the released HCl which is another catalytic factor in PVC degradation. Among all of these samples, PVC stabilized by 10 phr of the (Calcium-dipentaerythritol) showed less ageing and fewer colour changes at the end of the experiment, which is consistent with the TGA data available in section 4.6.

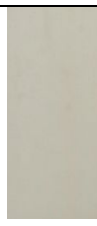












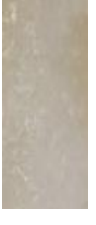


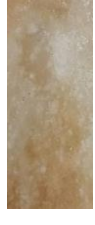


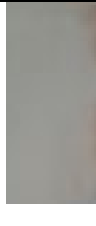




Stabilizer	Degradation time/ inspection time (min)					
	0	10	20	30	40	50
Pure PVC						
PVC+10 Phr ZnS						
PVC +10 Phr complex (Zn- dipentaerythritol)						
PVC +10 Phr complex (Ca- dipentaerythritol)						

Table 4-3 Results of thermal ageing test (180 °C)

## 4.8 Discussion

Principally, alcohols are weak acids but the acidity of polyols such as dipentaerythritol is higher than alcohols with only one hydroxyl group. Thus, dipentaerythritol reacts with a metal oxide to form Carbon—Oxygen—metal bonds, whilst water is released. This released water cools down the combustion environment.

In general, dipentaerythritol contains six hydroxyl groups and acts as a polydentate ligand. It has many points of attachment and can chelate to metal ions at two or more links, forming alicyclic structures. Chelates generally are more stable in comparison with non-chelated compounds of the same material. Additionally, the larger chelation-like chemical structure of dipentaerythritol can cause a more extensive number of ring closures to the metal ion and, consequently, forming a more stable compound. This is termed the chelate effect and it is because of the increase in entropy (thermodynamic quantity) that accompanies and conducts chelation. On the contrary, zinc as a metal atom is flexible with the number of ligands Zinc atom can be surrounded with. Complexes of zinc are also kinetically labile. For example, zinc bonding with its ligands, and exchange with other ligands rapidly. The most probable structure of zinc complexes is tetrahedral. However, octahedral complexes can also be made. Based on the theoretical literatures, zinc is able to hold a different number of OH or water ligands in its first coordination layer (four, five, or six ligands). The obtained isomeric complexes of the reaction do not have huge energy gaps and their energies differ by a few kilocalories per mole. In consequence, as tetrahedral complex of zinc has a lower energy level, tetrahedral structure is the most stable and probable product of this reaction. Furthermore, as this reaction is performed in the solid phase and cannot be completed to the end, the ultimate product may include a mixture of unreacted forms of reactants (Zinc Oxide and dipentaerythritol) and the complexes (structures I and II) as illustrated in Figure 4-14. In this study, structure (II) is considered a general product for the explanation of the mechanism. The enhancement of the thermal stability is related to the high reactivity of the product with HCl emitted from the Polymer. As illustrated in the reactions, the released chloride from PVC is captured by metal ions (zinc ions), avoiding the formation of free  $ZnCl_2$  which is a Lewis acid. In other words, the multiple hydroxyl groups available to Dipentaerythritol can form chelates with the produced  $ZnCl_2$  to avoid the catalytic dehydrochlorination which would be the result of independent Lewis acid. Accordingly, PVC stabilised by this compound shows long-term stability with no “zinc burning” effect. Moreover, OH moieties in the structure will be converted to water during thermal enhancement and result in the cooling down of the combustion zone and diluting the toxic environment caused by combustion.

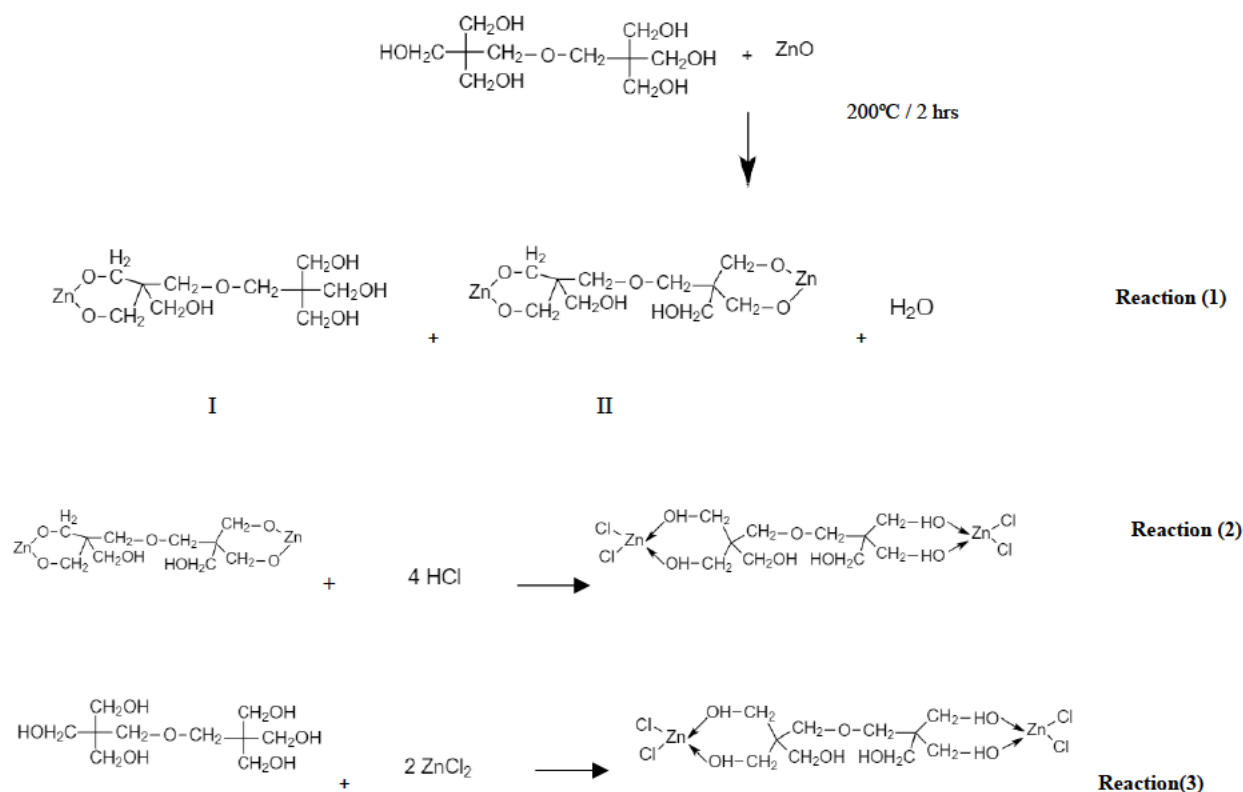


Figure 4-14 Chemical reactions of Dipentaerythritol and Zinc Oxide

On the contrary, some commercially used flame retardants in which zinc is not chelated to a ligand, including zinc borate or zinc stearate, can cause the formation of a free and independent Lewis acid which consequently accelerate the dehydrochlorination reactions and sudden black phenomenon. In other words, zinc chloride ( $\text{ZnCl}_2$ ) acts in the solid phase by accelerating dehydro-chlorination reaction in PVC and promoting cross-linking and char formation. The detailed mechanism is shown in Figure 4-15; as mentioned before,  $\text{ZnCl}_2$  is a Lewis acid, accepts a chloride from PVC and leads to carbonium ion which consequently decomposes to alkene and  $\text{ZnCl}_3^- \text{H}^+$ , the more stable ion pair than  $\text{HCl}$  and  $\text{ZnCl}_2$ . In the next stage, the unsaturated groups in PVC react with carbonium ions and ultimately crosslinking reactions take place in the same way resulting in char formation rapid colour change and low initial thermal instability.



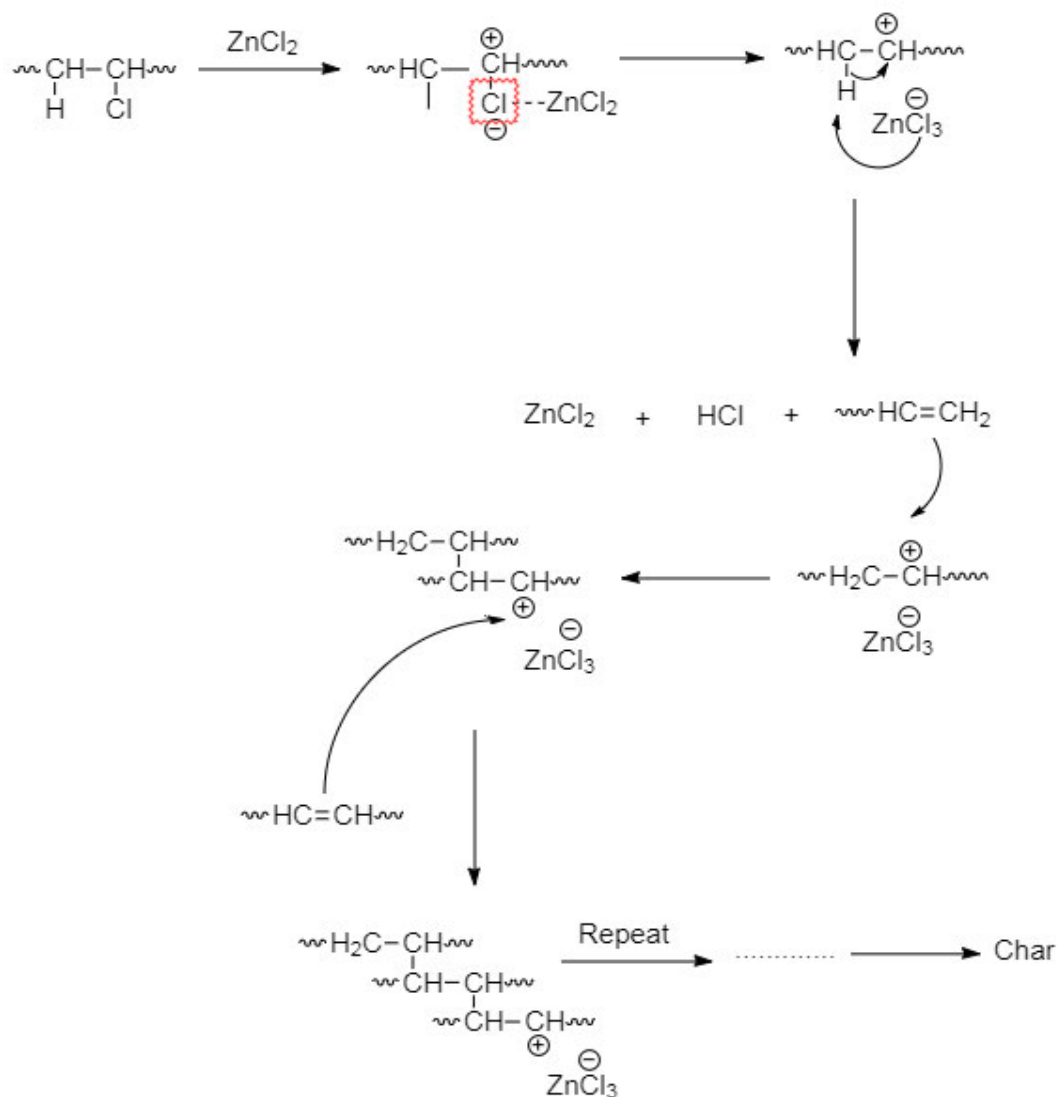


Figure 4-15 Mechanism involved for rapid colour caused by ZnCl<sub>2</sub>

Solving a problem for zinc burning phenomenon, which is a common issue among thermal stabilizers containing zinc, was the main purpose of this chapter. That is why this chapter is mainly focused on zinc as a metal complex with dipentaerythritol, although it shows the least efficient metal among other metal complexes investigated in this chapter.

Overall, the mechanism of action in this formulation involves:

- Chelating and capturing Lewis acid in the solid phase and avoiding catalytic dehydrochlorination and sudden black phenomenon.
- Capturing some amount of toxic HCl gas in the solid phase.

- c) Cooling down the combustion environment because of releasing water in the vapour phase.
- d) Diluting the corrosive and toxic HCl atmosphere because of releasing water in the vapour phase and capturing some amount of HCl in char (solid phase).

# CHAPTER 5

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia

## 5. Evaluation of cementitious compositions as a novel class of thermal stabilisers for PVC

### 5.1 Introduction

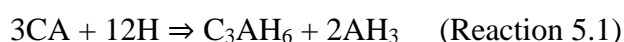
In this chapter a novel cementitious PVC composition was prepared and studied as an effective thermal stabiliser and HCl suppressing additive. The aim of this chapter is an improvement of the mechanism related to absorbing HCl released from thermally degraded PVC and decreasing its catalytic effect of dehydrochlorination. The first part of the chapter elaborates on hydrated calcium aluminate cement and the second part explains hydrated slag as the additive.

Calcium aluminate cement (CAC) with alternative names as High Alumina Cement (HAC) or Aluminous Cement is a special type of cement containing mainly  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ . These oxides combine to give mono calcium aluminate the main active phase which reacts with water during the hydration to produce hydrated calcium aluminate cement HCAC.

When Water is added to Calcium Aluminate Cement calcium ions ( $\text{Ca}^{2+}$ ) aluminate ( $\text{Al}(\text{OH})_4^-$ ) dissolves in the water. These ions can combine in the solutions forming different types of hydrate such as  $\text{AH}_3$ ,  $\text{C}_3\text{AH}_6$ ,  $\text{C}_2\text{AH}_8$ ,  $\text{CAH}_{10}$ , and defiantly crystallised gel-like phases. (cement notation: C= $\text{CaO}$ , A= $\text{Al}_2\text{O}_3$ , F= $\text{Fe}_2\text{O}_3$ , S= $\text{SiO}_2$ , H= $\text{H}_2\text{O}$ ).

The hydration of calcium aluminate cement is highly dependent on temperature so that it yields structurally and morphologically different hydration products at different temperatures [153, 154]

These different hydrated products can be mixed and recombined together to generate more stable phases. For all temperature ranges, the most stable hydrate phases of calcium aluminate cement are  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  (gibbsite). The following reactions are the most probable reaction during the hydration of Calcium aluminate cement.  $\text{C}_3\text{AH}_6$  has a cubic crystal structure while  $\text{AH}_3$  has a poorly crystalline morphology[155].



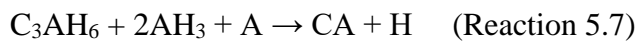
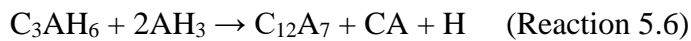
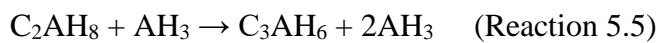
The other possible hydrates, that are less stable, will transform into these phases over time as follows [153, 156-158].



The conversion process is the name given to the above reaction in which the hydrated hexagonal  $CAH_{10}$  phase is converted to the cubic hydrated  $C_3AH_6$  phase, consequently, causing a decrease in the volume of the phase and an increase in the porosity of the matrix [157, 159, 160].

The metastable phases decompose at temperatures between 100–200°C, whereas the stable phases have decomposition peaks at 250–350°C [155].

In general, when the hydrated Calcium aluminate cement is heated, physically bound water (at 105°C) and Chemically bound water (200°C -800°C) are released from it [161]. Dehydration by heating follows the following reactions [162].



According to the literature, the dehydration temperatures of hydrated phases of calcium aluminate cement during heating are as follows [162, 163] :

At 100 °C: release of weakly bound water of the alumina gel (amorphous  $AH_3$  gel)

At 120 °C : dehydration of  $CAH_{10}$

170 - 195 °C: dehydration of  $C_2AH_8$

210-300 °C:  $AH_3$  (gibbsite)

240 to 370 °C:  $C_3AH_6$

In other words,  $AH_3$  loses two molecules of Water and produces  $AH$  during the heating to about 400 °C, while the third molecule of water is lost at 800 °C by transforming to  $A$  phase ( $\alpha-Al_2O_3$ ). During dehydration,  $C_3AH_6$  releases water and converts it to the anhydrous  $CA$  that can boost the thermomechanical properties of the compound [164, 165].

Moreover; exposure of the hydrated calcium aluminate cement to above 900°C leads to activation of the sintering process and ceramic bond formation which result in the densification of material and better mechanical properties. Above 1400 °C, the strongest ceramic bond is generated and apart from the existence of  $A$  phase,  $CA_6$  phase also develops in the structure.

[161]. The chemical reactions involved in the hydration and dehydration process of calcium aluminate cement and the formation of ceramic composition support and promote using this product as a thermal stabiliser and HCl suppressing additive for PVC. The PVC thermal decomposition is auto-catalysed by the HCl formed from the dehydrochlorination of PVC at about 150 °C. On the other hand, releasing the hydrated water from the hydrated cement at different temperature ranges as stated before will remarkably retard the thermal decomposing of PVC and enhance its decomposition temperature.

## **5.2 Thermal stability evaluation of PVC stabilised with HCAC by TGA**

Samples prepared in Ch.3.3 were evaluated by the TGA technique, adopting standard methods as detailed in Ch.3.2. The obtained thermograms for the PVC samples with different contents (phr) of HCAC are shown in Figures 5-1 to 5-5. The thermal stability characteristics extracted from the TGA curves are summarised in Table 5-1. The TGA thermograms show the heat tolerance of the samples and temperatures at which parts of the PVC composites decompose into gasses. According to the obtained graphs, all samples showed a two-step degradation pattern. The first step is known as the key step because at this step the cleavage of the Carbon-Chloride bond in the PVC takes place due to having a lower energy level than the Carbon-Carbon bond forming hydrogen chloride, which acts as an auto catalyst for further dehydrochlorination reactions and removal of chlorine from the polymer resulting in conjugated double bond polyene chains. The second step is related to the thermal degradation of the polyenes and breaking of the carbon chain yielding the formation of aliphatic compounds and volatile aromatics by the intramolecular cyclisation reactions of the conjugated chains forming cross-linked PVC containing Carbon Carbon double bonds.

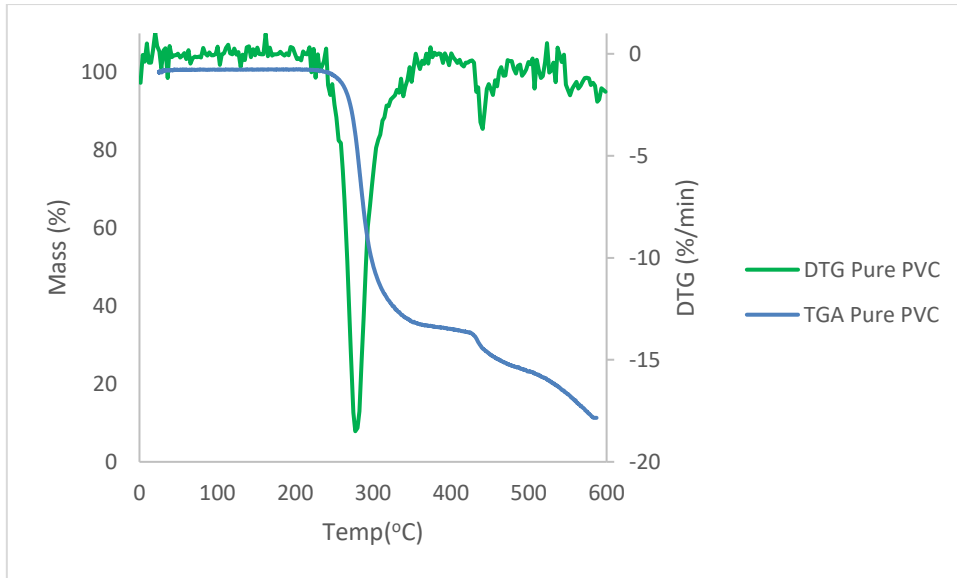


Figure 5-1 TGA and DTG curves of pure PVC

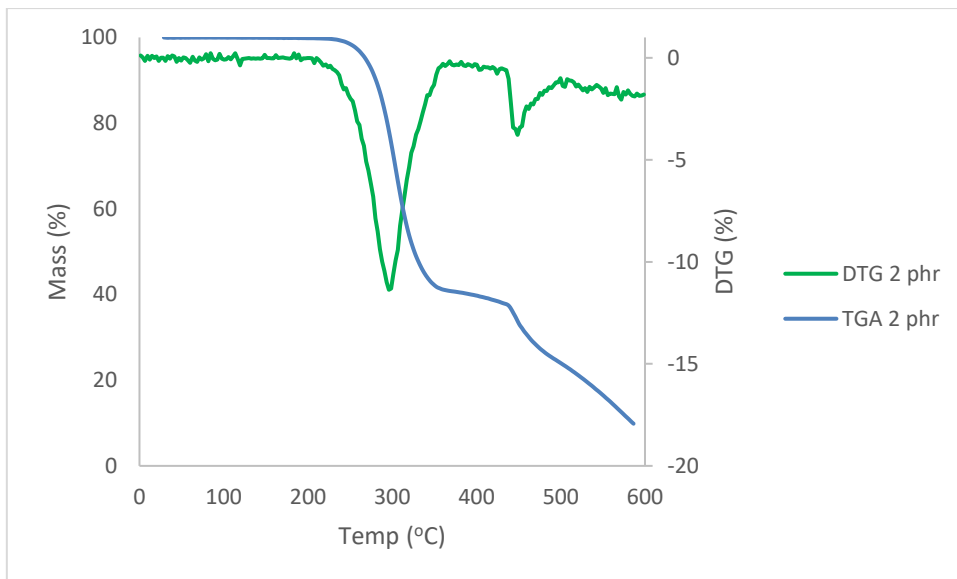


Figure 5-2 TGA and DTG curves of PVC stabilised with 2 phr of HCAC

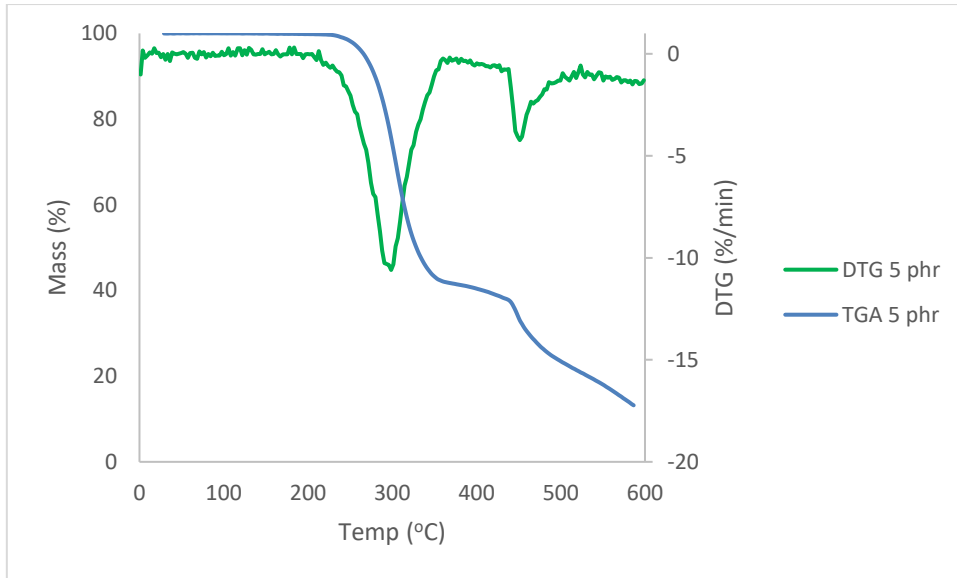


Figure 5-3 TGA and DTG curves of PVC stabilised with 5 phr of HCAC

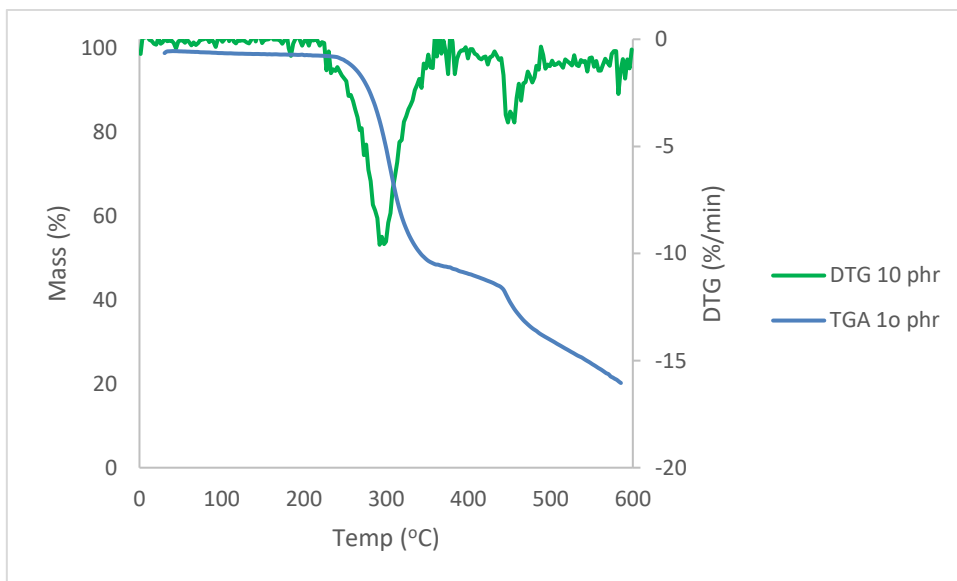


Figure 5-4 TGA and DTG curves of PVC stabilised with 10 phr of HCAC



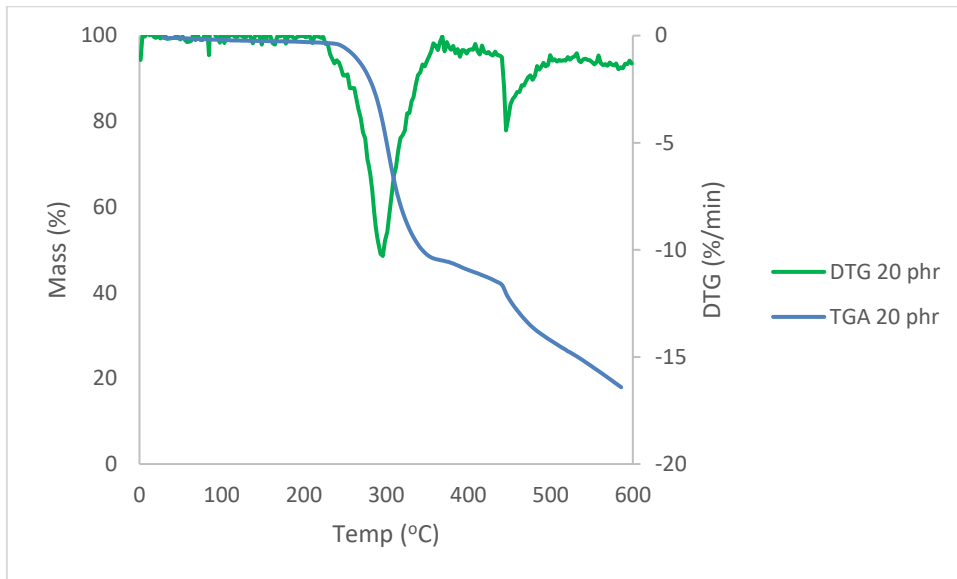


Figure 5-5 TGA and DTG curves of PVC stabilised with 20 phr of HCAC

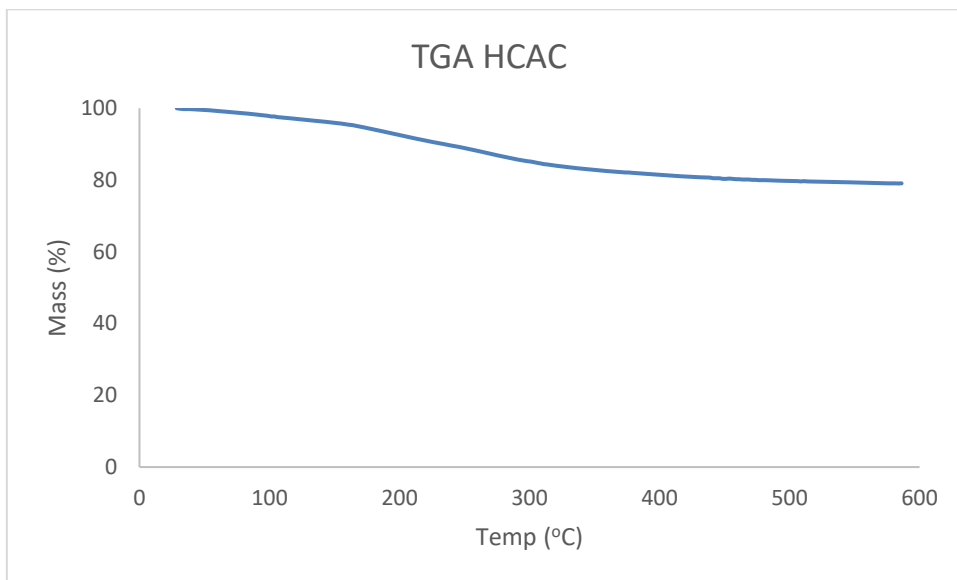


Figure 5-6 TGA curve of pure HCAC

Samples	T1 (°C)	T2 (°C)	Rate of degradation stage 1 (%/min)	Rate of degradation Stage 2 (%/min)	% RESIDUAL MASS at 587.1°C	% Mass change step 1
Pure PVC	268.2	431.1	-19.43	-3.68	10.03	-66.05
PVC+2 phr	277.7	438.9	-11.45	-3.85	10.26	-58.20
PVC+5 phr	277.8	440.1	-10.64	-4.37	13.63	-57.91
PVC+10 phr	278.5	440.9	-10.19	-4.47	20.05	-50.42
PVC+20 phr	279.5	441.1	-10.01	-4.92	23.75	-48.61
PVC+50 phr	281.7	448.3	-9.75	-4.95	29.12	-39.90

Table 5-1 Thermal stability characteristic (parameters) extracted from the TGA thermograms of PVC stabilised different phr of HCAC

T<sub>1</sub>= temperature of the first main degradation

T<sub>2</sub>= temperature of the second main degradation

According to TGA and DTG curves, as the amount of HCAC increases in the composites, the rate of degradation at the first stage of decomposition decreases. Even the existence of 2 phr HCAC in PVC, decreases the rate of degradation from 19.43 %/min in pure PVC to 11.45 %/min. On the other hand, as the content of HCAC increases in the composition, the rate of degradation at the second stage of decomposition increases, this can be related to the release of the chemically bounded hydrating water which dilutes the toxic gaseous phase of the combustion environment and decreases the temperature due to the absorbed heat for water evaporation of 540 cal /g.

Moreover, even the addition of 2 phr HCAC to PVC increases the initial decomposition temperature of the first stage from 268.2 to 277.7 °C. In general, as the contents of HCAC in PVC increase, the rate of degradation decreases and the decomposition temperatures at the first and second stages of degradation increase. Moreover, increasing the amount of hydrated cement cause an increase in the amount of residual mass at the end of the test (at the temperature of 587.1°C). Thermal gravimetric analysis shows that even a small amount of hydrated Cement

(2 phr) improves all thermal characteristics of PVC. As the temperature increases, the fully cured and dried HCAC undergoes dehydration. This process is endothermic which causes heat absorption from the combustion environment and the presence of the released water leads to the higher heat capacity of the gaseous phase. The water from dehydration of the HCAC dilutes the toxic gaseous phase of burned PVC. Furthermore, the mineral and inorganic nature of cement dilutes the organic and flammable nature of PVC and also leads to the higher heat capacity of the PVC before and after decomposition.

### 5.3 Thermal stability evaluation of PVC stabilised with HCAC by DSC

PVC samples stabilised with different content of HCAC prepared in Ch .3.3 were examined by DSC. The DSC scans for different samples containing different ratios of HCAC. are shown in Figure 5-7. The thermograms showed the enthalpy change characteristics as a function of increasing temperature indicating the phase transition of PVC-HCAC composition.

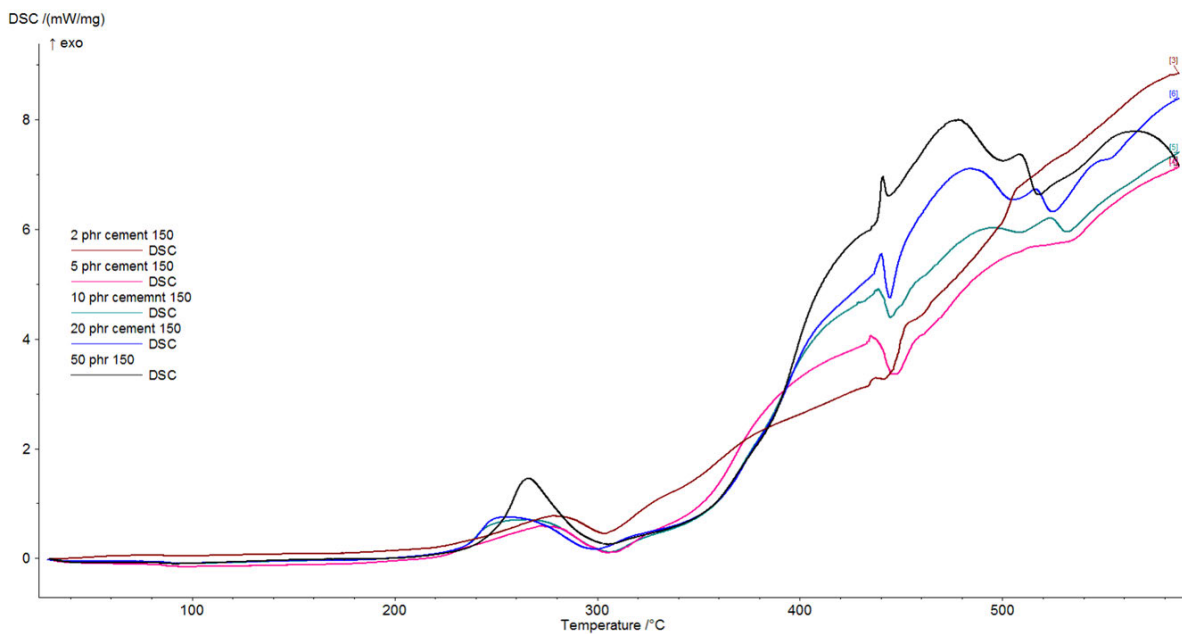


Figure 5-7 Comparison of DSC curves of PVC composite containing different ratio of HCAC

All the DSC graphs for different ratios of HCAC showed one exothermic peak below 300° C and 3 exothermic peaks above 400 ° C. It should be noted that as the ratio of hydrated cement increased, the exothermic peaks are stronger, and small endothermic peaks also appeared. For example, as can be seen in Figure 5-7, PVC containing high ratios of HCAC, such as 50 phr, showed 4 exothermic peaks, and an endothermic peak, while composite containing low ratios of HCAC (2phr) showed weak exothermic and one weak endothermic peaks above 400 ° C. The endothermic peaks of composites containing high ratios of HCAC are related to dehydration of the HCAC and evaporation of the chemically bonded water. Thus, as the amount of cement is increased, these endothermic peaks are larger. The exothermic peaks are also stronger as the amount of HCAC is increased. The exothermic peaks are very interesting which proves crystallization resulting from phase change with increasing temperature.

Figure 5-8 and Figure 5-9 illustrate the DSC thermograms for pure PVC and HCAC, respectively. Both PVC and HCAC showed only endothermic peaks, and completely different thermal decomposition behaviour than PVC-HCAC composites. Endothermic peaks in PVC are mainly related to dehydrochlorination and endothermic peaks in HCAC are related to dehydration.

Two endothermic peaks are obvious in Figure 5-8 related to pure PVC. The first is related to dehydrochlorination, due to the cleavage of C-Cl bond. The second is related to the volatiles which is mostly olefines, aliphatic, cyclic and aromatic hydrocarbons. The DSC curve of pure PVC is qualitatively matching with literature reported data [166, 167].

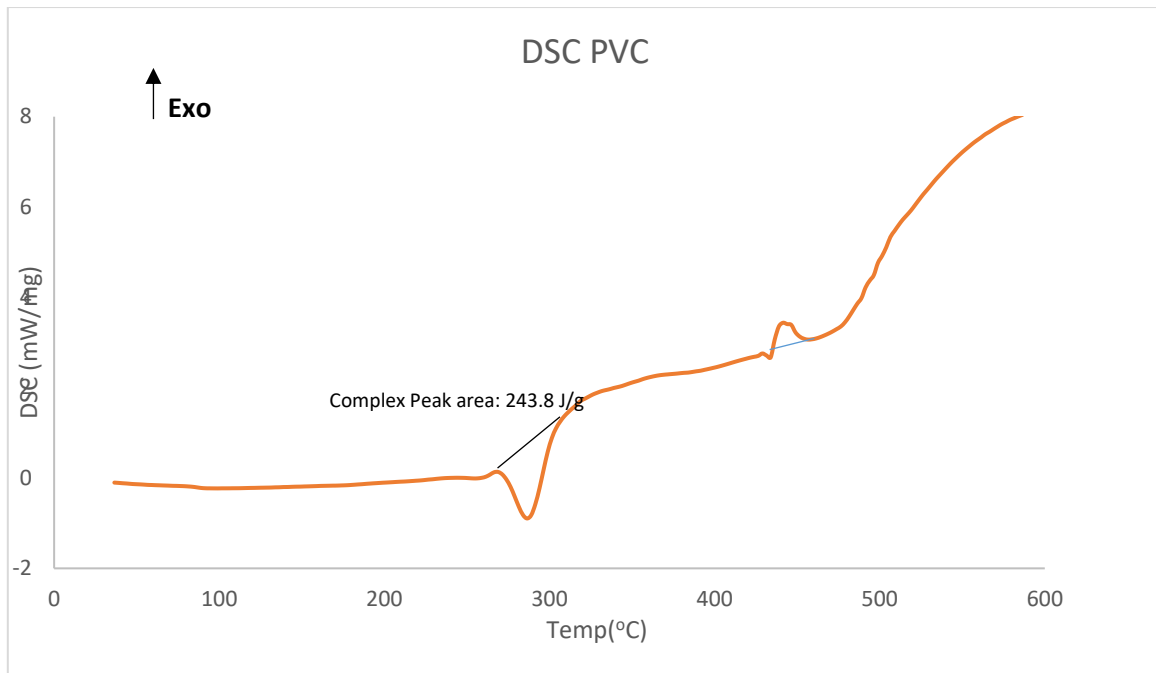


Figure 5-8 DSC curve of pure PVC

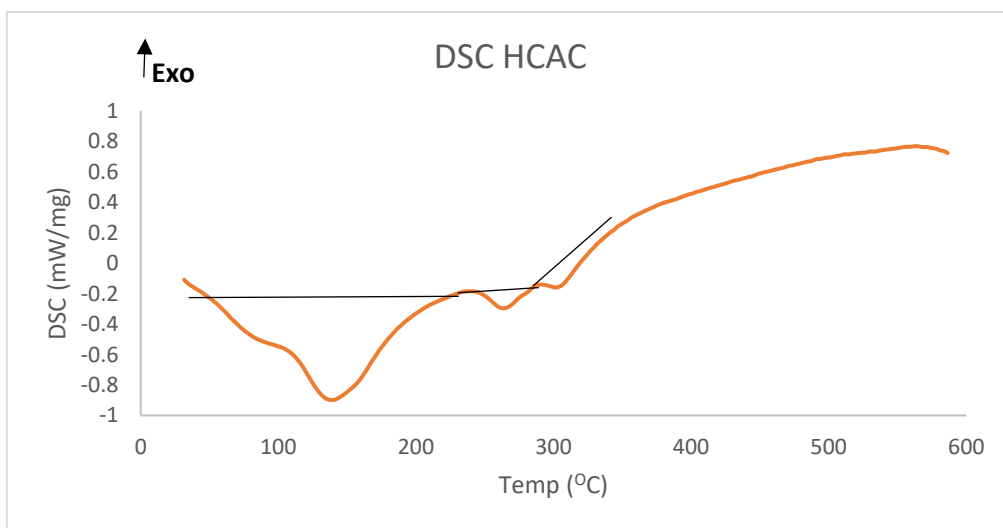


Figure 5-9 DSC curve of HCAC

The DSC curve of HCAC (Figure 5-9) shows large endothermic peaks attributed to the dehydration of phases which result in a considerable cooling down effect. Both PVC and HCAC showed endothermic peaks in their DSC thermograms (Figures 5-8 and 5-9), while the PVC-HCAC composites showed exothermic peaks (Figure 5-7 ). From the XRD result and

DSC thermograms, it can be concluded that crystallization takes place during the increasing temperature of PVC - HCAC composites.

Crystallization is a bond-making event in which particles of a chemical medium come together to produce an extremely ordered microscopic structure. Moreover, when elements are attached together to make new bonds, some energy and heat is released to reach the stable state. Thus, the crystallization and formation of new phases is a well-known exothermic process.

#### 5.4 Elemental analysis of the combusted residues by SEM-EDS

Suitable protection provided by the char enhances the fire resistance of substances during combustion. Therefore, the analysis of the char and ash residue will highlight and support the mechanism of fire resistance of the PVC matrix. To greater interpretation the function and microstructure of the protecting char residues of TGA, decomposed samples were systematically analysed by the coupling of SEM photographs and EDS spectra. Figures 5-10 to 5-12 show SEM and EDS results of the ashes residue from fully decomposed samples.

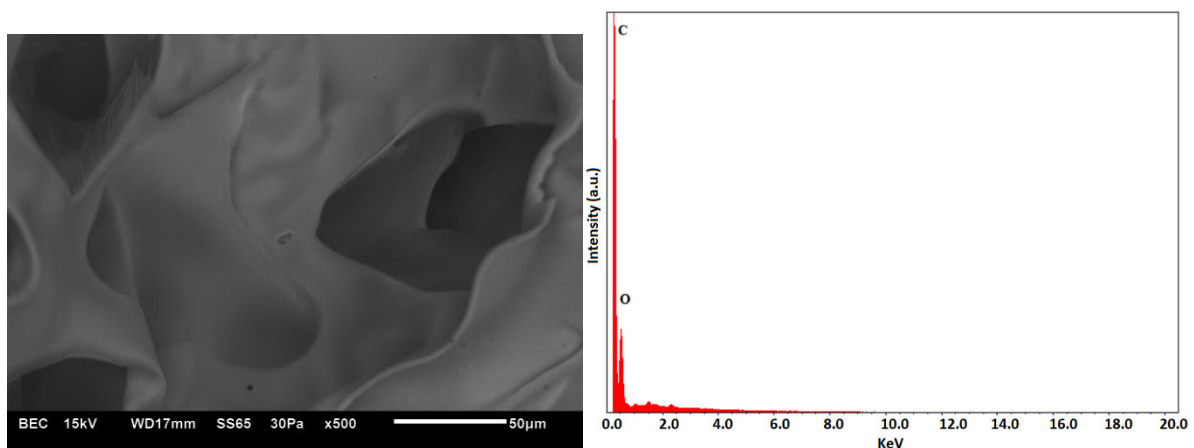


Figure 5-10 SEM (500 X) and EDS for ash residue of pure PVC thermal decomposition

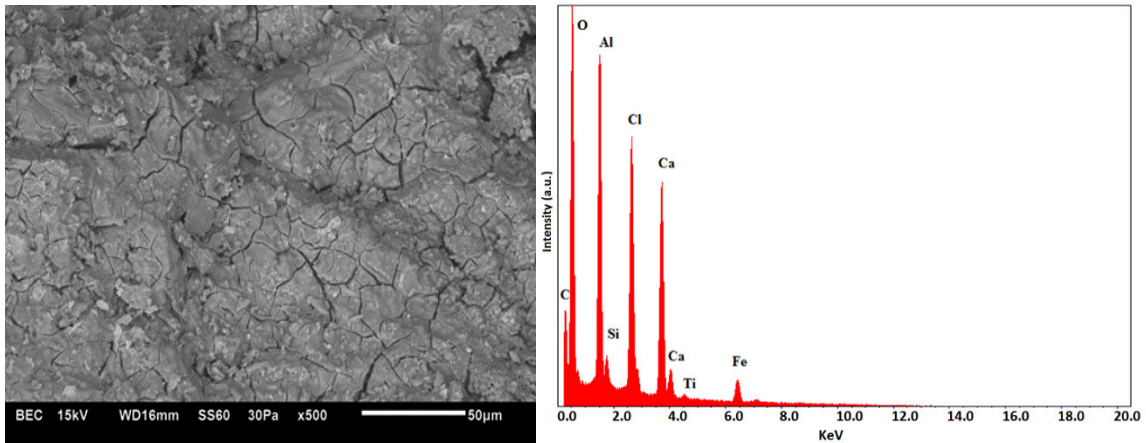


Figure 5-11 SEM (500X) and EDS for ash residue of PVC stabilised with 10 phr of HCAC

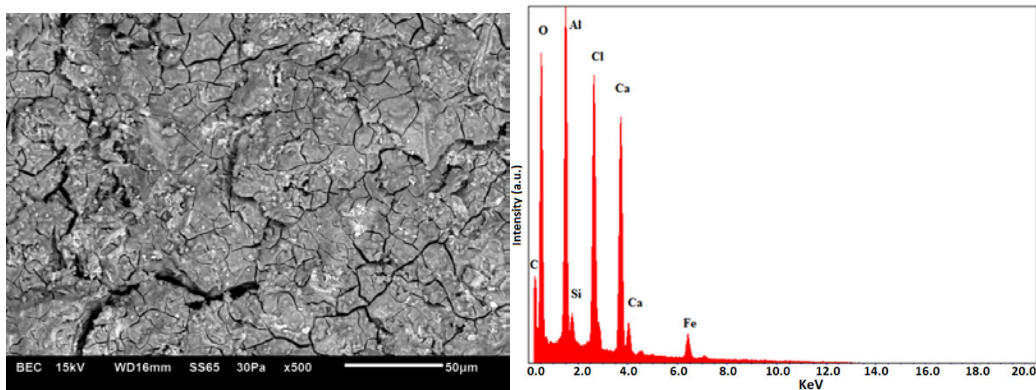


Figure 5-12 SEM (500 X) and EDS for ash residue of PVC stabilised with 50 phr of HCAC

A very interesting point about the comparison of EDS qualitative results (Figures 5-10 to 5-12) is that the ash residue from the PVC-HCAC composite showed a very strong chloride signal, while ash residue from the pure PVC sample didn't show any chloride signal. It means that during the combustion of pure PVC, HCl gas comes off from the samples, thus, leading to auto acceleration of PVC decomposition. Thus, a strong signal of Cl in the EDS spectrum of ash residue from PVC-HCAC composite proves that Cl released from the decomposition of PVC is reacted with hydrated calcium aluminate components, accordingly the auto acceleration reactions are retarded. Generally, HCl gas which is a toxic and corrosive gas is captured and stored in a solid phase and cannot emit into the environment. This proves a very good technological and scientific performance of the presented formulation by reducing the amount of toxic and corrosive hydrogen chloride released into the atmosphere. Thus, this formulation plays an important role in the assurance of fire safety by reducing fire toxicity.

## 5.5 Morphology study of the PVC stabilised with - HCAC by SEM technique

### 5.5.1 The SEM morphology of the stabilised PVC samples pre thermal degradation process

Samples before thermal degradation (pre TGA tests (Figures 5-13 to 5-15) prove successful homogenous incorporation and distribution of calcium aluminate cement additive into PVC texture. Observation of the surface morphology by SEM shows compatibility and homogeneous distribution of the additives within the polymer mixture. According to the SEM photographs, PVC samples with calcium aluminate cement additive show almost homogenous surface morphology with no high inner disconnection which exhibits the blend with good compatibility and miscibility.

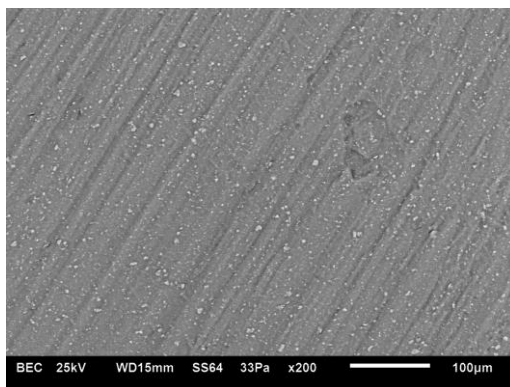


Figure 5-13 SEM of PVC stabilised with 2 phr HCAC



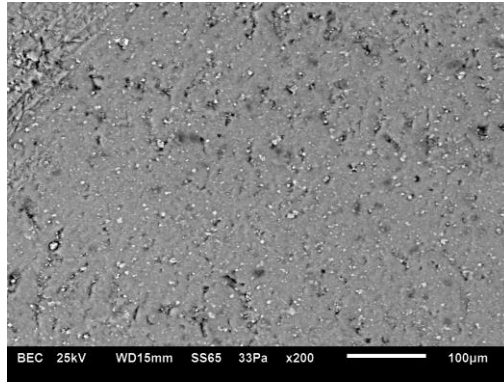


Figure 5-14 SEM of PVC stabilised with 10 phr HCAC

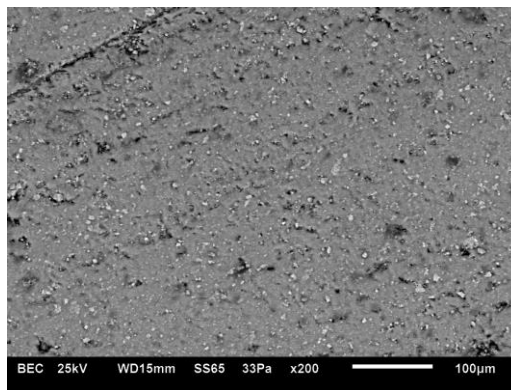


Figure 5-15 SEM of PVC stabilised with 20 phr of HCAC

### **5.5.2 The SEM morphology of the stabilised PVC samples with - HCAC post thermal degradation by TGA (char morphology study)**

SEM images of the ashes residue from PVC-HCAC compositions (Figures 5-11 and 5-12) showed a densified layer structure with some cracks and pores. In order to observe this densified structure in a smaller ratio of the area scanned of the sample, extra-magnified photos of 500 to 2000 were taken (Figure 5-16 to 5-17). All photos at different magnifications prove the formation of desired densified structure feature.

These interesting densified structures are ceramic layers. Calcium aluminate cement converts to ceramic at elevated temperatures and acts as the external shield for enclosed layers of polymer in fire incidents. The pores and cracks of the structure promote HCl capturing. The strong and densified structure of ceramic will reinforce the areas next to pores leading to a

mechanically stronger PVC matrix at high temperatures. As a result, this novel composition becomes stronger in fire incidents. This aggregated dense ceramic char layer provides a compact and durable shield to heat transfer, decomposition products, and volatile gases, and protects inner layers of PVC from heat source and Oxygen.

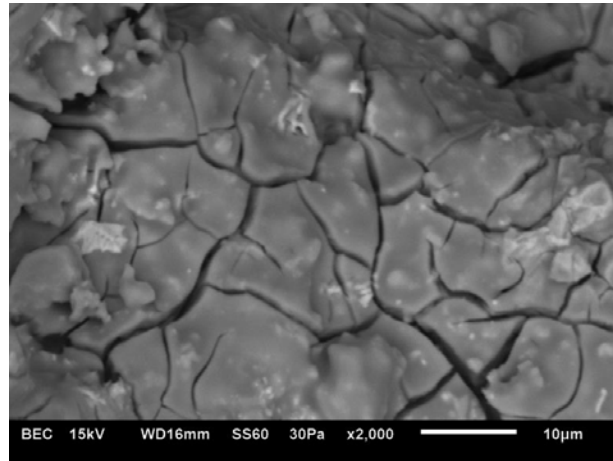


Figure 5-16 SEM (2000 X) for ash residue of PVC stabilised with 10 phr of HCAC

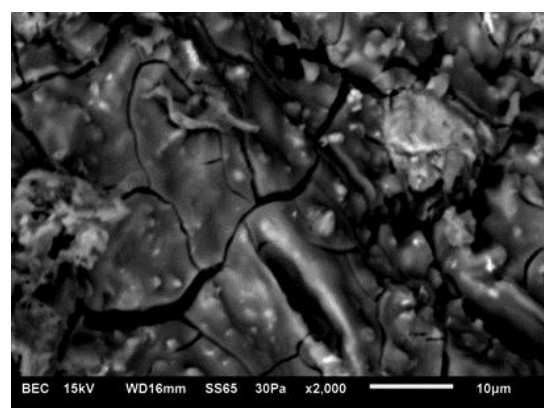
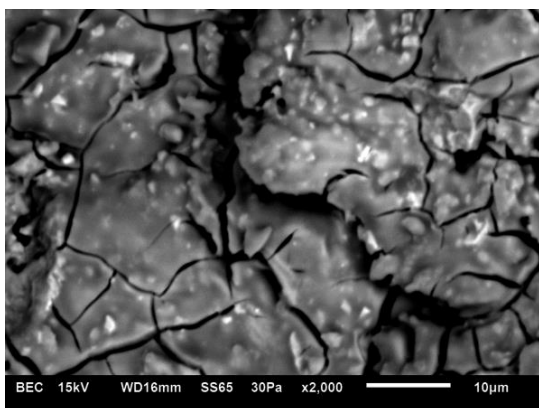


Figure 5-17 SEM (2000 X) for ash residue of PVC stabilised with 50 phr of HCAC in two different areas

In conclusion, the images of the samples pre TGA tests did not show any densified layer while after combustion a densified structure is clearly distinguishable in the char residues of the samples.

## 5.6 Crystallographic study of PVC stabilised with HCAC

In order to find the product formed due to the thermal decomposition of PVC stabilised with – HCAC, the XRD was performed on the ash residue of the decomposed PVC stabilised with HCAC. Typical crystallographs are shown in (Figure 5-18).

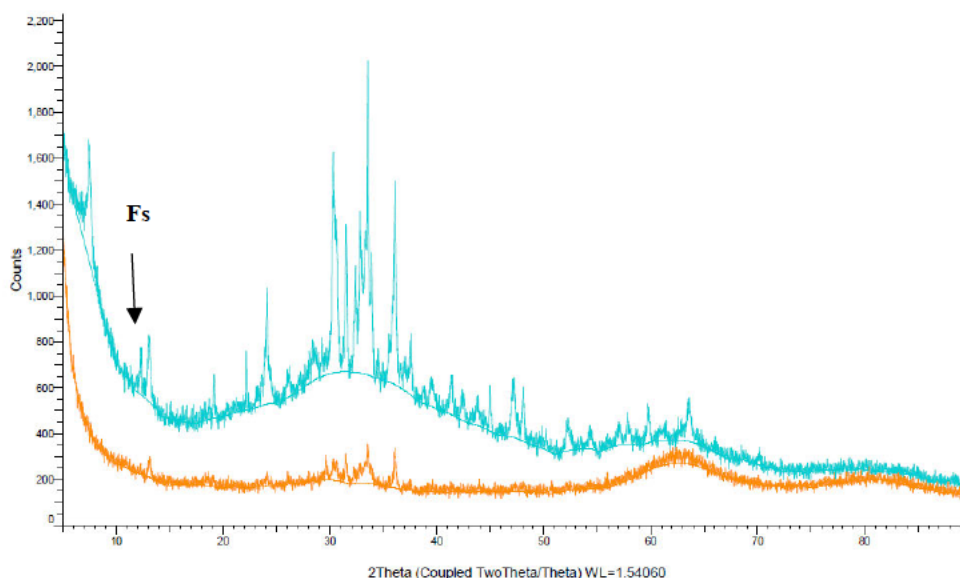


Figure 5-18 XRD comparison of the samples (blue ash from PVC-HCAC composite, orange: ash from HCAC)

According to X-ray diffraction spectra shown in Figure 5-18, samples from decomposed PVC-stabilised with HCAC showed more crystalline structure than ash samples from the decomposition of HCAC. New signals also appeared in the spectra of the combusted samples which also prove that new crystalline phases are generated during the combustion of PVC-HCAC composition. During the temperature range at which PVC is degraded and HCl gas is evolved by pyrolysis, It is trapped by HCAC constituents. From the XRD and EDS data, it can be concluded that the chloride is not only related to physical adsorption into the pores but it is also chemically reacted, forming new crystalline phases. In the XRD graph, there is an obvious crystalline phase labelled as Fs. This peak is the characterisation signal of the formation of Fridel's Salt crystal with the chemical formulation of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ . The existence of chlorine element in the chemical formulation of the new crystalline phase proves chemically linked chloride into the solid char layer.

### **5.6.1 Stabilisation of PVC based on the mechanism of Chloride binding and Chloride transport in PVC-Cementitious Compositions based on XRD, DSC and EDS analyses**

The obtained results from XRD, DSC and EDS analyses showed that HCAC adsorbs and binds chloride in two separate mechanisms including a physically adsorption mechanism, and a chemically anion-exchange mechanism. In other words, the transfer of chlorides into cement paste is a sophisticated process that may include permeation, diffusion, capillary suction and convective flow via the porous and micro-cracking system, followed by physical adsorption and chemical binding. Ionic transport chlorides penetrate the interconnecting pores in cement paste by convection, and chloride ions diffuse further into the saturated pore system. The diffusion process is governed by free chloride concentration gradients; therefore, the ability of the cement paste to physically adsorb and chemically react with chloride ions controls the number of free chloride ions in the cement paste.

In the adsorption and physically bonding mechanism, chloride penetrates the bulk via capillary pores and cracks of cement paste and finally goes further and is adsorbed to the inner and inferior layers of cement paste. Both the dehydration and conversion process in HCAC paste at elevated temperatures increase the porosity of the matrix and facilitate the physical penetration of toxic gas into the solid phase.

In the anion-exchange reaction and chemically bonding mechanism,  $\text{Cl}^-$  ions are exchanged with the  $\text{OH}^-$  ions of the hydrated cement phase to generate Calcium Aluminate Chloride and Calcium Aluminate Chloride Hydrate known as Friedel's Salt ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ) which can release its water during the elevated temperature of combustion environment. According to the literature, the main recognised peak of Friedel's Salt appears between 11-12 degrees in 2theta axis of the XRD pattern (in Figure 5-18 labelled as Fs).

An increase in the A/C ratio (higher amount of  $\text{Al}_2\text{O}_3$  in oxides of the clinker like in Calcium aluminate cement) causes an increase in the chloride ingress. In other words, the higher  $\text{Al}_2\text{O}_3$  content in calcium aluminate cement clinker would enhance and facilitate the formation of chloroaluminate hydrates, which is produced from a reaction between hydrated cement and Hydrogen Chloride gas. Thus, using calcium aluminate cement type is beneficial in this

research, due to the higher possibility of chloride reactive CA hydrations and Friedel's salt formation.

## **5.7 Production of PVC stabilised with HCAC on a pilot scale**

The outstanding thermal stability of PVC stabilised with HCAC has been of great interest to the "AFS Systems" industry. 5-10 kg samples were prepared and transformed into sheets by compression moulding. The TGA results (Figure 5-19) and those presented in Table 5-2 showed enhanced thermal stability behaviour of the samples in sheet form on the semi-industrial scale compared to the preliminary tests done on samples on the lab scale. This is due to more homogeneity and more consistent quality of the samples based on this method. In other words, Sheet samples have a more homogenous structure and show the same quality material from the surface to different layers of thickness. Thus, they show improved fire and thermal resistance in comparison with lab-scale tests. Table 5-2, compares the results of the sample made on the semi-industrial scale (homogenous sheets) with the results of the samples made by university facilities (preliminary tests in lab scale). Figures 5-20 and 5-21 illustrate a comparison of TGA and DTG curves of PVC with 2 phr HCAC made by different facilities, these figures prove an obvious improvement in samples made by industrial facilities even in a tiny amount (2 phr). Accordingly, it can be concluded that the novel formulation presented in this chapter showed very good improvement in the thermal behaviour of PVC at both the lab scale and mass scale when it is made homogeneously by advanced facilities.

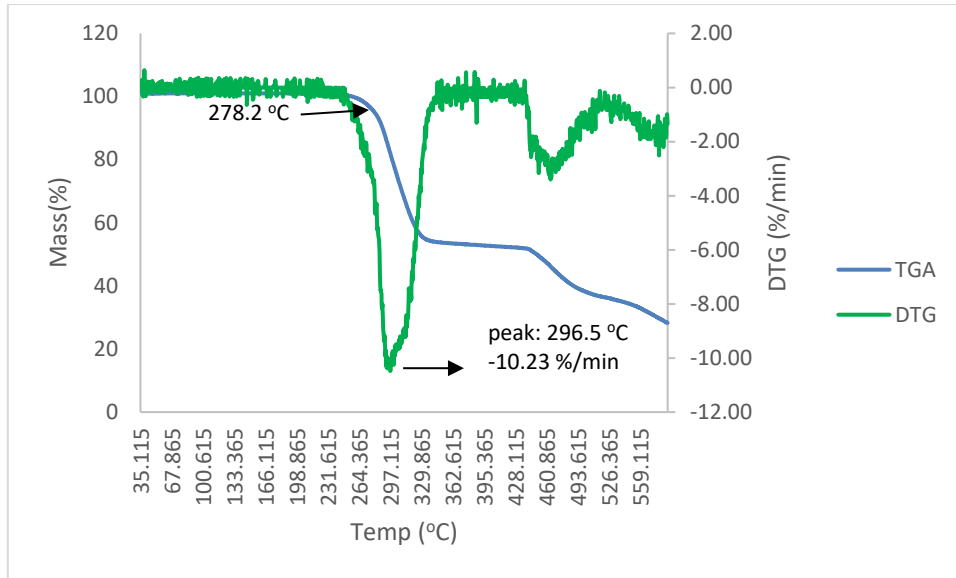


Figure 5-19 TGA and DTG curves of PVC composite with 2 phr HCAC (sheet form)

Samples	T1 (°C)	T2 (°C)	Rate of degradation stage 1 (%/min)	Rate of degradation Stage 2 (%/min)	% RESIDUAL MASS at 587.1°C	% Mass change step 1
Pure PVC	268.2	431.1	-19.43	-3.68	10.03	-66.05
PVC+2 phr preliminary test	277.7	438.9	-11.45	-3.85	10.26	-58.20
PVC+2 phr in sheet form	278.2	445.3	-10.23	-3.05	28.25	-48.47

Table 5-2 typical thermal stability characteristics and parameters extracted from TGA for the samples prepared on lab scale and semi industrial scale

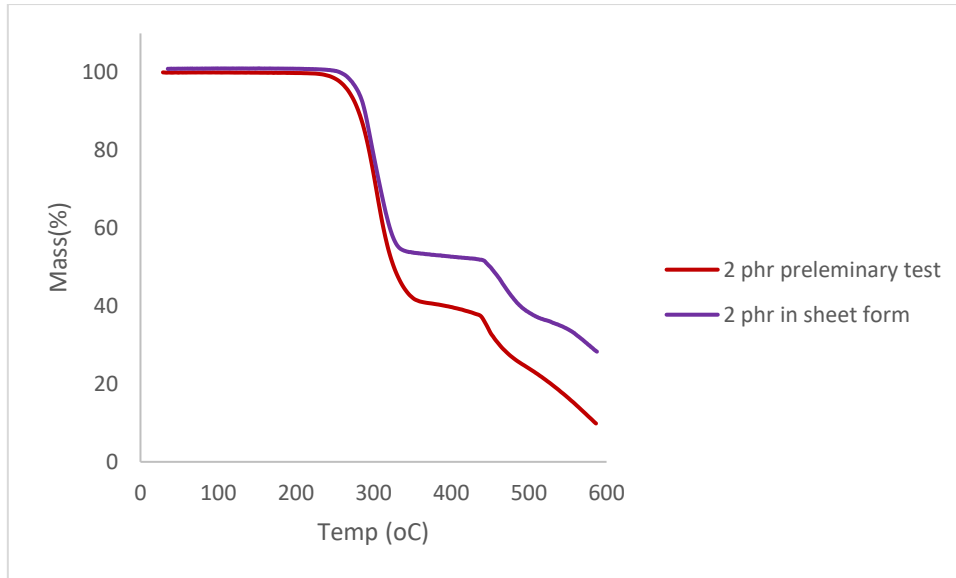


Figure 5-20 Comparison of TGA curves of PVC with 2 phr HCAC made by different facilities (Purple curve: homogenous sheet on semi industrial scale, Red curve: preliminary sample on lab scale.

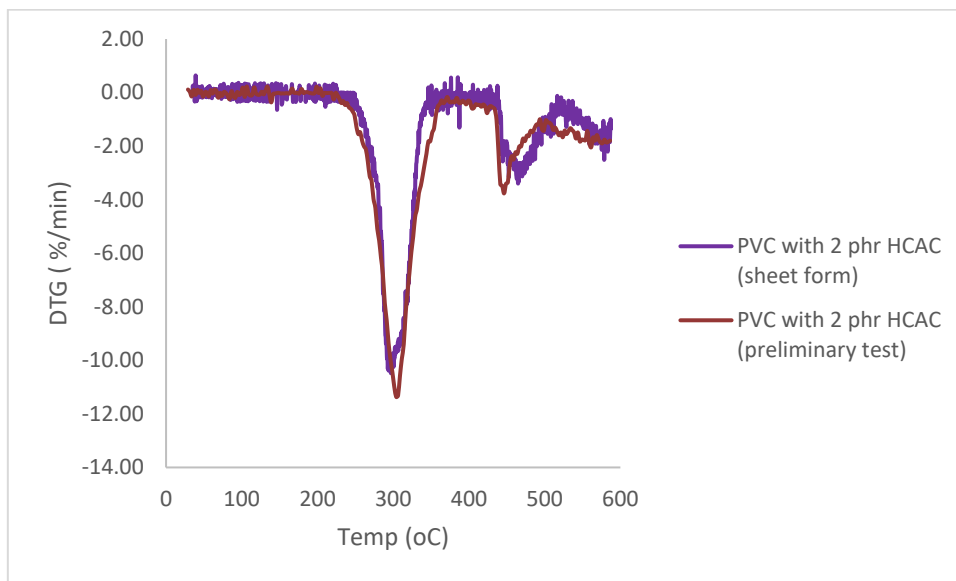


Figure 5-21 Comparison of DTG curves of PVC with 2 phr HCAC made by different facilities (Purple curve: homogenous sheet made on semi industrial scale, Red curve: lab scale samples.

## **5.8 Part II Stabilisation of PVC with activated /hydrated slag cement:**

### **5.8.1 Introduction**

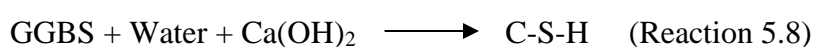
Slag cement is a cementitious substituent in the construction industry, it is also known as ground-granulated blast-furnace slag (GGBS). The hydration of GGBS is usually activated in an alkaline medium. Alkali activation is the reaction of a solid aluminosilicate precursor under alkaline conditions, to produce a compound which is formulated on alkali-alkali earth-aluminosilicate and/or hydrous alkali-aluminosilicate phases. The precursors for Alkali activated materials (AAM) are mainly by-products of industrial processes and should be rich in aluminosilicate for example, slag, fly ash or silica fume [168, 169]. Alkali activated materials (AAMs) are generally known as alternative green materials that can be used instead of Ordinary Portland Cement because of their more sustainability and cost effectiveness compared to ordinary Portland cement [170, 171]. In other words, the manufacturing of cement is accompanied by the generation of a large amount of CO<sub>2</sub> and energy which is harmful to the environment, whereas, aluminosilicate precursors are only waste products and, consequently, have a less negative impact on the environment [172, 173]. Additionally, several studies have shown that products based on hardened Alkali-activated materials (AAM) improve the heat and fire resistance of these products in comparison with Portland cement concrete [174, 175]. In recent years, (GGBS) has seen an increased uptake of usage in sustainable construction as a supplementary cementitious material. Blast furnace slag is a by-product in the manufacture of iron and steel and has a relatively smaller amount of CO<sub>2</sub> emission or embodied energy rather than OPC [176, 177]. Manufacturing 1 tonne of slag needs around 1300 MJ of energy and generates just 0.07 tonne of CO<sub>2</sub>. Whereas manufacturing of an equal amount of OPC needs 5000 MJ of energy and releases 1 tonne of CO<sub>2</sub> [178-180].

GGBS has also some other advantages such as its higher resistance to chloride ingress and chemical attacks [181, 182]. It lowers the risk of reinforcement corrosion and damages related to alkali-silica reaction. Blast furnace slag is mainly composed of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and Fe<sub>2</sub>O<sub>3</sub>. Raising the amount of CaO in the slag results in higher slag basicity and an increased compressive strength [183-185].



## 5.8.2 Mechanism of reactions and composition of the hydrated GGBS to promote its thermal efficiency as a stabiliser for PVC

The major hydration product of alkali activated slag is calcium silicate hydrate (CSH) regardless of the activator [186]. In this study, Ca (OH)<sub>2</sub> is used as an activator, so the pozzolanic reaction between slag and calcium hydroxide occurs as below (Reaction 5-1). Additionally, Ca (OH)<sub>2</sub> activator leads to products containing Calcium which is able to positively influence the comprehensive strength of the bind [187].



According to the above equation, the most abundant product of the paste is an inorganic hydrogel which contains calcium–silicate–hydrates. This hydrated gel is mostly amorphous as it is mixed with other phases such as AFm and ettringite phases (C<sub>2</sub>ASH<sub>8</sub> or C<sub>4</sub>AH<sub>13</sub>). Generally, hydration products include C–S–H, C<sub>6</sub>AFS<sub>2</sub>H<sub>8</sub>, M<sub>5</sub>AH<sub>13</sub>, C<sub>2</sub>ASH<sub>8</sub> and C<sub>4</sub>AH<sub>13</sub> [188]. Calcium silicate hydrate (C-S-H) is actually a porous media full of capillary pores and gel pores ranging from nanometres to micrometres. In other words, calcium silicate hydrates which are porous and nano-crystalline can be generated in an aqueous environment from calcium hydroxide and silica. In this situation, C-S-H forms and the higher the molar ratio of Ca/Si in a primary mix of solids, the higher the calcium amount of the equilibrium mixture and the higher Ca/Si ratio of C-S-H. Calcium silicate hydrate also plays an important role in the durability of cementitious materials.

In recent years, the reaction between chloride ions and C-S-H gel has been studied experimentally. There are also some molecular dynamic studies that prove the transportation of ions and water in the tiny channels (nano-meter) of the porous texture of calcium silicate hydrate gel [189, 190]. The studies demonstrate the dynamic and structural behaviour of calcium silicate hydrate samples when exposed to solutions containing chloride ions. Ramachandran [191] introduced three probable states of chlorides when they interact with calcium silicate hydrate which included interlayer chlorides, chemically absorbed chlorides and those which are firmly bound and confined in the lattice. However, more details were not presented because of the experimental methods' limitations. GeZhi [192] studied the adsorption of chloride, alkali and sulfate on the surface of the calcium silicate hydrate and its impact on the concrete durability. GeZhi put forward chlorides which may potentially be presented in the

adsorption as well as the diffusion surface of the C-S-H/solution interconnection. However, he only determined the amount of the adsorption and did not elaborate on the mechanism. Barberon and his team [193] studied the interaction between chloride and the aluminate and silicate hydrate phases available in the cement paste. Their study was based on the data of the nuclear magnetic resonance analysis on the stabilization and addition of the chloride ions in the hydration products and the detection of new phases possibly emerging because of chloride ingress. Based on their NMR results, they figured out that after exposure of the concrete samples to Sodium Chloride solution, only absorbed and condensed chlorides were detected in the concrete samples. Elakneswaran et al. [194] introduced a simulated model to estimate the chloride adsorption on the surface of C-S-H and gained a good complement compared with the evaluated results. Other studies on this concept have also been proposed [195-199].

According to Reaction 5.8, the major hydration product of alkali activated slag is calcium silicate hydrate (CSH). The water chemically captured in the paste highly impact the thermal and structural properties of the PVC composite. There is a two-level loss of water which comes from the dehydration of calcium hydroxide and dehydration of calcium silicate hydrates. Gradual release of water causes a cooling down effect in high temperatures. With the rising temperature in fire incidents, the bonded water of calcium silicate hydrate releases into the surrounding atmosphere, leading to the increase in the density of calcium silicate hydrate. Thus, the initially formed calcium silicate hydrate gel structures have the tendency to collapse to less porous, denser and more stable structures with large-scale pores of the gel, which consecutively increases the size and the amount of the capillary pores. Moreover, chloride ions of hydrogen chloride (the toxic and corrosive gas emitted from burning PVC) can be captured by calcium ions in the form of calcium chloride and additionally they can be transported and adsorbed in nano-pores of calcium silicate hydrate. Additionally, AFm is another major generated phase which plays an important role in chloride bonding. AFm is crystalline hydrate phase which represents alumina, ferric oxide, monosulfate phase in cement chemist notation. AFm is one of the major phases formed during the hydration of cementitious systems. It is relevant to the layered hydrates consisting positively charged layers and water together with charge-balancing anions.

In general, two major chloride bonding may take place (i) through physical adsorption by CSH phase due to its special surface and (ii) through chemical substitution by AFm compounds.

Based on the chemical reactions, structure and mechanism of activation and hydration of GGBS it has been selected as a novel thermos stabiliser for PVC to be investigated in this study by various techniques.

### 5.8.3 Evaluation of the thermal stability of PVC stabilised with Hydrated GGBS by TGA:

According to the comprehensive study done on HCAC in part I of this chapter, increasing the amount of hydrated cementitious materials (from 2 phr to 50 phr) causes an increase in improving the thermal behaviour of PVC through different mechanisms. Therefore, the amount of 20 phr of HGGBS was recommended by the industry to be analysed and compared with HCAC. 20 phr is high enough in cement-based content and also is less than half of the PVC which is a reasonable amount to be mixed with PVC as a single additive.

Figure 5-22 shows the TGA-DTG graph of PVC stabilised with 20 parts of HGGBS prepared as compression moulding method explained in Chapter 3. The results are compared with HCAC equivalent data and summarized in Table 5-3.



Figure 5-22 TGA and DTG curves of PVC stabilised with 20 phr HGGBS

Samples	T1 (°C)	T2 (°C)	Rate of degradation stage 1 (%/min) at Temp.....	Rate of degradation Stage 2 (%/min) at Temp...	% RESIDUAL MASS at 587.1°C
Pure PVC	268.2	431.1	-19.43	-3.68	10.03
PVC+20 phr HCAC	279.5	441.1	-10.01	-4.92	23.75
PVC+20 phr HGGBS	275.7	443.9	-8.10	-3.26	30.35

Table 5-3 comparison of TGA data for different cementitious-PVC composites

According to Table 5-3, HGGBS-PVC composition has a lower rate of degradation at both degradation stages in comparison with the HCAC-PVC composite. HBBBS-PVC also has higher char residue at the end of the TGA test compared to HCAC-PVC. In general, it can be concluded that hydrated slag was more effective than hydrated calcium aluminate cement in improving the thermal behaviour of PVC composites.

#### **5.8.4 Evaluation of the thermal stability of PVC stabilised with HGGBS by SEM-EDS**

PVC sample stabilised with 20 Phr of HGGBS prepared in Ch 3 was analysed by SEM and EDS techniques. The chemical characterization and elemental analyses related to the ash residue of this sample show a very strong signal of chloride (Figure 5-23). This proves the good functionality of hydrated GGBS (HGGBS) in physically and chemically capturing of HCl released from PVC at elevated temperatures. Figure 5-24 shows the SEM morphology of the composite after combustion. SEM image shows there are some crystalline phases in the ash of composites after burning which relates to chemical substitution and bonding of Cl from gaseous HCl to the solid ash and formation of new phases in the ash of composite sample.

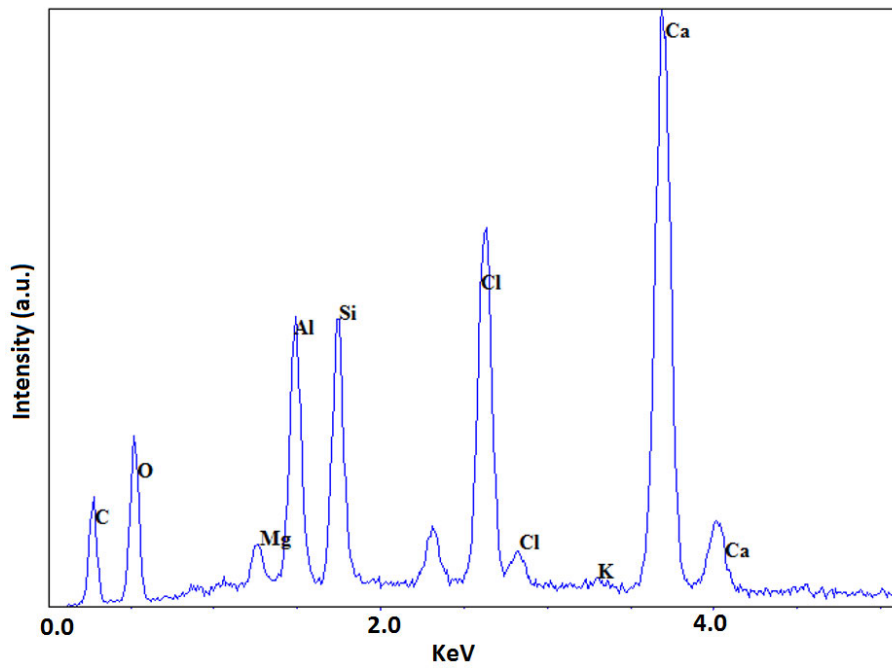


Figure 5-23 EDS analysis of ash residue related to PVC composite stabilised with 20 phr HGGBS

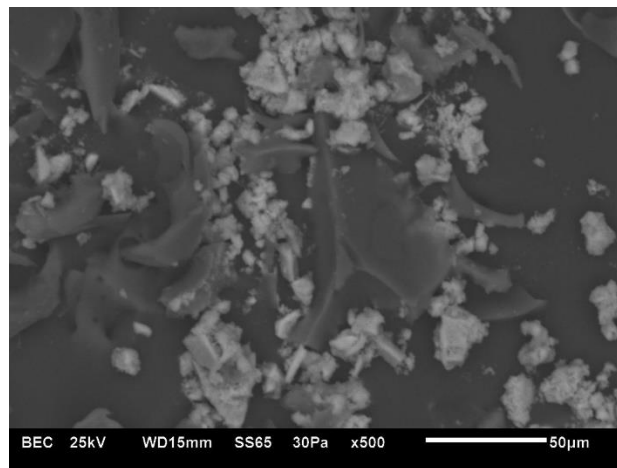


Figure 5-24 SEM of ash residue of PVC stabilised with 20 phr of HGGBS

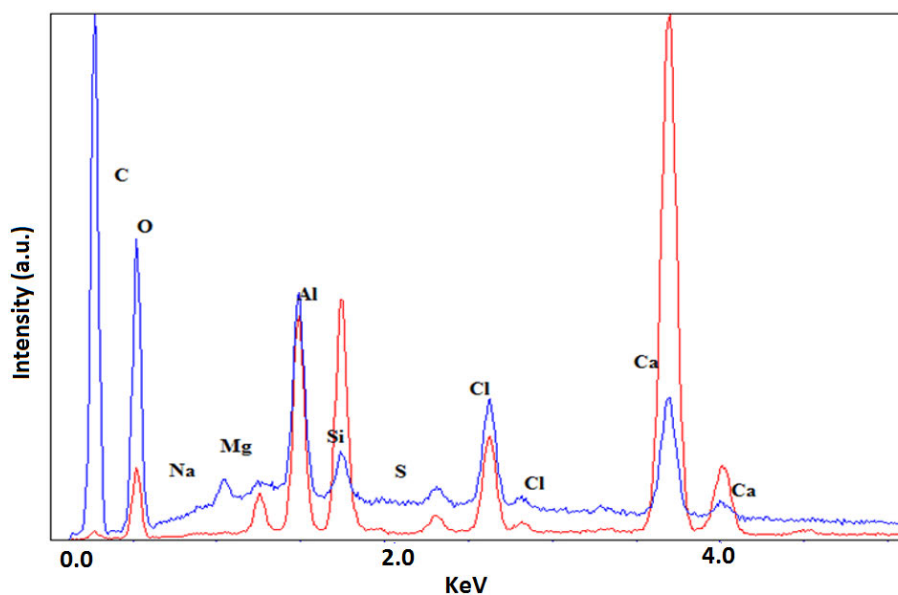


Figure 5-25 Comparison of elemental analysis in different parts of SEM photos from ash related to HGGBS-PVC (blue: darker areas of SEM, red: lighter areas of SEM)

Figure 5-25 compares the elemental analysis of bright and dark areas related to SEM photos which are presented in Figure 5-24. According to Figure 5-25, the difference is that the lighter area of the SEM image has a stronger signal for Si and Ca and a significantly weaker signal for C in its spectrum.

It is obvious that both areas have chloride attachment in their content. Thus, it can be concluded that GGBS has a good effect in scavenging toxic HCl gas released from burning PVC in all parts of its solid phase.

## 5.9 Discussion

Stabilisation of PVC based on the mechanism of auto conversion of calcium aluminate cement to ceramic was the main aim of this chapter.

According to the results, some phases in the composition begin to reach to crystalline state. As a result, fire incidents can cause residue and char integrity at high temperatures via ceramic formation. Most conventional fire retardants lose their effectiveness at extremely high temperatures when fire flames are at their most dangerous levels, while the presented novel

composition of PVC stabilised with HCAC releases water and automatically converts to ceramic. Consequently, it fuses to form an impervious permanent layer around the whole PVC matrix. As a result, it captures toxic HCl gas into a solid phase by chemical bonding (phase change) and physical adsorption (cracks on the surface of the residue). We also expect it might a) cool down the combustion environment by releasing water, b) provides a thermal barrier for the inner layers and undecomposed layer of the polymer, c) act as an oxygen barrier to delay and avoid further oxidation and accelerate the thermal degradation of PVC and its residue; d) provides a strong shield around the polymer matrix and acts as a smoke suppressant and can reduce smoke density; e) causes a compact and tough layer to hold and support the combustion residue/char together and consequently provides more structural integrity and more durability after combustion. All these benefits can prove that the claimed composite material is strong enough to retain the PVC on a vertical surface during a fire event.

# CHAPTER 6

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia



## **6. Evaluation of Sodium Hexametaphosphate as a new thermal stabiliser for PVC and its synergism effect**

### **6.1 Introduction**

Compounds containing Phosphorous such as inorganic phosphates, polyphosphates organophosphorus compounds, red phosphorus, and others have been investigated as good flame retardants for several years [200]. Elemental phosphorus is extremely flammable; however, its compounds were found to be suitable flame retardant additives in many polymers. In recent decades, the importance to reduce the toxicological hazards related to halogenated fire retardants has promoted the usage of phosphorous-containing compounds.

Sodium Hexametaphosphate also known as sodium multiple metaphosphate, polyvinylidene sodium or Graham salt has the chemical formulation of  $\text{Na}_{16}\text{P}_{14}\text{O}_{43}$ . It is a type of Sodium metaphosphate polymers with a white crystal appearance [201]. Sodium hexametaphosphate is completely safe and it is even used in the food industry. On the other hand, calcium metaborate belongs to the Boron family. Boron is well known to be able to act as a flame retardant in both gas and solid phases. melamine is usually used as a fire retardant in paints, plastics, and paper. Melamine and its salts are self-extinguishing and have low thermal conductivity. Melamine also named as 2,4,6-triamine-1, and 3,5-triazine is a crystalline solid with the nitrogen content of ~67% and the sublimation temperature of 350-355 °C.

In this chapter, the synergistic effect between sodium hexametaphosphate with calcium metaborate and melamine substances is investigated.

Synergism in fire retardancy generally means that the overall effect of two or more flame retardants shows better results than the sum of the single flame retardants. In recent years the advantages of synergism in fire retardancy are notably taken into account. For example, some synergistic systems based on nitrogen and phosphorous, metal hydroxides and salts have been introduced in recent years [202]. The synergistic effect is usually based on a combination of gas phase and solid phase reactions. Either of them might dominate depending on the class of flame retardant, its polymer nature, and the test condition [203, 204]. Since higher amounts of additives might affect the quality of the products, a synergist is sometimes beneficial to decrease the level of additives and lower the cost [205]. The high levels of additives used in

the composites have processing issues. It is of industrial and scientific importance to involve processing synergists to tackle this issue.

## 6.2 Thermal stability of PVC stabilised with Sodium hexametaphosphate / calcium metaborate as a synergistic stabiliser

PVC with 10 phr Sodium hexametaphosphate (SHMP) and 10 phr calcium metaborate (CMB) was prepared and the TGA laboratory testing is shown in the graph below (Figure 6-1).

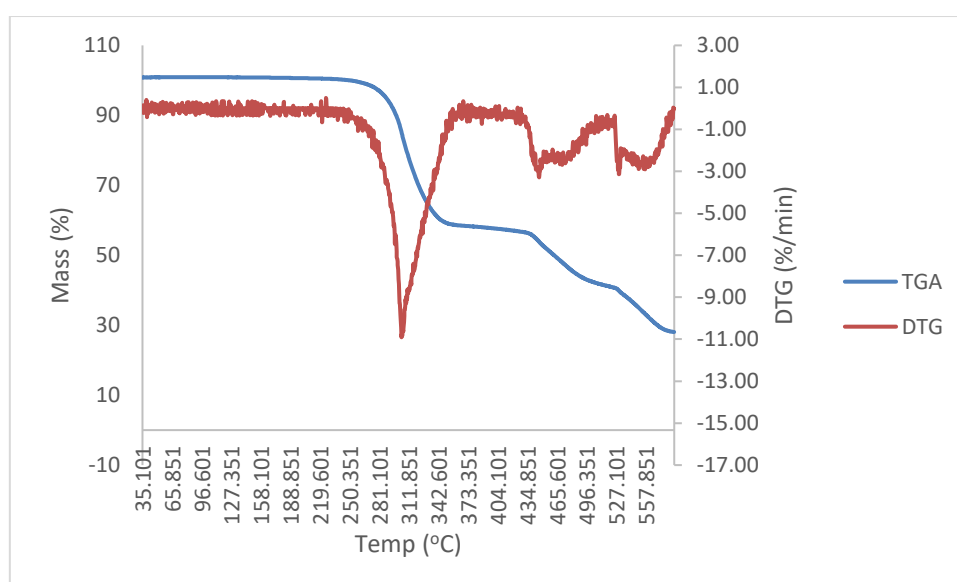


Figure 6-1 TGA and DTG curves of PVC stabilised with 10 phr SHMP + 10 phr CMB

The TGA and DTG thermograms of PVC stabilised with 20 phr of each component were also examined. The obtained curves are shown in Figures 6-2 and 6-3. The thermal stability parameters extracted from these thermograms are listed in Table 6-1.

The thermograms and the extracted thermal stability data showed that Sodium hexametaphosphate alone or calcium metaborate alone has a small effect as stabilisers on the thermal stability of PVC (Figure 6-2). Moreover, formulations with sodium hexametaphosphate alone or calcium metaborate alone showed a higher rate of degradation

(Figure 6-3) in comparison with the sum of the ingredients. The interesting point about the results is that the formulations which include both ingredients showed better efficiency as thermostabilisers than the sum of single results.

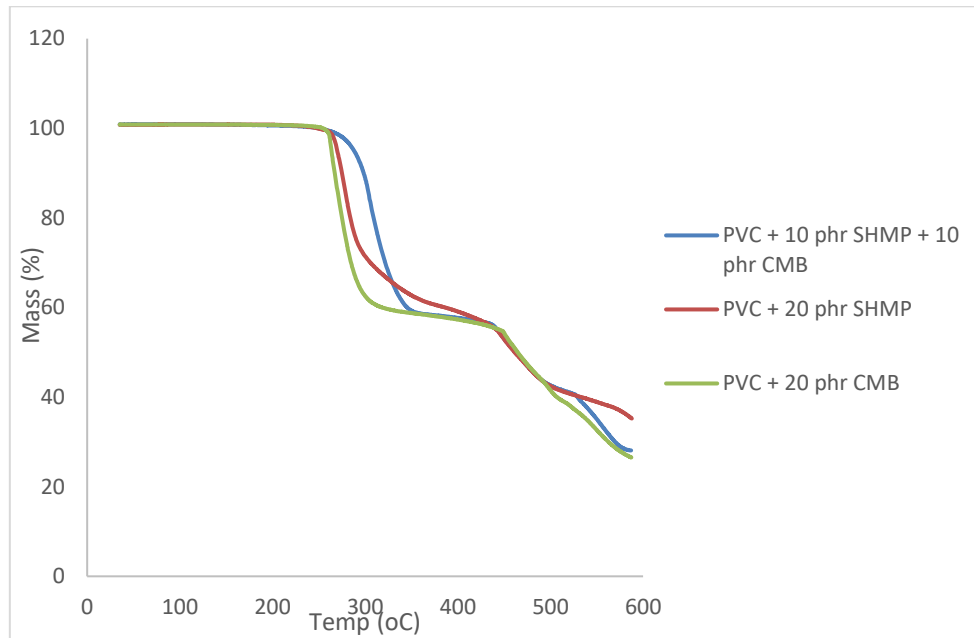


Figure 6-2 TGA comparison of different formulations of PVC with SHMP and CMB

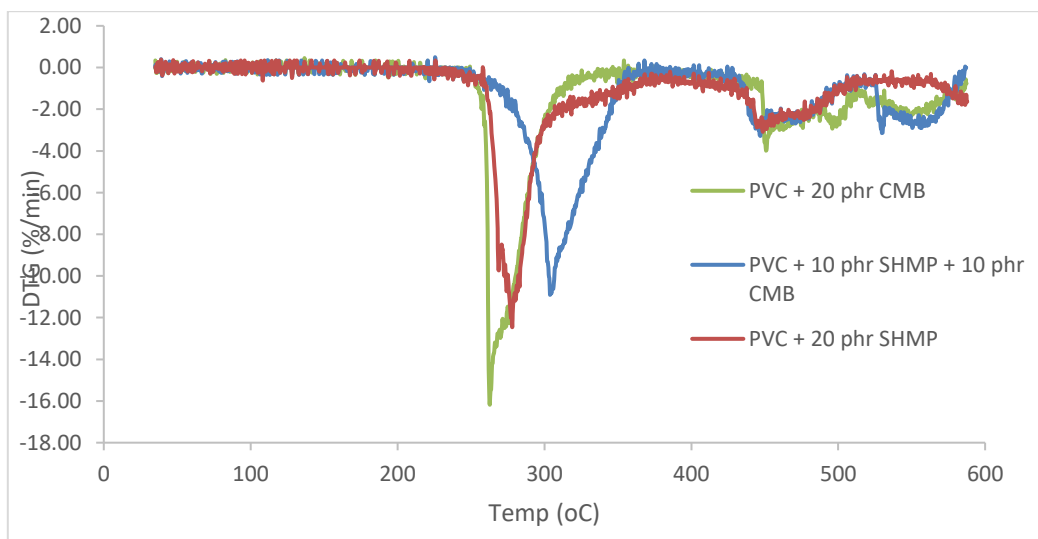


Figure 6-3 DTG comparison of different formulations of PVC with SHMP and CMB

Samples	T1 (°C)	Rate of degradation stage 1 (%/min)	% RESIDUAL MASS at 587.1°C
Pure PVC	268.2	-19.43	10.03
PVC+10 phr SHMP+10 phr CMB	287.7	-10.84	28.09
PVC+20 phr SHMP	265.6	-11.75	35.20
PVC+ 20 phr CMB	259.6	-14.87	26.51

Table 6-1 Summary of the data obtained from TGA and DTG graphs of PVC compositions with different amount of SHMP and CMB

### **6.3 Char morphology and elemental analysis of the solid phase of PVC stabilised with Sodium hexametaphosphate /, calcium metaborate and their synergistic combination**

In order to understand the thermal properties and elemental composition of the combusted particles in the composition. The chemical and morphological evaluation of the char related to the composite of PVC with SHMP (10 phr) and CMB (10 phr) was carried out by SEM-EDS analysis (Figure 6-4 and Figure 6-5 ).

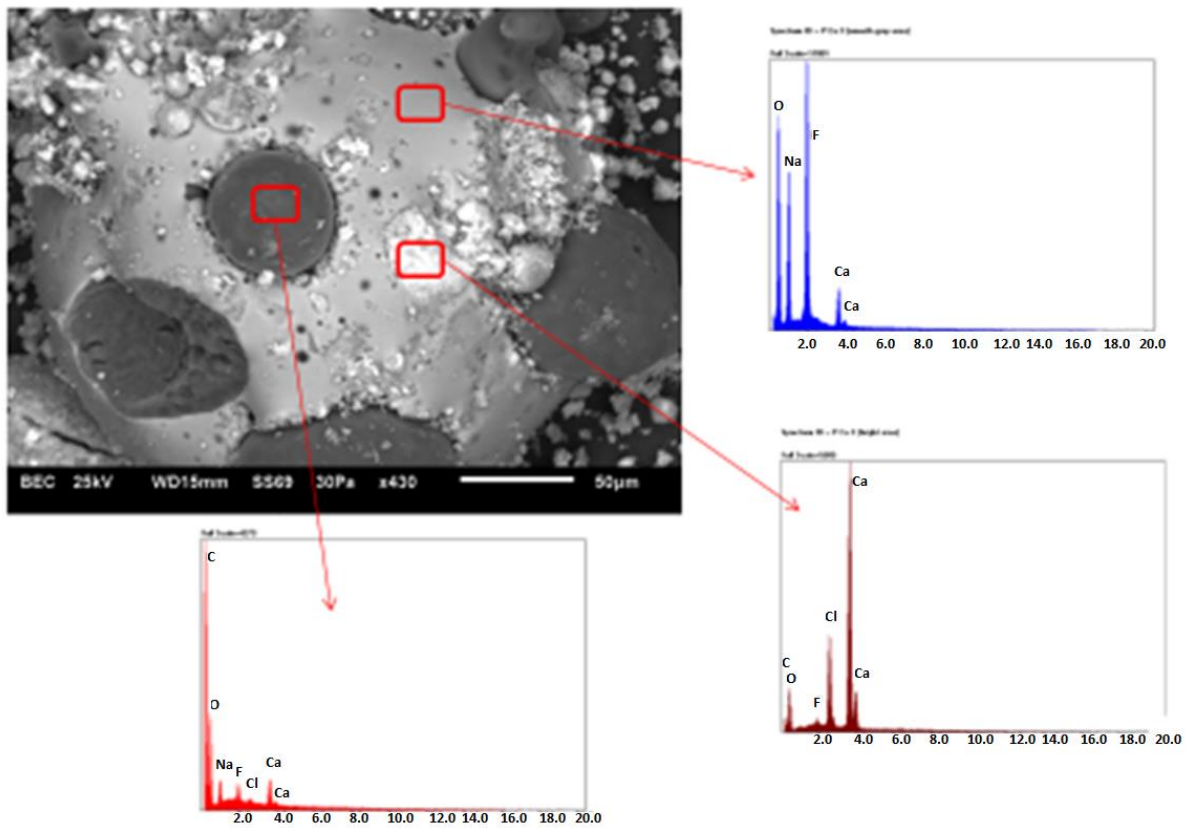


Figure 6-4 SEM-EDS analysis of ash residue of PVC stabilised with 10 phr of SHMP and 10 phr of CMB

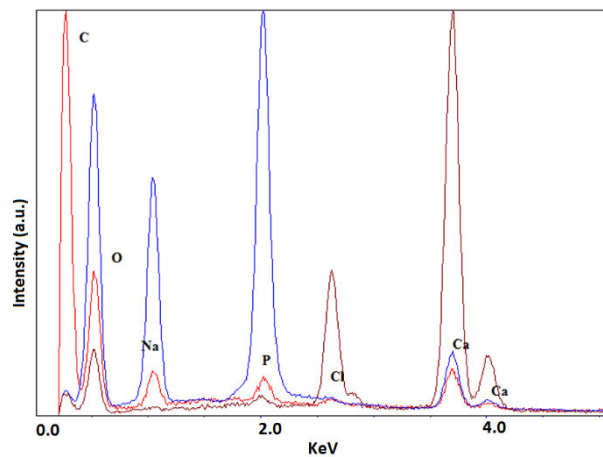


Figure 6-5 Comparison of EDS results in different areas of Char (Bright area = maroon, Grey area = blue, Dark circle = red)

SEM analysis shows that PVC with carbon-carbon and organic texture (Dark circle) was disconnected with inorganic sodium hexametaphosphate which has an inorganic and non-combustible texture (grey area). The interesting thing in the SEM photograph is the formation

of the crystals (bright area). EDS proves that the new crystals are calcium chloride. It means that some amount of corrosive and toxic hydrogen chloride evolved from PVC degradation was captured by calcium metaborate and converted to calcium chloride. EDS spectrum did not show the presence of boron elements structures which means that boron element in calcium metaborate was vaporized and exited from the solid phase. Grey area of SEM which is distinguished in the blue graph in the EDS spectrum shows no chlorine element which means sodium chloride was not formed in the solid phase. It means that the capture of hydrogen chloride was dominant by only calcium metaborate additive and not by sodium hexametaborate. In other words, sodium hexa metaphosphate did not convert to sodium chloride and multi-phosphoric acid. Generally, Compounds containing phosphorous which are able to convert to phosphoric or polyphosphoric acid are well known as the key substances in making carbon-rich polymer or intumescent systems. Thermal degradation of phosphorus-based compounds into phosphoric acid improves the carbonization of the polymer and converts the polymer into carbon-rich char. On the other hand, intumescent systems increase the cross-linked residue and expand to foam structure effectively in the presence of blowing agents. SEM image of the presented formulation doesn't show the foamed structure as there was no conversion in polyphosphoric acid and there was not a blowing agent in the combustion environment. According to the EDS spectrum, sodium hexametaphosphate was not able to capture HCl and form sodium chloride crystals in the residue. Thus, it can be seen that the dominant mechanism in improving fire retardancy is based on calcium metaborate additive as it is able to improve thermal stability properties in the solid phase (capturing HCl in char) and is also effective in the gas phase(diluting the combustion vapour by releasing its volatiles). The major role of sodium hexametaphosphate additive is based on the inorganic fillers mechanism in which inorganic particles replace polymeric texture per volume, and, therefore, cause a reduction of the total heat release. Moreover, Sodium hexametaphosphate remains in a char residue and definitely, each fire residue acts as a kind of shield for mass or heat transfer, suppressing the rate of heat released. In other words, this inorganic char simply decreases the rate of PVC decomposition; thus, reduces the accessible fuel to feed the flame. Subsequently, Sodium hexametaphosphate alone shows a lower effect in retarding the PVC degradation rather than calcium metaborate. However, a mix of them shows good compatibility and efficiency in improving thermal stability than a single stabiliser. Generally, some fire retardant synergists don't have outstanding fire and thermal resistance by themselves, whereas applying combined stabilisers leads to an increase in the total effectiveness of the thermal properties. Presence of synergism in the composition forms inorganic char in the solid phase and HCl interference in

the gas phase which improve the effectiveness and lower the amount of the fire retardant additives required.

#### **6.4 Mechanism of synergism stabilisation of polymers**

According to the literature, compounds containing phosphorus exhibit decomposition or chemical reactions with other substances, and their products are able to react forming solid or volatile products determined by the chemical surroundings in the combustion environment [206]. There are several different approaches to chemical compounds containing phosphorus. For example, phosphorus can act in the solid phase by increasing and building up residue [200, 206, 207], by producing intumescent, or by the formation of inorganic glass [208, 209]; and in the vapour phase by flame inhibition [210]. Generally, for a wide range of systems, a remarkable action has been found in both solid and vapour phases [211]. The efficiency and even the occurrence of the action seem to be highly dependent not only on the chemical formulation of the phosphorus-containing compound itself but also on the reactions and interactions during combustion with its surrounding environment, such as polymeric texture [206, 212]. However, a detailed and comprehensive understanding to ease the launch of selected approaches is lacking [206].

According to SEM images obtained of the presented formulation in this study, it is obvious that the condensed phase mechanism of sodium hexametaphosphate was more predominant than its vapour phase. This inorganic phosphorus compound remains in char and can improve thermal stability through both an inorganic barrier effect and increasing residue retention. In other words, the inorganic content of this salt decreases the flammable and organic texture of PVC. It can also cover and disconnect the carbon-carbon structure of PVC and, consequently, is able to decrease flammability and heat transfer. Also, an increase in the amount of inorganic residue, instead of organic residue, has the potential to cause a decrease in the level of generated combustible volatiles and consequently to a decrease in the amount of total heat release. Calcium metaborate, as the other additive, shows more principal mechanisms in the presented formulation than sodium hexametaphosphate [211]. According to SEM-EDS results, the capture of acidic and corrosive HCl gas was done by calcium content of calcium metaborate additive and not by sodium of sodium hexametaphosphate. Generally, Boron compounds are well-known flame retardants in both gas and condensed phases [201]. Under a fire situation,

Boron and halogen atoms produce the corresponding trihalide. Boron trihalides are Lewis acids, and, therefore, are able to improve crosslinking and reduce the decomposition of PVC into volatile flammable gases. Moreover, such trihalides are volatile and unstable; therefore, they volatilize into the flame and deliver halogen which acts as a flame inhibition, subsequently. Actually, halogen elements give good fire retardant properties to the polymer. Halogen radicals react with extremely reactive OH and H radicals and reduce the combustion kinetics [204]. Also, released trihalides during the combustion of PVC act as an inert diluent in the fire, particularly, calcium metaborate used in this study with chemical formulation  $\text{Ca}(\text{BO}_2)_2 \cdot 2\text{H}_2\text{O}$ , which reacts with hydrogen chloride evolved from burning PVC and products to water, non-volatile calcium chloride and volatile boron trichloride. Released water can cool down the combustion zone and boron trichloride can act as a gas phase flame retardant, but the main function is due to calcium chloride ( $\text{CaCl}_2$ ) which functions in the solid phase by catalysing dehydro-chlorination reaction in PVC and promoting cross-linking and char formation [211]. Calcium chloride itself is also a result of capturing corrosive and toxic gas of hydrogen chloride in the condensed phase.

## **6.5 Thermal stability of PVC stabilised with Sodium hexametaphosphate / melamine as a synergistic stabiliser**

Melamine also named 2,4,6-triamine-1,3,5-triazine is a crystalline solid which melts at 354°C. Its nitrogen content is about 67%. It sublimates and vaporizes at temperatures more than 200°C (below its melting point). Thus, it can dilute oxygen and fuel gases near the combustion zone. Sublimation of melamine during the high temperature of fire causes absorption 29 kcal/mole of heat. Also, the decomposition of melamine causes the absorption of 470 kcal/mole of heat. Thus, melamine can effectively drop heat levels in the fire. Moreover, Melamine absorbs UV radiation above 250nm. Fire retardants act by interference and obstruction with one of the three factors that begin and support combustion (heat, oxygen and fuel). Melamine has good flame retardant properties due to its capability to interfere with the combustion procedure in all steps and in many different modes. In the first step, melamine is able to retard ignition by sinking and dropping heat through endothermic sublimation at about 350°C. A subsequent larger heat sink is caused by the further decomposition of melamine vapours. Melamine is also considered



as a poor fuel. Actually, only 40% of the heat coming from the combustion of hydrocarbons belongs to melamine. Additionally, the nitrogen generated by combustion functions as an inert diluent. Subsequently, the breakdown and decomposition of the melamine or self-condensation of some portions of melamine which are not sublimed lead to the release of ammonia. Ammonia also acts as an inert diluent in the combustion zone. In the solid phase, under the impact of heat; melamine is reformed into a cross-linked structure suitable for char formation.

## **6.6 SEM analysis of PVC stabilised with Sodium hexametaphosphate / melamine synergistic stabiliser**

SEM images of the PVC stabilised with 10 phr of Sodium hexametaphosphate and 10 phr of melamine were taken at the same magnification (around 200X) before and after TGA (figures 6-6 and 6-7).

According to SEM images, the ash sample obtained after TGA analysis (Figure 6-7) shows a structure with much more holes and pores in comparison with its original sample before TGA analysis (Figure 6-6). In other words, several holes are uniformly distributed into the char surface of the composite after burning. This can be attributed to foaming by the released gas from melamine during combustion.

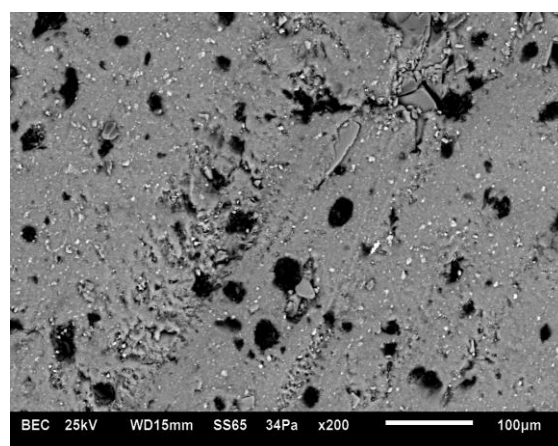


Figure 6-6 SEM of PVC composite with SHMP /melamine before TGA analysis

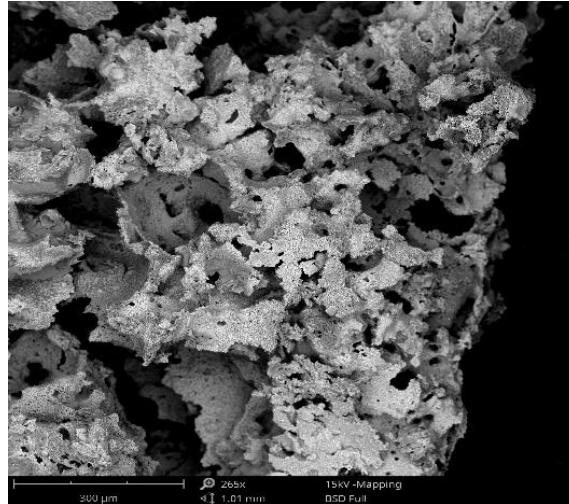


Figure 6-7 SEM of PVC stabilised with SHMP and melamine after TGA analysis

Figure 6-8 shows the surface morphology of the other side of the ash after TGA analysis. The inner and outer SEM images of char residue after the TGA analysis indicate that the char of the sample show foamed structure (Figure 6-7 and Figure 6-8) in comparison with its structure before combustion (Figure 6-6 ), it has the breakable and alveolate structure, with some crevasses, pores and crevasses in the surface. This porous structure is the result of gas emissions from melamine. The released gas act as an inert diluent in the combustion zone which is an advantage for improving the thermal stability of the composite. On the other hand, these generated pores and holes which make a very detached structure on the other side of the char layer lead to easy penetration of flammable volatiles and heat released from char into the fire zone which is a disadvantage for the thermal behaviour of the composite. These results indicate that the structure of char residue of the composite of sodium hexametaphosphate and melamine is not dense enough to isolate the heat effectively, thus the thermal behaviour of this sample is poorer compared to the previous sample which showed the more densified structure in all of its char surface (PVC composite with sodium hexa metaphostae and calcium metaborate), which agrees well with the TGA tests.

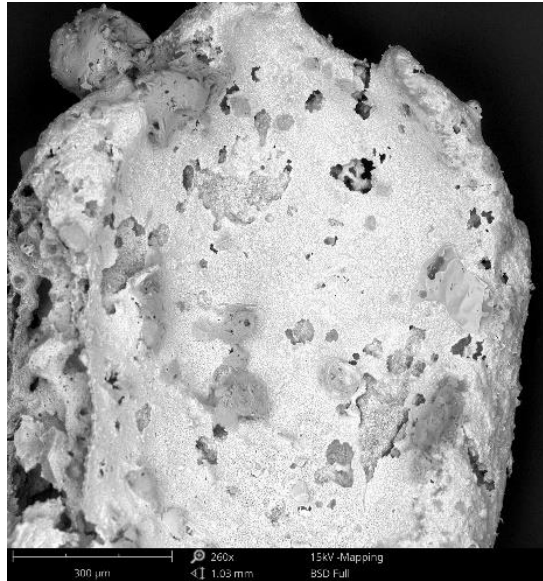


Figure 6-8 surface morphology of the lower side of ash related to PVC stabilised with SHMP /melamine

Generally, the outer layer of the composite (Figure 6-8) is the SHMP which is an inorganic coat and thus shields the solid combustible PVC. Melamine is also a blowing source of the char, causing swollen and intumescent behaviour. Moreover, melamine phosphates are other products made by a combination of nitrogen with phosphorus-containing components which can enhance char stability. The outer layer of the char, which is an inorganic shield, can dilute the organic and combustible texture of the polymer and stability of the overall char is increased by multi-ring arrangements such as melem generated due to self-condensation of the melamine.

## **6.7 TGA test of PVC composite with Sodium hexametaphosphate and melamine**

In order to find the component synergistic effect of phosphorus and nitrogen compounds in PVC, TGA and DTG, tests of PVC with 20 phr of each component were conducted and are summarized in Table 6-2. Accordingly, the formulations which include both ingredients show better efficiency and thermal behaviour than the sum of single results which is the key factor for the synergism effect.

Samples	T1 (°C)	Rate of degradation stage 1 (%/min)	% RESIDUAL MASS at 587.1°C
Pure PVC	268.2	-19.43	10.03
PVC+10 phr SHMP+10 phr Melamine	270.6	-11.93	29.14
PVC+20 phr SHMP	265.6	-11.75	27.60
PVC+ 20 phr Melamine	260.6	-14.93	26.60

Table 6-2 Data obtained from TGA and DTG thermograms of PVC stabilised with SHMP , melamine and their combination

## 6.8 Evaluation the stability of PVC sheets under the accelerated artificial UV Weathering conditions

All polymers, including PVC, need stabilisation against the harmful UV radiation of the sun. During formulation development, it is important to consider the effect of additives on stability and also look for methods to stop or reduce the damage originating from environmental factors such as air, light and heat. All commercial and synthetic polymers are subjected to photochemical degradation when exposed to sunlight. The degradation of PVC during storage, processing, compounding, and usage is a result of the elimination of HCl, leading to the formation of lengthy polyenes, which can cause discolouration, cracking, and a decrease in mechanical and chemical resistance. To prevent degradation, it is important to store PVC in a cool, dry place and to use appropriate compounding techniques and stabilizers during processing. Additionally, it is important to ensure that the PVC is used within its recommended temperature and chemical resistance range for optimal performance and longevity [213, 214]. In other words, the formation of polyenes is a result of several photochemical and thermal reactions that are started by C-Cl photolysis next to the double bond. Along with hydrogen detachment by the Cl radical, continuation of the conjugated length is attained and HCl is generated [215]. The spread of the conjugated polyenes is highly relevant to the source and spectral range of light.

In this part of the chapter, the aim was to test how the thermostabilised PVC with the synergistic formulation was an effective resistant to UV. Accordingly, the novel formulation of this chapter

(PVC composite with SHMP and CMB) was compared with the modified formulation (PVC composite with SHMP, CMB and 0.5 phr Titanium dioxide) and also compared with pure PVC and PVC with 0.5 phr TiO<sub>2</sub>. The mass loss in TGA analysis of PVC sheets subjected to UV irradiation for the interval of time was used as a measure of photodegradation stability. During UV radiation, a dehydrochlorination occurs which consequently leads to the elimination of HCl and the formation of polyene sequences. The PVC sheets with different formulations were artificially irradiated in the UV chamber for up to 300 hours according to the test scope mentioned in section 3.3.7 (ASTM G154). The mass loss of PVC sheets was evaluated according to Equation 6-1 where W<sub>1</sub> is the mass of the sample before radiation and W<sub>2</sub> is the mass of the sample after each radiation period. The white colour of the PVC sheet samples before radiation gradually turned brown and darkened after each inspection.

$$\text{Mass loss \%} = [(W_1 - W_2) / W_1] * 100 \quad (\text{Equation 6-1})$$

Figure 6-9 shows the mass changes of PVC samples upon the irradiation time. Accordingly, pure PVC showed the highest weight loss, whereas the PVC samples with CMB and SHMP showed less weight loss and, consequently, less degree of photodegradation. This can be attributed to minerals available in the second formulation which dilute the matrix. In the third formulation, which also has titanium dioxide additive, it significantly reduced the amount of mass loss in UV weathering. This proves even a tiny amount of titanium dioxide (0.5 phr) can play an important role as a UV resistant additive. Titanium Dioxide is commercially used as a UV stabiliser. As a result, this part of the study shows that the novel formulation of this chapter (PVC composite with CMB and SHMP) showed limited UV stabilising efficiency for photodegradation of the degradation of PVC. The current test of the PVC sample stabilised with CMB, SHMP and titanium dioxide improved the stability and delayed colour change and UV damage.

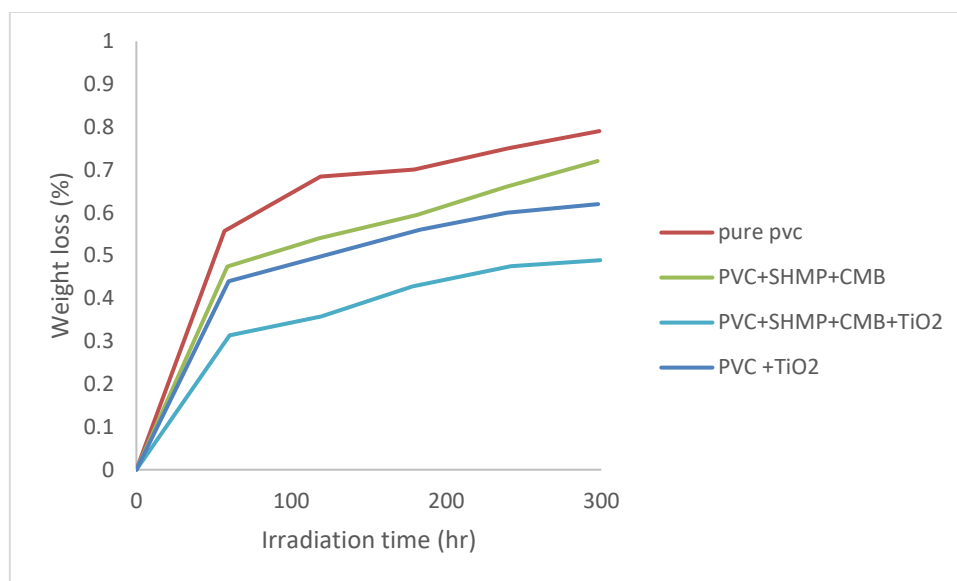


Figure 6-9 Changes of PVC samples versus irradiation time

## 6.9 Discussion

According to the literature, compounds containing Phosphorus exhibit decomposition or chemical reactions with other substances, and their products are able to react, forming solid or volatile products, determined by the chemical surroundings in the combustion environment [206]. There are several different approaches to chemical compounds containing phosphorus. For example, Phosphorus can act in the solid phase by increasing and building up residue [200, 206, 207], by producing intumescent, or by the formation of inorganic glass [208, 209]; and in the vapour phase by flame inhibition [210]. Generally, for a wide range of systems, a remarkable action has been found in both solid and vapour phases [211]. The efficiency and even the occurrence of the action seem to be highly dependent not only on the chemical formulation of the phosphorus-containing compound itself but also on the reactions and interactions during combustion with its surrounding environment, such as polymeric texture [206, 212]. However, a detailed and comprehensive understanding to ease the launch of selected approaches is lacking [206].

According to the SEM obtained from the presented formulation in this study, it is obvious that the condensed phase mechanism of sodium hexametaphosphate was more predominant than its vapour phase. This inorganic phosphorus compound remained in char and improve the thermal stability through both an inorganic barrier effect and increasing residue retention. In other words, the inorganic content of this salt decreases the flammable and organic texture of PVC. It can also cover and disconnect the carbon-carbon structure of PVC and, consequently, is able to decrease flammability and heat transfer. Also, an increase in the amount of inorganic residue instead of organic residue has the potential to cause a decrease in the level of generated combustible volatiles and, consequently, a decrease in the amount of total heat generated. Calcium metaborate as the other additive shows more principle mechanisms in the presented formulation than sodium hexametaphosphate. According to SEM-EDS results, the capture of acidic and corrosive HCl gas was done by calcium content of calcium metaborate additive and not by sodium of sodium hexametaphosphate. Generally, Boron compounds are well-known flame retardants in both gas and condensed phases. Under a fire situation, boron and halogen atoms produce the corresponding trihalide. Boron trihalides are Lewis acids, and, therefore, are able to improve crosslinking and reduce the decomposition of PVC into volatile flammable gases. Moreover, such trihalides are volatile and unstable; therefore, they volatilize into the flame and deliver halogen which acts as a flame inhibition subsequently. Actually, halogen elements give good fire retardant properties to the polymer. Halogen radicals react with extremely reactive OH and H radicals and reduce the combustion kinetics. Also, released trihalides during the combustion of PVC act as an inert diluent at the fire, particularly, calcium metaborate used in this study with chemical formulation  $\text{Ca}(\text{BO}_2)_2 \cdot 2\text{H}_2\text{O}$  reacts with hydrogen chloride evolved from burning PVC and yields to water, non-volatile calcium chloride and volatile boron trichloride. Released water can cool down the combustion zone and boron trichloride can act as a gas phase flame retardant, but the main function is due to calcium chloride ( $\text{CaCl}_2$ ) which functions in the solid phase by catalysing dehydro-chlorination reaction in PVC and promoting cross-linking and char formation. Calcium chloride itself is also a result of capturing corrosive and toxic gas of hydrogen chloride in the condensed phase.

# CHAPTER 7

**WESTERN SYDNEY**  
UNIVERSITY



Centre for Infrastructure Engineering,  
Western Sydney University (UWS)  
Kingswood Campus, Kingswood, NSW 2747, Australia



## 7. Conclusion and future work

### 7.1 Conclusion

The importance of materials and compositions in fire design considerations of plastic formworks is focused on in this study. Actually, this study investigates how ingredients in building materials formulations may influence the fire resistance of buildings, and the safety of the occupants and the environment. This work also shows the importance of chemical properties of formworks such as heat resistance, UV resistance and smoke suppressant properties in the future development and performance of formwork products. Since a suitable formwork system plays an important role in the construction of a project, the significant impact of quality, time and cost of presented materials are also considered thoroughly in this study.

There are three principal commissions in this work.

- 1) Development and evaluation of new metal complexes (Zn, Ca, Mg) with dipentaerythritol which showed outstanding efficiency in comparison with some commercial stabilisers currently used in the thermal stabilisation of PVC based on a new mechanism for thermal stabilisation of PVC.
- 2) A novel thermostabiliser composition of PVC stabilised with hydrated cementitious materials HACC and GGBS was made and investigated which showed good efficiency with the advantage of low cost and multi-functionality and multi routes for stabilising PVC.
- 3) Developing and evaluating a new synergistic thermo stabiliser based on Sodium Hexametaphosphate and calcium meta borate as a new thermo stabiliser for PVC which showed good efficiency as a thermostabiliser with limited efficiency as a UV photo degradative stabiliser system.

These mentioned tasks were accomplished based on logical fire design approaches, characterizing new materials, analysing and testing their mechanism of action, and understanding structure-to-structure fire spread. The important thermal degradation procedures of each additive for fire retardancy workability have been studied utilizing thermogravimetry.

Structural changes were investigated utilizing Fourier transform infrared and X-ray diffraction spectroscopy. The morphology of the stabilised system was also covered by advanced techniques such as SEM and EDS.

Based on the outcomes of the experimental investigations, it can be summarized that the thermal resistant performance of the PVC stabilised with hydrated cementitious materials HCAVC and GGBS (Chapter 5 showed higher efficiency in the stabilisation of PVC than metal chelates of dipentaerythritol (Chapter 4) or synergistic stabilisers of sodiumhexametaphosphate /calcium meta borate (Chapter 6).

Chapter 4 of the study focuses on the use of zinc as a metal complex with dipentaerythritol to stabilize PVC. The zinc complex proves to be more effective than traditional stabilizers such as ZnS, offering not only early discolouration prevention but also long-term thermal stability. Dipentaerythritol was selected as the ligand due to its high concentration of OH groups, which serve as chelating agents, preventing catalytic dehydrochlorination. The mechanism of action in the solid phase involves capturing Lewis acids and HCl gas to avoid catalytic dehydrochlorination and sudden blackening, while in the vapour phase, it works by releasing water which cools the combustion environment and dilutes the corrosive HCl atmosphere. Additionally, some HCl is captured in the solid phase and causes further improvement.

In Chapter 5, Calcium Aluminate Cement (HCAC) and slag are used instead of Ordinary Portland Cement (OPC) for their various advantages. Calcium Aluminate Cement has a higher chloride binding ability and refractory properties. Slag is a waste product of steel making and is more environmentally friendly compared to OPC. The chapter focuses on using these materials to reduce waste and increase productivity in the building materials industry.

HCAC and PVC form a good ceramifying composition when exposed to high temperatures, as a portion of HCAC will convert to ceramic, creating a physical self-supporting barrier that protects the PVC from fire. The high water/cement ratio caused a high amount of hydration which resulted in the maximum amount of dehydration. As a result, it causes a release of water during combustion and cooling down the environment, as well as reducing the emission of hydrogen chloride (HCl) which can cause corrosion.

Samples containing HCAC also improve the thermal characteristics of PVC, lowering the rate of degradation, and increasing T1 and T2 temperatures, and residual mass. The novel formulation presented in Chapter 5 addresses the corrosive effects of smoke from PVC fires,

reducing the emission of HCl gas by capturing it in the solid phase of the novel composite. This leads to a minimum of corrosion and damage to building equipment and facilities in the vicinity of the fire.

The materials used in Chapter 5 are highly economical, environmentally friendly, and compatible with each other, attracting great interest from the industry. The chapter's approach, combining cooling and protection from fire, results in a cost-effective and efficient solution for hazardous waste management and the building materials industry.

In Chapter 6, CMB along with SHMP improved the thermal behaviour of PVC due to the additional ability of CMB to react with the evolved HCl from burning PVC and positively influence the thermal behaviour of PVC in three different mechanisms. The products of the reaction of CMB and evolved HCl are water (cooling down the action in the vapour phase), non-volatile calcium chloride (capturing some amount of toxic gas action in the solid phase) and volatile boron trichloride (gas phase flame retardant). The synergism effect of sodium hexametaphosphate with melamine showed to be less effective than CMB, although melamine was used in the synergistic composition based on its high melting and sublimation point 356C and emits NH<sub>3</sub> gas which acts as an inert diluent at high temperatures enhancing the thermal stability of PVC.

## **7.2 Outlook**

The PhD thesis presents different novel formulations that improve the thermal stability of PVC. Hydrated cement-based materials are confirmed as the best thermal stabilizers for PVC and are therefore the best option for use in the PVC formwork construction industry. The novel formulation has attracted interest from the industry and is undergoing further testing for commercial use in the production of PVC formworks. It is also potentially cost-effective, with a cost analysis planned for future study.

### 7.3 Recommendations for future work

- The fire safety analysis procedure could be extended to involve other methods and facilities which evaluate the toxicity, flammability and by-products of combustion. methods and could involve gas chromatography-mass spectrometry (GC-MS) and limiting oxygen index (LOI). GC-MS is a test that could be applied to determine the volatile products produced during the heating of the samples. LOI also could be used to evaluate the relative flammability of samples, by determining the minimum oxygen concentration. LOI could be applied to analyse the relative flammability of the samples and compare the functionality of additives and their mechanisms. Throughout this thesis, TGA, SEM, FT-IR, XRD and EDS are the main techniques that were implemented to investigate the thermal and fire safety behaviour of PVC.
- Evaluation of the cementitious thermal stabilisers for PVC implementing the global and extensive flammability test methods issued by Australian and New Zealand building code requirements, Underwriters' Laboratories (UL), American Society for Testing and Materials (ASTM), and International Conference of Building Officials (ICBO) is essential to be carried out to support industrial applications of the product.
- Production of a standard master batch of PVC composition which contains all the additives such as plasticisers, UV stabilisers, antioxidants, thermostabilisers, and other additives. Testing such standard composition side by side with currently used thermo stabilisers is vital to support any industrial application of the product.
- Extending the synergistic study to cover various combination ratios and compositions.
- Extending the UV stability of different synergistic compositions.
- Applying tests done on ZINCDPE to cover all the other mentioned metal complexes with dipentaerythritol.

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