

CHAPTER I

INTRODUCTION

1.1 Background

Uncontrolled fire is a danger to modern life and property. Unfortunately, this period has also seen a dramatic increase in the number of serious fires, and the number of deaths and injuries in fires remains appealingly high. Fire creates a complex toxic environment involving flame, heat, oxygen depletion, smoke, and toxic gases. Fire deaths are normally violent in nature, and smoke inhalation and not fire itself is the killer that accounts for over 80% of fire deaths [1]. A prime cause of this fire hazard is the use of natural and synthetic flammable materials.

The last two decades have seen a major growth in the use of synthetic polymers. Nowadays plastics are considered as essential materials for construction, insulation, packaging, upholstery and transport applications. The advantages over metallic and other materials, e.g. rapidity, cost saving manufacture of complex mouldings and reducing assembly cost, and by consumer demands for more comfort and better design, lower weight, lower maintenance and running costs can frequently be achieved only by the increased use of plastics. Because plastics are synthetic organic-based materials with high carbon, and often high hydrogen content and will burn under the proper condition.

However, the susceptibility to fire can be reduced, and the spread of flame can be decreased by the incorporation of additives. Additives called “flame retardants” help reduce the ignition of the plastic and the rate of flame propagation. The use of flame retardants in polymers has increased dramatically in recent years, in parallel to the growth of the plastics industry. Flame retardants play an important role within the polymer industry accounting for 27% of plastics additives market [2] (Figure 1-1).

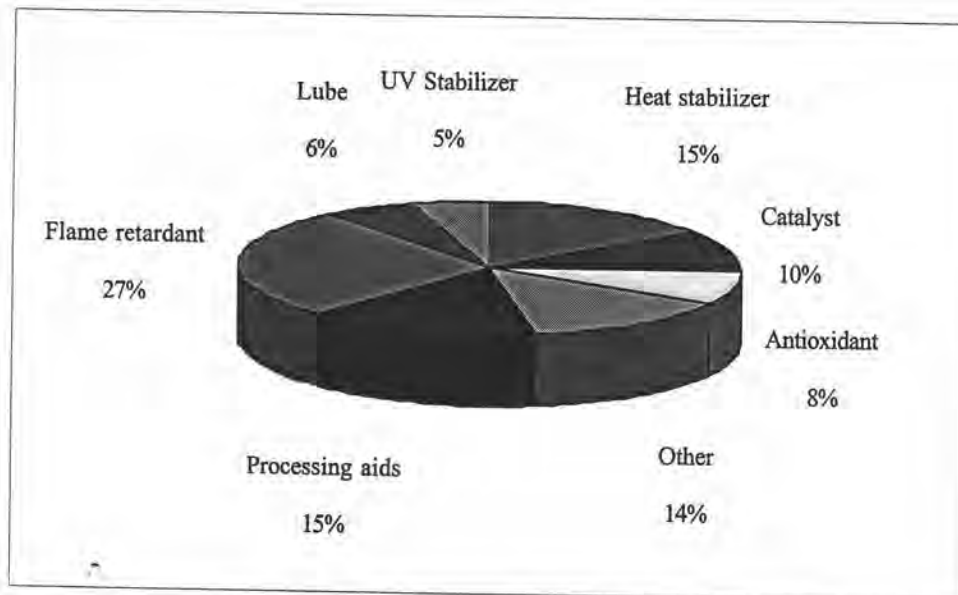


Figure 1-1 : Global plastic additives (1995).

The requirements of flame-retardance are becoming more rigorous as these markets are penetrated, as test methods become more realistic and sophisticated, and as awareness of the inherent danger in using flammable materials increases. This awareness has been accentuated by the total destruction, by fire, of buildings that were supposedly fireproofed, due to combustible contents, furnishings, and decorations.

HIPS resins are well known in the synthetic organic polymer art as a class of thermoplastics which offers excellent mechanical properties. The general characteristics of HIPS resin are known for their ease of processing, good dimensional stability, impact strength and rigidity. Because of their properties and their moderate cost, they have been found a wide range of applications in many fields. However, they have restricted usage due to their flammability the same as other thermoplastic resins [3].

Therefore, this research focused on the technology required to develop ignition-resistant HIPS and evaluated various carefully-selected flame retardants. It represents a systematic approach to gain a more detailed, fundamental understanding of how the properties of flame retardants affect those of the final HIPS compound and to correlate the characteristics of the flame retardant with the properties of the final compound.

1.2 Objectives

1. To study the effect of flame-retardant structure on HIPS performance.
2. To study the dispersion of flame-retardant in HIPS.

1.3 Scope of the investigation

The flame retardance of plastic material can be determined by many methods. In this research, the minimum concentration of oxygen that will just support combustion or LOI test will be used as the criteria for determination of flame retardance property. The necessary procedures may be as follows :

1. Preparing the specimens of HIPS after blending with flame retardant by the following procedure :

- All of the blends were made from individual components and passed through an extruder.

- The pellets are injection molded in order to provide specimens for testing mechanical property.

2. Varying the ratio of flame retardant in order to attain the appropriate LOI value, as good as commercial HIPS, and compare with the use of other bromine compound.

3. Investigating the properties of HIPS composition such as impact strength, melt flow index, tensile strength etc.

CHAPTER II

THEORY

2.1 Theoretical Background

2.1.1 The combustion process

The combustion of plastics is a process comprising many steps. A simplified schematic representation of the various phenomena which take place during the combustion of plastics is shown in Figure. 2-1 [4].

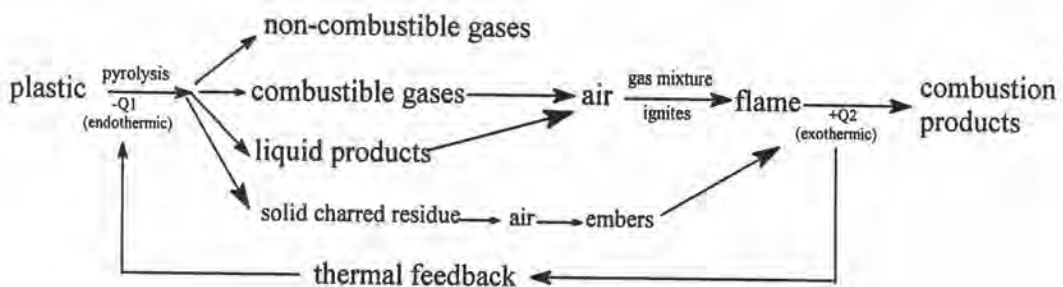


Figure 2-1 The combustion process.

There are 3 necessary states to initiate the actual combustion process of the polymer.

1. Heating

As a material is exposed to a fire and its temperature rises, several phenomena may occur. In thermoplastics, the polymer chain acquires vibration energy, with the bonds becoming more active until the solid becomes a highly viscous liquid. This change occurs at the glass-

transition temperature. As the polymer is heated still further, the vibrationally excited bonds begin to break.

The solid plastics is heated by thermal “feedback” or by an external heat sources. In this initial phase thermoplastics tend to soften or melt and start to flow. Thermosetting plastics have a cross-linked molecular structure which prevents softening or melting. If further supply energy, polymer must decompose before vaporizing.

2. Decomposition

Decomposition is an endothermic process. As the individual plastics differ in structure, their decomposition temperature ranges vary within certain limits. Table 2-1 gives the range of decomposition temperatures (Td) for some plastics, and for the natural products, cellulose.

Table 2-1 Decomposition temperature of some plastics and cellulose [5].

Plastic	Td (°C)
Polyethylene	340 - 440
Polypropylene	320 - 400
Polystyrene	300 - 400
Polyvinyl chloride	200 - 300
Polytetrafluoroethylene	500 - 550
Polymethyl methacrylate	180 - 280
Polyacrylonitrile	250 - 300
Polyamide 6	300 - 350
Polyamide 66	320 - 400
Cellulose	280 - 380

Various decomposition products depending on the constitution of the polymer :

- (a) Almost gaseous products are formed; for instance the depolymerization of polymethyl methacrylate results in the formation of over 90 % monomer and the degradation of polyethylene leads to the formation of saturated and unstaturated hydrocarbons.
- (b) Gaseous products and carbonaceous residues are formed; for instance in the pyrolysis of poly (vinyl chloride) hydrogen polyene sequence forms aliphatics and aromatics in a second step. These escape as gaseous products or remain as solid carbonaceous residues as a result of crosslinking reactions.
- (c) Almost carbonaceous residues are formed; for example in the case of polyacrylonitrile or high temperature resistant plastics such as polyamides.

3. Ignition

The flammable gases formed by pyrolysis mixture with atmospheric oxygen, reach the lower ignition limit and are either ignited by an external flame or, if the temperature is sufficiently high, self-ignite. The flash-ignition and self-ignition temperatures of various polymers given in Table 2-2 [5,6].

Table 2-2 Flash-ignition and self-ignition temperatures of various plastics by ASTM D 1929.

Plastic/natural product	Flash-ignition temp. (°C)	Self-ignition temp. (°C)
Polyethylene	340	350
Polypropylene	320	350
Polystyrene	350	490
Poly (vinyl chloride)	390	450
Polytetrafluoroethylene	560	580
ABS	390	480
Polymethyl methacrylate	300	430
Polyacrylonitrile	480	560
Polyamide 6	420	450
Polyamide 66	490	530
Polyurethane (rigid foam)	310	415
Cotton	210	400

Ignition depends on numerous variables such as oxygen availability, temperature and the physical and chemical properties of the polymer. The reaction of the combustible gases with oxygen is exothermic and, if sufficient energy is available, overrides the endothermic pyrolytic reaction and initiates flame spread. The last state continue from heating, decomposition and ignition is flame spread.

4. Flame spread

A phenomenological description of flame spread along a polymer surface is given in Figure 2-2. The diffusion flame advances over the decomposed polymer surface.

The other factors which determines the extent of flame spread is the heat of combustion of the polymer.

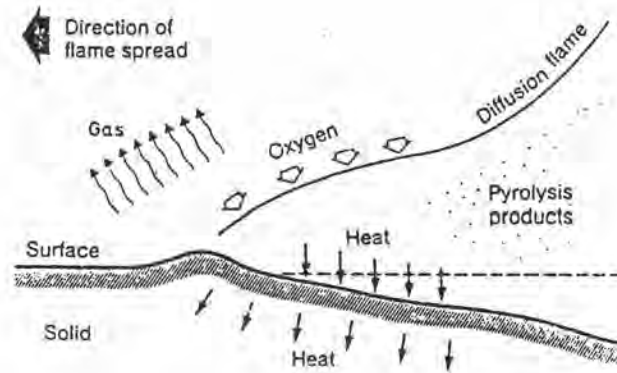


Figure 2-2 Schematic of flame spread [7].

2.1.2 Flame retarded mechanism

Flame retarded mechanism of the flame retardant in polymer systems could be grouped into the following three categories :

1. Vapor-Phase Mechanism

In the vapor-phase mechanism, the flame retardants or the modified polymer unit, on heat exposure, release a chemical agent which can remove free-radical intermediates or which can replace the major propagating species. Flame retardation could be implemented by incorporating flame-retardant additives, impregnation the material with a flame-retardant substance, or using flame-retardant comonomers in the polymerization or grafting. Halogenated flame-retardants have been commonly used in flame-retarding plastics. They are postulated to

function by a vapor-phase flame inhibition mechanism which characterized by following criteria :

- Flame-retardant element is lost from the substrate.
- Flame inhibition is insensitive to substrate structure.
- Flame retardant is sensitive to oxidant (e.g., O₂ or N₂O).
- Flame retardant does not change the composition or amount of volatile.

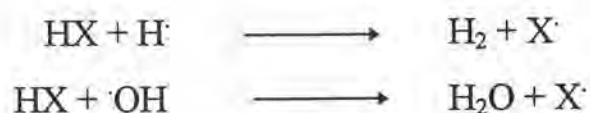
Halogen-containing flame retardants act by interfering with the radical chain mechanism taking place in the vapor phase. The high-energy HO[·] and H[·] radicals formed by combustible gases are removed by the halogen-containing flame retardant. At first the flame retardant breaks down to radicals, where X is Cl or Br.



The halogen radical X[·] reacts by hydrogen abstraction from the substrate RH to form hydrogen halide.



It interferes with the radical chain mechanism by reaction with the high-energy H[·] and OH[·] radicals and by replacing them with X[·] radicals of lower energy. The actual flame retardant effect is thus produced by HX.



2. Condensed-Phase Mechanism

The flame retardant that function by this mechanism have the ability to increase the conversion of polymeric materials to a char residue during heat exposure. The char formed protects the substrate by interfering with the access of oxygen and act as a heat shield for base material.

Phosphorus-containing flame retardant influence mainly the reactions taking place in the condensed phase. They are particularly effective in materials with high oxygen content, such as oxygen-containing plastics as well as cellulose and its derivatives. Many of the phosphorus compounds are liquid and possess plasticizing properties.

The following are the indicators of a condensed-phase operation for a flame retardant :

- Flame-retardant results in enhanced char formation.
- Flame-retardant elements is retained in the substrate.
- Flame-retardant elements is often ineffective in the vapor phase.
- Flame-retardant is sensitive to the substrate structure.
- Flame-retardant is sensitive to oxidant (e.g., O₂ or N₂O).
- Flame-retardant changes the composition of volatiles.

3. Miscellaneous Mechanism

Apart from vapor-phase and condensed-phase mechanisms, flame retardant could also function in a number of other ways. The followings are some other alternative model of flame inhibition :

- Large volumes of noncombustible gases produced which can dilute oxygen supply to flame and/or dilute the fuel concentration.
- The flame retardant may act as a thermal sink to increase the heat capacity of the combustion system or to reduce the fuel content to a level below the lower limit of flammability.
- The endothermic decomposition of the flame retardant could lower the polymer surface temperature and retard pyrolysis of the polymer.

2.1.3 Synergism

The effect of a mixture of two or more flame retardant may be additive, synergistic, or antagonistic. Synergism is the case in which the effect of two or more components taken together than the sum of their individual effects. The concept of synergism is very important, since the development of synergistically efficient flame retardant 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 trioxide to halogen containing polymers.

Antimony trioxide shows no perceptible flame retardant action on its own. However, it produces a marked synergistic effect with halogen containing compounds. The most important reactions take place in the gas phase. They are the result of an effect on the radical chain mechanism. Antimony trioxide reacts with hydrogen chloride and forms antimony trichloride and various antimony oxychlorides, which act as radical interceptors like HCl or HBr. Antimony trichloride is formed via

the intermediate SbOCl which is actually the effective agent. Antimony trioxide and hydrogen chloride first yield SbOCl and other oxychlorides, which give off antimony trichloride over a relatively wide temperature range [8].

2.1.4 Flame retardant materials

There is general agreement that plastics cannot be made fireproof. Plastics are organic-based materials and will burn under the proper conditions. However, the susceptibility to fire can be reduced, and the spread of flame can be decreased by the incorporation of additives. The flame retardant help reduce the ignition of the plastic and the rate of flame propagation.

An ideal flame retardant should be :

1. retard flame effectively and efficiently.
2. withstand ordinary processing temperature.
3. non-toxic.
4. compatible with plastics.
5. no bleeding.
6. no effect on properties.
7. not corrosive.
8. low smoke and low cost.

2.1.5 Flame retardants in polymer

2.1.5.1 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.

- Bromine-containing flame retardants

Bromine can be bound aliphatically or aromatically in flame retardants. The more effective aliphatic brominated compounds are easier to break down and hence are less temperature resistant than aromatic flame retardants. Their suitability depends on the plastic and the method of incorporation.

Flame retardants with aromatically bound bromine have the highest market share [3]. They can be subdivided into several classes on the following types of chemical structures:

- compounds with two benzene rings.
- tetrabromophthalic acid and derivatives.
- oligomeric and polymeric flame retardants.

- Chlorine-containing flame retardants

Chlorinated flame retardants are used in plastics mainly in the form of chlorinated hydrocarbons or chlorinated cycloaliphatics. They are low cost and offer good light stability. To achieve the required flame retardancy, however, formulations with high amounts of the respective flame retardant are necessary. This can adversely affect the properties of the polymer.

2.1.5.2 Phosphorus-containing flame retardants

Phosphorus-containing flame retardants influence mainly the reactions taking place in the condensed phase. They are particularly effective in materials with high oxygen content, such as cellulose.

2.1.5.3 Inorganic flame retardants

Few inorganic compounds are suitable for use as flame retardants in plastics, since such compounds are usually too inert to be effective in

the range of decomposition temperatures of plastics, between 150 and 400 °C.

Apart from antimony trioxide, which interferes with the combustion process chemically in combination with halogen-containing flame retardants, the most widely used inorganic flame retardants such as aluminum hydroxide and boron-containing compounds affect the combustion process by physical means. Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat ; rather they decompose, giving off nonflammable gases such as water or carbon dioxide, which dilute the mixture of flammable pyrolysis gases and shield the surface of the polymer against oxygen attack and thermal feed-back.

2.2 Literature review

J.G. Uhlmann, J.D. Oelberg, K.D. Sikkema, and R.G. Nelb [9] reported a systematic approach to gain a fundamental understanding of how the properties of flame retardants affect those of the final ignition-resistant ABS compound. Evaluation of nine flame retardants, selected on the basis of their cost, molecular structure, and property data developed for the final compounds. Properties of the final compound that were considered included morphology (measured via transmission electron microscopy, TEM), mechanical properties (izod impact strength, tensile strength, flexural strength), thermal properties (Vicat), rheology (melt flow rate) and flammability (UL 94).

L. Ojog, D. Panaitescu [10] was studied that the using of a programmed experimental system (ternary cubic programme) for the flammability and impact properties of ABS/PVC blends. The triangular diagrams were analysed and the optimum PVC/antimony oxide ratio was established. The models were applied to the selection of concentrations of ABS, PVC and antimony oxide which led to compositions with optimal impact strength and fireproof properties.

R.L. Markezich, R.F. Mundhenke [11] reported the flame retardation of ABS using chlorinated flame retardants. It was shown that using the smaller particle size flame retardant improves the notched izod impact strength of ABS. The improved UV stability, increased heat distortion temperature, high thermal stability and non-blooming nature of the flame-retarded ABS were considered.

Some of the additives used in plastics formulations, such as flame retardants, synergists, fillers and pigments, can have a detrimental effect on the impact resistance of the material. Impact modifiers can sometimes be used to correct for the detrimental effects of these additives by boosting the impact performance of the material.

Janis C. Stevenson [12] found that impact modifiers provide a boost to the impact resistance of plastics. They can often be used to help correct the detrimental effects of other additives on the impact resistance of a formulation. Impact modifier improves the impact resistance of a plastic by facilitating the ability of the polymer matrix to shear yield and / or craze.

Antimony oxide and antimony synergists are well known to producers of flame retarded plastics. Most formulations require relatively minor amounts of these synergists, yet they have a major impact on the flammability of the base resin.

Irv Touval [13] presented that not all antimony synergists behave the same. Particle size plays an important role with antimony oxide. Its efficiency in the oxygen index test is inverse to its particle size. The larger the particle size the less the flame retardant efficiency and very large particles are more detrimental to impact strength than small particles.

In case of high impact polystyrene, not much study on the flame retardancy has been reported. This research work has thus designed to achieve the acceptable HIPS with a flame-retardant.