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Research Note

Fire Retardation of Polymers

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In this paper, an overview of fire retardants along with discussion about their types is presented. Retardation effects of three additive flame retardants, magnesium hydroxide, aluminium hydroxide and antimony trioxide, were examined in a cone calorimeter. Results demonstrate that $Mg(OH)_2$ reduces heat release rate, CO formation and smoke density and increases ignition time; Sb_2O_3 and $Al(OH)_3$ also exhibited the same trend.

INTRODUCTION

During the past twenty years, there has been a steady growth in the use of synthetic polymers as materials for the construction industry, packaging, upholstery and transport applications, areas where the behavior of materials under fire conditions is crucial to personal safety [1]. For these reasons, most polymeric materials need to become flame retarded, which is achieved through the addition of chemical substances to the polymer that will suppress, reduce or delay the propagation of flame through the mass or surface of the polymers. Flame retardants are not like other additives, which enhance the physical properties, aid processing or increase the service life of a plastic. In contrast, flame retardants tend to degrade the host polymer, causing processing problems and their inclusion in the formulation can shorten the useful life of the product. The use of flame retardant is, therefore, a compromise achieving fire retardancy at the expense of other properties [2]. The use of flame retardants is influenced by a number of regulatory groups, including building codes, independent certifiers, insurance underwriters and military. Without these regulatory actions and mandatory standards, flame retardant chemicals probably would not be used to any appreciable extent. As in the case of some developing countries where building codes and state law do not require fire standards and therefore, fire retardant is an unknown subject in their polymer industry. In this report, an overview of the fire retardant chemicals is provided and their characteristics are discussed. The types of flame retardants used for different types of polymers will be reviewed. The retardation effects of three additive flame retardants are examined on polyethylene utilizing ASTM 1354-90 heat release rate.

TYPE AND SELECTION OF FLAME RETARDANTS

Two types of flame retardants are known, additive and reactive. A reactive fire retardant is directly incorporated into the chemical structure of the polymer. Examples include various halides. They operate through releasing halide compounds during combustion process, which act as combustion inhibitors, through combining with the free radicals. Without these free radicals, combustion chain reaction will terminate [3].

$$\mathrm{HCl} + \mathrm{OH}^- \longrightarrow \mathrm{H2O} + \mathrm{Cl}^-$$

$$\mathrm{Cl}^- + \mathrm{H}^+ \longrightarrow \mathrm{HCl}\ .$$

Additive fire retardants are physically mixed with the host polymer during the last stage of production. Examples include aluminium trihydrate, antimony oxide and magnesium hydroxide. These chemicals do not burn and implement fire resistance to the polymer. Some of these additives decompose endothermically during combustion to produce water according to the following reaction:

$$\mathrm{Mg(OH)_2} \rightarrow \mathrm{MgO} + \mathrm{H_2O} + 1301\ \mathrm{J/g},$$

when decomposition occurs around 30.9% of $Mg(OH)_2$ weight is released as water [4].

In Table 1, the USA market for flame retardants in 1991 is shown. Approximately 65% of the total FR (Fire Retardant) is used in plastics. Rubber accounts

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Table 1. Flame retardant market in 1991.

Fire Retardant	%
Plastics	65
Rubber	25
Textiles	5
Coatings/adhesives	3
Wood/paper	2

for about 25% of the total fire retardant, which is mostly alumina trihydrate, used in carpet underlay [2]. In Figure 1, the consumption of FR additives in several important thermoplastics is shown, requirement for PVC is the largest while engineering plastics such as PET and PBT account for a relatively small amount.

Among thermoset resins, the largest consumers of flame retardants are epoxy resins where the reactive tetrahydra tetrabromobisphenol A is used. Flexible and rigid polyurethane use chlorinated phosphate additives. Figure 2 demonstrates world consumption of flame retardants in 1991 among halogenated flame retardants, bromine compounds have the highest application. The following criteria should be considered when a flame retardant is being selected:

- Efficiency
- Reactive or additive
- Process stability
- Processability
- Compatibility
- Effect on properties
- Aging
- Smoke and combustion products
- Enviromental effects
- Cost

Efficiency is the most important parameter; with higher FR efficiency, a smaller amount will be needed, resulting in fewer side effects.

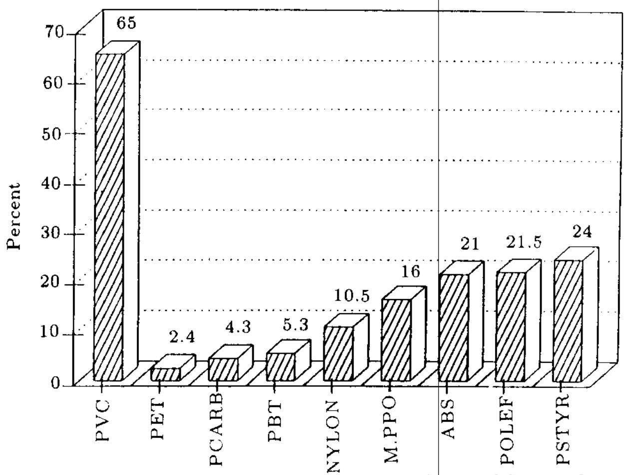

Figure 1. Consumption of flame retardant additives by thermoplastics type.

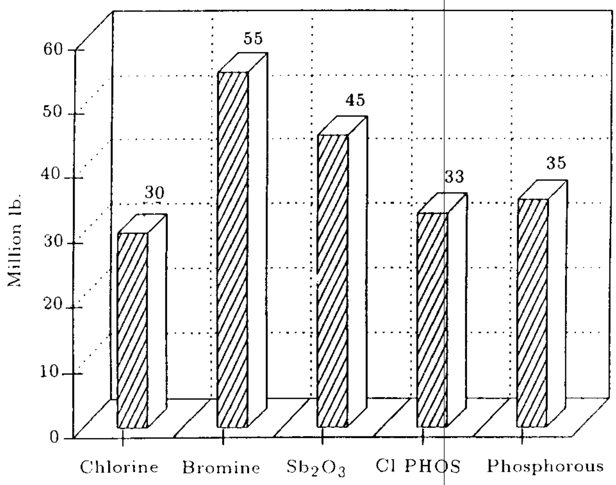

Figure 2. World consumption of flame retardants (1991).

EXPERIMENTAL

Rate of heat release is determined in a cone calorimeter with horizontal specimens. The data for sample size 100 × 100 mm was obtained at constant heat flux level of 50 kW/m^2. Besides HRR data, ignition time, CO concentration, mass loss rate and smoke density were also determined. (Full experimental methods are given elsewhere [5].) Materials used here had the following specifications; polyethylene was low density, LFO-075, magnesium hydroxide, alominium hydroxide and antimony trioxide were supplied by Merk in powder form with mesh size below 60 and purity over 99 percent.

EXPERIMENTAL RESULTS

A case study is considered on the retardation effects of the three most important additive fire retardants, namely $Mg(OH)_2$, $AL(OH)_3$ and Sb_2O_3 with polyethylene. Polyethylene is the major component of a wide variety of plastic cables including power cables, signal control cables and special general purpose cables. To develop a cable flammability criteria for classification of cables, three types of tests are recommended: 1)Ignitabion, 2)Fire propagation (using external heat flux) and 3)Large scale validation. In this work, the results of ignition and heat release rate tests are reported. In order to reduce electrical fire risks, thermal behavior and stability of PE is improved by the addition of fire retardants.

When considering the fire characteristics of a material via cone calorimetry, the selected heat flux to which samples should be exposed has a very important role (for details see [6]). In this study, a fixed irradiance of 50 kW/m^2 was used, which represents a medium strength fire at pre-flashover stage.

In Figure 3, the influence of three different additive flame retardants on the ignition of PE is compared. The highest ignition time is obtained with $Mg(OH)_2$. With the increase of $Mg(OH)_2$, ignition time increases up to 120 sec. $Al(OH)_3$ shows an adverse effect compared to PE. Sb_2O_3 is normally used in small quantities as a synergist accompanying other fire retardants. Addition of 10 percent Sb_2O_3 increases the burning time by 50 percent. Maximum rate of heat release is the most important parameter in assessing construction materials. It is an indication of the rate of fire growth and the time taken for fire to spread to other parts of a building. From a life safety point of view, the rate of heat release is a measure of the available egress time for the occupants.

In Figure 4, the maximum heat release rate for pure and fire retarded PE is compared. It can be seen that the addition of Sb_2O_3 has little influence on this parameter. However, $Mg(OH)_2$ and $Al(OH)_3$ both reduce the heat release rate. When the amount of these additives is 60 percent and above, this effect is more significant. After the ignition of each sample, fire propagates on the surface, generating heat, smoke and other gases. Smoke and gases generated by fire reduce visibility and can be toxic.

Generation of CO is the major cause of death in fires [7]. In order to determine the smoke density and gas toxicity, the effluent gases were directed through a laser smoke measurement system and a gas analyser. The results are shown in Table 2. It can be seen that $Mg(OH)_2$ and $Al(OH)_3$ both reduce CO formation, whereas Sb_2O_3 increases the CO concentration. A

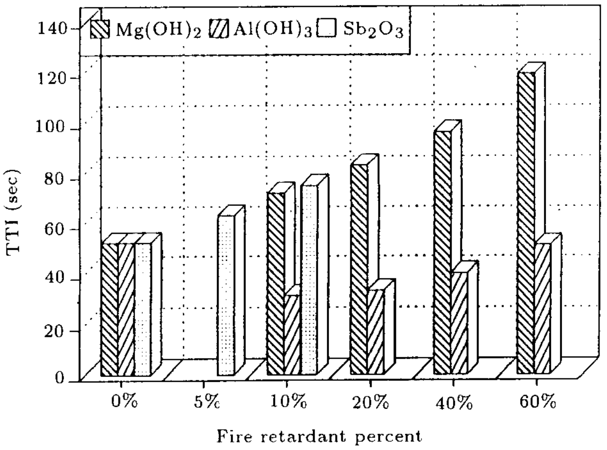

Figure 3. Comparison of the influence of various fire retardants on ignition of polyethylene.

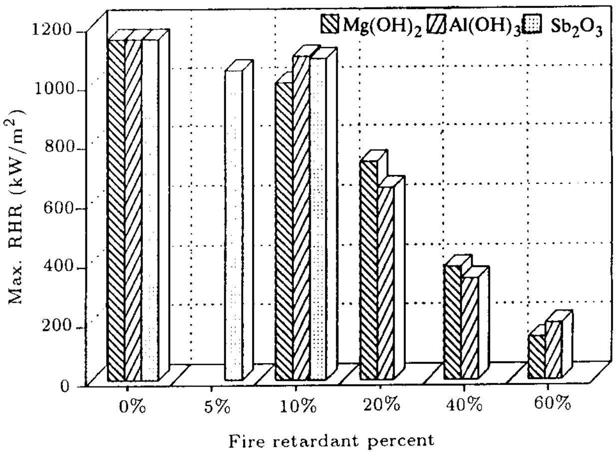

Figure 4. The maximum heat release rate of pure and fire retarded polyethylene.

Table 2. The most important fire parameters of polyethylene and its mixtures with fire retardants, obtained at incident radiation 50 kW/m^2.

Sample	1	2	3	4	5	6	7
PE	52	1152.9	493.1	363	0.020	40.8	45.1
PEMG10	72	1004.4	509.5	273.1	0.015	39.1	71.6
PEMG20	83	734.4	552.9	266.2	0.013	45.6	113
PEMG40	96	381.4	295	244.9	0.011	34.2	251.6
PEMG60	119	145.6	112	134	0.009	21.3	817.3
PEAL10	31	1093	530.6	318	0.017	41.8	28.4
PEAL20	33	648	482.5	318	0.015	41	51
PEAL40	40	343.3	259.7	241.7	0.011	32.8	116.5
PEAL60	51	191.8	126.2	150.2	0.009	17.4	266
PESB5	63	1045.5	448.3	419.9	0.018	41.1	60.3
PESB10	75	1085.7	593.6	462.3	0.026	45	69

1. Time to ignition (sec).
2. Maximum heat release rate (kW/m^2).
3. Average heat release rate three minutes after ignition (kW/m^2).
4. Specific extinction area three minutes after ignition.
5. CO mass ratio three minutes after ignition (kg/kg).
6. Effective heat of combustion (MJ/kg).
7. Ratio of time of ignition to peak heat release rate (m^{2}s^2/MJ).

similar influence is observed for smoke density. With $Mg(OH)_2$, smoke density is reduced, whereas with Sb_2O_3 smoke density increases. Magnesium hydroxide is found to be a suitable fire retardant in PE wire cable jackets, where corrosive gases and smoke are objectionable. This is believed to be due to its higher temperature of decomposition compared with $Al(OH)_3$ which is thermally unstable [8].

CONCLUSIONS

Studies on fire retardation characteristics of PE with three additive retardants demonstrated that $Mg(OH)_2$ reduces heat release rate, CO formation and smoke density, and increases ignition time. These trends were not observed in the case of Sb_2O_3 and $Al(OH)_3$. Magnesium hydroxide has a higher thermal stability and on decomposition at higher temperatures releases water. $Mg(OH)_2$ is, therefore, particularly suitable for electrical cables.

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