

CHAPTER II

LITERATURE SURVEY

2.1 Theoretical Background

2.1.1 The Burning of Polymeric Materials.

A burning polymer is a complex combustion system. To create a basis for fire retardant research, it is important to clarify the combustion mechanisms of polymers. The process by which a polymer burns can be summarised in a combustion cycle which are shown below ;

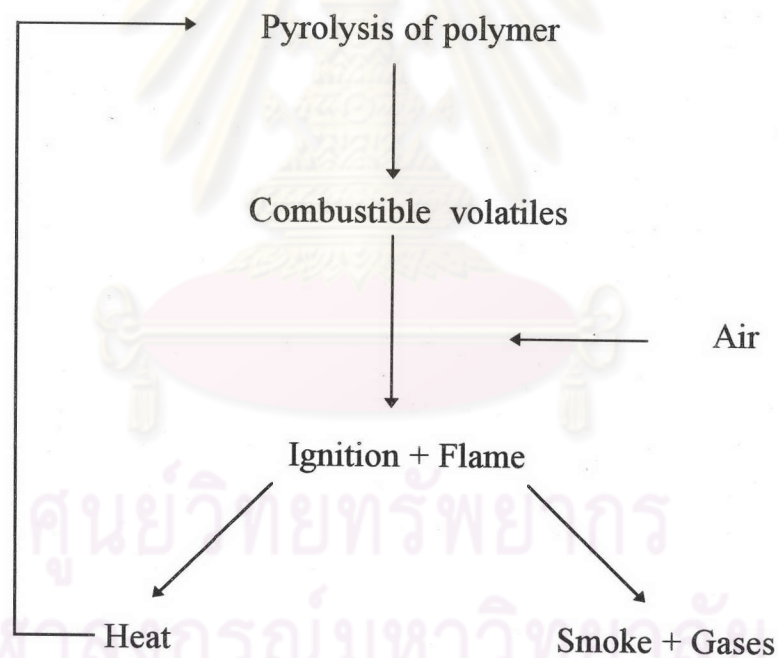


Figure 2-1 Burning of polymers

Polymers ignite and burn in a three-step process. The first step is fuel production in which heat from an outside source causes a temperature rise in the fuel, with subsequent breaking of chemical bonds and production of volatile

flammable gases which diffuse into the surrounding air environment. The second step is the ignition of these flammable gases. Ignition cannot be achieved until interdiffusion of the flammable gases with air has produced a flammable mixture of some minimum volume. Then, this mixture must be heated, by the external heat source, to its ignition temperature. This time, the combustion which is an exothermic reaction, is initiated. The third step is that of flaming combustion, a strictly gas phase process, but one that is coupled with the fuel, in that heat is transferred from the flame back to the condensed phase to continue the process of gaseous fuel production. While the ignition step must be accomplished in a flammable premixed volume of fuel vapour and air, flaming combustion of solid or liquid fuels continues by a process that is a diffusion flame. Hence, polymer combustion may be retarded or prevented if the flame retardant affects the equilibrium of combustion, i.e. in the rate of evolution of pyrolytic gases, the rate of mixing with oxygen in air, ignition, the rate of reaction with oxygen and of the rate of heat flow back to the polymer.

The reactions occurring in a burning polymer may be classified according to the site of action, i.e. in the condensed phase or in the gas phase.

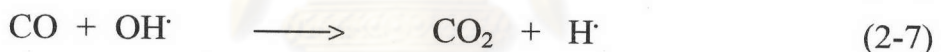
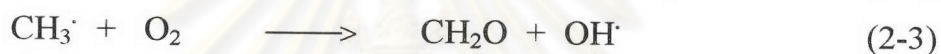
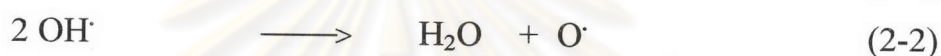
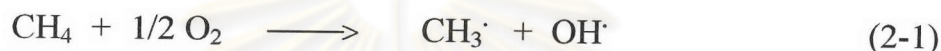
2.1.1.1 Condensed Phase Reactions.

On combustion, high molecular weight polymers decompose before vaporisation. Sufficient thermal energy (typically, 200-400 kJ/mole) is required to rupture a C-C or C-X bond and although, once initiated, the cleavage process proceeds rapidly, because of propagating chain reactions. Each bond rupture produces two radicals which react with a low activation energy (20-40 kJ/mol), with other polymer chains. As a result, the polymer breaks down to give the gaseous monomer or cross-linking agent and to give an involatile char, according to the nature of the polymer being burnt.

2.1.1.2 Gas Phase Reactions.

The processes involved in the flames of burning polymer systems are complex and are not well understood. The mechanism of combustion of methane involves several radical reactions which are shown below ;

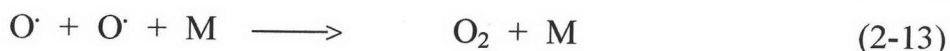
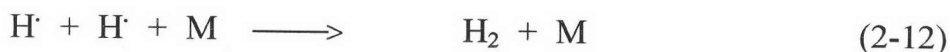
Chain propagations.



Chain branching



Termination (three-body reaction).



Where M is a solid catalyst.

Overall reaction.



In more complex fuel-rich flames, initial attack by atoms rather than OH radicals probably occurs since the concentration of the latter specie is low, thus resulting in the formation of CO, H₂, H₂O and solid carbon as the major products.

2.1.2 Flame Retardants. [8,9]

Flame retardants may be divided into two types ;

a) Additive flame retardants are incorporated into polymers by being physically mixed with polymer, normally after the polymerisation is completed. They do not affect the chemical structure of the monomeric units.

b) Reactive flame retardants appear to be most versatile in thermosetting materials, in which substitution of compounds can be effected at a stage much closer to end use than might be the case with thermoplastics. Additive type flame retardants appear to be most versatile in thermoplastics.

A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread.

It is almost universally accepted that flame retardants which inhibit the combustion process by chemical action are more effective than those which act by physical means. In many cases, however, the boundary between chemical and physical effects is so indistinct that it is difficult to evaluate their respective contributions.

2.1.2.1 Physical Action

There are several ways in which the combustion process can be retarded by physical action :

a) By cooling : Endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process.

b) By formation of a protective layer (coating) : The condensed combustible layer can be shielded from the gaseous phase with a solid or gaseous protective layer. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, the oxygen necessary for the combustion process is excluded and heat transfer is impeded.

c) By dilution : The incorporation of inert substances (e.g. fillers) and additives which evolve inert gases on decomposition dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded.

2.1.2.2 Chemical Action

The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases :

a) Reaction in the gas phase.

The radical mechanism of the combustion process which takes place in the gas phase is interrupted by the flame retardant. The exothermic processes are thus stopped, the system cools down and the supply of flammable gases is reduced and eventually completely suppressed.

b) Reaction in the solid phase.

Here two types of reaction can take place. Firstly, breakdown of the polymer can be accelerated by the flame retardant causing pronounced flow of the polymer and, hence, its withdrawal from the sphere of influence of the flame which breaks away. Secondly, the flame retardant can cause a layer of carbon to form on the polymer surface. This can occur, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These form the carbonaceous layer by cyclizing and cross-linking.

2.1.3 Synergism in Flame Retardation.

The effect of a mixture of two or more fire retardants may be additive, synergistic, or antagonistic. Synergism is the case in which the effect of two or more components taken together is greater than the sum of their individual effects. The concept of synergism is very important, since the development of synergistically efficient fire retardants can lead to less expensive polymer systems with reduced effects on other desirable properties. One of the classical illustrations of synergism observed in flame retardation is the addition of antimony (III)oxide to halogen containing polymers.

In polymer systems containing Sb_2O_3 and halogen, it has often been suggested that fire retardance is mainly due to the gas phase flame inhibition by the volatile antimony trihalide, since maximum flame retardancy is observed when the mole ratio Sb/X is 1:3. It is believed that HCl formed by the degradation of the chlorinated additive reacts with Sb_2O_3 to yield SbOCl as an intermediate, and the subsequent reactions are responsible for the increased flame retardancy. The formation of an intermediate by the combination of Sb_2O_3 and a chlorine source was also confirmed by thermoanalytical data.

2.1.4 Example of Flame Retardants in Polymers.

2.1.4.1 Halogen-Containing Flame Retardants.

The effectiveness of halogen-containing flame retardants increases in the order $F \ll Cl < Br < I$. Fluorine- and iodine- based flame retardants are not used in practice because neither type interferes with the combustion process at the right point. Fluorine cannot become effective as a radical interceptor in the gas phase because of its strong bond to carbon. Iodine in contrast is attached to carbon so loosely that it is liberated by even a negligible energy supply.

Of the two remaining halogens, bromine is the more effective since its weaker bonding to carbon enables it to interfere at a more favourable point in the combustion process. Bromine is believed to perform in the gaseous phase whereas the flame retardant function of chlorine is in both the gaseous and condensed phases. The chemical reaction may involve halogenation followed by dehydrohalogenation to yield a polymeric residue rich in double bonds which is then converted to carbon.

2.1.4.2 Phosphorus-Containing Flame Retardants. [10]

Phosphorus-containing flame retardants mainly influence the reactions taking place in the condensed phase. They are particularly effective in materials with high oxygen content, such as cellulose. The flame retardant is converted by thermal decomposition to phosphoric acid which in the condensed phase extracts water from the pyrolysing substrate, causing it to char.

2.1.4.3 Boron-Containing Compounds. [11]

Boron-containing compounds can be effective in the condensed phase, and in some cases, in the gas phase as well. A major application of borates is the use of mixtures of boric acids and borax as flame retardants for cellulose. Boron-containing compounds act by endothermic, stepwise release of water and formation of a glassy coating protecting the substrate.

2.1.4.4 Antimony Compounds.

Antimony appears to be ineffective when used by itself. It is principally used as a synergist with the halogens, particularly bromine and chlorine. The increased effectiveness is probably due to the longer residence time of bromide as antimony tribromide, relative to bromide as hydrogen bromide. The greater effectiveness of bromide compared to chloride is also observed char.

Unfortunately, antimony trioxide-halogen system tends to increase smoke production during combustion of the associated polymer, and also result in undesirable rigidity and/or brittleness, in addition to a strong pigmentation. Furthermore, recent health and environmental issues have focused attention on the possible toxicity/carcinogenicity of Sb_2O_3 , and consequently, its use as a flame retardant has been subject to intense scrutiny.

2.1.5 Development of Tin-based Flame Retardants.

Despite the fact that tin salts have been known as fire retardants since the mid-nineteenth century, until very recently their industrial use has been limited to specialized treatments for woolen sheepskins and rugs. In view of the increasing demand for novel, non-toxic, fire-retardant additives for synthetic polymers, a program of research was initiated in the laboratories of the International Tin Research Institute during the mid-1980s, to develop tin chemicals as fire retardants and smoke suppressants for plastics, elastomers and related materials. Preliminary studies demonstrated the effectiveness of tin(IV) oxide, SnO_2 , both in its anhydrous and hydrous forms as a flame- and smoke- inhibitor for halogen-containing polymer formulations such as PVC, halogenated polyester resins and polychloroprene. Subsequent work was aimed at developing tin additives with improved activity compared to tin(IV) oxide. This led to the conclusion that, of a series of metal hydroxystannates and stannates, $\text{MSn}(\text{OH})_6$ and MSnO_3 respectively, the zinc compounds were clearly the most effective with regard to fire retardant and smoke suppressant performance.

The choice of zinc hydroxystannate (ZHS) and zinc stannate (ZS) for further study at I.T.R.I. was to prove a significant step in the quest for tin-based fire retardants for synthetic polymers. Some important properties of these compounds are shown in Table 2-1.

Table 2-1 Properties of zinc hydroxystannate and zinc stannate [12]

Properties	ZHS	ZS
Chemical formula	ZnSn(OH) ₆	ZnSnO ₃
Appearance	white powder	white powder
Analysis (approx.) :		
Sn	41%	51%
Zn	23%	28%
Cl	< 0.1%	< 0.1%
free H ₂ O	< 1%	< 1%
Specific gravity	3.3	3.9
Decomposition temp (°C)	> 180	> 570
Toxicity	very low *	very low *

* Acute oral toxicity, LD₅₀(rat) > 5000 mg/kg

2.1.6 Acrylonitrile-butadiene-styrene copolymer (ABS)

Acrylonitrile-butadiene-styrene (ABS) plastics represent an extremely large volume for a material that was originally classified as an engineering plastic [13,14]. It is available in many grades, depending upon the end-use requirements and the composition of the final compound.

The ignition temperature of ABS is in the range of 415-490 °C. depending on its composition. It will begin to melt (soften) in the range of 88-125 °C. It burns with a smoky flame, producing large amounts of soot (characteristic of polystyrene) and may smell of burnt rubber (owing to the presence of polybutadiene). ABS will burn with a luminous yellow flame and will support its own combustion (that is, it will continue to burn after the

igniting flame has been removed). In some cases, the molten drops from burning ABS will burn as they fall.

It is important to check with the manufacturer to determine whether the ABS compound contains any flame retardant material, since this will certainly affect the way the article burns. For example, many plastic television cabinets are made from ABS, and for many appliance applications a flame retardant must be used to reduce the product's combustibility. An ABS part made from a compound containing flame retardant will burn only with great difficulty, and only if the flame is very hot and in contact with the part throughout the burning process.

2.2 Research Work.

ABS plastics are useful in many commercial applications such as automotive, business machines, electronics manufacture, etc., where fire resistance is required, as well as in the production of molded articles. The use of brominated and/or chlorinated compounds by themselves or in combination with other materials such as antimony trioxide and boron compounds as flame retardant for ABS compositions are well known :

Thomas and Greenville [2] suggested a flame-retarded ABS composition comprising 5-35 wt% bis(2,4,6-tribromophenoxyethyl)tetrabromobisphenol A ether and about 1-10 wt% of an enhancing agent, preferably antimony trioxide.

Enric, Nicolai and Dennis [15] disclosed an ABS plastic composition containing halogenated unsymmetrical higher alkyl bisphenoxy alkane and an enhancing agent which retarded or suppressed the blooming of composition. The compositions of this material preferably comprise about 50-90 % ABS thermoplastic resin, 5-30% halogenated unsymmetrical higher alkyl bisphenoxy alkane and 1-10 % enhancing agent, all by weight of the composition.

Davie, Janet and Susan [16] investigated a flame-retarded ABS formulations with high impact strength. This resin includes at least about 50 wt% ABS resin, about 5-30 wt% halogenated flame retardant (selected from the group consisting of tetrahalobisphenol A, bis-halophenyl compounds, halogenated polystyrene), 2-6 wt% flame retardant synergist (a particularly effective and preferred synergist is antimony trioxide) and about 8-38 wt% polymeric impact modifier. The method comprises master batching the flame retardant and polymeric impact modifier, dry-blending the masterbatch with the ABS resin and the flame retardant synergist and extruding the resultant blend to form the formulated ABS resin.

Although antimony trioxide is efficient as a flame retardant synergist in ABS compositions, but it is found to increase the amount of smoke and toxic gases. Recent studies to develop flame retardant formulation have used inorganic tin compounds such as zinc hydroxystannate and zinc stannate.

Cusack, Monk, Pearce and Reynold [17] indicated that zinc hydroxystannate and zinc stannate; at incorporation levels of 1-10 phr; impart flame, smoke and carbon monoxide suppressant properties of brominated polyester. These improvements in performance are superior to those exhibited by tin (IV) oxide or antimony (III) oxide.

In addition, these investigators examined that the surface area and degree of dispersion of the additive affect its fire retardant efficiency. Hence, colloidal SnO_2 has been found to be more effective as flame retardant than powdered SnO_2 .

Bains, Cusack and Monk [18] examined the retardant properties of zinc hydroxystannate, compared to those of antimony trioxide in brominated polyester resin containing various inorganic fillers. The effectiveness of $\text{ZnSn}(\text{OH})_6$ and ZnSnO_3 as flame retardants depended on several factors including incorporation level of the additives and fillers, and bromine content

of the resin. In general, Sb_2O_3 gave optimum performance in alumina trihydrate-filled resin, whereas $\text{ZnSn}(\text{OH})_6$ exhibited a flame retardant synergism with anhydrous Al_2O_3 . Furthermore, the $\text{ZnSn}(\text{OH})_6$ - Al_2O_3 combination inhibited the evolution of carbon monoxide from burning polymers and was clearly an excellent overall fire retardant system for this type of polymer.

Cusack, Heer and Monk [19] examined zinc hydroxystannate and found that it exhibited flame-, smoke- and toxic gas-retardant properties in unsaturated polyesters based on the halogenated compounds, chlorendic anhydride (CA) or dibromoneopentylglycol (DBNPG). In addition, they suggested that the fire-retardant action of the tin additive involved both the condensed and vapour phase in the DBNPG resin, whereas its effects in the CA system appeared to be almost exclusively due to vapour phase activity.

Chaplin and Tingley [5] investigated a formulation for halogenated polymers without added antimony trioxide. The formulation contained a synergistic flame retardant combination consisting of 10-400 phr of an aluminum magnesium hydroxide and 0.5-80 phr of a tetravalent tin compound which is a tin oxide or a metal stannate or hydroxystannate. It was reported this significant increases flammability resistance.

Chaplin [20] found that the combination of a zinc borate and a divalent metal stannate, particularly zinc stannate in halogen-containing polymeric compositions, provides an increased fire-retardant effect and also suppresses smoke production. The fire-retardant compositions comprise, by weight percent, 40-94% polyamide, 5-40% halogen-containing organic fire retardant, 1-20% of a mixture of zinc borate and a divalent metal stannate, preferably in a weight percentage ratio of about 50:50. The suitable stannates that can be used are zinc stannate, zinc hydroxystannate, calcium hydroxystannate and magnesium hydroxystannate. Preferably the stannate is zinc stannate.

Hornsby, Winter and Cusack [21] considered the influence of tin (IV) oxide and zinc hydroxystannate on fire retardancy of chlorosulphonated polyethylene. Both tin compounds can confer large improvements in oxygen index with corresponding reductions in smoke emission, particularly when used with chlorinated paraffin wax. It was apparent that tin acted mainly in the condensed phase by a char formation. At high Cl/Sn ratios, volatilisation of tin chloride or oxychloride might occur, resulting in a vapour phase flame retardation.

Andre, Cusack, Monk and Seangprasertkij [22] have found that zinc hydroxystannate (ZHS) and zinc stannate (ZS) are effective flame retardants and smoke suppressants in unsaturated polyester resins when used in conjunction with additive-type halogenated compounds such as chlorinated paraffin wax and decabromodiphenyl oxide. At a 5 phr (parts per hundred of resin) incorporation level, the tin-containing additives gave limiting oxygen index (LOI) elevations of ca. 2-3 units in resins containing 10% halogen, and ca. 3-6 units in 20% halogen formulations, with observed reductions in maximum smoke density of ca. 20-40%. Thermoanalytical experiments suggested that ZHS and ZS operate as fire retardants by combined condensed/vapour phase action.

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