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FLAME RETARDING AND MECHANICAL PROPERTIES OF MELAMINE PHOSPHATE-EVA COMPOUNDS

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ได้ศึกษาผลของสาร 3 ชนิดในกลุ่มเมลามีนฟอสเฟตเมื่อใช้เป็นสารเติมแต่งในเอทิลีนไวนิลเอซิเทต (อีวีเอ) โคพอลิเมอร์ ต่อสมบัติเชิงความร้อน สมบัติการหน่วงไฟ และสมบัติเชิงกล เทียบกับสมบัติเดียวกันของสารประกอบของอะลูมินัมไทรไฮดรอกไซด์ (เอทีเอช)-อีวีเอที่ใช้อยู่ทั่วไปได้เตรียมสารประกอบอีวีเอที่มีเมลามีนฟอสเฟต เมลามีนไพโรฟอสเฟต เมลามีนพอลิฟอสเฟต และเอทีเอชในปริมาณต่างๆ และได้ตรวจวัดสมบัติเชิงกลเช่น เทนไซล์ และ ค่าการยืดตัว นอกจากนี้ได้ตรวจวัดสมบัติเชิงความร้อนโดยการวิเคราะห์ด้วยทีจีเอ ตรวจสอบการเผาไหม้โดยใช้มาตรฐานต่างๆ และวัดค่าดัชนีออกซิเจนจำกัด อัตราการเผาไหม้ เวลาที่ใช้ในการเผาไหม้ อุณหภูมิของสารประกอบเมื่อน้ำหนักหายไปที่เปอร์เซ็นต์ต่างๆ ได้เตรียมสารประกอบที่มีเอทีเอชและซิงค์บอเรตขึ้นด้วย และได้ตรวจสอบสมบัติในลักษณะเดียวกันเพื่อเปรียบเทียบด้วย ผลการทดลองแสดงให้เห็นว่าสารประกอบทั้งสามได้แสดงสมบัติหน่วงไฟได้ในอีวีเอเมื่อใช้ในปริมาณที่เพียงพอ (ตั้งแต่ 30% ขึ้นไป) สมบัติหน่วงไฟจะเพิ่มขึ้นเมื่อใช้สารเติมแต่งเหล่านี้ในปริมาณเพิ่มขึ้น แต่สมบัติเชิงกลจะลดลง เมื่อใช้เมลามีนโพลีฟอสเฟตร่วมกับเอทีเอชหรือร่วมกับซิงค์บอเรคเป็นสารเติมแต่งไม่พบว่าให้สมบัติที่เสริมกัน ในบรรดาสารในกลุ่มสารผสมเมลามีน ฟอสเฟตทั้ง 3 ชนิด สารที่ให้ผลดีที่สุดคือเมลามีนโพลิฟอสเฟต

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The effects of three additives in melamine phosphate group, in ethylene vinyl acetate (EVA) copolymer, on the thermal, flame-retarding, and mechanical properties were studied in comparison with those of the conventional aluminum tri hydroxide (ATH)-EVA compounds. Various amounts of melamine phosphate, melamine pyrophosphate, and melamine polyphosphate, and ATH were mixed with EVA by twin screw extruder. Tensile strength and elongation of these samples were evaluated. In addition Thermal decomposition, as measured by thermogravimetric analysis, and other burning standard methods, were determined in terms of Limiting oxygen index, burning rate, burning time, and the temperature at different % weight loss EVA compounds with ATH and an addition of zinc borate were also prepared. It was found that all compounds in the melamine phosphate group can exhibit flame retarding properties when adequate amounts were used (more than 30% by weight). Flame retarding properties increased, at the expense of mechanical properties, with increasing amount of additives. Synergistic effect was not observed when melamine polyphosphate was used in combination with ATH or zinc borate. Among the three melamine phosphate compounds tested, the melamine polyphosphate gave the best results.

Field of Study Petrochemistry and Polymer Science Student's Signature ....
Academic year 2005 .... Advisor's Signature ....

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LIST OF ABBREVIATIONS

^{o}C	: Degree Celsius
g	: Gram
min	: Minute
PCDD	: Polychlorinated Dibenzo-Dioxin
PCDF	: Polychlorinated Dibenzo-Furan
LDPE	: Low density polyethylene
VA	: Vinyl Acetate
mm	: Millimetre
kg	: Kilogram
cm	: Centimeter
Gy	: Gray
EPR	: Ethylene propylene rubber
s	: Second
PE	: Polyethylene
ESC	: Enviroment Stress Craking
CSP	: Chloro sulphonated polyethylene
PCP	: Polychloroprene

CHAPTER I

INTRODUCTION

In recent years, there has been an increasing level of public awareness of the importance of limiting the progression and effect of fire. Fire can kill in many ways, *e.g.* by asphyxiation, poisoning, or burning. Most accidental fires begin with smoldering and the evolution of smoke and other combustion products, and it is known that in most fires the phenomenon that first threatens human life is the loss of visibility on escape routes.

In 1990's, over 3 million fires leading to 29,000 injuries and 4500 deaths were reported in the United States. The direct property losses exceed $8 billion and the total annual cost has been estimated at over $100 billion. Today a fire in a structure occurs every 60 seconds, residential fires every 82 seconds, every 85 seconds in a vehicle and every 34 seconds in an outside property in the United States. These add up to 1.8 million fires a year. This resulted in 3,570 civil deaths and 21,875 injuries in 1999, from the early 1990's (1). The public awareness on fire prevention has resulted in significant advance in identifying and eliminating the causes of fire, and minimizing the risks to human life and property when fires do occur.

In the cable industry, there has been considerable activity to promote cable for use in emergency circuits to withstand the effects of fire and particularly to continue to function during the inset of a fire or for use in vertical cable runs which reduce the hazard of propagation of fire along the installed runs.

In recent years, increasing attention has been paid to use of polyvinyl chloride (PVC) and halogen containing flame retardant polyolefins in the wire and cable industry because these halogen-containing materials can cause some problems, such as toxicity, corrosion and smoke. These have promoted the development of halogen-free flame retardant material.

Aluminium tri hydroxide (ATH) has been extensively used as additive in halogen-free flame retardant polymeric materials. However, more than 60% ATH loading is require to obtain an adequate level of flame-retardant properties, whereas high loading levels of ATH could be greatly detrimental to the mechanical properties of the filled polymeric materials.

Objective

1. Determine mechanical, thermal, flame retarding properties of EVA blended with compounds in the melamine phosphate group compared to EVA blend with ATH.
2. EVA-melamine phosphate compounds with good flame retarding and mechanical properties for use in cables and wires.

CHARTER II

THEORETICAL BACKGROUND

2.1 Ethylene Vinyl Acetate Copolymer

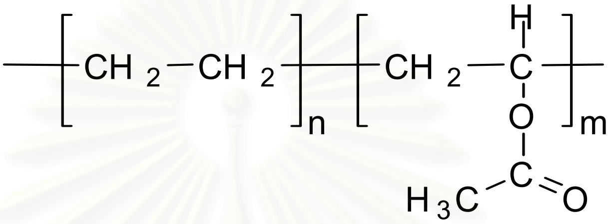


Figure 2.1 Ethylene Vinyl Acetate Copolymer.

Ethylene Vinyl Acetate Copolymer (EVA) in Fig 2.1 is produced by copolymerization of ethylene and vinyl acetate (VA). With increasing proportion of the polar comonomer VA, the products change from modified PE to rubber-like product. EVA is mainly recognized for its flexibility and toughness (even at low temperatures), adhesion characteristics and stress-cracking resistance. Compared to LDPE, EVA is more polar and less crystalline due to the acetate groups. With increasing VA content, EVA copolymer becomes softer due to decreased crystalinity. Up to a VA content of 10 wt.-%, the density decreases and the crystalline structure is not destroyed. While higher densities usually mean higher stiffness and a higher glass transition temperature, the opposite is true in the case of EVA copolymers. Transparency increase with increasing VA content, the product becomes rubber elastic and the ultimate tensile strength passes through a maximum.

Products with up to 10 wt.-% VA are more transparent, more flexible, and tougher than LDPE. The high resistance to ESC is especially useful for cable isolation. Between 15 and 30 wt.-% VA the products are comparable with plasticized PVC. They are very soft and flexible. Compounds with 30 to 40 wt.-% VA are soft, elastic, and highly fillable. Strength and adhesion are the desirable properties for coating and adhesives. Between 40 and 50 wt.-% of VA rubber-like properties predominate and these products can be cross-linked as cable insulation by either peroxide or radiation.

Copolymers with 70 to 95 wt.-% VA are used for manufacturing of emulsion paints, adhesives and film coating.

EVA is resistant to dilute mineral acids, ketones, and aromatic or chlorinated hydrocarbons. The resistance to ESC increase with increasing VA content and decreasing melt index. It is significantly higher for EVA copolymers than comparable LDPE

2.2 Principal of Flame Retardant

2.2.1 Thermal Degradation

In the case of the polymers, an external heat source is needed to ignite the substrate. The heat, to which the material is exposed to, causes the high molecular weight polymer to thermally decompose. On thermal decomposition, the polymer releases smaller volatile compounds that act as fuel to the fire. These combustible species mix with the oxygen in the air to form an ignitable mixture. Exothermic oxidation of the volatile occurs and the material burns. Light and more heat are generated. The process becomes self-sustaining and functions with a feed back loop as can be seen in the fire triangle (Figure 2.2). The product of the fire differs for each combustible compound. In the case of polymers, the gases produced by combustion tend to be mainly carbon dioxide (CO_2), carbon monoxide (CO), and water vapor (H_2O). The solid residue is mostly carbon (C) and ash (oxidized metals) (5).

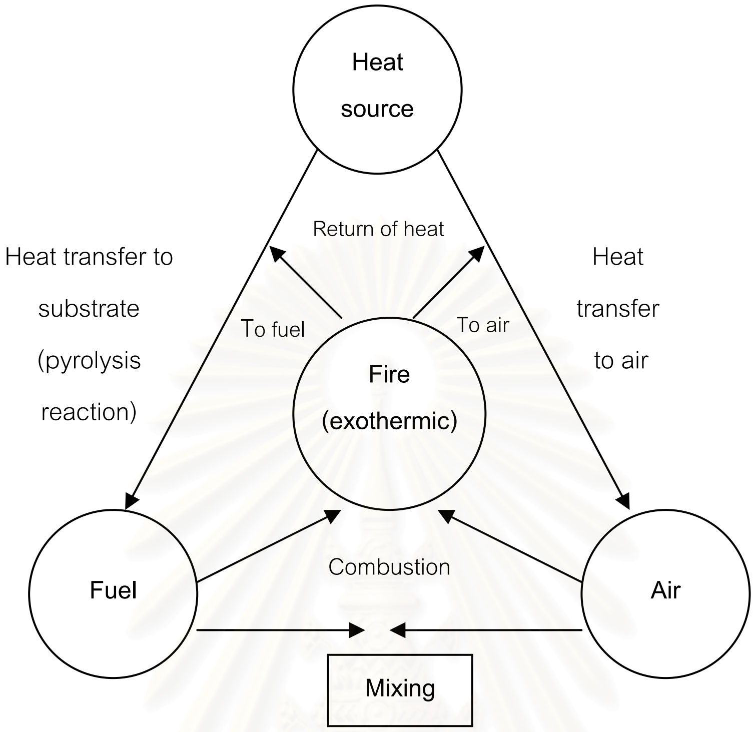


Figure 2.2 Combustion Process

2.2.2 Combustion Process

Flammability is an interaction of pyrolysis, ignition, combustion, fire propagation, and flame extinction processes. The first four processes are brought about by the heat exposure of the material. The heat exposure must be of sufficient strength to satisfy the requirements of the pyrolysis process.

Pyrolysis is generally an endothermic process, characterized by the softening, melting, discoloration, cracking decomposition, and vaporization and so forth of the material and release of products. The boundary of the pyrolysis process is defined as the pyrolysis front

Ignition is a process in which the pyrolysis products mix the air and form a combustible mixture, and the mixture ignites by itself or is ignited by a flame, a hot of the pyrolysis process is defined as the pyrolysis front.

Combustion is a process in which the pyrolysis products react with oxygen from air, with a visible flame. Heat and products are released in this process.

Fire propagation is a process in which the pyrolysis front, accompanied by the flaming or nonflaming combustion process, moves beyond the point of origin at a certain rate, defined as the fire-propagation rate. Heat and products are released at an increasing rate during the propagation process.

Flame extinction is a process in which the pyrolysis, ignition, combustion, and fire-propagation processes are interrupted by external agents such as water. Heat and products are released at a decreasing rate until flame extinction. Pyrolysis products continue to be released past the flame extinction as long as the heat within the materials continues to satisfy the requirements of the pyrolysis process.

2.2.3 Mechanism of Action of Flame Retardant

Flame retardant systems act in five basic ways

1. Inert gas dilution: large quantities of inert and non combustible gases are produced on thermal decomposition of the additive. The concentration of oxygen and combustible species are reduced and the fire dies.
2. Thermal quenching: the surface temperature of the polymer is reduced or kept low by the endothermic degradation of the additive. Due to the lower substrate temperature, less combustible products are produced and the thermal degradation is retarded.
3. Physical dilution: large quantities of inorganic fillers are added to the polymer matrix. The amount of flammable material is thus reduced and the substrate's fire resistance increased.
4. Chemical interaction: some flame retardants thermally dissociate into radical species that then interferes with the gas phase combustion of the combustibles.
5. Protective char: on thermal decomposition, the additive forms an insulating char barrier on the surface of the oxygen to the area of decomposition and diffusion of combustibles to the flame zone, retarding the combustion.

The flame retardant must not decompose at temperature below the processing temperatures of the polymer. Its decomposition temperature should be several degrees higher than the polymer processing temperature.

2.3 Type of flame retardants

A distinction is made between reactive and additive flame retardants. Reactive flame retardants are reactive components chemically built into a polymer molecule. Additive flame retardants are incorporated into the polymer either prior to, during or following polymerization.

2.3.1 Inorganic flame retardants

Inorganic fillers act as flame retardants due to their endothermic decomposition which withdraws heat from the fire and simultaneously release inert gasses such as H_2O, CO_2, NH_3 that dilute the oxygen and volatile fuel supplies to the fire. These inorganic compounds are non-combustible polymer in the solid phase. Metal oxide residues are formed during the decomposition of the inorganic systems. These metal oxides may catalyze further oxidation of the condensed phase. The latter includes the carbonaceous residues formed during the charring step and the remaining polymer (6).

The very high concentrations (50 to 80%) required to impart flame retardancy often adversely affect the mechanical properties of the polymer into which they are incorporated.

2.3.1.1 Aluminium hydroxide, also known as alumina trihydrate (ATH) is the largest volume flame retardant in use today. It decomposes when exposed to temperatures over 200°C, which limits the polymers in which it can be incorporated. Magnesium hydroxide is stable to temperatures above 300°C and can be processed into several polymers.

$$2Al(OH)_3 + 300\ kJ/mol \xrightarrow{200\ ^0C} Al2O_3 + 3H_2O$$

Figure 2.3 Decomposition mechanism of ATH

The utility of aluminium trihydrate as a flame retardant is based on its endothermic dehydration to aluminium oxide and water (Fig. 2.3) In absorbing some of the heat of combustion and lowering the temperature of the substrate near the flame, the hydrate functions as a chemical heat sink. The water vapor provided by such action dilutes the gaseous reactants in the flame until all the water of crystallization is exhausted. Aluminium trihydrate also can be as the only fire-reactant ingredient in the production of fiber-board. However, other research indicates that it is more effective when used in combination with other chemicals

2.3.1.2 Antimony oxides and antimonates must be converted to volatile species. This is usually accomplished by release of halogen acids at fire temperatures. The halogen acids react with the antimony-containing materials to form antimony trihalide or antimony halide oxide. These materials act both in the substrate (condensed phase) and in the flame to suppress flame propagation. In the condensed phase, they promote char formation, which acts as a physical barrier to flame and inhibits the volatilization of flammable materials. In the flame, the antimony halides and halide oxides, generated in sufficient volume, provide an inert gas blanket over the substrate, thus excluding oxygen and preventing flame spread. These compounds alter the chemical reactions occurring at fire temperatures in the flame, thus reducing the ease with which oxygen can combine with the volatile products. It is also suggested that antimony oxychloride or trichloride reduces the rate at which the halogen leaves the flame zone, thus increasing the probability of reaction with the reactive species. Antimony trichloride probably evolves heavy vapours which form a layer over the condensed phase, stop oxygen attack and thus choke the flame. It is also assumed that the liquid and solid antimony trichloride particles contained in the gas phase reduce the energy content of the flames by wall or surface effects (7).

2.3.1.3 Boron compounds such as borax (sodium borate), zinc borate, barium metaborate ($BaB_2O_4xH_2O$) are well known retardant systems. Boron compounds act in both the composed and vapor phase as fire suppressants. Most boron complexes are Lewis acids, which promote crosslinking of the polymeric material on thermal degradation and thus minimizing decomposition and volatile combustibles. Boron compounds can also react with the hydroxyl group in polymers containing such groups to form a glassy ester. This ester forms a char coating on the substrate surface and reduces solid-state carbon oxidation by protecting the underlying material.

2.3.1.4 Phosphorus compounds such as red phosphorus and ammonium polyphosphate (APP) are used in various plastics.

Red phosphorus was first investigated in polyurethane foams and found to be very effective as a flame retardant. The flame-retarding effect is due, in all probability, to the oxidation of elemental phosphorus during the combustion process to phosphoric acid or phosphorus pentoxide. The latter acts by the formation of a carbonaceous layer in the condensed phase. The formation of fragments that act by interrupting the radical chain mechanism is also likely.

Ammonium polyphosphate is mainly applied in intumescent coatings and paints. Intumescent systems puff up to produce foams. Because of this characteristic they are used to protect materials such as wood and plastics that are combustible and those like steel that lose their strength when exposed to high temperatures. Intumescent agents have been available commercially for many years and are used mainly as fire-protective coatings. They are now used as flame-retardant systems for plastics by incorporating the intumescent components in the polymer matrix, mainly polyolefins, particularly polypropylene (7).

2.3.2 Halogenated flame retardant

Halogen based flame retardants function in the vapor phase. On heating, they decompose to form halogen radicals. These halogen radicals interfere with the oxidation of the volatile fuels. They react with the oxygen and hydrogen radicals in the gas phase, thereby reducing their concentration and extinguishing the fire (8).

2.3.3 Non intumescent - phosphorus flame retardants

Phosphorous containing flame retardants include phosphate esters and inorganic phosphates. Phosphorus-based flame retardants work in both condensed and vapor phases, interact according to both physical and chemical mechanisms. Phosphorus and boron compounds are well known to act as inhibitors of carbon oxidation. Phosphorus systems prevent this glowing combustion.

Flame retardants occurs both as already stated in the vapor phase and in the condensed phase. Phosphorus acts primarily in the condensed phase by promoting charring. Some reports indicated that certain organic phosphorus compounds may also work in the gas phase by scavenging free radicals.

2.3.3.1 Condensed phase

It is charring or altering thermal degradation processes. Phosphates and other phosphoric acid derivatives decompose thermally to form phosphoric acid, which is a good flame retardant due to its own low volatility. The phosphoric acid acts as dehydration catalyst in cellulose or in the presence of hydroxyl rich compounds or polymers. It forms polyphosphoric acid when strongly heated. The polyphosphoric acid is an even more effective dehydration catalyst of cellulose than phosphoric acid itself. Char and water are formed during the dehydration step. The char formed is coated by phosphoric acid, making it less permeable and protecting the char from solid phase oxidation or afterglow (9).

This is however not a general phenomenon and some nitrogen compounds are antagonistic. The compound used depends on the polymer flame retardant system. Some polymers, the phosphorus rich flame retardants cause an initial crosslinking reaction through the polymer. This implies that the polymer is prevented from volatilizing and thus less combustible species are forms. The phosphorus containing additives can also catalyze the clipping of the polymer chains thereby reducing its molecular weight. This reduces the viscosity of the polymer melt allowing it to drip away from the fire zone. This dripping removes material that can burn from the fire zone.

2.3.3.2 Vapor phase

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

$$H^{\cdot} + O_2 \longrightarrow {}^{\cdot}OH + O^{\cdot}$$

Figure 2.4 The hydroxyl and oxygen radicals react

The volatile phosphorus compounds produced during the thermal decomposition of the phosphorus based flame retardants, are effective flame retardants Mass spectroscopy studies have shown that triphenyl phosphate thermally degrades to form small volatile species such as P_2, PO, PO_2 and HPO_2. These volatile phosphorus species interfere and inhibit the branching step in the vapor phase. They extinguish the flame by reducing the hydrogen atom concentration in the vapor phase. Phosphorus based flame retardants form water during a fire situation. This water is volatiled forming inert water vapor. The presence of water vapor may help to extinguishing the flame: it dilutes the combustible and starves the fire of O_2 (9).

2.4 Halogen Free Flame Retardant Compounds

Halogen belongs to the main group VII in the periodic table of the elements. In this order: fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). They easily react with hydrogen, and create the following acids: HF, HCl, HBr, and HI. The Acids are reactive and create salts if they make contact with metals.

The cable industry uses several halogen containing polymers. Those containing chlorine are the most widely known. This includes polyvinyl chloride (PVC), neoprene, and chlorinated polyethylene (CPE). Brominated butyl rubber is the only polymer containing bromine. It is not used in cable production. However, bromine can be added to polymers to reduce the flammability. Halogen containing polymers features

1. good mechanical properties.
2. good chemical resistance
3. good weather resistance
4. improved flame retardancy

Polyvinyl chloride (PVC), a representative of halogenated materials, is widely used for both insulation and sheath of wire and cables. It is considered that hazardous dioxins evolve during incineration of halogenated materials under inadequate conditions, and to disperse harmful lead ions from lead stabilizers into underground water supplies on reclamation. In addition, phthalic esters used as plasticizers of PVC have recently been reported as suspected endocrine disrupters (2).

To understand why we want halogen free flame retardant cables instead of PVC. It is important to be aware of the character of the halogenated acids (3). Toxic gases are given on the combustion and pyrolysis conditions. During combustion and pyrolysis of pure PVC in cable sheathing in an air atmosphere, PCDD and PCDF are formed in significant amounts up to the ppm range. In general furans were formed predominantly. Especially higher levels of octa and heptachlorinated furans were generated in the pyrolysis experiments, whereas lower chlorinated furans were produced predominantly by combustion (3). Studies have been carried out on the flammability, of the level of smoke production and of the amount of char remaining after combustion, for a variety of chlorinated polymers. The chlorine level of the sample ranged between that in ordinary PVC and 70 wt%. The intrinsic viscosity of the PVC from which these resins were produced ranged between 0.6 and 1.1. PVC has exceptionally good fire properties. The LOI increase from a level of 45-49 to over 70 and to pure oxygen (for sustained flaming combustion at 70 wt% Cl). A flammability property was defined which corresponds to sustained flaming combustion, some of the highly chlorinated samples require pure oxygen atmosphere to achieve an LOI of 100. the amount of smoke evolved also decrease drastically with increasing chlorinated systems of equations which give very good predictions of the properties to be measured (4).

Cable users have expressed concern over the amount of hydrochloric acid which is evolved when conventional cable compounds based on materials such as PVC, PCP, and CSP are burned as this acid can cause extensive damage to electrical equipment not involved in the fire itself. It must be appreciated that, even in an installation where the main requirement is one of fire resistance, other fire related factors cannot be ignored. Therefore, halogen free flame retardant compounds are developed for this requirement to be halogen free fire retardant cables.

2.5 Intumescent - phosphorus flame retardants

Intumescent flame retardants are thus those that reduce flame spread and fire risk through the formation of a swollen, bubbled or foamed up char residue on the material’s surface.

The early formulations were based on ammonium polyphosphate and nitrogen rich compounds. The main function of an intumescent coating is to shield the underlying material from the heat of a fire. For a mixture to be an efficient intumescent system, three elements are needed (10):

1. The inorganic acid (dehydrating agent)
2. The polyhydric materials rich in carbon: a carbonific or char former
3. The blowing agent: spumific

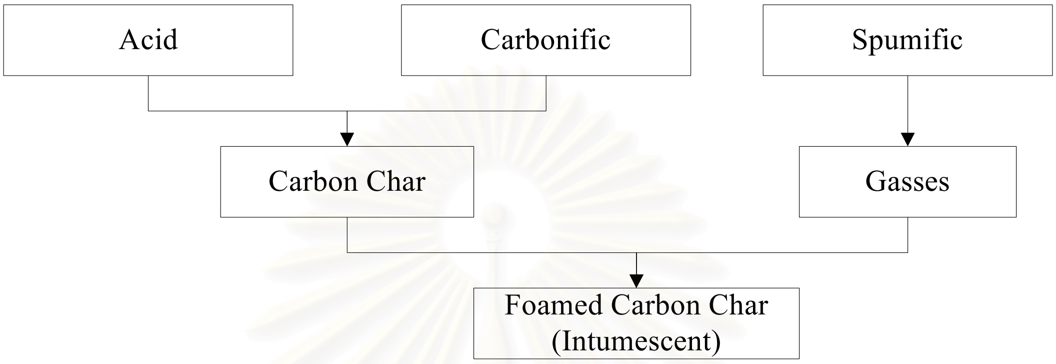


Figure 2.5 Schematic diagram for acid catalyzed intumescent

The fire fighting capabilities of the intumescent flame retardants is due to the swollen of foamed char formed on the surface of the burning material. The char forms a physical protective barrier for heat transfer to the surface of the combustible material acting as a “shield” to the polymer from the fire. This lowers the temperature of the surface beneath the char and causes a lag in the surface temperature rise. The char layer furthermore hinders the diffusion of oxygen to the site of combustion. Dripping of the molten plastic is reduced by char formation thereby eliminating a possible source of further propagation. Compounds that promote the formation of char under fire conditions are good flame retardants and can improve current systems. Charring also reduce the amount of the polymer that is converted into volatile fuels. There is a positive correlation between char yields and flammability of a polymer when the LOI is used as the measure of fire resistance.

The char formation in intumescent systems is often expressed in terms of simple acid catalyzed dehydration reaction of hydroxyl compound. The mechanism for carbon-carbon double bond formation is indicated below. The formation of $-CH=CH_2$ fragment leads to carbon rich residues or char. Pentaerythritol and dipentaerythritol are polyalcohols frequently used as carbonifics.

The acid catalyst for the char formation is phosphoric acid derivatives. Phosphoric acid is produced when phosphate containing flame retardants degrade thermally. The phosphoric acid reacts with polios (polyhydroxyl compounds) to form polyol phosphates. These polyol phosphate can break down to firm material rich in carbon-carbon double bonds (char). Water is released during the reaction (10).

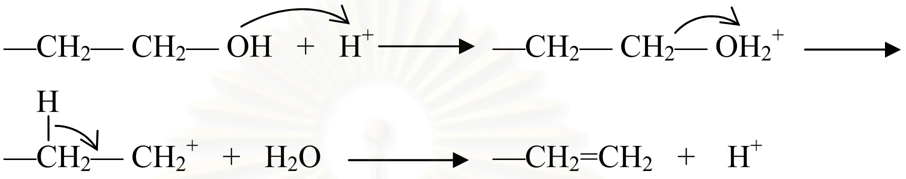


Figure 2.6 Acid catalyzed dehydration of a hydroxyl compound

The water evolved during the reaction also acts as the blowing agent. The blowing agent forms gasses during the degradation reaction that cause the carbon residue to foam, bubble, or intumesce.

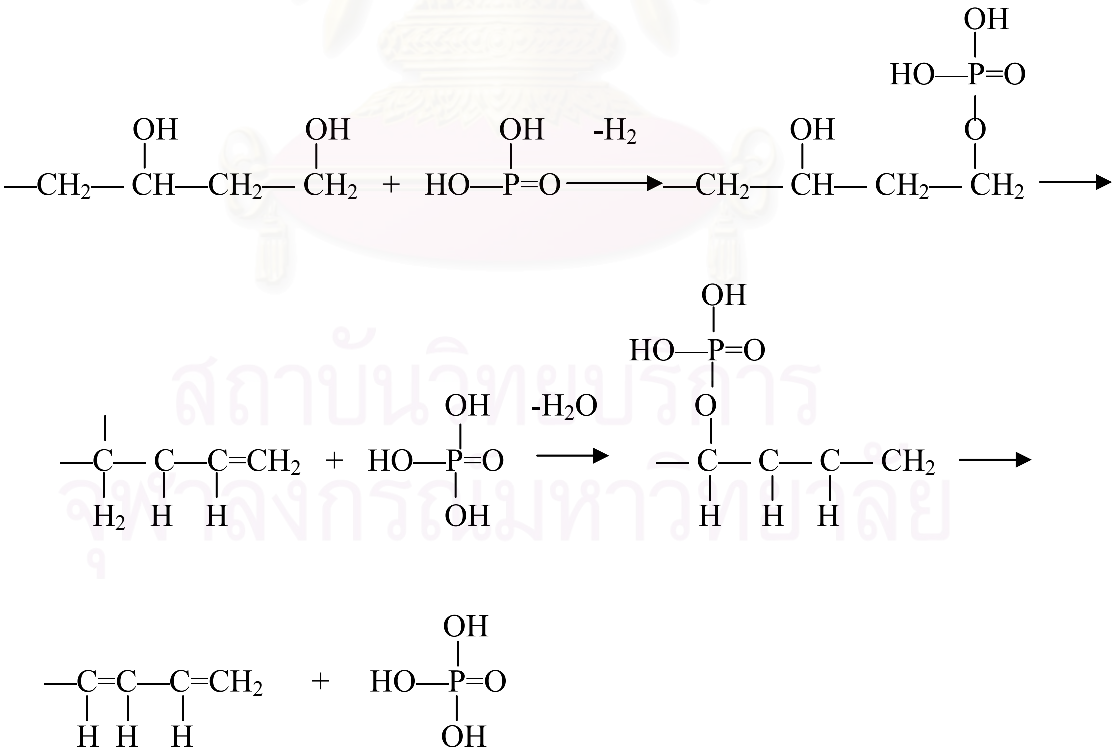


Figure 2.7 The action of the phosphate acid in char formation mechanism

Nitrogen rich compounds are nearly always in intumescent systems. Such compounds improve char yield and intumesces the carbon through the formation of gasses-acting as the spumific. Nitrogen compounds are environmentally friendly; they do not produce corrosive gasses, are easily disposable, produce fewer toxic gasses and less smoke than for example halogen based systems.(11) Melamine is often used as a compound in an intumescent flame retardant system and melamine-based compounds have shown promise as fire retardants (12) .

2.6 Melamine Phosphate

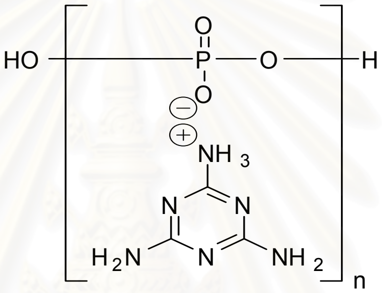


Figure 2.8 Melamine Phosphate

During the last years a large interest has arisen in melamine-phosphate-based flame retardants (MPBFR's). These non-hazardous and environmental-friendly materials are considered to be an attractive to replace halogen-containing flame retardants. The latter releases toxic and corrosive gases during combustion. MPBFR's are salt of melamine and phosphoric acid, either orthophosphate or condensed forms of phosphate, such as pyrophosphate and polyphosphate that result from a thermal condensation. Often in these compounds the melamine moiety is a cation (melaminium) with an endocyclic nitrogen being protonated, due to hydrogen transfer from a phosphate.

MPBFR's are polycrystalline materials with a high thermal stability and a very low solubility in water and organic solvents. MPBFR's are active in the condensed phase: during combustion an organic-inorganic porous char layer is formed at the surface of the polymer that shields off the polymer from heat, air and intumescences process (swelling) that leads to the char layer as blowing agent, the precise flame-retardant mechanism of MPBFR's and the role the individual components therein have not been clarified completely.

Melamine Phosphate (MP) is decomposed under high temperature (normally above 300 ^{o}C) if undergoes endothermic decomposition thus acting as a heat sink and cooling the combustion source. The released phosphoric acid acts to coat and therefore shield the condensed combustible polymer or surface of the combustible materials. The phosphoric acid along with the fuel source thus reducing the amount of oxygen present at the combustion source. The melamine releases in its gaseous form furing the reaction also helps to reduce the oxygen present at or around the combustion source.

Melamine polyphosphate (MpolyP) are known as char forming or intumescent flame retardants (13). Unlike the halogenated flame retardants, which act by way of chemical inference with the radical chain mechanism taking place in the gas phase (14), intumescent systems are active in the condensed phase. As a result of a series of physical/chemical processes during the combustion process, a char layer is formed, which isolates the polymeric material from the action of heat and oxygen. Melamine polyphosphate also blocks, the transfer of flammable materials into the gas phase, thus leading to extinguishing of the fire. The barrier properties of the char layer are most effective if it is expanded, when the process is termed "intumescent" (15) is clear that polymer degradation and interaction with melamine polyphosphate play a decisive part in char formation (16). Experiment of Shahab Jahromi, Wouter Gabriëlse and Ad Braam, The thermal degradation of melamine polyphosphate as a function of time at different temperatures has revealed that this flame retardant depolymerizes above 350 ^{o}C and 450 ^{o}C in compounds with both polyamide 66 (PA66) and polyamide6(PA6). It has been established that phosphoric acid forms when PA66 and MolyP mixtures are heated. The frequency dependent rheological experiments demonstrated that MolyP induces significant cross linking in PA66 and leads to a dramatic depolymerization of PA66. These results are used to explain the performance of MolyP as a intumescent flame retardant in both PA66 and PA6 (17).

2.7 Zinc Borate

Zinc borate is a boron-based fire retardant with a chemical composition of $xZnOyB_2O_3zH_2O$. The most commonly used grade have the following structure:

$2ZnO.3B_2O_3zH_2.3,5H_2O$. Zinc borate can be used as a fire retardant in PVC, polyolefins, elastomers, polyamides, epoxy resins. In halogen-containing systems, zinc borate is used in conjunction with antimony oxide, while in halogen-free systems, it is normally used in conjunction with aluminium trihydrate, magnesium hydroxide, or red phosphorus. In some particular application Zinc Borate can be used alone.

Zinc borate acts through:

- Zinc halide or zinc oxyhalide that accelerate the decomposition of halogen sources and promote char formation.
- the B_2O_3 moiety released, a low melting glass, that can stabilize the char. B_2O_3 released can also promote the formation of ceramic formation in systems containing ATH or magnesium hydroxide.
- the endothermic, stepwise release of water that can promote the formation of foamy char.

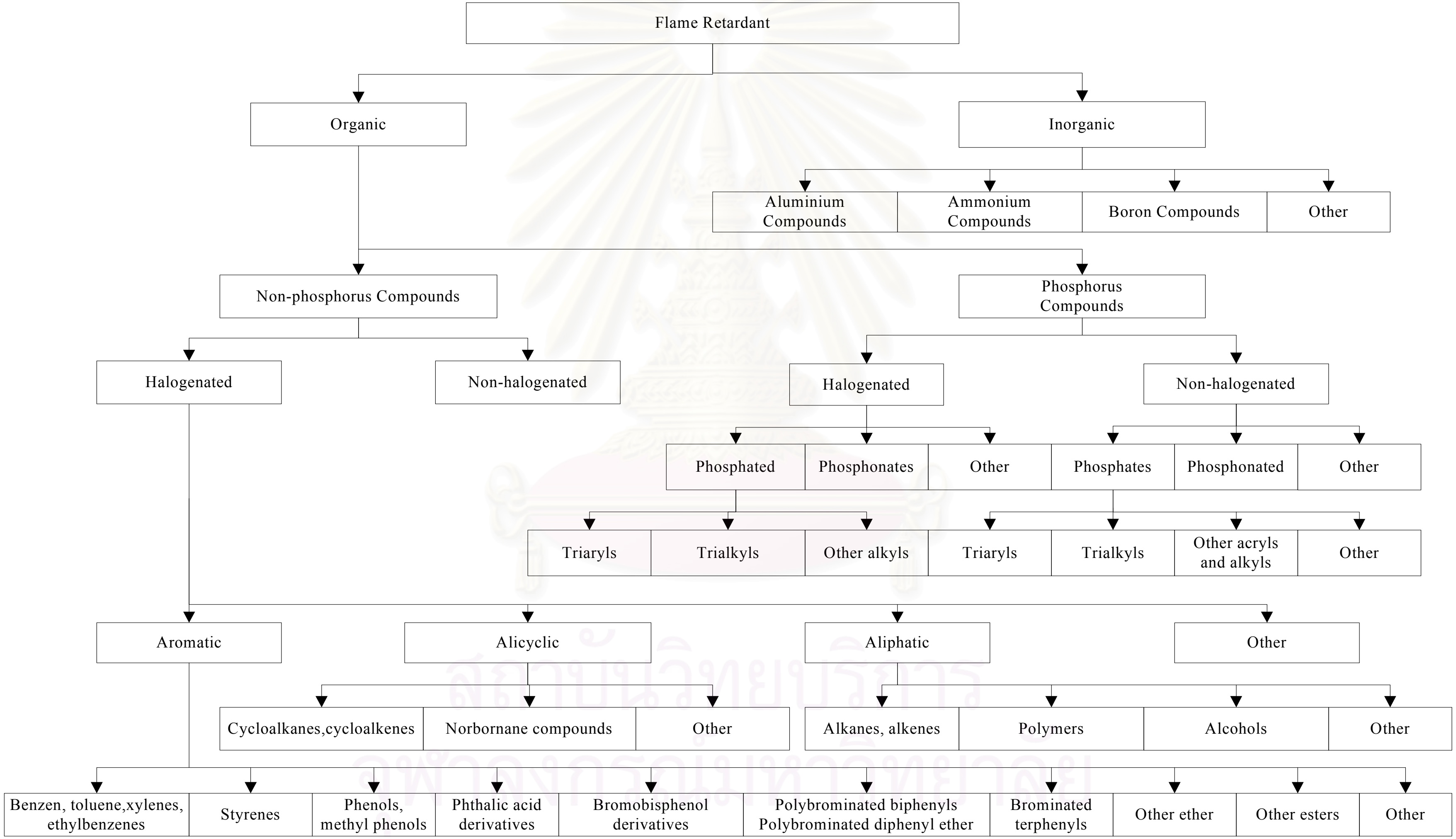
Hydrated zinc borate has been proposed as a challenger for the ATH filler. It is able to lose more than 10% of its own weight as water molecules in a range of temperature comprised between 300 ^{o}C and 450 ^{o}C. Moreover, during the thermal treatment, zinc borate is converted into a glassy phase which acts as a temporary insulating barrier against combustion. The combination of zinc borate and ATH offers also good perspectives due to their ability to form a solid residue at relatively high temperature allowing the maintenance of good mechanical and electrical properties (2) meet the silicon ethylene propylene diene monomer (EPDM) blend containing ATH and hydrate zinc borate that can fuse and form a ceramic-like hard residue. This strong char can act as a thermal barrier and prevents burning drip. However, first-tests of wires with that composition, performed at 950 ^{o}C, failed due to short-circuit revealing the presence of a conductive compound in the burnt insulating layer (18).

2.8 Tests and Standards

2.8.1 Thermogravimetric Analysis (TGA)

Thermogravimetry is a technique in which the mass of the sample is monitored against time or temperature of the sample, in specified atmosphere. The chief use of this technique has been to study the thermal decomposition of polymeric materials and to accumulate kinetic information about such decomposition. A sample is suspended on a sensitive balance that measures the weight as it is exposed to a furnace. Air, nitrogen, or another gas flows around the sample to remove the pyrolysis or combustion products. Weight loss is recorded as a function of time and temperature. In isothermal TG, the change in weight of the sample is recorded as a function of time as the temperature remains constant. In dynamic or nonisothermal thermogravimetry, the change in weight is a function of both temperature and time as the temperature is raised at a given heating rate. With the use of a derivative computer, the rate of weight loss as a function of time and temperature can also be determined. The computer allows a more accurate determination of peak temperature transitions (19).

Figure 2.9 Breakdown of flame retardant chemical types



2.8.2 Limiting Oxygen Index (LOI)

Oxygen index methods, which describes the tendency of a material to sustain a flame, are widely used as a tool to investigate the flammability of polymers. They provide a convenient and reproducible means of determining a numerical measure of flammability. A further attraction is that the test method uses inexpensive equipment and only requires a small sample size. These methods have been used to systematically investigate the relative flammabilities of fire-retarded materials, frequently comparing the effectiveness of fire-retardants and fire-retardancy mechanisms.

The quintessential feature of oxygen-index methods is that the sample is burnt within a controlled atmosphere. The standard procedure is to ignite the top of the sample, using a gas flame which is withdrawn once ignition has occurred, and to find the lowest oxygen concentration in an upward flowing mixture of nitrogen and oxygen which just supports sustained burning. The criticality criterion typically takes the form of a minimum burning length: either specifying that the sample must burn for a certain length of time or that a specified length of material be consumed. The effectiveness of fire retardants is measured by the change in the critical oxygen concentration that they induce as a function of their concentration.

The limiting oxygen index (LOI), also called the critical oxygen index (COI) or oxygen index (OI), is defined as:

$$\mathrm{LOI} = \frac{[O_{2,cr}]}{[O_{2,cr}] + [N_2]} \qquad \text{equation~(1)}$$

where $[O_{2,cr}]$ and $[N_2]$ are the minimum oxygen concentration in the inflow gases required to pass the "minimum burning length" criterion and the nitrogen concentration in the inflow gases, respectively. If the inflow gases are maintained at constant pressure then the denominator of equation~(1) is constant since any reduction in the partial pressure (concentration) of oxygen is balanced by a corresponding increase in the partial pressure (concentration) of nitrogen. Limiting oxygen index is more commonly reported as a percentage rather than fraction.

Since air comprises about 20.95% oxygen by volume, any material with a limiting oxygen index less than this will burn easily in air. Conversely, the burning behaviour and tendency to propagate flame for a polymer with a limiting oxygen index greater than 20.95 will be reduced or even zero after removal of the igniting source. Self-sustaining combustion is not possible if LOI>100, such values are not physically meaningful.

Several researchers have suggested that materials with a limiting oxygen index greater than 28 are generally self-extinguishing .We describe materials satisfying 28.00 < LOI < 100 as being "self-extinguishing". The threshold LOI = 20.95 is of great practical interest and we define materials with a limiting oxygen index of 20.95 as being "marginally stable". We follow and refer to materials that are between the marginally stable and self-extinguishing thresholds, i.e., 20.95 < LOI < 28, as being "slow-burning".

It should be realized that our classification of materials (flammable, slow-burning, self-extinguishing, intrinsically non-flammable) is specific to the limiting oxygen index test, *i.e.*, a material that is self-extinguishing here is not necessarily self-extinguishing in another test method. The tenet in the limiting oxygen index is that the higher the value of the LOI the "safer" the material. However, we stress that results from one test method do not necessarily agree with another. Thus throughout this thesis an assignment of a material as being self-extinguishing is short-handed for ``self-extinguishing in the limited oxygen index test".

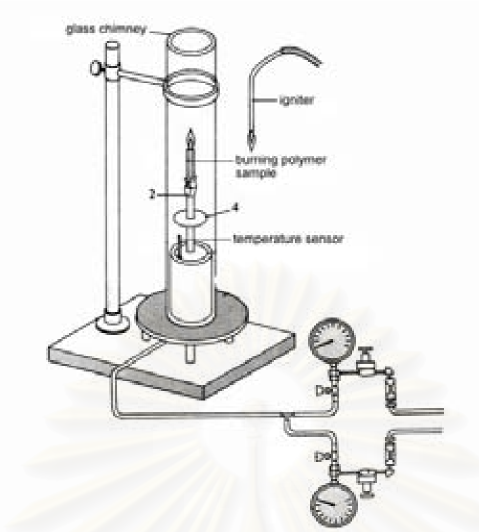


Figure 2.10 Limiting Oxygen Index Tester

2.8.3 Fire safety standards

A large set of British Standards exist relating to flame retardancy of product. Fire safety standards are also produced by the European Committee for Standardization (CEN), and the American Society for Testing and Materials (ASTM). Compliance is determined by performance of flame retarded products in specially designed standard tests to assess factors such as ignition, the rate and temperature to burn, and the by-products released during combustion.

Underwriters Laboratories Inc., an independent product safety testing and certification organization, has also developed generic standard test methods for plastics (UL94), which are widely applied in this industry. The performance in vertical and horizontal burn tests is assessed and the product is classified accordingly (V0-2; if the vertical test is not passed, HB; if the horizontal test is not passed (not classified) and the highest rating is V0.

Types of fire safety standards vary for different applications. One particularly important area is electrical and electronic equipment (EEE), *e.g.* in equipment housings. The EU fire safety standard for IT appliances, EN 60950, cover different approaches for achieving fire safety in EEE, including the use of flame retardants. Classification V0 in UL94 is typically required for monitor housings, while television sets in the EU often meet only UL94-HB, though some companies are increasing the level of fire safety of such products (20).

UL 94 tests for flammability of plastic materials giving a preliminary indication of their suitability for a particular application. The apparatus is supplied as a complete system incorporating all the features necessary for ease of use and safety. It conforms to all five UL 94 horizontal and vertical Bunsen burner tests and associated international standards. These are: -

1. Horizontal Burning Test; UL 94HB (ASTM D 635, ISO 1210, IEC 60695-11-10 or IEC 60707).
2. Vertical Burning Test; UL 94V-0, V-1, or V-2 (ASTM D 3801, IEC 60695-11-10, IEC 60707 or ISO 1210).
3. 500 W (125mm) Vertical Burning Test; 5VA or 5VB (ASTM D 5048, IEC 60695-11-20, IEC 60707 or ISO 9772).
4. Thin Material Vertical Burning Test; VTM-0, VTM-1, or VTM-2 (ASTM D 4804 or ISO 9773).
5. Horizontal Burning Foamed Material Test; HBF, HF-1, or HF-2 (ASTM D 4986 or ISO 9772).
6. Burners (ASTM D 5025, ASTM D 5207, ISO 10093, ISO 10351)

2.8.3.1 Horizontal Testing (HB)

Procedure: A specimen is supported in a horizontal position and is tilted at 45°. A flame is applied to the end of the specimen for 30 seconds or until the flame reaches the 1 inch mark. If the specimen continues to burn after the removal of the flame, the time for the specimen to burn between the 1 and 4 inch marks are recorded. If the specimen stops burning before the flame spreads to the 4 inch mark, the time of combustion and damaged length between the two marks is recorded. Three specimens are tested for each thickness.

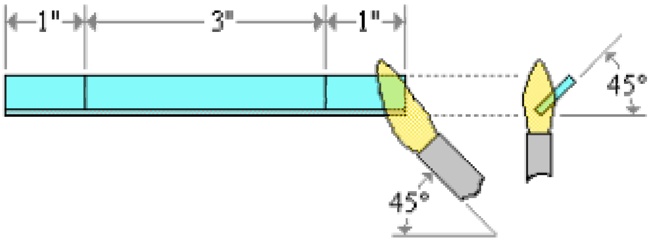


Figure 2.11 Horizontal Flame Test

Table 2.1 Horizontal Flame Test

Horizontal Rating	Requirements
HB	- Specimens must not have a burning rate greater than 1.5 inches/minute for thicknesses between 0.120 and 0.500 inches and 3 inches/minute for thicknesses less than 0.120 inches. - Specimens must stop burning before the flame reaches the 4 inch mark.

2.8.3.2 Vertical Testing (V-0, V-1, V-2)

Procedure: A specimen is supported in a vertical position and a flame is applied to the bottom of the specimen. The flame is applied for ten seconds and then removed until flaming stops at which time the flame is reapplied for another ten seconds and then removed. Two sets of five specimens are tested. The two sets are conditioned under different conditions.

Table 2.2 Vertical Flame Test

Vertical Ratings	Requirements
V-0	• Specimens must not burn with flaming combustion for more than 10 seconds after either test flame application. • Total flaming combustion time must not exceed 50 seconds for each set of 5 specimens. • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. • Specimens must not drip flaming particles that ignite the cotton. • No specimen can have glowing combustion remain for longer than 30 seconds after removal of the test flame
V-1	• Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application. • Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens. • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. • Specimens must not drip flaming particles that ignite the cotton. • No specimen can have glowing combustion remain for longer than 60 seconds after removal of the test flame.
V-2	• Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application. • Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens. • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. • Specimens can drip flaming particles that ignite the cotton. • No specimen can have glowing combustion remain for longer than 60 seconds after removal of the test flame

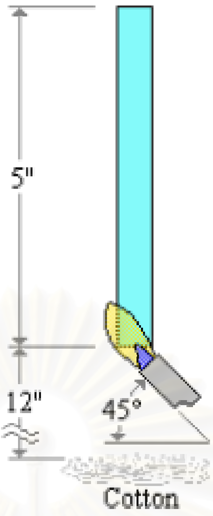


Figure 2.12 Vertical Flame Test

2.8.3.3 Vertical Testing (5V, 5V-A, 5V-B)

Testing is done on both bar and plaque specimens.

Procedure for Bars: A bar specimen is supported in a vertical position and a flame is applied to one of the lower corners of the specimen at a 20° angle. The flame is applied for 5 seconds and is removed for 5 seconds. The flame application and removal is repeated five times. Procedure for Plaques: The procedure for plaques is the same as for bars except that the plaque specimen is mounted horizontally and a flame is applied to the center of the lower surface of the plaque.

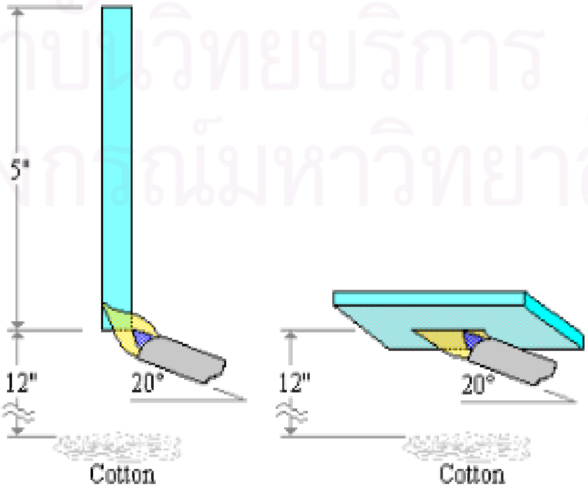


Figure 2.13 Vertical Flame (5V Type) Test

Table 2.3 Vertical Flame Test

Vertical Rating	Requirements
5V	• Specimens must hot have any flaming or glowing combustion for more than 60 seconds after the five flame applications. • Specimens must not drip. • Specimens must not be destroyed in the area of the flame
5V-A	• Specimens must hot have any flaming or glowing combustion for more than 60 seconds after the five flame applications. • Specimens must not drip flaming particles that ignite the cotton. • Plaque specimens must not exhibit burnthrough (a hole).
5V-B	• Specimens must hot have any flaming or glowing combustion for more than 60 seconds after the five flame applications. • Specimens must not drip flaming particles that ignite the cotton. • Plaque specimens may exhibit burnthrough (a hole).

2.8.3.4 Vertical Testing of Thin Materials (VTM-0, VTM-1, VTM-2)

This test is used for materials that are thin, or are too flexible or may distort, shrink or flex during ordinary vertical testing. Procedure: An 8x2 in specimen is rolled longitudinally around a 1/2 in diameter mandrel and taped on one end. When the mandrel is removed the specimen forms a cone. The cone is supported in a vertical position and a flame is applied to the bottom of the specimen. The flame is applied for three seconds and then removed until flaming stops at which time the flame is reapplied for another three seconds and then removed. Two sets of five specimens are tested. The two sets are conditioned under different conditions.

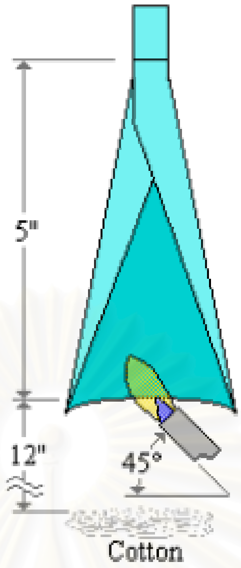


Figure 2.14 Vertical Flame Test for Thin Materials

Table 2.4 Vertical Flame Test for Thin Materials

Vertical Rating	Requirements
VTM-0	• Specimens must not burn with flaming combustion for more than 10 seconds after either test flame application. • Total flaming combustion time must not exceed 50 seconds for each set of 5 specimens. • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. • Specimens must not drip flaming particles that ignite the cotton. • No specimen can have glowing combustion remain for longer than 30 seconds after removal of the test flame. • No specimen shall have flaming or glowing combustion up to a mark 5 inches from the bottom of the specimen.

Table 2.4 Vertical Flame Test for Thin Materials (cont'd)

Vertical Rating	Requirements
VTM-1	• Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application. • Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens. • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. • Specimens must not drip flaming particles that ignite the cotton. • No specimen can have glowing combustion remain for longer than 60 seconds after removal of the test flame. • No specimen shall have flaming or glowing combustion up to a mark 5 inches from the bottom of the specimen.
VTM-2	• Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application. • Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens. • Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. • Specimens can drip flaming particles that ignite the cotton. • No specimen can have glowing combustion remain for longer than 60 seconds after removal of the test flame. • No specimen shall have flaming or glowing combustion up to a mark 5 inches from the bottom of the specimen.

2.8.4 Fire safety standard methods for the selection of electronic cables, wire and insulated parts

The instruction prescribes standard test methods for selecting suitable materials for the insulation and sheathing of power, control and signal cables and wires with respect to their resistance to fire and ionizing radiation. It summarizes the required properties for the difference materials and cable types, giving criteria for their specification, selection, and testing. It is applicable to all kinds of cables and wires and other insulated parts to be used in CERN installations, including equipment for prototyped. Tests and experiments (power, control, signal, high and low voltage, high and low frequency, fiber optics, etc.).

The requirements for all types of cables are the following

- Electrical, mechanical, thermal and environmental endurance properties conforming to the appropriate standards
- Flame retardant characteristics satisfying the relevant standards
- Halogen and sulphur fee
- Low smoke density
- Low toxicity of gases from fires
- Low corrosively of gases from fires
- Retention of functional capabilities up to an integrated doses of 10^6 Gy for general purpose cables and 10^7 Gy for special radiation resistant cables

2.8.4.1 Criteria for the specification and selection of cable insulating materials

Applicable standards

The required properties are described in this section and summarized together with the standards in Table 2.5. Independent laboratories capable of carrying out fire.

Flame propagation and fire resistance

Electric cables and wire can be classified in three categories with increasing fire resistance

1. flame retardant cables tested under single configuration (IEC 332-1 and 332-2)
2. flame retardant cables tested under bunched configuration (IEC 332-3)
3. fire resistant cables (IEC 331)

A distinction is made between the fire properties of materials and those for cables. Only categories (1) and (2) will be considered in this document. Cables in Category (3) are those which must continue to function for a defined time during and after a fire. They are mainly used for safety installations and will not be considered further in the present document.

Materials

The value of the temperature index measured according to BS 2782. Part1, shall be greater than 260 ^{o}C for all materials and compounds except primary insulation and dielectrics.

Remark Cables with sheath materials satisfying this requirement must also satisfy the fire test for the finished product.

Finish cables

Small, single-core, insulated wires conductor smaller than 0.8 mm diameter (0.5 mm^2) shall be tested according to IEC 332-2.

Single-core insulated wires with conductors greater than 0.5 mm2 and all multiconductor cables, round or flat of any dimension, shall pass IEC 332-1. For flat cables the flame shall be applied to one edge of the cable with the axis of the burner tube in the same plane as the major axis of the cables.

All types of finished cables having an outer diameter exceeding 10 mm must pass the IEC 332-3 test, Category CF.

Table 2.5 Required properties for the selection of electric cables and wires with respect to fire safety and radiation resistance

Property	Standard	Requirements	Remarks
Flame and fire propagation	IEC 332-2	Pass	Applied to all single wires
	IEC 332-1	Pass	Applied to all cables and to all single wires > 0.5 mm^2
	IEC 332-3	Pass	Applied to all cables with outer diam. > 10mm., category CF
Fire resistance	IEC 331	Pass	For cables with special safety functions (eg. emergency lighting, alarms, lifts, etc.)
Smoke density	ASTM E662 (or ASTM F 814)	Ds<250 in the flaming and non-flaming modes	For all cables
	IEC 1034-1 and 2	Pass	For all major CERN cables contracts
Toxicity of fire gases	ABD 0031	HF < 100 HCl < 150 HCN < 150 $SO_2 + H_2S < 100$	Mean value in ppm of at least 3 sample obtained within 4 minutes under flaming and non-flaming conditions
	BSS 7239	CO < 3500 $NO + NO_2 < 100$	
Corrosive of fire gases	IEC 754-2	pH>4 and conductivity < 100 µs/cm	Cables shall be halogen and sulphur free (less than 0.1% by weight)
UV resistance	IEC 68-2-5	No discoloration No stickiness	Procedure C, 10 days, 40 °C

Table 2.6 Summary of required properties for the selection of electric cables, wires and insulated part with respect to fire safety and radiation resistance

Property	Standard	Requirements	Remarks
Radiation resistance	IEC 544-2 and 4	Radiation Index > 5. 7	Elongation at break (ISO 37) 50% of initial value at absorbed dose of 5.105 Gy Test at high-dose rates (greater than 1 Gy/s)
Temperature Index of sheath	BS 2782, Part1	Pass	FT >260 °C Length burnt < 50 mm

Summary of required properties for the selection of electric cables, wires and insulated part with respect to fire safety and radiation resistance:

All cables and wire

a) Flame retardant characteristic satisfying the appropriate standards

b) Halogen and sulphur free

c) Low smoke density

d) Low toxicity of fire gases

e) Low corrosively of fire gases

f) Retention of function capabilities up to an integrated radiation dose of 106 Gy

<u>Remark</u> on b), c), d) and e): These requirements exclude some very commonly used materials such as PVC, Hypalon, Neoprene, fluorocarbons and other halogenated or sulphur containing compounds (e.g. Teflon).

on f) : This requirement is considered satisfied if, after an exposure of the insulation and sheath material to an integrated dose of ionizing radiation of 5 x 105

Gy, the elongation at break (ISO 37) is greater than 50% of the initial value. The irradiation is performed at high dose rates (greater than 1 Gy/s). The Radiation Index (RI)* according to IEC 544-4 is then > 5.7. The supplier must either this radiation resistance or supply test samples in order to carry out radiation tests by CERN.

The supplier must provide test results or certificates to prove that the cable satisfies the test requirement defined in Table 2.7.

Power Cables

Both the insulation and outer sheath materials should preferable be made EPR or EPDM. Supplier may propose alternative materials for insulation and outer sheaths (e.g. EVA or polyolefin). They must, however, prove that all specification requirements are fulfilled.

Control and signal cables and wires

The recommended material for insulation is PE and for the outer sheaths a flame retardant material such as EVA or a polyolefin copolymer.

Electrical and electronic equipment

Internal wiring of electrical and electronic equipment should follow the same rules as applied for power, control and signal cables. The same applies for all other kinds of organic materials used in this equipment such as connectors, conduits, terminal boards, frames, covers, spacers.

*RI = log10 of the absorbed dose in gray above which the appropriate critical property value has reached the end-point criterion.

Table 2.7 Quoted Standards (the most recent version will apply)

ASTM E 662 & ASTM F 814	Standard test method for specific optical density of smoke generated by solid materials
BS 2782	Parts, plastics: methods 143A and 143B. Determination of flammability. Temperature of materials
IEC 68-2-5	Simulated solar radiation at ground level
IEC 331	Fire-resisting characteristics of electric cables
IEC 332	Tests on electric cables under fire conditions 332-1 Part1: test on a single vertical insulated wire or cable 332-2 Part2: test on single small vertical insulated copper wire or cable 332-3 Part3: test on bunched wires or cables amendments No 1 and 2
IEC 544	Guide for determining the effects of ionizing radiation on insulating materials 544-1 Part1: radiation interaction 554-2 Part2: procedures for irradiation and test 554-3 Part3: classification system for service in radiation environments
IEC 695	Fire hazard testing Part2-2: needle flame test Part3-1: examples of fire hazard assessment procedures
IEC 707	Methods of test for the determination of the flammability of solid electrical Insulating materials when exposed to an igniting source
IEC 754-2	Test on gases evolved during combustion of electric cables
IEC 1034 Part1 and 2	Test for the measurement of smoke density of electric cables burning Under defined conditions
ISO 37	Rubber, vulcanized-determination of tensile stress-strain properties
UL-94	Standard for flammability of plastic materials for parts in devices and appliances

CHAPTER 3

EXPERTIMENTAL SECTION

3.1 Materials

1. Ethylene Vinyl Acetate Copolymer with vinyl acetate content at 18% was purchased from Thai Petrochemical Industry Public company limited (TPI.)

2. The following flame retardants were obtained from the Budenheim Ibérica Commercial, Spain

   : melamine phosphate (Budit 312)

   : melamine pyrophosphate (Budit 311)

   : melamine polyphosphate (Budit 3141)

3. Aluminum trihydrate (Apyral 40CD) was purchased from Nabaltec GmbH.

4. Zinc borate (Firebrake® ZB-2335) was purchased from U.S Borax Inc.

3.2 Instruments, Apparatus, and measurements

1. Twin screw extruder: Nanging Giant Machinery Co., Ltd.

2. Tensile testing machine Model LFPlus 1 kN (225 lbf): Lloyd Instruments

3. Flammability measurements: were performed at Plastics Industry Research and Training Centre (PIRTC), Patumthani

4. Limiting Oxygen Index (LOI): were measured at Thailand Institute of Science and Technological Research (TISTR), Patumthani

5. Thermogravimetric Analyzer (TGA): Model TGA/SDTA 851. The measurements were performed at the National Metal and Materials Technology Center (MTEC) at the National Science and Technology Development Agency (NSTDA), Patumthani

6. UL-94: were measured at the Electrical and Electronics Institute, Bangpoo Industrial Estate

3.3 Procedure

3.3.1 Sample preparation

The compositions were blended on twin rotor extruder of 20 mm diameter. The resulting mixtures were then compression molded at 120 ^{o}C, into sheets (2.5 mm thickness) under a pressure of 25 psi for 10 min. The sheets were cut into suitable size specimens for fire testing. The samples were prepared into dumbbell-shaped for the tests of mechanical properties.

3.3.2 Measurements of Properties

3.3.2.1 Tensile Properties (ASTM D 638)

Tensile strength and elongation of each sample were determined following the ASTM D 638 method. The plastic was stamped with a compressed sample cutter into a dumbbell shape (Type C). The specimens were cut from a 2.0 mm thickness plastic sheet. The testing was performed on a tensile machine. Results reported for each sample are on average values of 5 specimens. Measurement condition is as follows.

3.3.3 Flammability Measurements (ISO 9773)

1. Specimens are 125 mm long, 12 mm wide, and 2.5 mm thick. The overlapping portions of the specimens were secured within the upper 75 mm segment above the 125 mm mark .
2. All specimens were tested in a laboratory atmosphere of 15 ^{o}C to 35 ^{o}C, and 45 % to 75 % relative humidity.
3. The specimen is clamped from the upper 6 mm of its length with the longitudinal axis vertical by a heavy spring clamp or other device, so that the upper end of the tube is closed to prevent any chimney effects during the test. The lower end of the specimen should be 300 ± 10 mm above a horizontal layer

of 0.05 g to 0.08 g of cotton wool of area approximately 50 mm × 50 mm and maximum thickness 6 mm (see Figure 3.1)

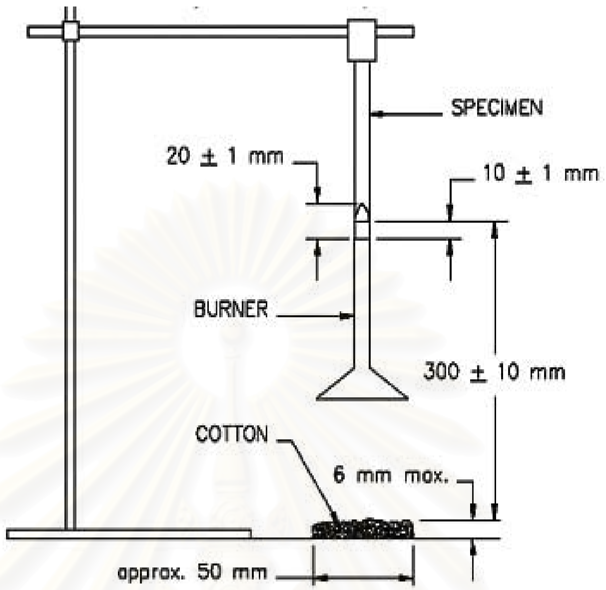


Figure 3.1 UL94 Test for Flammability for V0, V1, and V2 categories.

4. The desired burner flame was obtained by adjusting the supply and air ports of the burner until a yellow tipped blue flame of height 20 mm ± 1 mm was produced. The air supply was increased until the yellow tip just disappeared. The height of the flame was measured again and corrected to 20 mm ± 1 mm if necessary.
5. The flame of the burner was applied centrally to the middle point of the bottom edge of the unlapped section of the specimen so that the top of the burner is 10 mm ± 1 mm below that point of the lower end of the specimen, and was maintained it at that distance for 3 s ± 0.5 s, moving the burner as necessary in response to any change in the length. If the specimen drips molten or flaming material during the flame application, the burner was tilted at an angle of up to 45^o and withdrawn just sufficiently from beneath the specimen to prevent material from dropping into the barrel of the burner while maintaining the 10 mm ± 1 mm spacing between the center of the outlet of the burner and the remaining portion of the specimen, ignoring any strings of molten material. After the application of the flame to the specimen for 3 s ± 0.5 s, the burner was

immediately withdrawn at a rate approximately 300 mm/s to a distance of at least 150 mm away from the specimen and the timing device was simultaneously used to commence measurement, to the nearest second, of the first after flame time t1. The t1 was recorded.

6. After flaming of the specimen ceased, even if the burner has not been withdrawn to the full 150 mm distance from the specimen, the flame of the burner was again immediately placed under the specimen and maintain the burner at a distance of 10 mm ± 1 mm from the remaining portion of the specimen for 3 s ± 0.5 s while moving the burner clear of dripping material as necessary as described in 5. After this application of the flame to the specimen for 3 s ± 0.5 s, the burner was immediately or removed extinguished it at a rate of approximately 300 mm/s to a distance of at least 150 mm from the specimen and simultaneously, using the timing device, commence measurement to the nearest second of the second afterflame time t_2 and the afterglow time t_3 of the specimen. The t_2 and t_3 were recorded. It was also noted whether the afterflame or afterglow progresses up to the 125 mm mark and whether the cotton wool layer below the specimen is ignited by material dropping from the specimen.
7. The total afterflame time was calculated using the equation

$$t_{Fi} = t_1 + t_2$$

where : t_{Fi} is the total afterflame time for the individual specimen

t_1 is the first afterflame time

t_2 is the second afterflame time

Table 3.1 Category paths

Requirements	Category paths			
If : every individual afterflame time t_1 and t_2 is	≤10s	≤10s	≤30s	>30s
and: total set afterflame time (t_{FS}) is	≤50s	≤250s	≤250s	>250s
and: every individual afterglow time after the second flame application (t_3) is	≤30s	≤60s	≤60s	>60s
and: afterflame or afterglowing progresses up to the 125 mm mark	No	No	No	Yes
and: cotton indicator ignited by flaming particles or drops.	No	No	Yes	Yes or No
Then: category is	V-0	V-1	V-2	A)
A) materials that cannot be categorized by this procedure. Use method A of ISO 1210 to categorize material burning behavior.				

3.3.4 Measurement of the Limiting Oxygen Index (LOI)

The Limiting Oxygen Index for each sample indicates the minimum concentration of oxygen that will just support flaming combustion of a sample in a flowing mixture of oxygen and nitrogen. In the measurement, a specimen is positioned vertically in a transparent test column and a mixture of oxygen and nitrogen, the flow of which can be controlled, is forced upward through the column. The specimen is ignited at the top. The oxygen concentration is adjusted until the specimen just supports combustion. The concentration reported is the volume percent.

Preparation of the test specimens

Table 3.2 Test Specimens

Specimen	Length (mm)	Width (mm)	Thickness (mm)	Usage
I	80 to 150	10	4	Molding materials
II	80 to 150	10	10	Cellular materials
III	80 to 150	10	<10.5	Sheet materials (as received)
IV	70 to 150	6.5	3	Alternative size for molding or sheet materials. For electrical purposes.
V	140	52	10.5	Flexible film or sheet
VI	140 to 200	20	0.02 to 0.1	Thin film (as received)

1. Specimens were 125 mm long, 10 mm wide, and 3.0 mm thick. They are prepared at least 88 hours prior to the measurement and were kept at 23±2 ^{O}C, 55±5 % humidity before testing.
2. The starting point was marked on the sample 1 cm from the top of the sample. The burning distance of 50 mm was required, therefore, the other mark was made for end point, accordingly.
3. The flow rate of N_2 and O_2 were initially adjusted to be at 10.1-11.1 L/min
4. The volume of O_2 was adjusted to the required value.
5. The specimen was installed in the oxygen index testing apparatus.
6. The burning was started at the top of the specimen and the time taken for the specimen of 50 mm length, as designated by the starting and the end points marked earlier, to burn was measured.
7. If the fire extinguished before reaching the end point, Step 4 has to be repeated. This is a good indication that the amount of the oxygen is not enough to sustain the fire.
8. Step 4 was iteratively performed until the minimum volume of O_2 gas, that can sustain the fire until the desired length of specimen was all burned, was obtained
9. The amount of oxygen is recorded as the LOI.

3.3.5 Thermogravimetric Analysis (TGA) Model TGA/SDTA 851

Experimental set up

Weight of sample:	10 mg
Heating Rate:	10 °C/min
Environment:	N_2 Atmosphere
Heating Temperature:	100 °C – 800 °C

3.4 Formulation of the compounds in the experiments

The samples used in this research were prepared as described in section 3.3.1 by varying the amount of additives according to what the detail in Table 3.3. Additives in comparison are ATH, MP, MPP, MPoP.

Table 3.3 Formulation of the compounds in the experiments

Entry	Code	EVA	ATH	MP	MPP	MPoP	ZB
1	original	100	-	-	-	-	-
2	A1	80	20	-	-	-	-
3	A2	70	30	-	-	-	-
4	A3	60	40	-	-	-	-
5	A4	55	45	-	-	-	-
6	A5	50	50	-	-	-	-
7	A6	45	55	-	-	-	-
8	A7	40	60	-	-	-	-
9	MP1	80	-	20	-	-	-
10	MP2	70	-	30	-	-	-
11	MP3	60	-	40	-	-	-
12	MPP1	80	-	-	20	-	-
13	MPP2	70	-	-	30	-	-
14	MPP3	60	-	-	40	-	-
15	MPoP1	80	-	-	-	20	-
16	MPoP2	70	-	-	-	30	-
17	MPoP3	60	-	-	-	40	-
18	MPoP4	55	-	-	-	45	-
19	MPoP5	50	-	-	-	50	-
20	MPoP6	45	-	-	-	55	-
21	AMP1	60	30	-	-	10	-
22	AMP2	60	20	-	-	20	-
23	AMP3	60	10	-	-	30	-
24	ZMP1	60	-	-	-	10	30
25	ZMP2	60	-	-	-	20	20
26	ZMP3	60	-	-	-	30	10

CHAPTER IV

RESULTS AND DISCUSSION

This research is focused on the study of effect of different additives in ethylene vinyl acetate (EVA) copolymer on the properties of the compounds obtained. In general Aluminium tri hydrate (ATH) are used as on additive in polyolefin. However, a high percentage of ATH (*ca.* 60%) is required in order for the polymer to exhibit desired flame retarding effects. This may alter physical and mechanical properties of the polymer. Therefore, we are interested in finding an alternative class of additive to be used in EVA which would provide adequate level of flame retardancy while physical and/or mechanical properties remain within range for practical use.

The additives of interest belong to the melamine phosphate group consisting of melamine phosphate (MP), melamine pyrophosphate (MPP), melamine polyphosphate (MPoP). These compounds have been shown to give good flame retarding properties through char forming or intumescent mechanisms (17). We would like to compare the effect of using melamine phosphates to those of ATH. In addition, the effect of adding MPoP to EVA in the presence of zinc borate which is known, when combined with ATH, to form a solid residue at relatively high temperature allowing the maintenance of good mechanical and electrical properties (2) was also investigated. Basic thermal properties and burning properties were determined by certain measurements while mechanical properties were closely monitored in parallel at various amounts of additives.

4.1 Preparation of EVA compounds

The samples were prepared by blending the additive of interest in various amounts with EVA as described in the experimental section (Chapter 3). The amount of ATH mixed with EVA was in the range of in 20-60% (entries 2-8). The amounts of MP (entries 9-11) and MPP (entries 12-14) added were 20, 30, and 40%. In the case of MPoP, the added amount was extended to 55% since preliminary experiments indicated good results (*vide infra*) (entries 15-20). It was worth exploring if ATH and any melamine phosphate compound would exhibit a synergistic effect.

Therefore, samples having both ATH and MPoP (which appeared to be better than MP and MPP) at varying ratios were blended with EVA (entries 21-23). The total amounts of the combined additives in these cases were kept at 40%. Finally, in order to investigate if zinc borate could be used with MPoP, samples where both compounds are mixed with EVA were prepared. In these samples, the combined amount of the 2 additives was again kept at 40% (entries 21-23). The data are as shown in Table 3.3. All data were compared to those of pure EVA (entry 1).

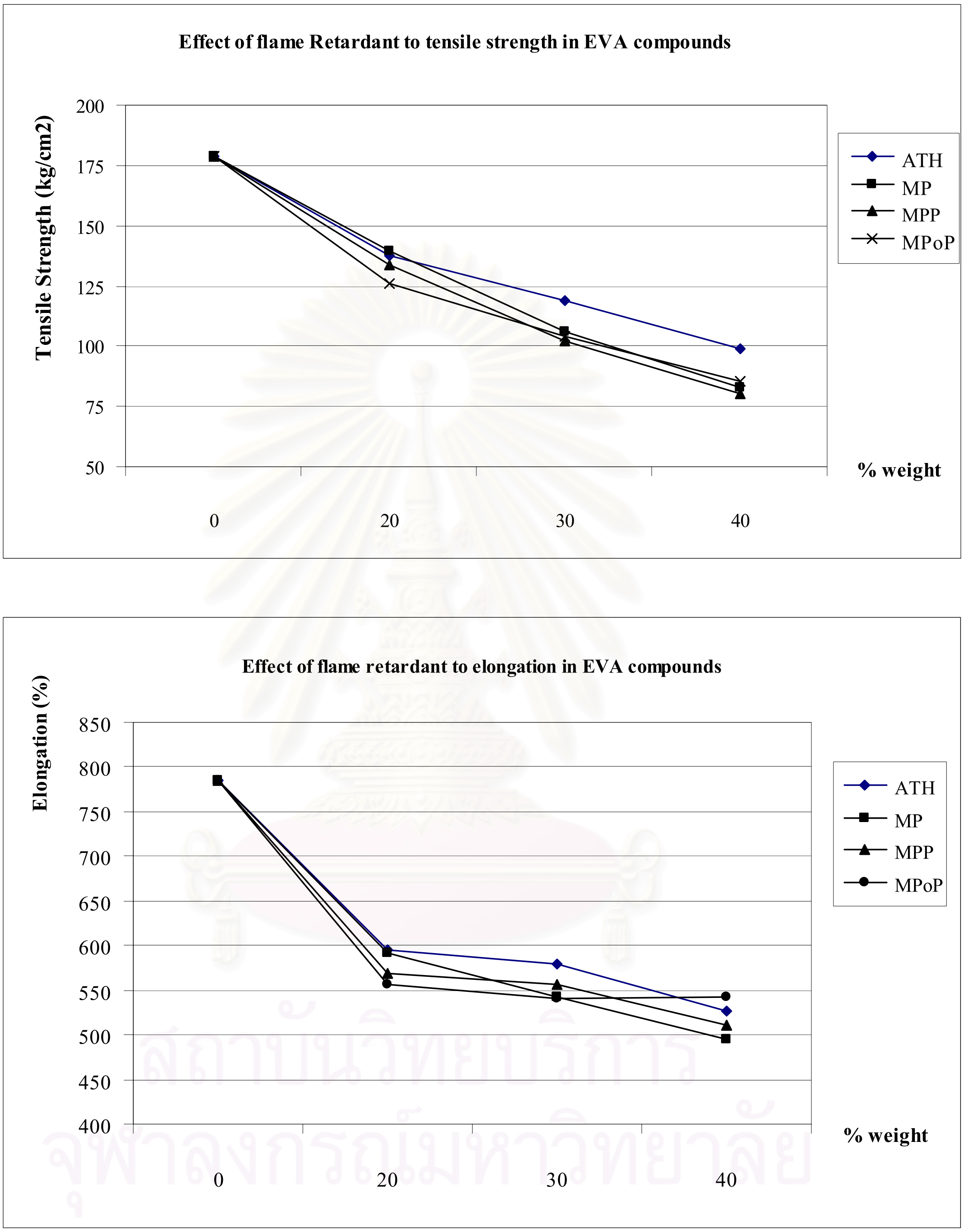
4.2 Testing of EVA blended with flame retardants

4.2.1 Determination of mechanical properties

The prepared samples were subjected to measurement of tensile strength and percent elongation at break. The results are shown in Table 4.2. In general, the data show that EVA additive samples, regardless of additive type and amount, gave lower tensile strength and elongation at break than those of pure EVA. The plots of the amount of additive in the samples against measured tensile strength and the plots of the amount of additive against percent elongation at break are shown in Figures 4.1 and 4.2, respectively.

Table 4.1 Mechanical properties of pure EVA *vs.* EVA with varying amounts of additives.

Entry	Additive	Amount (%)	Code	Tensile strength (kg/cm^2)	Elongation at break (%)
1	-	-	Original	178.96	785.41
2	ATH	20	A1	137.42	594.81
3		30	A2	119.16	578.65
4		40	A3	99.04	526.65
5		45	A4	74.50	498.04
6		50	A5	65.86	472.85
7		55	A6	63.86	424.81
8		60	A7	63.89	66.51
9	MP	20	MP1	139.35	592.37
10		30	MP2	105.85	542.66
11		40	MP3	82.98	495.69
12	MPP	20	MPP1	133.64	568.17
13		30	MPP2	101.90	556.41
14		40	MPP3	80.19	510.71
15	MPoP	20	MPoP1	125.80	557.29
16		30	MPoP2	103.79	541.26
17		40	MPoP3	85.54	542.41
18		45	MPoP4	68.48	478.13
19		50	MPoP5	75.98	423.97
20		55	MPoP6	64.60	367.62



(b)

Figure 4.1 (a) Effect of flame retarding additives on tensile strength. (b) Effect of flame retarding additives on elongation at break.

Both figures clearly illustrated that the mechanical properties of EVA that were blended with the same amount of any melamine phosphate compounds were more or less in the same range of values. However, EVA-ATH compounds showed a slightly higher tensile strength and elongation at break than EVA-melamine phosphate compounds at almost all concentrations. Among the three melamine phosphate compounds, they all gave comparable properties when the same amounts of flame retardants were used.

The effect of the concentration of flame retardant additive on the mechanical properties of filled EVA is quite dramatic. Apparently, tensile strength and elongation at break decreased with increasing amount of the flame retardant additives. In comparison to pure EVA, the tensile strength decreased from ~180 kg/cm^2 to ~86 kg/cm^2, and the elongation at break decreased from ~785% to ~520% when flame retardant loading increased to 40%. These results indicate that the mechanical properties of the filled EVA were greatly deteriorated, especially at high loading of flame retardant additive. Therefore, in the present work, the amount of additive was controlled to avoid causing serious drop to the mechanical properties of the filled EVA while other factors will be explored.

4.2.2 Determination of Thermal and Flame Retarding Properties

4.2.2.1 Thermogravimetric analysis (TGA)

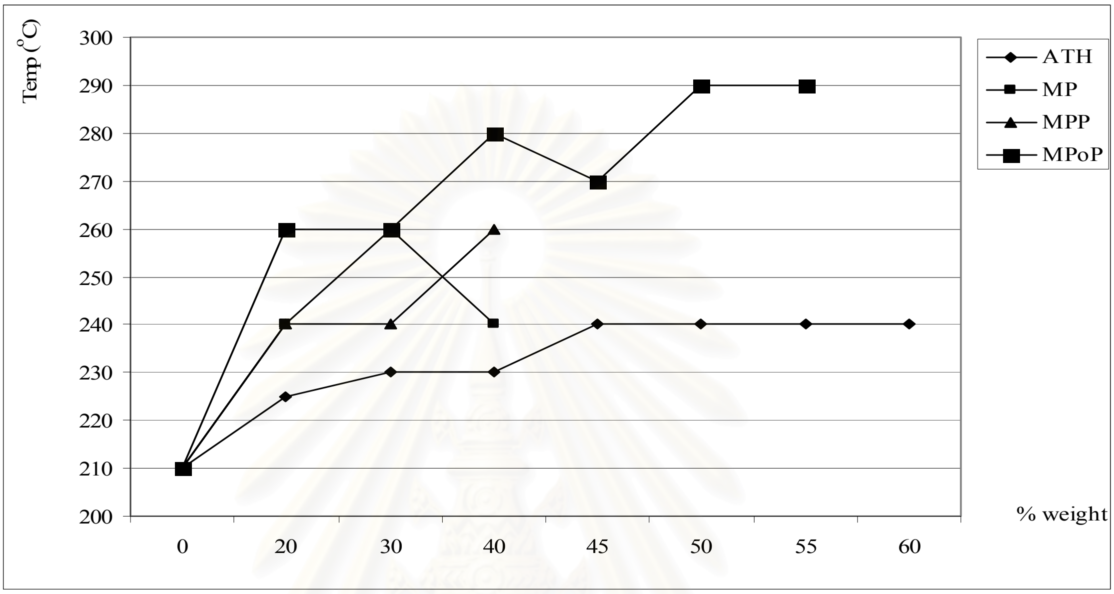
All samples were prepared and subjected to thermogravimetric analyses. Interests were placed on the initial burning temperature at certain percent weight loss of the samples. The results are shown in Table 4.3. The trend in the increase of initial burning temperature and temperature can be observed in Figure 4.2.

It can be seen that the initial burning temperature of EVA blended with high amounts of any of the three compounds in the melamine phosphate group is higher than those of the EVA blended with ATH (230-240 ^{o}C) and pure EVA (210 ^{o}C). EVA-MP offered initial burning temperatures in the range of 240-260 ^{o}C at 20-40% loading, while EVA-MP gave 270-275 ^{o}C and EVA-MPoP gave up to 280-290 ^{o}C at the same range of loading. These are significantly highest than in the case of pure EVA and EVA-ATH

Table 4.2 Thermal properties of pure EVA *vs.* EVA with varying amounts of additives.

Entry	Additive	%	Code	TGA			
				Initial burning temp (^{0}C)	**Temp at % weight loss**		
					20%	**50%**	**80%**
1	-	-	Original	210	380	450	490
2	ATH	20	A1	225	410	470	500
3		30	A2	230	400	470	490
4		40	A3	230	410	475	500
5		45	A4	240	430	470	550
6		50	A5	240	430	475	550
7		55	A6	240	420	480	550
8		60	A7	240	430	470	550
9	MP	20	MP1	240	400	470	490
10		30	MP2	260	390	470	490
11		40	MP3	240	430	475	550
12	MPP	20	MPP1	240	400	470	490
13		30	MPP2	240	410	475	500
14		40	MPP3	260	410	470	550
15	MPoP	20	MPoP1	260	390	470	490
16		30	MPoP2	260	410	470	550
17		40	MPoP3	280	420	480	540
18		45	MPoP4	270	430	470	550
19		50	MPoP5	290	440	480	500
20		55	MPoP6	290	430	470	600

Among the three melamine phosphates, MPoP gave the highest initial burning temperature. From the results, when MP was used at 20, 30, and 40%, the initial burning temperature increased to 240-270 ^{o}C. This shows that at 40% loading of MP, the sample starts burning at the same temperature as pure EVA. However, when the temperatures at different percent weight loss are concerned, EVA-MP compounds gave a better performance, *i.e.*, higher temperature is required to burn the compound to the same amount of the pure EVA. The increases of initial burning temperatures as well as temperatures at various percent weight loss was more pronounced in the case of EVA-MPP and EVA-MPoP. In both systems, even at only 20% addition of MPP or



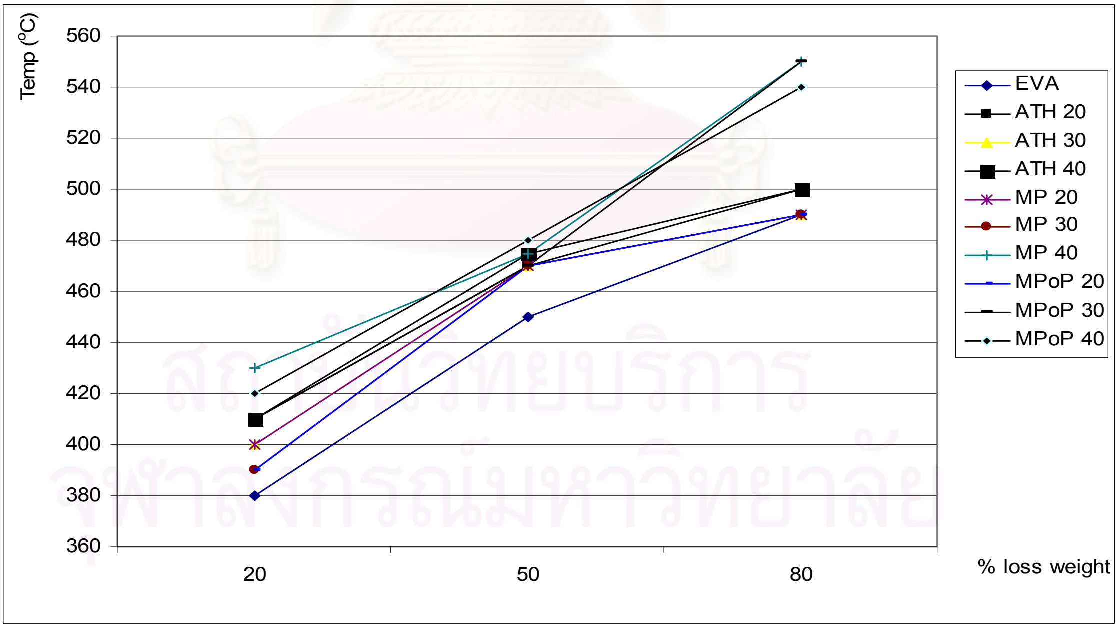


Figure 4.2 (a) Effect of flame retarding additives on initial burning temperature.

(b) Effect of flame retarding additives on % weight loss

MPoP, the initial burning temperatures and percent weight loss were better than those of pure EVA. Since MPoP appeared to offer best results, samples with higher amounts of MPoP namely; at 45, 50, and 55% were prepared (entries 18-20). However, the initial burning temperatures at these higher concentrations of the additive appear to have, more or less, reached a plateau of about 285-290 °C. While the initial burning temperatures seem to change to a small degree, at these higher percent loading, the temperatures at various percent weight loss were increased.

Therefore, the efficiency of improving thermal properties (initial burning temperature and temperature at different percent weight loss) of all samples under investigation is as follows: EVA-MPoP > EVA-MPP > EVA-MP ~ pure EVA > EVA-ATH. In other words, all three compounds in the melamine phosphate group under investigation exhibit flame retarding effects in EVA even at about 20% loading and offer very good performance at higher concentration as illustrated in the examples of EVA-MPoP.

The reason as to why the melamine phosphate group seems to have increased initial burning temperature could be because these compounds themselves have higher decomposition temperatures (of about 300 °C, (26)) an that of EVA. Similarly, addition of ATH gave a reversed effect probably because ATH itself has an initial start decomposition temperature of 180°C which can cause the decrease in the initial decomposition temperature of EVA.

4.2.2.2 Determination of burning rate and burning time

Each sample was tested in a flame test where burning rates and burning times were measured. All data are tabulated in Table 4.3.

Table 4.3 Thermal and flame retarding properties as reflected by burning rates and burning time of pure EVA *vs.* EVA with varying amounts of additives.

Entry	Additive	Amount (%)	Code	Burning rate (mm/min)	Burning Time (s)
1	-	-	Orig.	14.70 ± 2.36	312 ± 42
2	ATH	20	A1	9.22 ± 0.83	491 ± 41
3		30	A2	8.96 ± 1.41	512 ± 74
4		40	A3	6.19 ± 0.10	727 ± 58
5	MP	20	MP1	21.42 ± 0.81	210 ± 8
6		30	MP2	19.12 ± 0.72	236 ± 9
7		40	MP3	16.07 ± 3.72	291 ± 59
8	MPP	20	MPP1	31.59 ± 2.60	143 ± 12
9		30	MPP2	20.00 ± 1.18	226 ± 9
10		40	MPP3	16.43 ± 3.12	283 ± 58
11	MPoP	20	MPoP	16.19 ± 3.27	287 ± 54
12		30	MPoP	17.84 ± 1.78	254 ± 28
13		40	MPoP	14.38 ± 2.43	320 ± 25

The data clearly show that at each concentration used, EVA-ATH samples (entries 2-4) burn at slower rates than EVA-melamine phosphate group and the EVA itself (14.71±2.36 mm/min). On the other hand, MP (entry 7) and MPP (entry 10), even at 40% the samples burned faster than the pure EVA. When MPP was used at 40%, only a comparable result was obtained compared to those of pure EVA. Apparently, these additives have to be used in high amounts in order for the polymer blend to burn more slowly. ATH performed better than compounds in the melamine phosphate group possibly because upon burning, ATH decomposes and gives water which helps cool down the surrounding environment and retards the flame. In addition, EVA-ATH samples did not give high flames, therefore, reducing the chance of getting the surrounding fuels to burn.

The fact that compounds in the melamine phosphate group have to be used in high amounts to exhibit slow burning rate, as represented by the numbers shown, is due mainly to the criteria to which the burning tests are based on. In the burning tests, (c.f. experimental details in chapter 3) the times were recorded when the flame starts from one end of the specimen and reaches the other end (as marked). However, the burning nature of the flames from the burning of EVA-ATH and EVA-MP Group were different and can be described as follows. The EVA-ATH samples starts burning from one end when material at each point was consumed the flame gradually moved towards the direction of the other end. Therefore, the starting and ending times were a long period. While in the case of compounds in the EVA-MP group, once ignited, the flame expanded and quickly burned almost the entire surface area of the specimen. This resulted in a very short period from which the flame started at the starting end and reached the other end of the specimen. This is actually misleading because the flame would burn mostly on the surface but once the char was formed the flame gradually extinguished itself and the inner part of the specimen was still intact.

4.2.2.3 Determination of LOI and percent char formed

The effect of the concentration of flame retardant additive on the LOI values of the filled EVA were determined using the LOI apparatus (as described in chapter 3). The data on LOI values and % char obtained are presented in Table 4.5. A relative change can be seen from the curves in Figures 4.3 and 4.4.

Table 4.4 Limited oxygen indexes and percent char of pure EVA *vs*. EVA with varying amounts of additives.

Entry	Additive	%	Code	LOI (%)	Char (%)
1	-	-	Original	21.6	0
2	ATH	20	A1	21.7	11.64
3		30	A2	23.0	15.29
4		40	A3	23.1	19.32
5		45	A4	23.4	26.25
6		50	A5	25.0	33.28
7		55	A6	27.8	36.02
8		60	A7	**30.1**	**40.12**
9	MP	20	MP1	21.8	6.37
10		30	MP2	22.4	8.08
11		40	MP3	23.3	12.59
12	MPP	20	MPP1	22.1	9.36
13		30	MPP2	22.5	9.82
14		40	MPP3	23.7	16.07
15	MPoP	20	MPoP1	21.6	8.69
16		30	MPoP2	22.5	12.13
17		40	MPoP3	22.4	15.28
18		45	MPoP4	22.7	18.92
19		50	MPoP5	23.7	21.15
20		55	MPoP6	25.2	29.75

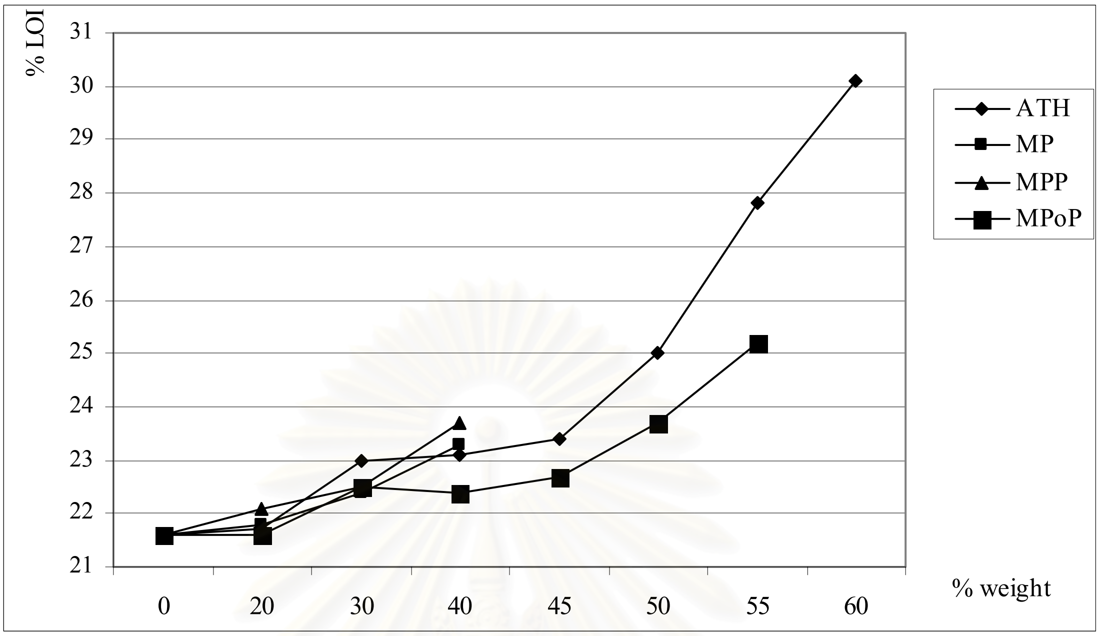


Figure 4.3 Effect of flame retarding additives on LOI.

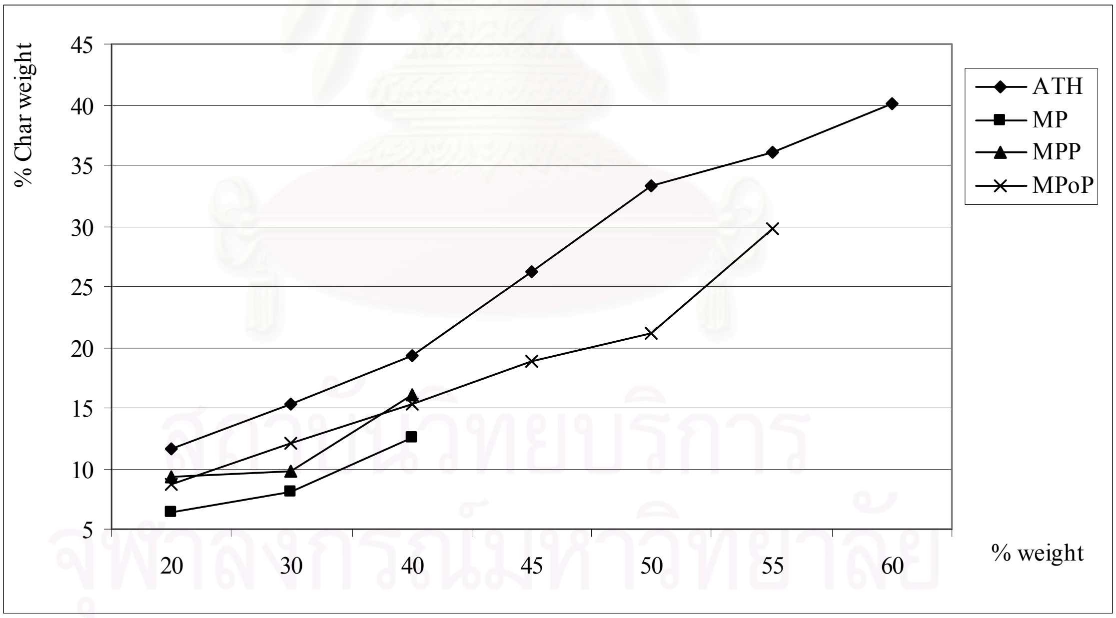


Figure 4.4 Effect of flame retarding additives on % char weight

In the case where ATH was used, the LOI and percent char formation increased with increasing amount of flame retardant additive. LOI of about 30 was obtained when ATH was used at 60% (entry 8). Even at lower flame retardant percent loading increase, the LOI value of 23 and higher were observed. Char formation was also observed especially when high percentages of ATH were used. It appeared that ATH can increase LOI values of EVA to a higher extent than melamine phosphate group at higher than 50% by weight.

The LOI values of EVA blends increase gradually with increasing amount of flame retardant from 20 to 60 % by weight. The LOI values of EVA blended with melamine phosphate group were 23.1 % at 40% by weight. This is comparable to the LOI values of EVA-ATH at 40% by weight. MPoP appeared to give the best performance among its analogs. The LOI value of EVA blended with melamine polyphosphate at 55 % by weight is the highest in the melamine phosphate groups at 25.2%.

As mentioned earlier that since the air comprises about 20.95% oxygen by volume, any material with a limiting oxygen index less than this will burn easily in air. Conversely, the burning behavior and tendency to propagate flame for a polymer with a limiting oxygen index greater than 20.95 will be reduced after removal of the ignition source. Therefore, the results show that all melamine phosphate compounds tested could enhance, though not greatly, flame retardancy of the polymer.

4.2.2.4 Char formation and characteristics

Representative samples of EVA-ATH were ignited in a crucible. The characteristics of flame, residue, and smoke were recorded. In comparison, the EVA blended with compounds in the melamine phosphate group were also performed. The results are shown in Figure 4.5.

It was observed that the entire piece of EVA samples blended with ATH would burn slowly. It was found that in the samples where ATH was used < 55% by weight, the molten samples which were still burning would start to flow. On the other hand, when the amount ATH were used 55% and 60% or higher the burning samples were more viscous and did not flow. All EVA-ATH samples gave white powdery ash after burning. They do not form lumps.

Figure 4.5 Char of EVA-ATH, EVA-MP, EVA-MPP, and EVA-MPoP samples after burning tests.

As for EVA blended with compounds in the melamine phosphate group, the flame would start on the surface of the samples. In the case where less than 30% of the additive was used, the burning and melted surface of the sample surface would started dripping from the sample (horizontal burning tests). Once it dropped, the flame on the burning sample would extinguish. When the fire stopped, the dropped sample became a black solid and congealing. In addition, EVA samples blended with melamine polyphosphate has higher amount of intumescence char than EVA samples blended with melamine pyrophosphate and melamine phosphate, respectively.

The reason why all EVA-ATH samples gave white powdery ash after burning may stem from the fact that ATH is an inorganic compound. Upon burning, this type of salt would naturally yield powdery ash. On the other hand compounds in the melamine phosphate group has a higher organic characters than ATH. Therefore, upon burning, char-like residue was obtained. This appears to be advantage since the inner part of the specimen was, hence, protected from the fire by the char.

The burning test results can help categorize the samples by UL-94 standard as shown in Table 4.5.

Table 4.5 EVA *vs.* EVA with varying amounts of additives catagorized by UL-94.

Entry	**Additive**	**Amount (%)**	**Code**	**UL-94**
1	-	-	Original	A
2	ATH	40	A3	V-2
3		55	A6	V-1
4		60	A7	V-0
5	MP	40	MP3	A
6	MPP	40	MPP3	V-2
7	MPoP	40	MPoP3	V-2
8		55	MPoP6	V-1

When different aspects of results reflecting thermal and mechanical properties of the samples were taken into consideration, the results may be analyzed as follows. To compare the effect of each additives, it was found that EVA-ATH have increased

LOI values which reflects the higher mount of oxygen gas required to ignite and sustain the fire. EVA mixed with compounds in the melamine phosphate group, disappointingly, requires higher amount of the additives in order to obtain similar range of LOI values as the EVA-ATH. The melamine phosphate group, on the other hand, improve thermal resistance of the sample as indicated by the TGA results. Higher temperature is needed for EVA samples blended with compounds in the melamine phosphate group to start the burning and decomposition. In addition, their weights are reduced more slowly than those of the EVA samples blended with ATH when compared at the same temperature since the char helps protect the inner samples from being burned (retarding effect).

From the flammability test determining burning rate, burning time, and the UL-94. EVA-ATH systems required longest burning time and slowest burning rate. ATH can decompose to give water which makes the surrounding surface cooler. This helps slow down the spread of the fire to other parts and the flame wouldn’t arise.

A good characteristic of compounds in the melamine phosphate group, in addition to a higher initial temperature required to start the flame, is that the samples would get burn mostly on the surface. This will create a hard layer of char covering the surface of the rest of the polymer. Therefore, the inner materials can be protected from the flame. Even in the case where the melted burning surface could drip, the dropped sample would stop burning relatively easily. In general, the phosphorus containing additives can also catalyze the clipping of the polymer chains thereby reducing its molecular weight. This reduces the viscosity of the polymer melt allowing it to drip away from the fire zone. This dripping removes material that can burn from the fire zone.

Although the results on LOI and flammability tests demonstrated that ATH is an efficient flame retardant than the melamine phosphate group, more than 60% weight of ATH in EVA is required in order to obtain that level of flame retardancy. This would affect mechanical properties of EVA. In addition ATH is not suitable to be used in polymer to be processed at high temperature since at 180 °C ATH starts to decompose. Melamine phosphate group, on the other hand are more superior because they start decomposing at temperature higher than ATH making it harder for EVA to ignite in fire. As seen earlier that the TGA data helps support this observation. Moreover, they promote char formation, which acts as a physical barrier to flame and inhibits the volatilization of flammable materials.

Among the three compounds in the melamine phosphate group tested, the results indicate that melamine polyphosphate possesses better thermal and flame retarding properties than melamine pyrophosphate and melamine phosphate, respectively.

Different classes of flame retardants perform via different mechanisms, therefore, we were interested in mixing 2 types of flame retardants together. Synergistic effect may increase the efficiency. Melamine polyphosphate was mixed with ATH because ATH decomposes to give water at lower temperature than melamine polyphosphate, while, at higher temperature, melamine polyphosphate decomposes to produce char which can cover surface of material. It is envisaged that the mixing may improve flame retarding properties of materials and reduce the amount of flame retardants needed.

4.3 Determination of properties of EVA blended with flame retardants and zinc borate

In addition to comparing properties of EVA compounds mixed with ATH and the melamine phosphate group, we were also interested in mixing zinc borate (ZB) with melamine polyphosphate because it is known that ZB can reduce the smoke and it is also a char promoter that may be reinforcing strong char of melamine polyphosphate.

Experiments were, therefore, performed on samples prepared from EVA-MPoP with added ZB. The combined amounts of MPoP and ZB in EVA specimen were kept at 40% with varying ratios of MPoP and ZB. It appeared that if the flame retardants were used at higher amount than 40% by weight, the mechanical properties of the polymeric materials would be reduced. It has always been kept in mind that improving physical and mechanical properties of a polymer, in general, is easier than improving its flame retarding properties. In other words, once a composition of polymer and additives can give the desired level of flame retardancy, the mechanical and physical properties may be adjusted to the need by adding other suitable materials.

4.3.1 Determination of Mechanical Properties

Mechanical properties of samples with both MPoP and ZB added are as shown in Table 4.6. A trend can be seen from Figures 4.6 and 4.7. The increase of flame retardant amount can decrease the physical properties, especially the tensile strength which is reduced to around 50% when flame retardant was used at 40%. From the testing results, ZB decrease tensile strength more than melamine polyphosphate and ATH.

Table 4.6 Mechanical properties of pure EVA vs. EVA with varying amounts of additives compared with those where zinc borate

Table	Additive	%	Code	Tensile Strength (kg/cm^2)	Elongation at break (%)
1	-	-	Original	178.96	785.41
2	ATH	40	A3	99.04	526.65
3		55	A7	63.89	66.51
4	MPoP	40	MPoP3	85.54	542.41
5	ATH : MPoP	30 : 10	AMP1	113.32	631.36
6		20 : 20	AMP2	103.44	541.44
7		10 : 30	AMP3	99.78	552.81
8	MPoP : ZB	30 : 10	ZMP1	93.68	545.12
9		20 : 20	ZMP2	84.73	550.70
10		10 : 30	ZMP3	86.75	462.82

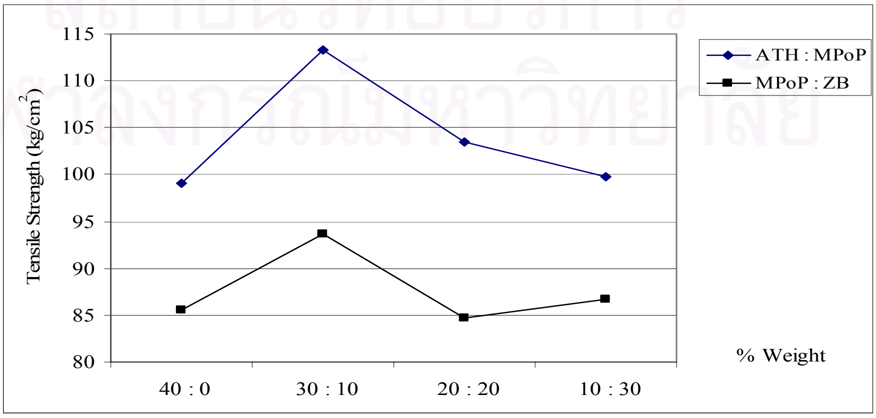


Figure 4.6 Effect of the mixing flame retarding additives on tensile strength.

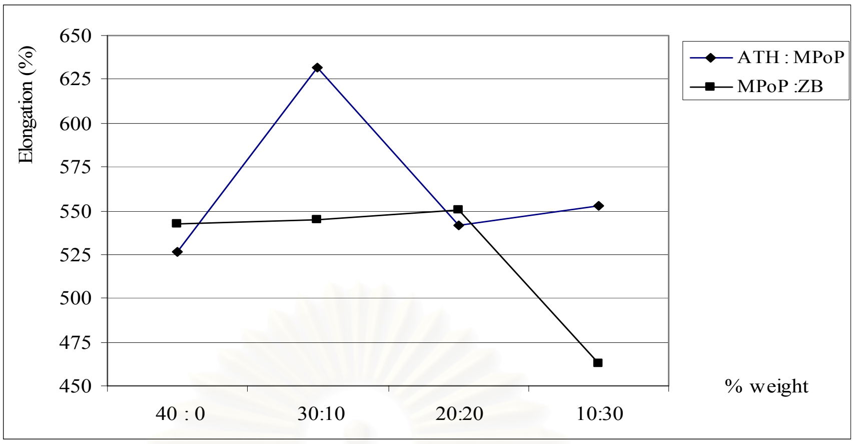


Figure 4.4 Effect of flame retarding additives on elongation.

4.3.2 Determination of Thermal and Flame Retarding Properties

4.3.2.1 Thermogravimetric analysis (TGA)

As shown earlier, a good result can be observed in the case of MPoP: the initial burning temperature from the use of MPoP of 10% of ATH is increase to be 240 °C, initial burning temperature of mixing 40% of ATH is 230 °C and it use increase temperature from 500 °C to be 550 °C at 80% weight loss. The results from the use of ZB instead of MPoP are summarized in Table 4.7.

Table 4.7 Thermal properties as reflected by TGA of pure EVA *vs.* EVA with varying amounts of additives.

Entry	Additive	%	Code	UL-94	Init. Burn Temp (°C)	Temp at % wt. loss		
						20%	50%	80%
1	-	-	Origina	A	210	380	450	490
2	ATH	40	A3	V-2	230	410	475	500
3		55	A7	V-0	240	430	470	550
4	MPoP	40	MPoP3	V-1	280	420	480	540
5	ATH	30 : 10	AMP1	V-2	245	420	480	550
6		20 : 20	AMP2	V-2	250	425	480	650
7		10 : 30	AMP3	V-2	250	420	480	540
8	MPoP :	30 : 10	ZMP1	A	270	430	470	550
9		20 : 20	ZMP2	A	260	410	465	550
10		10 : 30	ZMP3	A	220	390	470	550

At a 10% loading; ZB resulted in a lower initial burn temperature than that of the mixing only with MPoP at 40%, but ZB did not affect temperature at certain percent weight loss that much.

According to the testing method of UL-94 discussed earlier, there was no difference in flame retardancy when mixing MPoP and ATH or when only ATH was used. The UL-94 result were V-2 level for both systems. However, when mixing ZB with MPoP, the testing result of UL-94 decreases to from V-2 to A level. The results are as shown in Table 4.7.

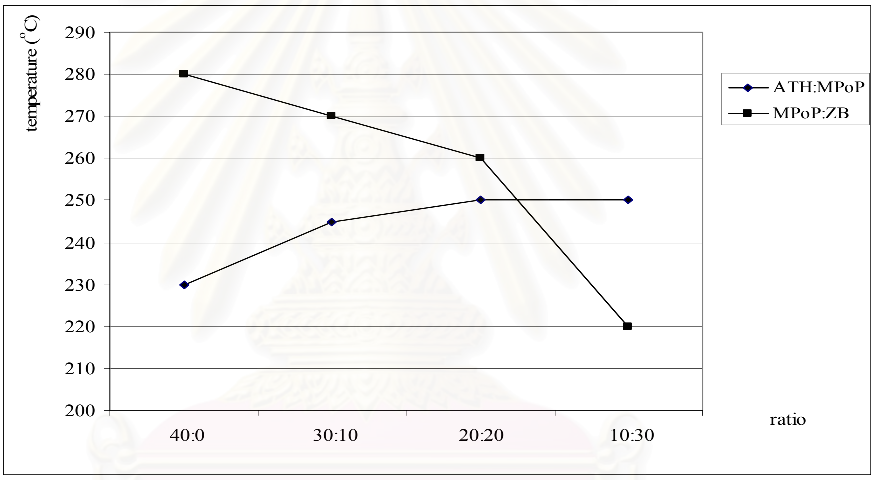


Figure 4.8 Effect of the mixing flame retardant on initial burning temperature

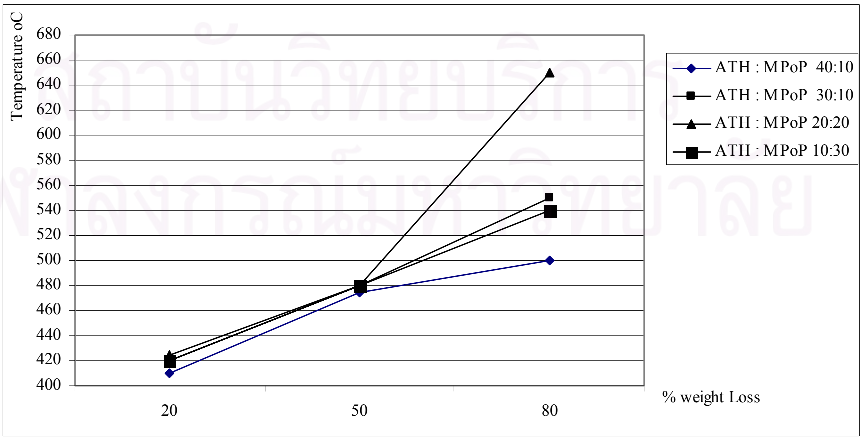


Figure 4.9 Effect of the mixing ATH with MPoP on % weight loss.

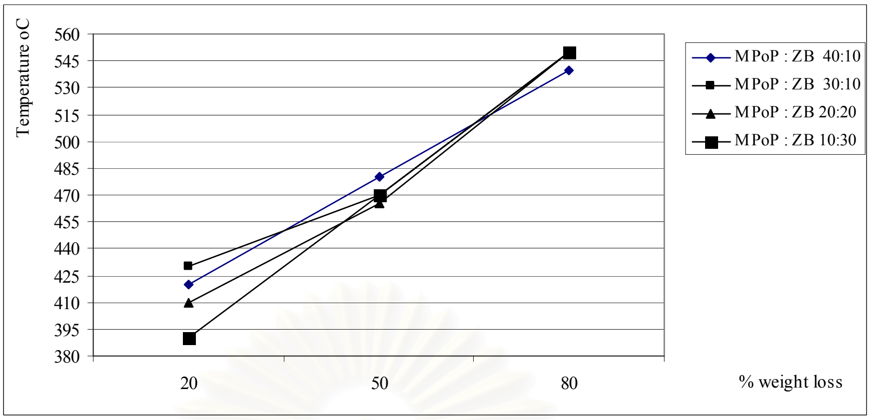


Figure 4.10 Effect of the mixing MPoP with zinc borate on % weight loss.

4.3.2.2 Determination of LOI and percent char formed

As shown previously, LOI result of the mixing between melamine polyphosphate and ATH were lower than when only ATH was mixed. From the testing result, LOI at 40% of ATH is 23.1%, when mixing MPoP instead of 10% of ATH, the LOI is 22.8%.When ZB was used in comparison, the data was compiled in Table 4.8. Also a plot showing a change in LOI with the change in the amount of the additive is illustrated in Figure 4.11.

Table 4.8 Thermal properties as reflected by LOI and char of pure EVA *vs.* EVA with varying amounts of additives.

Entry	Additive	Amount (%)	Code	LOI (%)	Char (%)
1	-	-	Original	21.6	0
2	ATH	40	A3	23.1	19.32
3		55	A7	33.6	40.12
4	MPoP	40	MPoP3	22.4	8.25
5	ATH : MPoP	30 : 10	AMP1	22.8	23.06
6		20 : 20	AMP2	22.6	19.78
7		10 : 30	AMP3	22.4	16.70
8	MPoP : ZB	30 : 10	ZMP1	21.3	10.44
9		20 : 20	ZMP2	21.1	11.75
10		10 : 30	ZMP3	20.7	15.01

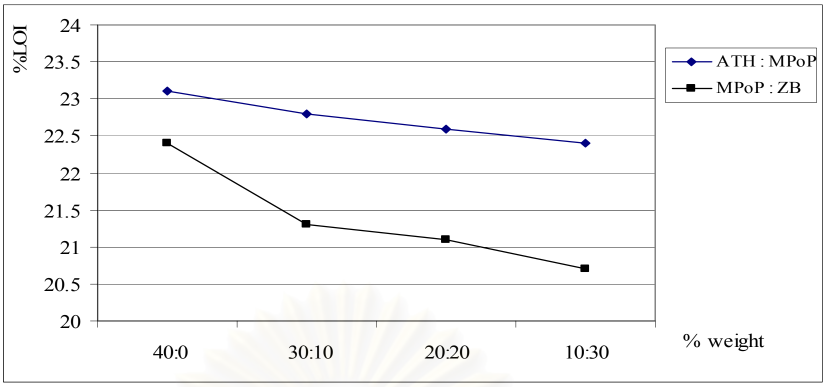


Figure 4.11 Effect of the mixing flame retardant additives on LOI.

When ZB was used instead of ATH at 10%, the LOI is 21.3% which is lower than when only MPoP at 40% was used (LOI of 22.4%). ZB did not seem to give a better result.

4.3.2.3 Determination of burning rate and burning time

As described previously, when some part of 40% ATH was replaced with compounds in the melamine polyphosphate group, burning rates increase and burning times decreased around 33-38%. Apparently, these compounds burn faster than when only 40% ATH was used. The reason was explained earlier. Here, the effect of inclusion of zinc borate in burning rate and burning time was also examined. The data are included in Table 4.9.

Table 4.9 Thermal properties as reflected by burning rates and burning time of pure EVA *vs.* EVA with varying amounts of additives.

Entry	**Additive**	**%**	**Code**	**Burning rate (mm/min)**	**Burning Time (sec)**
1	-	-	Original	14.70 ± 2.36	312 ± 42
2	ATH	40	A3	6.19 ± 0.10	727 ± 58
3	MPoP	40	MPoP3	14.38 ± 2.43	320 ± 25
4	ATH : MPoP	30 : 10	AMP1	20.76 ± 0.76	217 ± 8
5		20 : 20	AMP2	21.29 ± 0.69	212 ± 7
6		10 : 30	AMP3	23.78 ± 3.84	193 ± 27
7	MPoP : ZB	30 : 10	ZMP1	17.31 ± 1.05	268 ± 20
8		20 : 20	ZMP2	19.67 ± 3.55	236 ± 51
9		10 : 30	ZMP3	28.85 ± 0.57	156 ± 3

As shown, burning rates increased and burning time decreased around 12-20% compared to when 40% ATH was used. Apparently, zinc borate can decrease thermal properties of melamine polyphosphate.

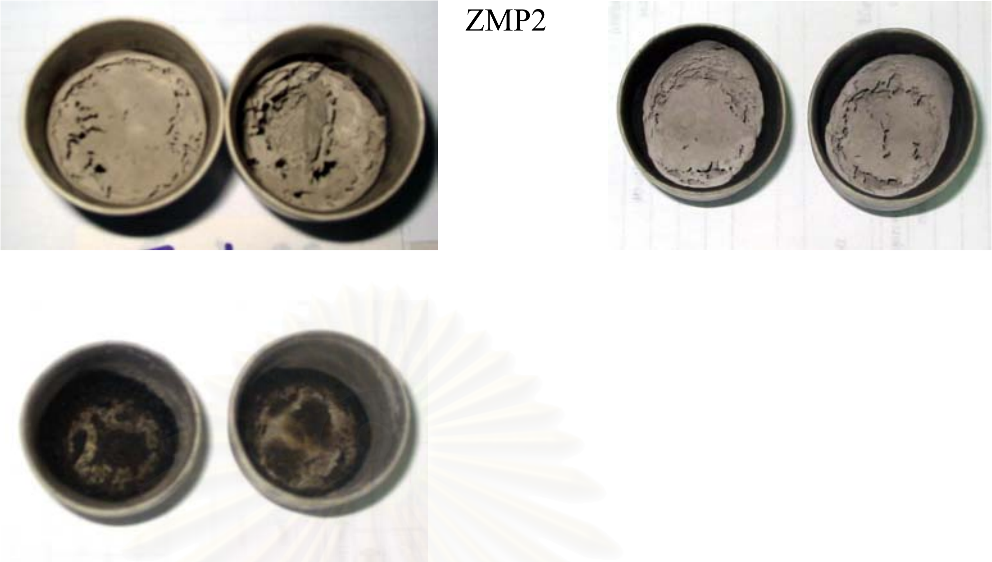
4.3.2.4 Char formation and characteristics

The samples with ZB as a composition were subjected to a burning test. Sample photo of char of samples when ZB was included are shown in Figure 4.12.

AMP1

AMP2

AMP3



ZMP3

ZMP2

ZMP1

Figure 4.12 Char and residues of EVA-ATH-MPoP and , EVA-MPoP-ZB

In comparison, the mixing of EVA and ATH provides % weight of char higher than the mixing of ZB and MPoP. From Figure 4.12, char from the mixing of ATH and MPoP is coagulate and swell, but char from only ATH is a powder. The char from the mixing of MPoP and ZB isn't coagulate which is different the char from MPoP. Since ZB is also an inorganic compound, the characteristic of the char obtained in the cases where ZB was included is similar to when ATH was used in the sense that they both gave powdery char or ash. The inclusion of MPoP helps reduce this characteristics since it is an organic compound.

It is obvious from all data obtained on samples where zinc borate was added that all properties deteriorated. Apparently, using either ATH or MPoP alone gave better results than when ZB was introduced.

From all the results, the following points were observed and discussed. EVA-melamine phosphate compound group has some advantage over ATH because they can give higher heat resistance than EVA-ATH as confirmed by TGA results. Therefore, it is harder for , EVA-melamine phosphate compound group to ignite. Even though at this stage the results showed that LOI of the EVA-melamine phosphate compound group were not greatly better than EVA-ATH, comparable or better results maybe obtained upon further adjustment of the amounts added. What was clearly observed was that melamine polyphosphate is best flame retardant in MP groups. Although, flammability test of EVA-MPs group shows poorer result than EVA-ATH, but TGA, LOI and UL-94 results are comparable.

When 2 flame retardants were mixed in EVA namely ATH mixed with melamine polyphosphate and Melamine polyphosphate mix with Zinc borate, the following were observed. In the case of ATH-MPoP, it is possible that with different flame retarding mechanisms, they may enhance the other mechanism therefore improve efficiency of EVA. When ATH was mixed with melamine polyphosphate in EVA, best thermal properties was observed which gives nearly the same LOI and UL-94. In addition, it was observed that the char of ATH changed from powder to foam. Therefore, if ATH-melamine polyphosphate is used at higher than 40% in EVA, good flame retardant properties maybe obtained. Nonetheless, it was observed that when 2 flame retardants were mixed, the flame retarding properties are not better than using each one separately.

In the case of MPoP-ZB, char maybe formed with higher strength and can protect lower layer of substrate from fire. Zinc borate cannot improve flame retarding properties, it reduce char forming of melamine polyphosphate.

Although, the mechanical properties of EVA-MPs groups are not higher than EVA-ATH, but MPs groups are organic which should mix well with polymer more than ATH which is inorganic. If particle size of MPs groups were reduced, they may increase mechanical properties. Melamine polyphospahte (MPoP) is best flame retardant in MPs group at 55% by weight. It gives flame retardant properties nearly the same as ATH and better thermal properties than ATH. Melamine polyphosphate can be applied for use in the industry where high heat resistance is required in polymer processing such as PP, PE and PA.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

Samples of EVA in the presence of various additives were prepared. Performances of additives in the melamine phosphate group were compared with those of ATH additive. The results showed that all compounds tested can exhibit flame retarding properties for the EVA. It was also observed that flame retarding properties increased with increasing amounts of additives. The results also showed that ATH has to be used at least 55% to show desirable properties. Among MP, MPP, and MPoP, the additive which gave the best thermal and flame retarding properties in MPoP. When ATH was used in combination with MPoP at the total amount of 40%, no obvious synergistic effect was observed. Using each compounds alone in EVA appeared to give better results. In similar manner, when MPoP was used with ZB, it was found that poor flame retarding properties were observed. Apparently, zinc borate cannot improve the amount of char which is produced from decomposition of the compound even in the presence of MPoP.

From the test results, it was observed that EVA-MPoP compound decomposed at higher temperature and at a slower decomposition rate than EVA-ATH. In addition, higher amount of char covering the surface of substrate was produced in EVA-MPoP than in EVA-ATH. Preliminary result suggested that MPoP can be applied for use in the cable industry which required production of material with heat resistance and flame retarding properties since MPoP makes it harder for the material to ignite. This is clearly seen from the TGA results where initial burning temperatures were significantly increased when the amount of the MPoP increased. However, a solution needs to be found in order to maintain or improve the material’s mechanical properties for practical use.

5.2 Suggestion

1. It would be interesting to investigate if more pronounce synergistic effect would be observe if ATH and MPoP are mixed and used in EVA at increased percentage, e.g., 50 % or 55%.
2. It is worth exploring the effect of mixing MPoP with polyethylene or polypropylene.

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APPENDIX A

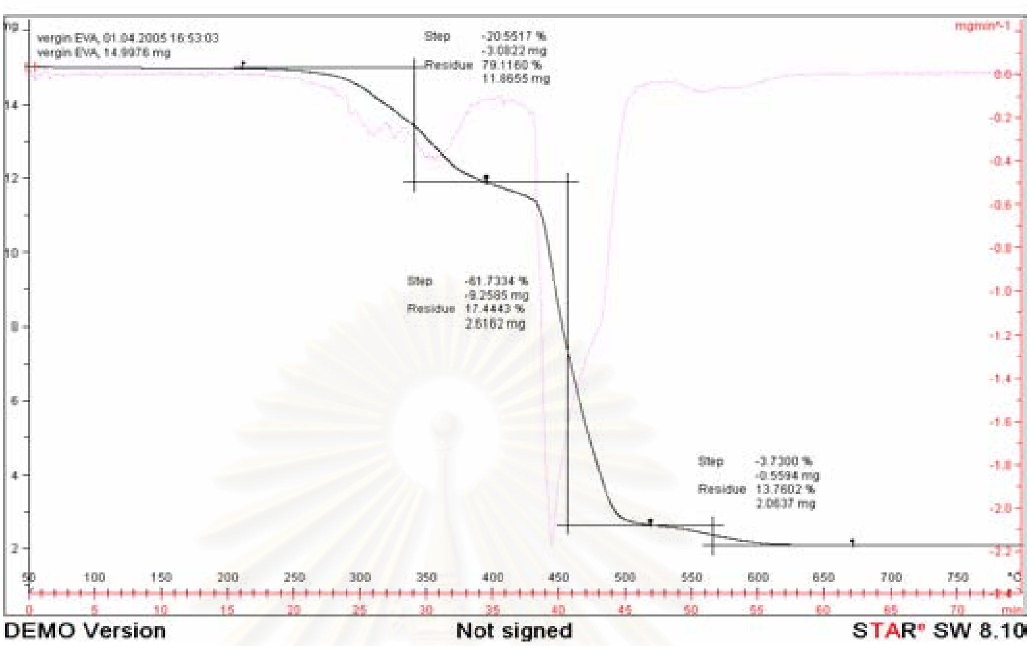


Figure A.1 TGA cures of EVA

Figure A.2 TGA curves of ATH-EVA compound (20:80)

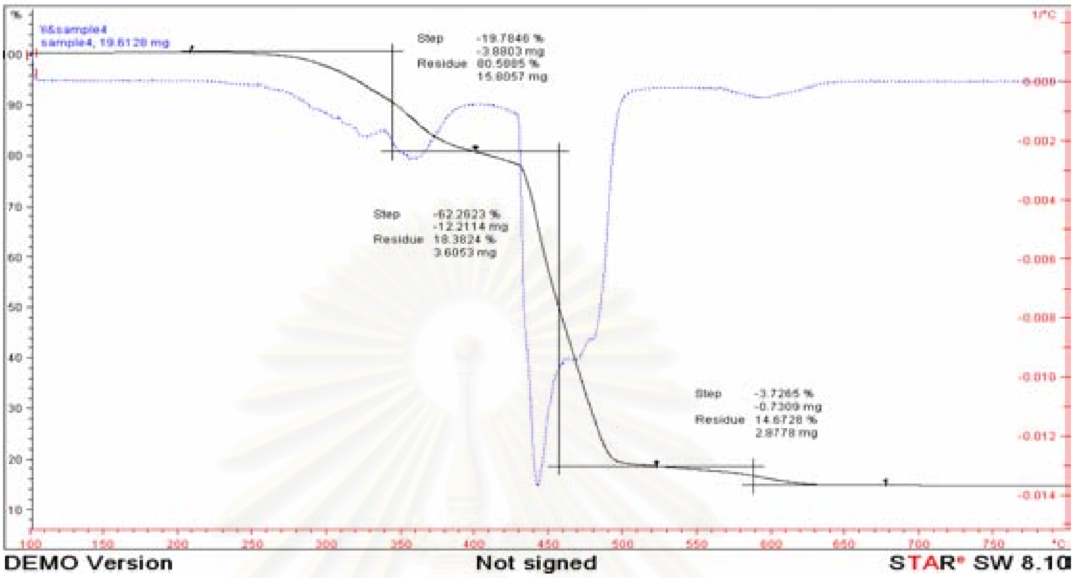


Figure A.3 TGA curves of ATH-EVA compound (30:70)

Figure A.4 TGA curves of ATH-EVA compound (40:60)

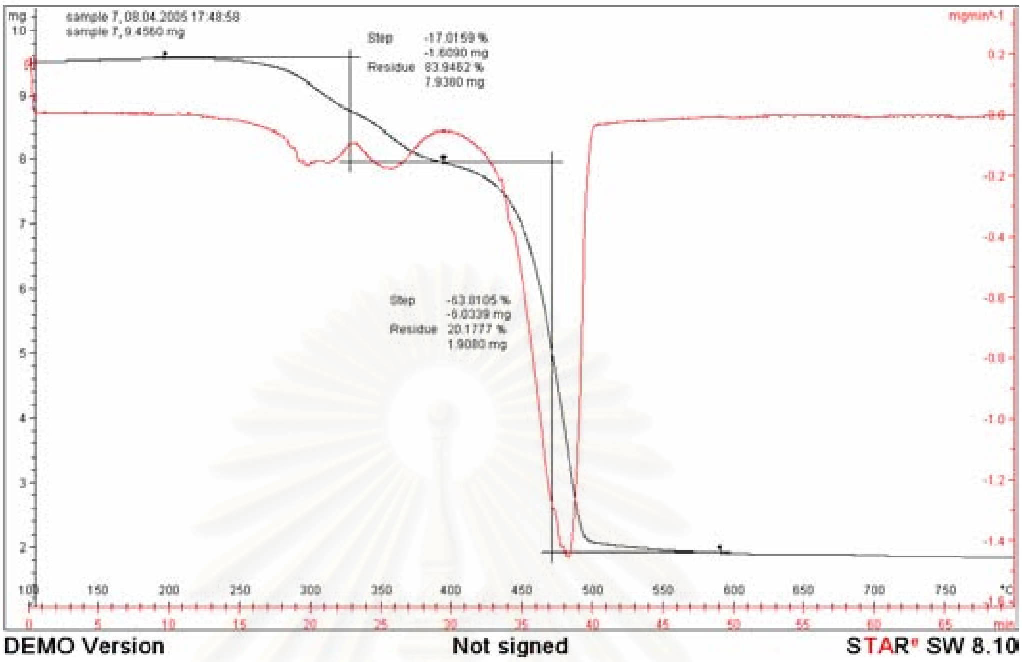


Figure A.5 TGA curves of ATH-EVA compound (45:55)

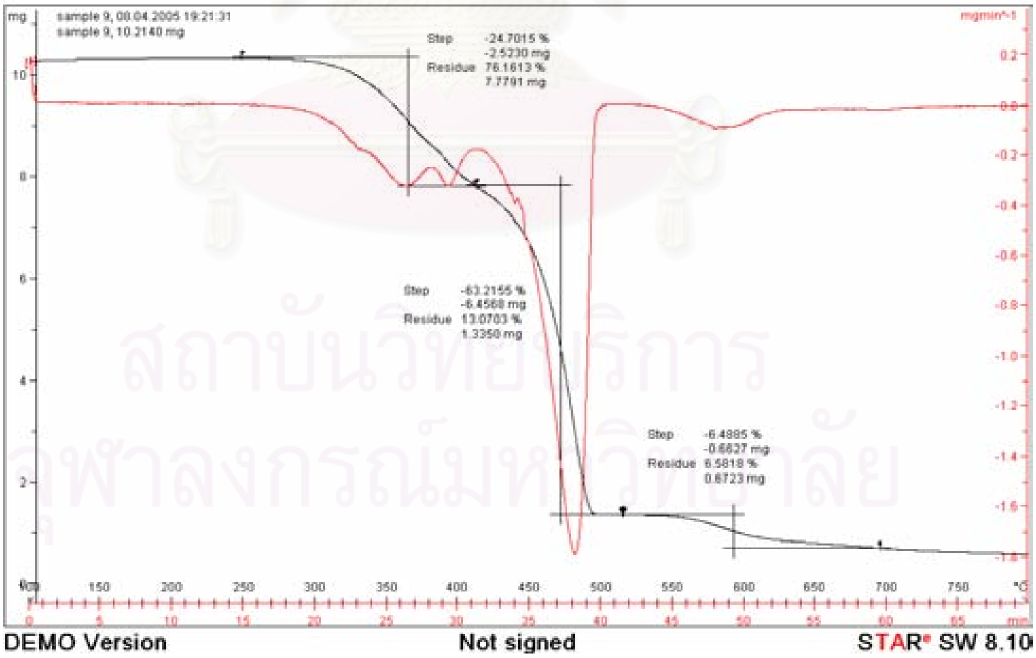


Figure A.6 TGA curves of ATH-EVA compound (50:50)

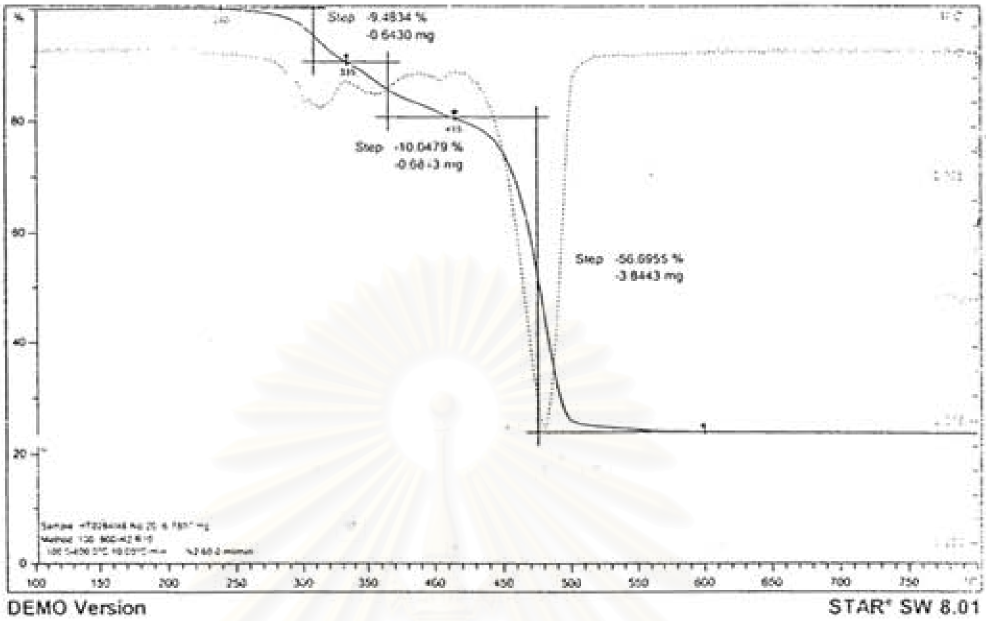


Figure A.7 TGA curves of ATH-EVA compound (55:45)

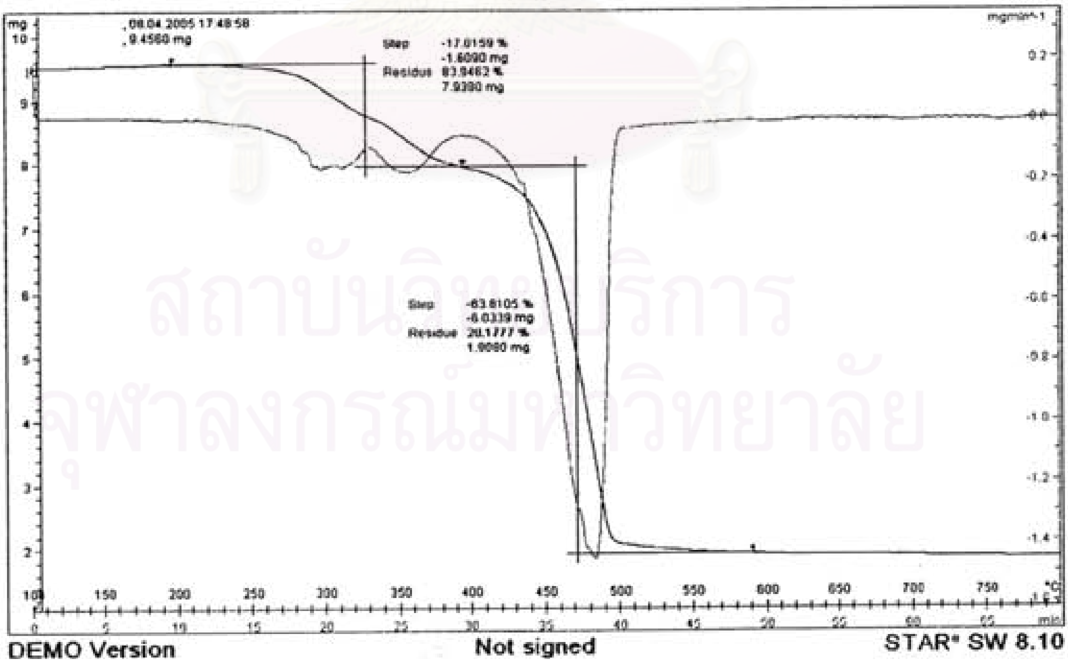


Figure A.8 TGA curves of ATH-EVA compound (60:40)

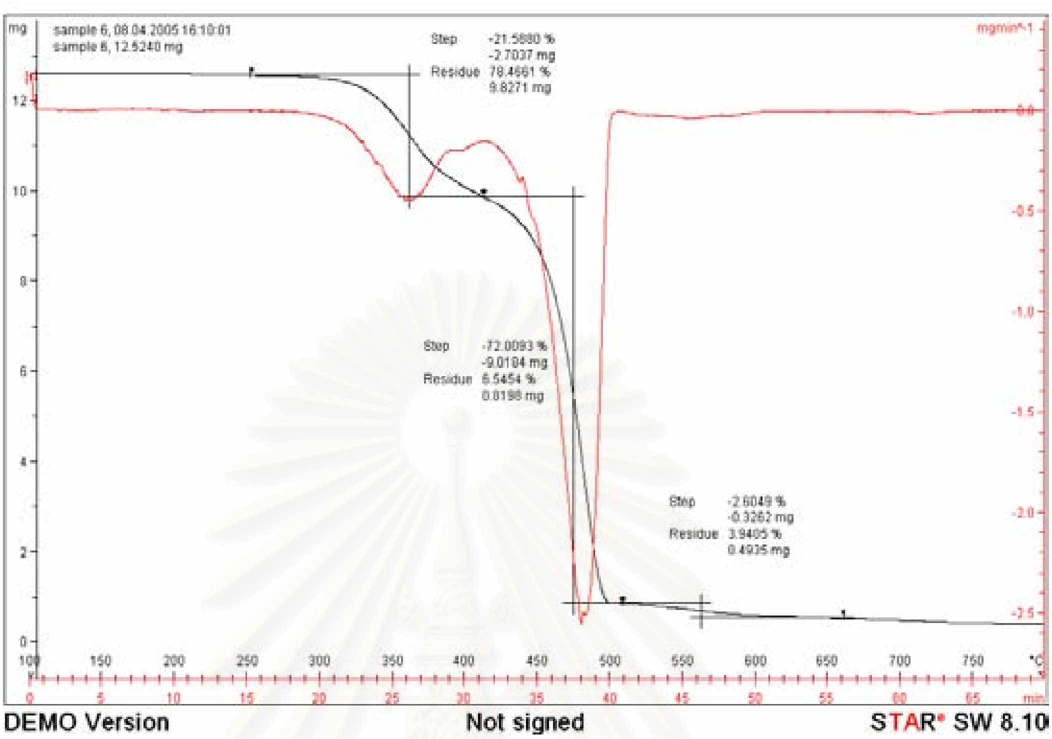


Figure A.9 TGA curves of melamine phosphate-EVA compound (20:80)

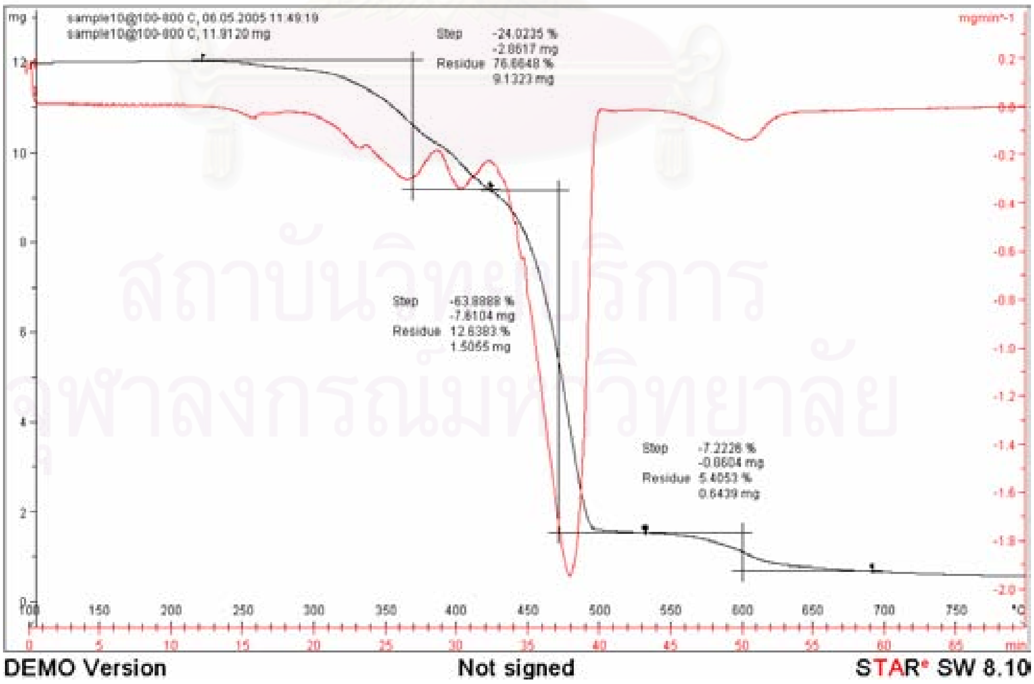


Figure A.10 TGA curves of melamine phosphate-EVA compound (30:70)

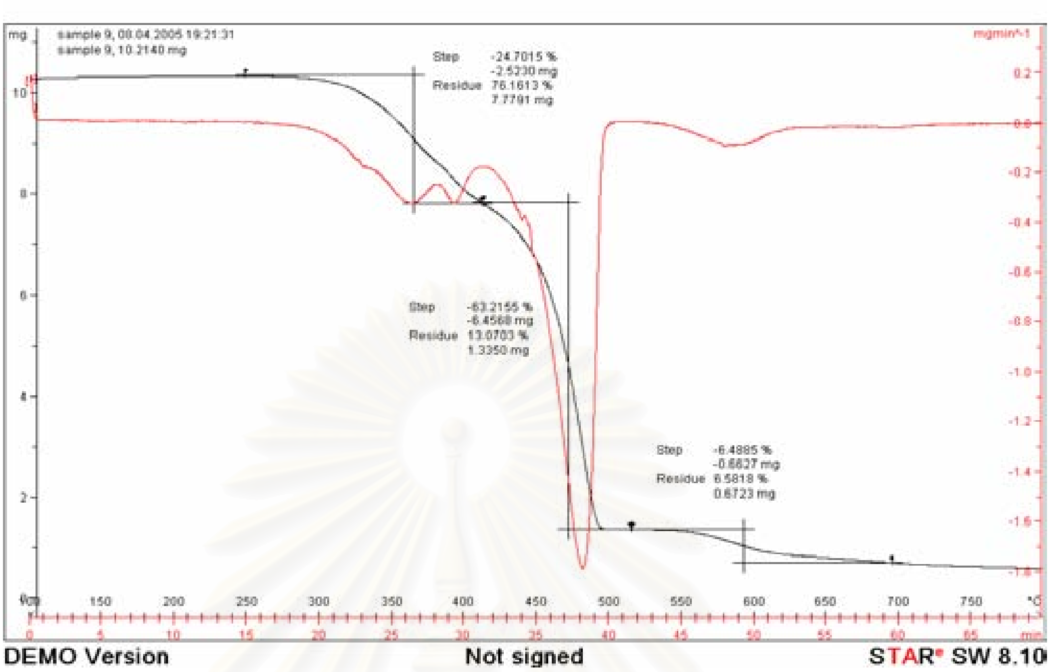


Figure A.11 TGA curves of melamine phosphate-EVA compound (40:60)

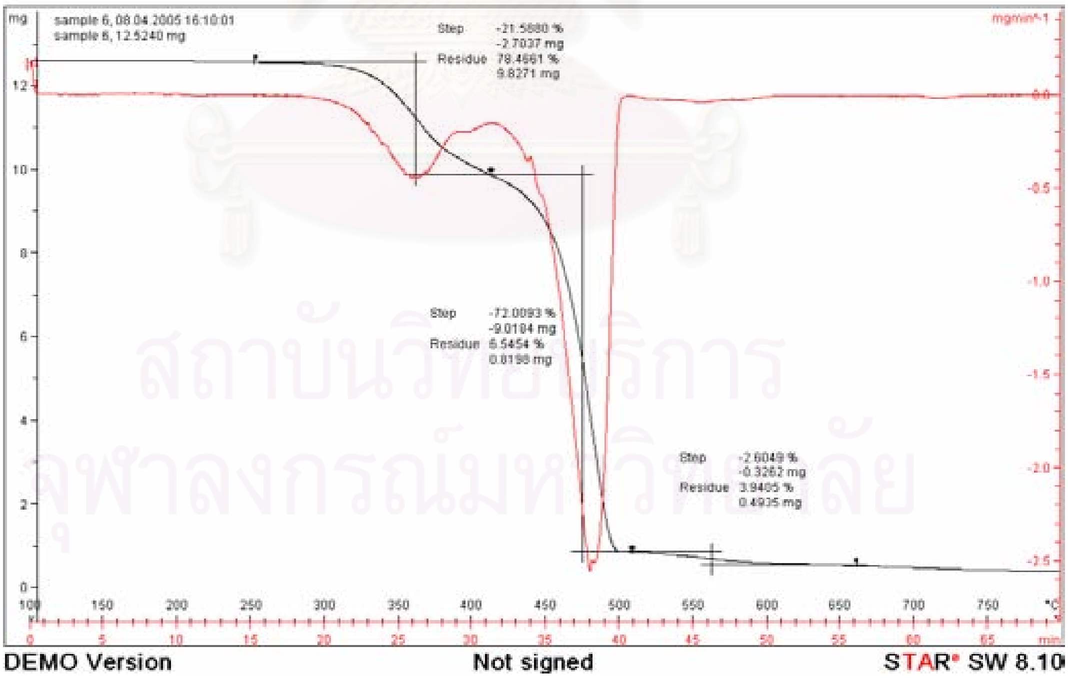


Figure A.12 TGA curves of melamine pyrophosphate-EVA compound (20:80)

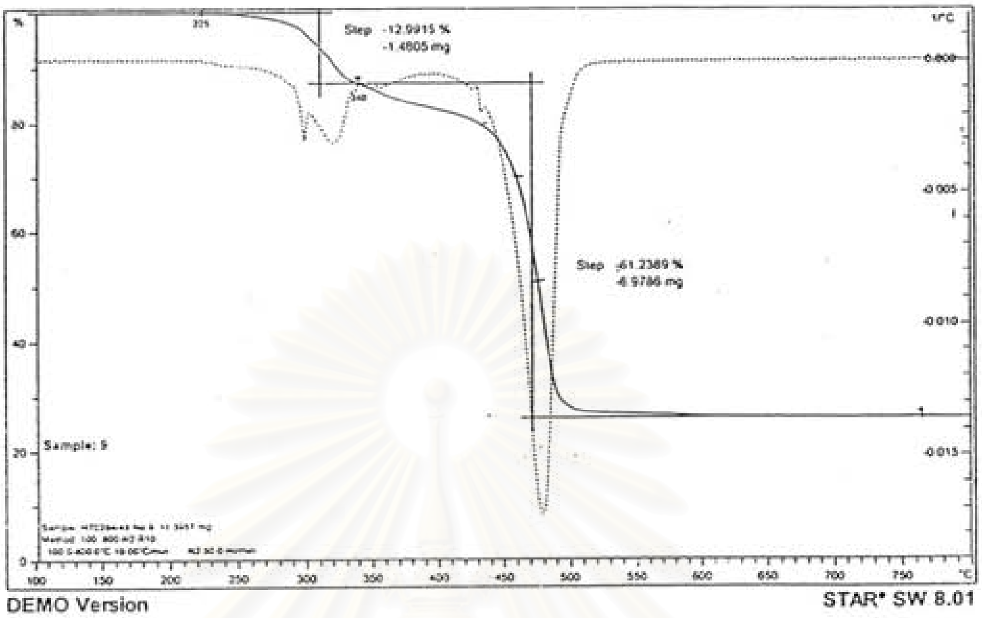


Figure A.13 TGA curves of melamine pyrophosphate-EVA compound (30:70)

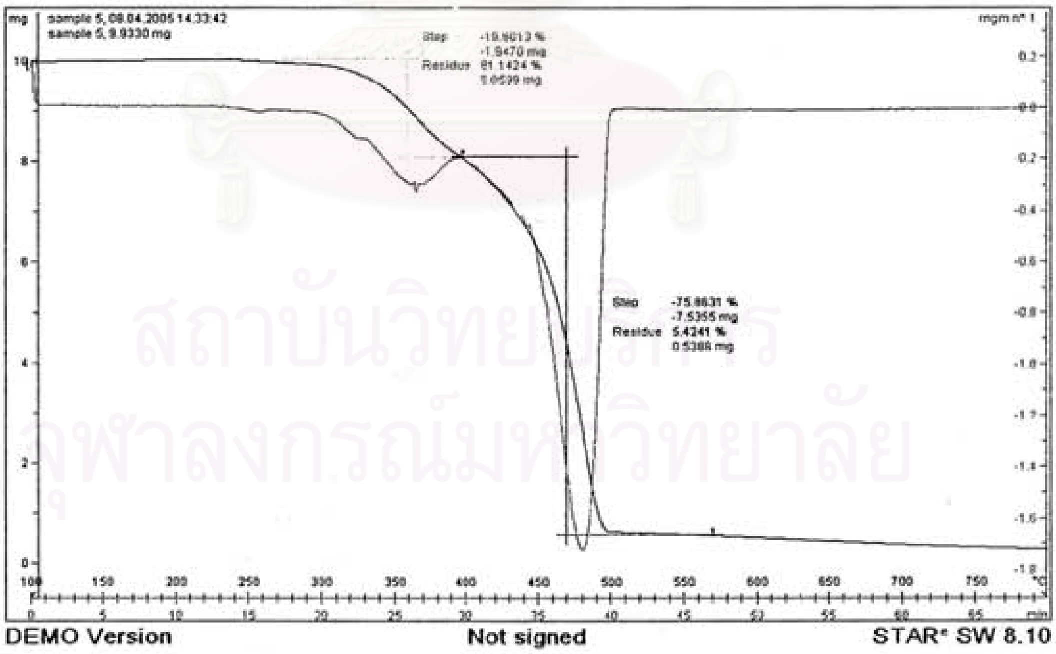


Figure A.14 TGA curves of melamine pyrophosphate-EVA compound (40:60)

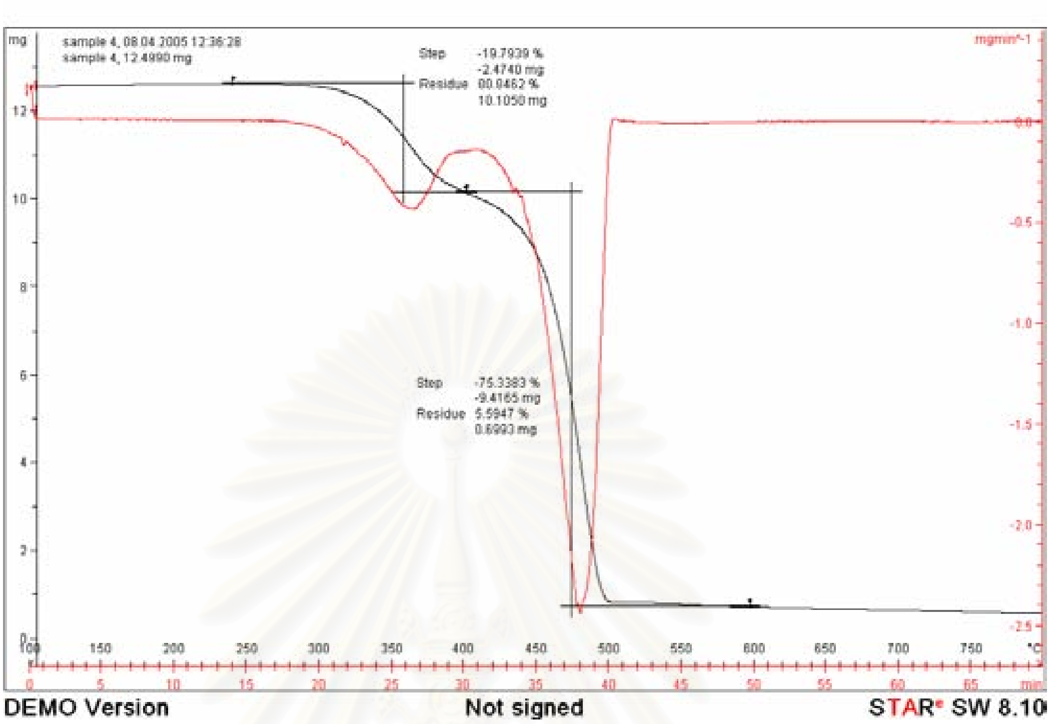


Figure A.15 TGA curves of melamine polyphosphate-EVA compound (20:80)

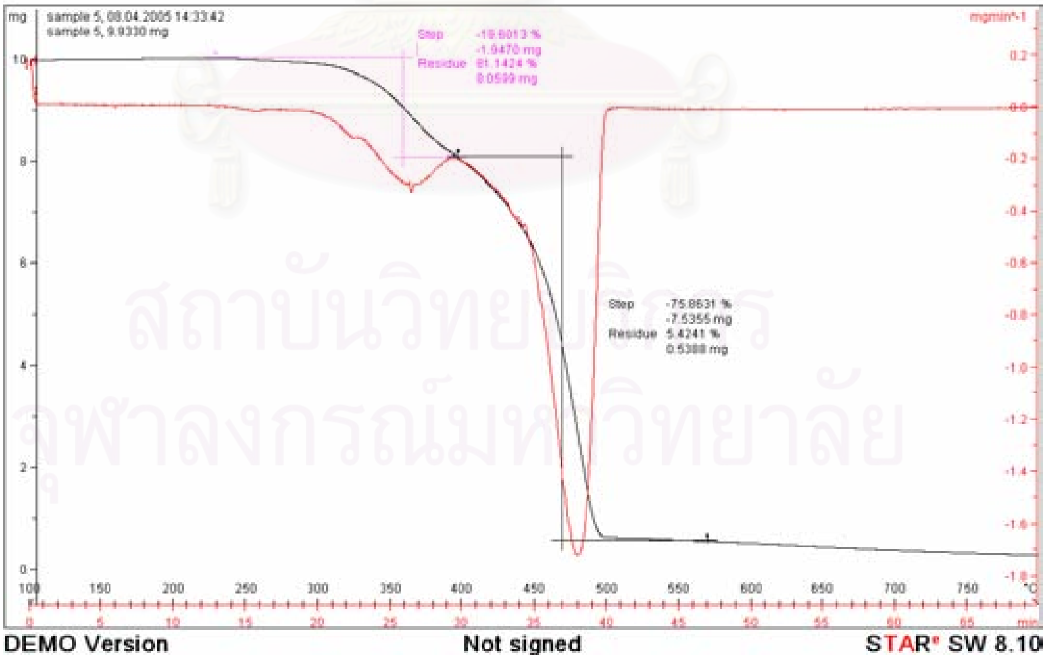


Figure A.16 TGA curves of melamine polyphosphate-EVA compound (30:70)

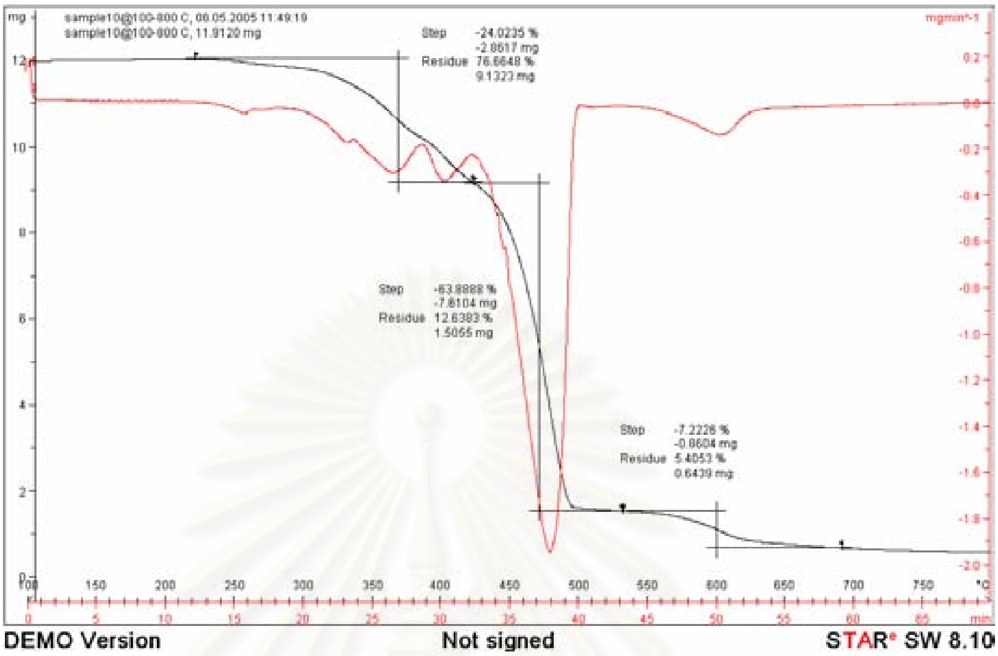


Figure A.17 TGA curves of melamine polyphosphate-EVA compound (40:60)

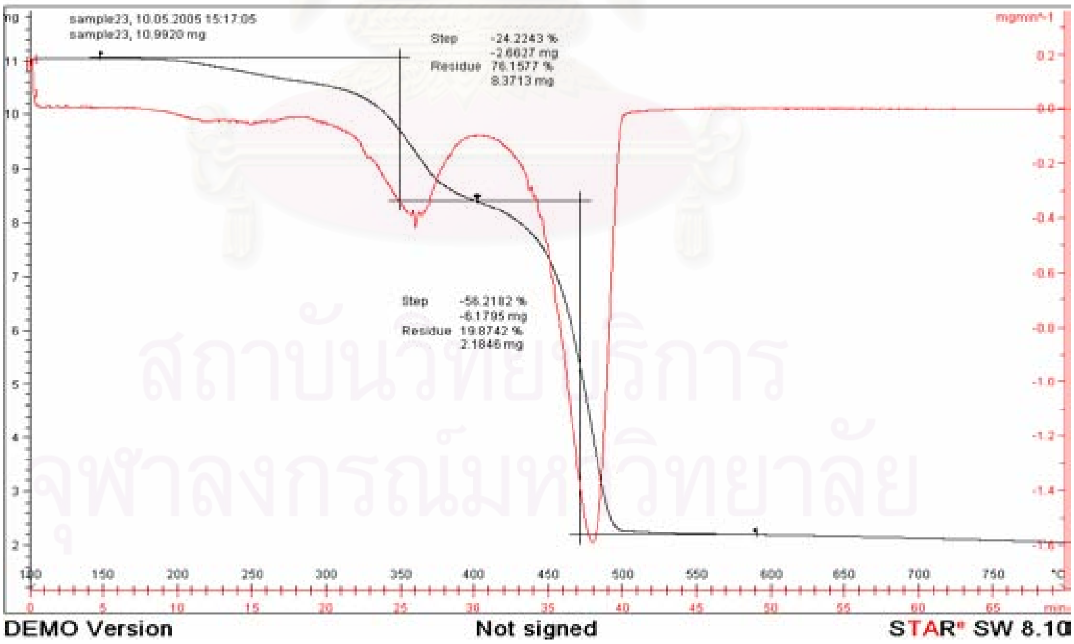


Figure A.18 TGA curves of melamine polyphosphate-EVA compound (45:55)

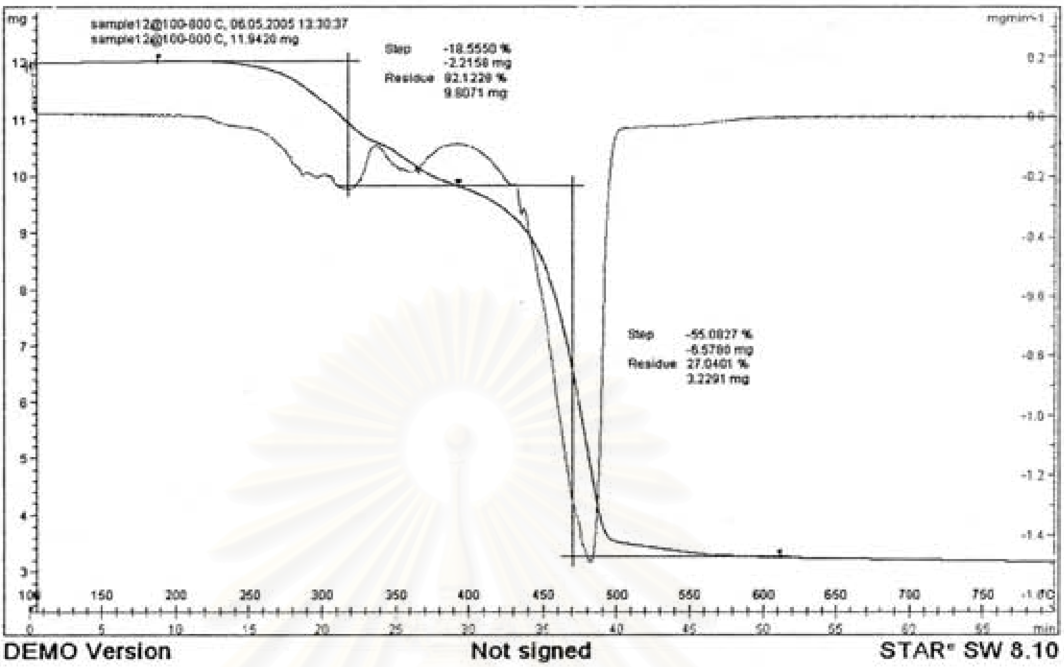


Figure A.19 TGA curves of melamine polyphosphate-EVA compound (50:50)

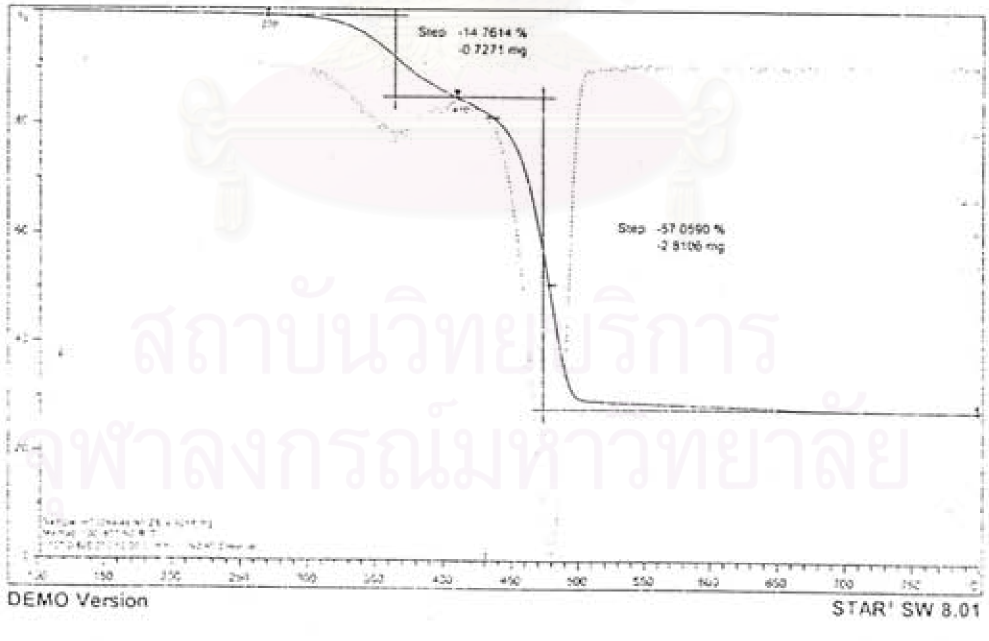
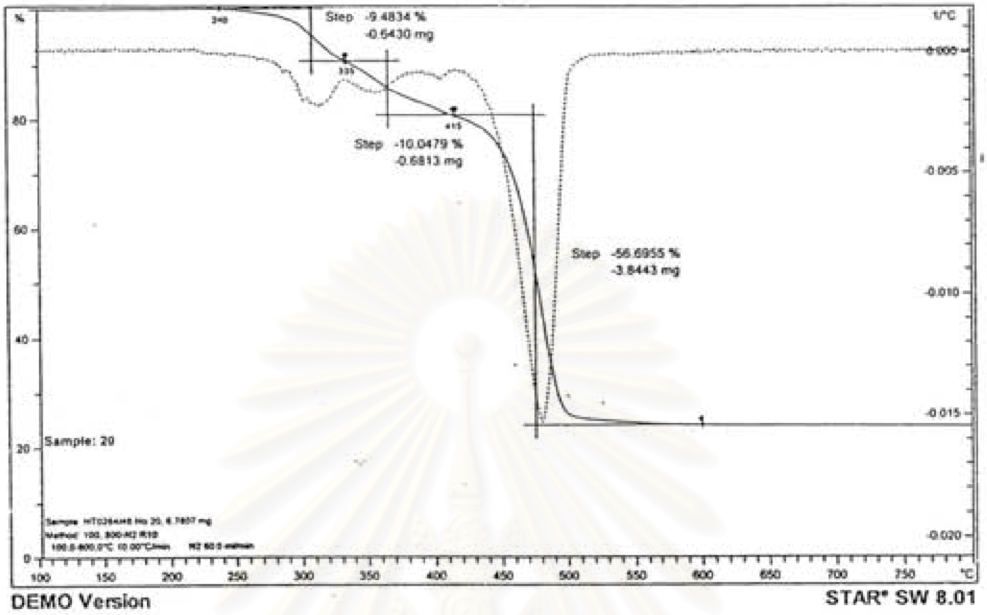
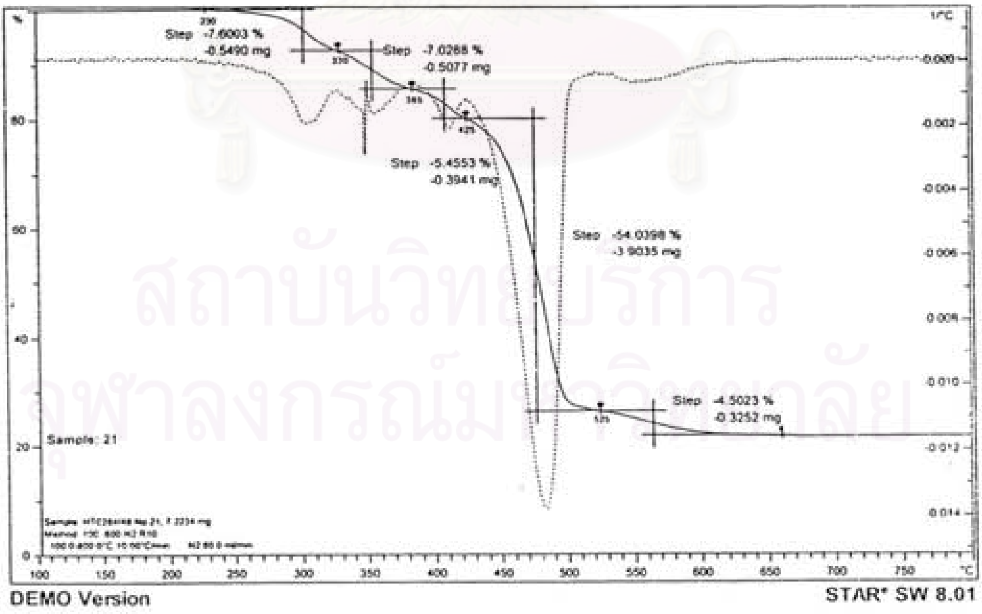


Figure A.20 TGA curves of melamine polyphosphate-EVA compound (55:45)



FigureA.21 TGA curves of ATH-melamine polyphosphate-EVA compound (30:10:60)



FigureA.22 TGA curves of ATH-melamine polyphosphate-EVA compound (20:20:60)

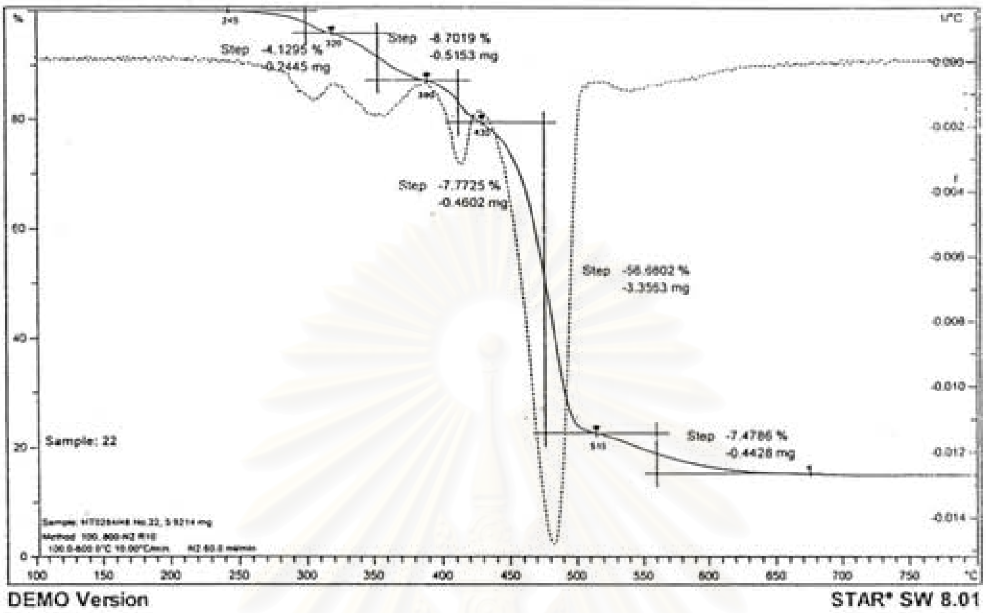
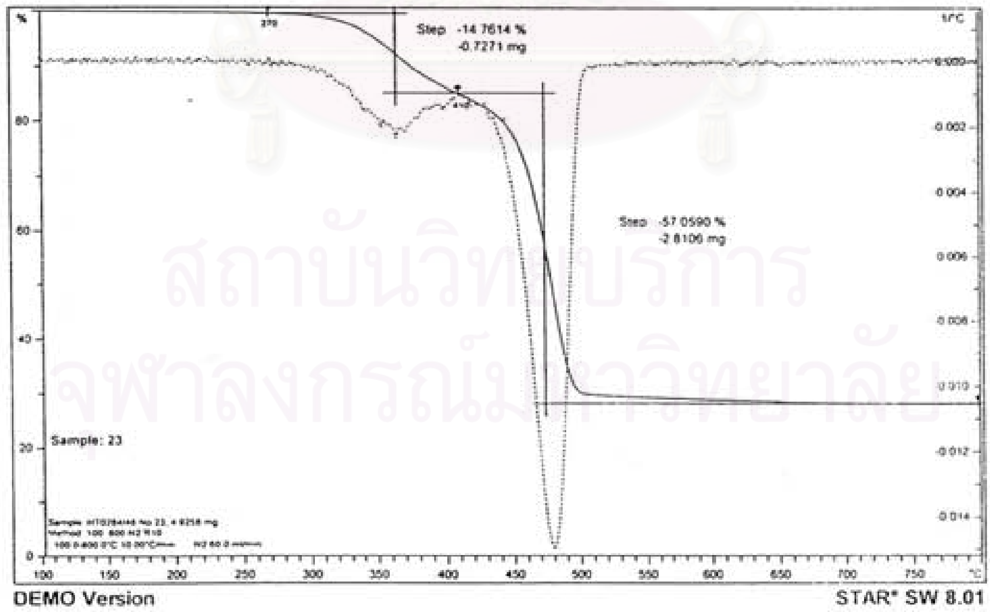
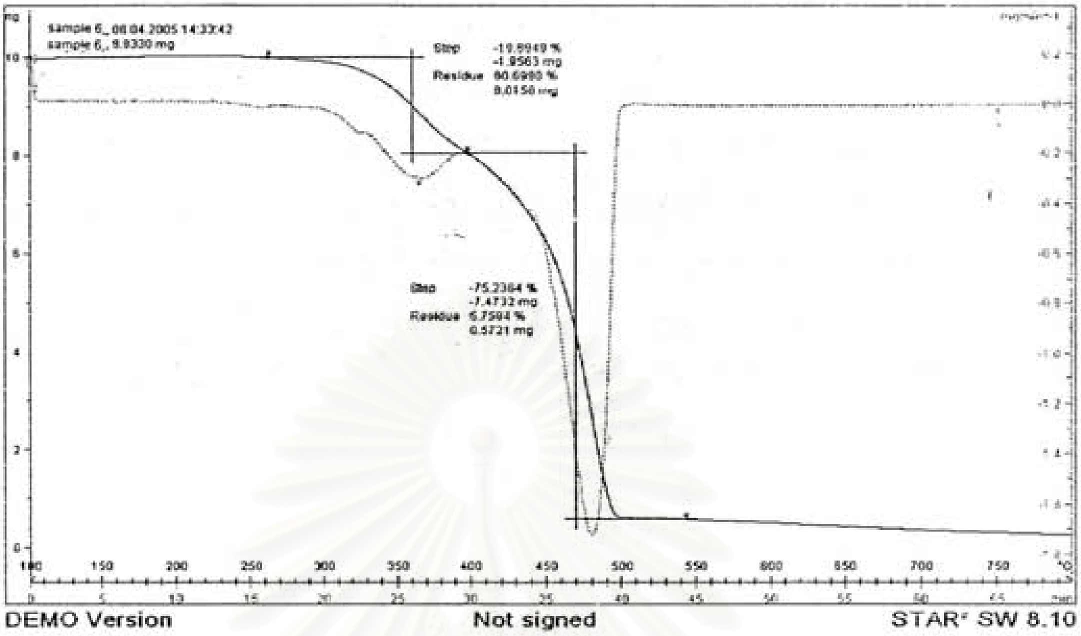


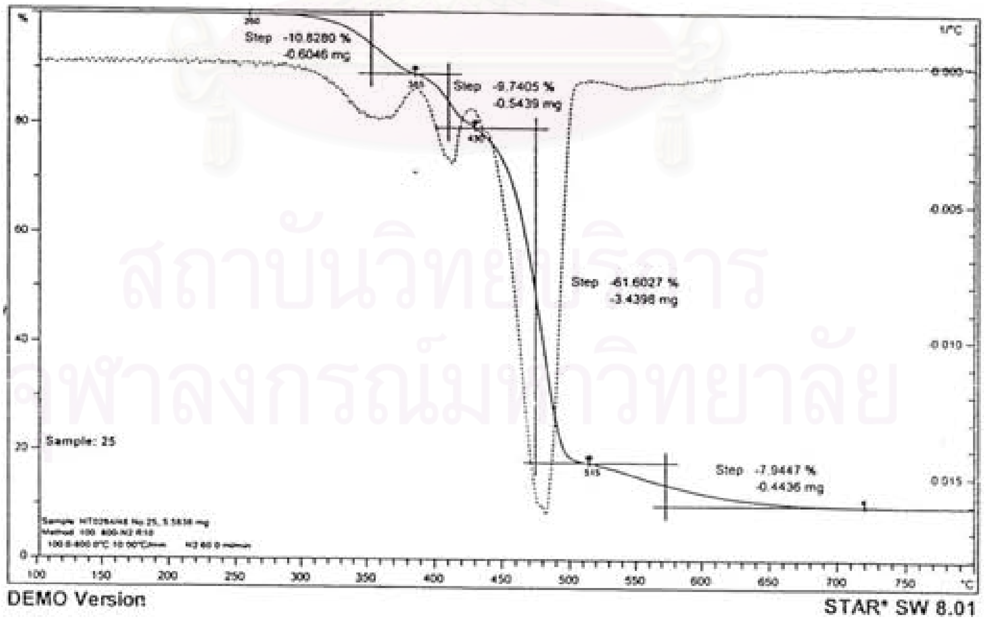
Figure A.23 TGA curves of ATH-melamine polyphosphate-EVA compound (10:30:60)



FigureA.24 TGA curves of melamine polyphosphate-zinc borate-EVA compound (30:10:60)



FigureA.25 TGA curves of melamine polyphosphate-zinc borate-EVA compound (20:20:60)



FigureA.26 TGA curves of melamine polyphosphate-zinc borate-EVA compound (10:3:60)

VITAE

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