State-of-art study for the flame-retardancy

of polymeric materials with some experimental results

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State-of-art study for the flame-retardancy

of polymeric materials with some experimental results

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Contents

Summary

This study describes the basic mechanisms, which controls the flammability of polymeric materials. Based on these mechanisms, various measures reported in the literature to improve the flammability of polymer materials has also been summarized in this report.

The literature survey shows that there are numerous ways to improve the flammability of materials. The best and the cheapest ways are by adding suitable additives including both halogenated and halogen-free additives. The study reveals that in order to restrict the amount of additives to limited levels and also to avoid hazardous additives, it is essential to select flame-retardant (FR) additives, which functions as flame-retardants through different mechanisms. In order to obtain optimised formulations, it has been suggested that more than one fire-retarding mechanisms should be used. The amount of additives are restricted to minimum levels both in order keep the price of the final product at a reasonable level and also to avoid their influence on the physical and processing properties of the polymers.

In order to assure the flammability of polymers and optimise the polymer compositions with respect to FR-properties, the importance of testing methods has also been emphasised in this report. Since, effectivity of additives are very much dependent on the polymer types and their degradation mechanisms, the subjective tests based on different standard methods for different products are not enough according to the discussions presented in this report. This clearly suggests that fire-parameters such as oxygen index (OI), onset degradation temperatures for polymers, various thermal transition temperatures both for FR additives and polymers, degradation rate, activation energies for thermal degradation, char yield, peak heat release rate (HRR), emission products as a result of pyrolysis are very essential to measure. Beside these fire-relating properties, influence of these additives on the mechanical and the processing properties for the specific polymers are also very important to estimate.

In order to investigate how flame retardancy was obtained in a few commercially available polymer materials, such material samples were analysed in our laboratory and the results are summarized in this report. For our evaluation we selected one sample on expanded polystyrene (EPS), one sample of electrical contact based on polyolefin and one sample of furniture stuffing material based on Neoprene. The analytical results show that in all the cases only thermal stabilization mechanism has been used and also the additive effects on thermal stabilization of the materials are very marginal, which really raises the question on the usefulness of these additives as FR additives although they fulfil the FR requirement according to material standards.

Based on these findings, proposals for future developmental work, to solve the environmental problems associated with the use of halogenated FR additives have been presented in this report. It has been proposed that our first measure should be to replace the brominated FR belonging to polybromobiphenyl (PBB), polybromodiphenylethers (PBDE) and tetrabromobisphenol-A (TBBA) groups as discussed in this report. Further, we should try to minimise the concentration of alternative FRs by incorporating other FR-mechanisms proposed in this report. These developmental efforts should also be complemented with the evaluation of other FR additive systems as proposed in this report.

Detta projekt genomfördes för att ta reda på hur brandegenskaperna för några vanliga polymerer kan påverkas med och utan tillsatser. Kunskap om detta kan visa på vägar att förbättra dessa egenskaper.

Sammanfattning

Studien beskriver viktiga parametrar som påverkar brännbarheten hos polymeriska material. Olika metoder för att förbättra brandegenskaper för dessa material har summerats.

Litteraturöversikten visar att där finns ett antal sätt att förbättra brandegenskaperna.

För att klara brandkrav och optimera polymerens egenskaper diskuteras olika testmetoder. Eftersom effekten av flamskyddsmedlen är beroende av de olika typerna av polymerer och deras nedbrytning bör detta beaktas vid val av testmetoder. Utöver dessa brandrelaterade egenskaper måste tillsatsernas inverkan på själva polymerens egenskaper bedömas.

För att undersöka hur flamskyddet åstadkoms har ett par kommersiella polymerer använts. Det var expanderad polystyren, polyolefin från en elektrisk kontakt och stoppningsmaterial baserat på neopren. Analysresultat visar att additiven bara används för att påverka den termiska stabiliteten och effekten bedöms som marginell. Nyttan och användbarheten av dessa

additiver kan därför ifrågasättas även om materialet klarar de krav som ställs vid brandtester.

Som resultat av studien föreslås fortsatt utvecklingsarbete. En inriktning bör vara att minska koncentrationen av flamskyddsmedel genom att också utnyttja andra flamskyddsmekanismer. I första hand föreslås arbete för att ersätta bromerade flamskyddsmedel som hör till grupperna PBB, PBDE och TBBA.

1 Flame retardant mechanisms

Almost all polymeric materials are comprised of organic materials. The major shortcoming of polymeric materials is their burning characteristics. The flammability of some polymers is higher than wood and natural fibres. The calorific values for same common polymers such as polyethylene, polypropylene, polystyrene, and polymethylmethacrylate are 46000-27000 kJ/kg, whereas this value for wood is 19000 kJ/Kg. In addition, smoke and soot formation, droplets and emission of highly toxic products accompany the combustion of some polymer materials depending on the polymer type. Thus, the wide application of polymer material makes it necessary to develop fire-retarded materials. An important and cheapest way to obtain flame-retarded materials is to add suitable types of fire-retardant additives. The activities of such additives as flame retardants are very much dependent on the mechanisms in which they interact with the material and thereby reduce the flammability of the materials. Burning process for the polymers can schematically be shown as in fig 1 below:

Figure 1
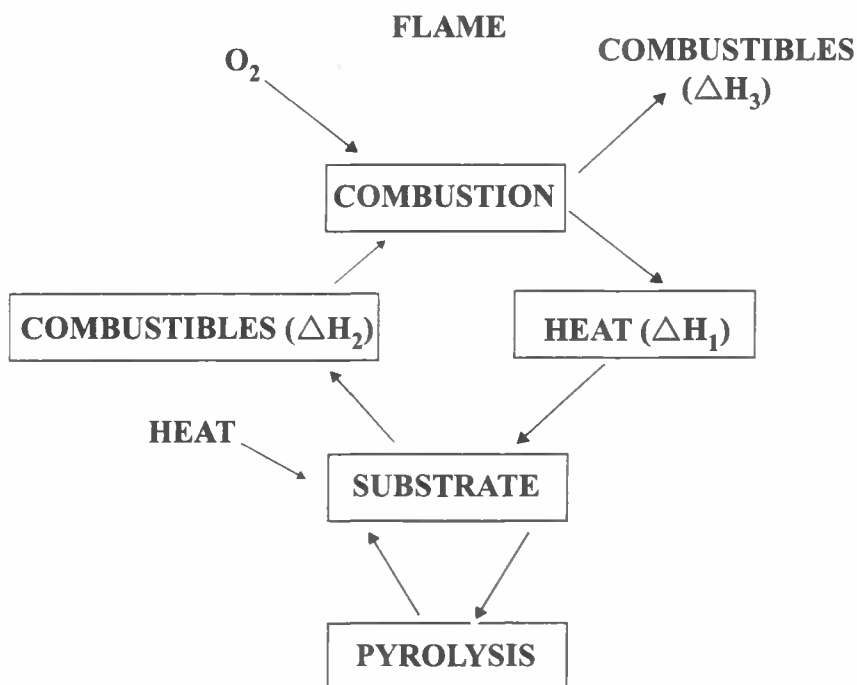
Here DH represents heat of enthalpy generated as a result of combustion

As evident from the figure, heat is generated under fire conditions. This results into pyrolysis of the polymeric materials forming combustible gases. These combustible gases in presence of oxygen create flame and smoke. Since combustion is an exothermic process, it generates more heat resulting into more pyrolysis of the materials and thereby supplying more fuel for the fire. This means that as soon as the material starts burning, the flame reactions just accentuates and it is difficult to stop the flaming process.

The above process sequence suggests that in order to reduce the flammability of materials, following measures are required:

1   Increase the thermal stability of materials.
2   Increase the amount of char formation.
3   Decrease the diffusion of combustible gases from the material, formed as a result of pyrolysis, to the flame.
4   Reduce the amount of heat generated as a result of fire.
5   Insulate the material surface in order to reduce transfer of heat from the fire to the material.
6   The materials generate inert gases as a result of combustion.

This suggests that in order to control the flammability of materials under fire situation, it is essential to control both the condensed-phase reactions in the polymer and the gas-phase reactions in the volatile phase under fire conditions. Condensed-phase reactions in the polymer mainly involve changes of the pyrolytic path of the polymer, which reduces formation of gaseous combustibles. Formation of lower amounts of combustible gases under fire conditions results into less generation of heat and thereby reduces flammability.

The general strategies, reported in the literature, to prepare thermally stable materials with inherently low flammability are to introduce following in the structure:

1   Incorporation of halogen or phosphorus.
2   Increasing the C to H ratio.
3   Increasing the nitrogen content.
4   Incorporation of conjugation either through aromatic or heteroaromatic ring systems.
5   Incorporation of rigid structure such as semi-ladder or ladder polymers.
6   Incorporation of strong interactions between polymer chains.
7   Incorporation of high degree of crystallinity or cross-linking.

As mentioned above, flame retardancy of the materials can also be improved if the extent of charring for the materials could be increased under fire conditions. This, in turn, reduces the amount of combustibles formed under fire conditions. In the sections below, basic reactions occurring in the gas-phase and the condensed-phase and different factors affecting such reactions will be described very briefly.

11

1.1 Gas-phase reactions

So far the gas-phase reactions are concerned, all polymeric materials undergo pyrolysis forming combustible gases. These gases are capable of forming hydrogen and hydroxyl radicals, which in turn, may react with oxygen as below:

$$H\cdot + O_2 \rightarrow OH\cdot + O\cdot \qquad (1)$$

$$O\cdot + H_2 \rightarrow OH\cdot + H\cdot \qquad (2)$$

The main exothermic reaction in the flame comprise of:

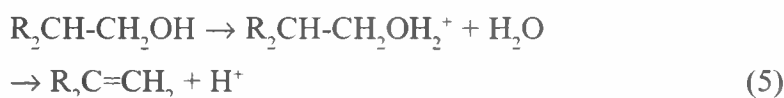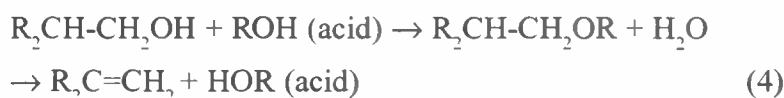$$OH\cdot + CO \rightarrow CO_2 + H\cdot \qquad (3)$$

In order to slow down or stop combustion, it is essential to stop these reactions.

1.2 Condensed-phase reactions

Such reactions have been shown to include interaction between the FR and the polymer and occur at temperatures lower than the decomposition temperature of the polymers. Condensed-phase reactions generally comprise of dehydration and cross-linking.

Dehydration is used very frequently in flame retardancy and several ways to achieve such phenomena are reported in the literature. Dehydration may result due to chemical reaction of the hydroxyl groups present in the polymer chains. This occurs for cellulosics in the presence of phosphorus and sulfur derivatives. It has been reported in the literature, that in cases where hydroxyl groups are not present in the polymer backbone, the effectivity of such additives are very low. For example, phosphorus and sulfur additives are effective at very low concentrations ($\gg 2\%$) for cellulosics whereas for polyolefins concentrations in the range of 5-15% of P are required.

Two alternative mechanisms have been suggested for the dehydration reaction of cellulosics with acid forming P and S derivatives and both mechanisms lead to char formation. These reactions can be represented as below:

$$R_2CH\text{-}CH_2OH + ROH \text{ (acid)} \rightarrow R_2CH\text{-}CH_2OR + H_2O$$

$$\rightarrow R_2C{=}CH_2 + HOR \text{ (acid)} \qquad (4)$$

$$R_2CH\text{-}CH_2OH \rightarrow R_2CH\text{-}CH_2OH_2^+ + H_2O$$

$$\rightarrow R_2C{=}CH_2 + H^+ \qquad (5)$$

Reaction (4) involves esterification followed by ester decomposition whereas reaction (5) involves formation of carbonium ion followed by its decomposition. Sulfur derivatives follow the latter mechanism.

Cross linking reactions have also been shown, in general, to enhance the fire retardancy of the materials. This is because latter reactions promote stabilization of polymers and thereby result into increased char formation. Cross linking has also been shown to increase the melt-viscosity of the polymers and thereby lowering the rate of transport of the combustible gases as a result of pyrolysis. Influence of cross linking on the flame retardancy of cellulosics, PS and polyesters has been reported in the literature.

1.3 Physical effects

Physical effects such as "dilution effects", "heat sink effects" and endothermic transitions in the additives have been used to obtain flame retardancy of polymers. Dilution effects involve dilutions of the organic part of the structure and dividing it into small-insulated domains. This means that on pyrolysis, larger amounts of heat are required to reach pyrolysis temperature; therefore less combustible gases are formed thereby generating less heat. The latter effect is also referred to as "heat sink effect". Thus additives having high specific heats and low thermal conductivities exhibit enhanced flame retardancy. Also the endothermic decompositions of additives have been used to reduce the flammability of materials.

Another physical effect, which has been used in flame retardancy is through the formation of impermeable skin of glass or char that hinders the passage of the combustible gases from the pyrolysing polymer to the flame front and at the same time act as an insulating layer for the transfer of heat from the flame to the polymer surface. The latter helps to reduce the pyrolysis of polymers and thereby decreases the formation of combustible fuel gases.

The only limitation in obtaining fire retardancy by physical effects is that relatively large amounts of additives (50-65%) are required. Addition of such large amounts of additives may have a substantial influence on the mechanical and processing parameters of the polymers.

In the case of additives functioning based on physical effects, it has been shown that particle size- surface area plays an important role because they influence greatly the melt flow of the polymer and also the crystal size of the additive. Factors such as dispersibility and the "surface free energy" of such additives have also a great influence on their affectivity as flame retarding agents. Good dispersibilty helps a uniform distribution of the additive in the polymer matrix whereas "surface free energy" determines their reactivities with the acidic groups in polymers, which might produce cross linking and reduce melt flow, as well as with acidic groups in air, i.e. CO_2 or acid rain, which might cause the "chalking effect" and decrease flame retardancy.

In a patent, it has been shown that addition of a few metallic catalysts to endothermic additives improves the flame retarding properties of such additives by increasing the char behaviour and OI-values for the polymers. However, nickel (III) oxide and metal acetylacetonates have been showed to give negative results. Similarly co-precipitation of transition metals with magnesium hydroxides as solid solutions have also been shown to enhance the affectivity. This was assumed to be due to the facilitation and lowering of the dehydration temperature of the additive, dehydrogenation of polymer, increase of carbonisation and improvement of acid resistance. The mechanisms of the catalytic and the antagonistic activities of the metallic compounds are not yet well understood.

1.4 Intumescent systems

In intumescent systems suitable combinations of additives are used which undergoes a series of chemical and physical processes under fire situations and thereby reduces the flammability of the materials.

Flame retardancy by intumescence is also considered to be a special case of a condensed phase mechanism. In these cases also the amount of fuel produced is greatly diminished and instead char is formed. This intumescent char functions as a two-way

barrier i.e. hinders passage of combustible gases and molten polymer to the flame and shield material from the heat of flame. Basic mechanisms and a few examples on such systems will be considered later in this report.

Based on these basic mechanisms, all the additives reported in the literature and which have been used to reduce the flammability of polymeric materials, can be classified in the following general groups as shown below in fig 2:

Figure 2

PRIMAR

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┌──────────────┐              ┌──────────────┐        ┌──────────────┐
│ CHEMICAL     │              │ PHOSPHORUS   │        │ HALOGEN      │
│ ACTIVITY     │              └──────────────┘        └──────────────┘
└──────────────┘                  ↓  ↑                    ↓   ↑

         SYNERGISTIC                                  ┌──────────────┐
         ──────────────                   ↑           │ ANTIMONY     │
                                                      └──────────────┘
                                                            ↑

┌──────────────┐                              ┌────────────────────────┐
│ PHYSICAL     │     ADJUNCTIV                │ ALUMINA TRIHYDRATE      │
│ ACTIVITY     │                              │ BORON COMPOUNDS         │
└──────────────┘                              │ SILICATES               │
                                              │ CARBONATES              │
                                              └────────────────────────┘
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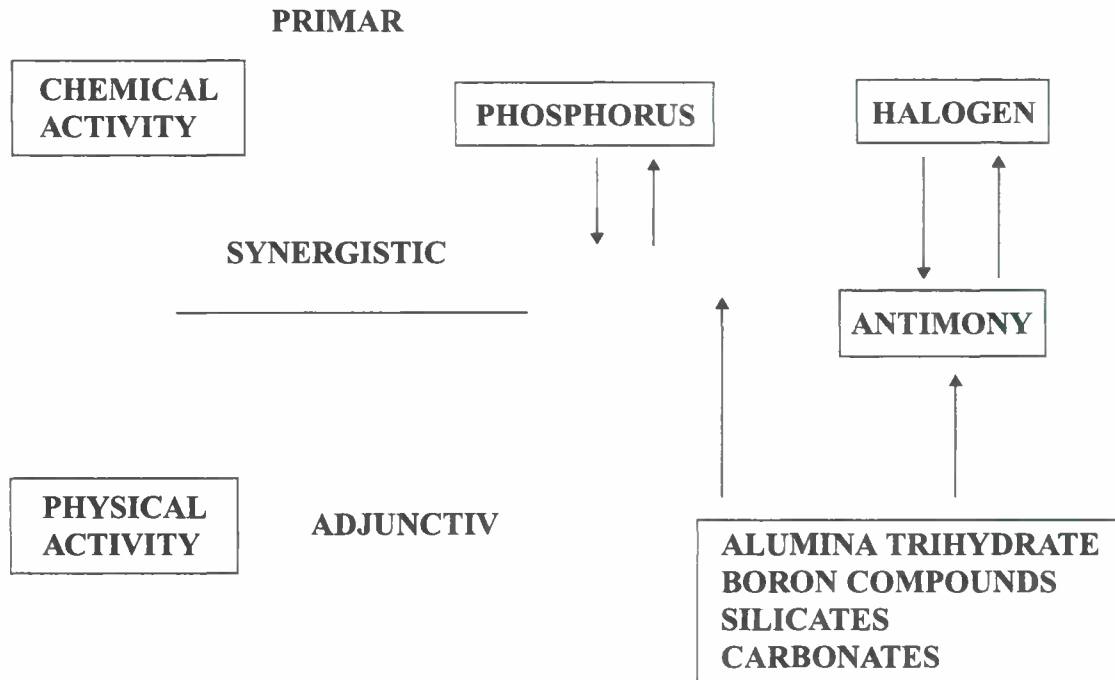
Examples of different flame retardant additives and how they function will be discussed later in this report. An ideal flame retardant for a polymer should be easily incorporated into the polymer, be compatible with the plastic, and not alter its mechanical properties. It should be colourless; exhibit good light stability, and have resistance to ageing and hydrolysis. In the selection of flame-retardants, it is essential to match the decomposition temperature of the FR with the polymer. In general, the effect of FR must begin below the decomposition temperature of the polymer and continue over the whole range of its decomposition.

2 Testing methods for the evaluation of flammability of materials

Testing methods used to evaluate the flammability of the materials have been reviewed earlier in the literature, where both the full scale and the bench scale test methods have been described. Full-scale methods of interest were mainly based on the oxygen consumption principle. According to this principle a definite amount of heat (J) is generated for a fixed number of oxygen removed from the exhaust.

It has been showed that for most combustible materials including polymers, 13.1 MJ of heat is released for each kg of oxygen consumed from the air with a deviation of ±5% from this value. It was also showed that the material does not need to burn fully for the above relation to hold. The above value holds very well for all hydrocarbons with only a very few exceptions where materials contain significant fractions of O, N, Cl, Br, F or S. Detailed values of this constant for many combustibles have been reported elsewhere in the literature.

Since, testing methods are essential from the point of view of quality control assurance in manufacturing and for the product development, it is necessary to develop bench-scale test methods which are not only simple to run, but also could predict the full-scale performance of the materials. Such bench-scale test methods are necessary to determine the following fire related properties of the materials:

1) Ignition

2) Flame spread

3) Rates of heat release and production of smoke, toxic gases and corrosive products

So far ignition is concerned, it is of interest to determine ignition of materials as a result of external source of heat or fire. ISO 5657 describes a radiant exposure ignitability test for specimens in a horizontal orientation. Such tests can also be performed in Cone Calorimeter and LIFT (Lateral Ignition and Flame Spread Test) apparatus, which will be described later. LIFT apparatus tests specimens are oriented vertically, while the Cone Calorimeter is used for testing in either orientation. Since radiant ignitability is only a small component of the fire development process, no efforts have been made to provide direct large-scale validation for the bench-scale data.

Since in a fire process, materials gets progressively involved as a result of gradual spreading of flame, it is important to determine the fire spreading behaviour of materials. Such test methods have been described in ASTM and ISO standards E 1321 and DP 5658 respectively and the test apparatus used is named LIFT. In this case also validation of LIFT apparatus data against large-scale data is not available.

Another method of interest to evaluate the flammability of polymeric materials is oxygen index (OI) method. According to this method a vertically clamped polymer sample is burned in a stream of oxygen and nitrogen. The strip is ignited at the top. OI is the volume percentage of oxygen at which the material no longer self-extinguishes. In general, higher the OI-value better is the flame retardation. For example, for carbon, which is considered to be non-flammable, the OI is 60%.

In electronic industry, the flammability of materials is determined according to Glow-wire test described in IEC 695-2-1, 1994. According to this method a glow-wire

comprising of a specific loop of Ni/Cr (80/20) wire is heated to 960°C and horizontally contacted with the specimen at a force of 0.8 to 1.2 N. The contact is maintained until the glow-wire or the specimen moves horizontally towards one another over a distance of at least 7 mm. The specimen is considered to pass the test if following of the two conditions are fulfilled:

1 There is no flame or glowing.

2 If flames or glowing extinguishes within 30s after removal of the glow-wire.

Cone Calorimeters have been developed to determine all the necessary fire properties of materials and the test methods have been described in ASTM standards E 1354and STP 983 and ISO standard DIS 5660. The apparatus makes use of an electric heater in the form of a truncated cone where the heater is capable of being set to a wide variety of heating fluxes (0-100 kW/m^2). Basics and the technical features of Cone Calorimeter have been reported in several references.

The main features of Cone Calorimeter can be summarized as below:

1 Specimens can be both oriented horizontally and vertically.

2 All types of specimens can be tested.

3 Mass loss as a result of fire can be measured continuously.

4 Heater operation is controlled by a feedback loop.

5 A heat flux meter with in-built alignment fixture calibrates heat flux.

6 Heat release rate is calibrated using methane metered with mass flow container.

7 Smoke generated can also be measured using both laser-beam photometer and gravimetrically.

8 It is possible to analyse combustible gases such as CO, CO_2, H_2O, HCl.

In Cone Calorimeter measurements, Heat Release Rates (HRR) are reported in kW/m^2, smoke data in specific extinction area (m^2) generated per mass (kg) of specimen decomposed. The smoke data are expressed in m^2/kg. Efforts are being made to validate Cone Calorimeter data with full-scale tests data.

In recent report, very good correlations have been reported between the Cone Calorimeter data and other testing methods such as UL 1581 for several cable samples where the peak heat release rate (HRR) was compared with damage length.

Beside the above-mentioned measurements several other quantitative analytical techniques such as Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) have also been found very useful in the evaluation of fire retardancy. From DSC measurements, it was possible to determine the melting and decomposition temperatures of FR additives whereas TGA can be used to evaluate the FR efficiency of such additives by estimating the changes in the polymer decomposition temperatures, rate and activation energies for weight losses, extent of char formation etc.

In the development or evaluation of FR additives, the following testing strategy should be used:

1. Evaluate the transition temperatures of the FR additives using DSC.

2. Evaluate the thermal degradation behaviour of both the FR additive alone and in combination with polymers.

3. After the basic screening of different FR additives either alone or in combinations, perform Oxygen Index (OI) and Cone Calorimeter tests to obtain the fire-related properties.

4. After these screening evaluations, determine the mechanical and the processability properties of the interesting formulations.

In order to evaluate the fire retardancy efficiency of different additives and final material compositions, it is essential that parameters controlling flammability of materials are measured and compared and the evaluations are not based only on the subjective tests according to the various standard methods, which are applicable for different product groups. Quantitative measurements of controlling parameters are essential when more than one fire-retarding mechanisms are used in the designing of suitable FR compositions.

In the later part of this report, we shall demonstrate the application of one of the quantitative methods to evaluate the difference between a few fire-retarded and non fire-retarded commercially available material composition.

3 Flame retardant additives

3.1 Halogen based flame-retardants

Halogen based flame-retardants functions mainly through the gas-phase reactions. Halogen atom reacts with the fuel forming hydrogen halide. The latter is believed to function as flame inhibitor and consumes hydrogen and hydroxyl radicals as below:

$$H \cdot + HX = H_2 + X \cdot \qquad (6)$$

$$OH \cdot + HX = H_2O + X \cdot \qquad (7)$$

Reaction (6) was found to be twice as fast as (7) and has been shown to be the main inhibiting reaction. The inhibiting effect was shown to be dependent on the extents of reaction (6) and (1). This is because reaction (1) produces two free radicals for each H-atom consumed, whereas reaction (6) produces one halogen radical, which recombines to the relatively stable halogen molecule. The latter results into lower heat generation and thereby renders fire retardancy.

The flame retardant effectivity of halogens has been reported to be directly proportional to their atomic weights i.e.:

$$F : Cl : Br : I = 1.0 : 1.9 : 4.2 : 6.7$$

Because of higher effectivity of bromine compounds than chlorine compounds, they are used at lower concentrations. It has been shown that on a volumetric basis 13% bromine was found to be as effective as 22% chlorine. Iodine and fluorine compounds are not industrially interesting because the former is less stable and very expensive whereas the latter is very stable. For bromine compounds, their effectivity is also dependent on the type of bromine i.e. if the bromine is an aliphatic or an aromatic one. In general, aromatic bromine is much stable and volatile than the aliphatic ones therefore these compounds evaporate before they could decompose and thereby furnish halogen to the flame. Beside radical trap mechanism, flame retardancy is also affected by physical factors such as density and mass of the halogen, its heat capacity and its dilution of the combustible gases in the flame.

Following general rules are used in the selection of halogenated FR:

1 Effectivity/ cost.
2 Compounding ease.
3 Thermal stability. The decomposition temperature should be higher than the processing temperature of the polymers and lower than the decomposition and flash ignition of polymer.
4 Corrosivity.
5 Effect on physical properties of the materials.
6 Appearance e.g. colour and surface.
7 Permanency or compatibility i.e. plating out on mould surfaces and blooming on parts.
8 On pyrolysis of FR, HBr formation should be favoured in cases where polymers do not form H_2 on pyrolysis otherwise Br formation is favoured.
9 Toxicity and environmental safety.
10 Light stability.

11 Electrical properties e.g. dielectric strength, volume and surface
    resistivity, arc and track resistance.
12 Combustion products.

In general, halogen based systems are undesirable because it has been shown that aromatic halogenated fire retardants may give super toxic halogenated dibenzodioxines and dibenzofurans on heating.

3.1.1 Brominated flame retardants (FR)

Several types of brominated FR has been described in the literature which includes compounds belonging to families of diphenylether (DPE), Bisphenol-A (TBBA), tribromophenol (TBP) and phthalic anhydride. Use of such FR additives depends mainly on the type of polymers.

Copolymerizable fire retardants such as tribromostyrene and pentabromobenzyl acrylate for polystyrene and acrylic polymers respectively have also been reported in the literature. Thermally stable brominated isocyanurate FR, has been found suitable for PET, PBT and ABS plastics Brominated phthalates have also been reported to provide efficient flame retardancy for several polymers without affecting the processing properties. For glass filled PBT, brominated phosphate was shown to be very suitable. Ethylene bis (tetrabromophthalimide) has been shown to function as FR for ABS plastics. A few new types of brominated FR not belonging to diphenyloxide family have been recently described in the literature. These additives have been evaluated for HIPS, ABS, PBT, nylon and PP and have been found to be effective FR without affecting the properties and processability of these plastics.

Although the use of brominated FR is still growing by 5% per year, their use has been strongly questioned based on environmental grounds. In a report from Räddnings-verket, it has been shown that on burning organobrom compounds they form 95% bromine and not HBr, which is very reactive and toxic. The hygienic and short-term threshold values for bromine according to AFS (1996) are 0.1 ppm and 0,3 ppm respectively. However, when brominated FR´s were incorporated in polymers, no free bromine was detected.
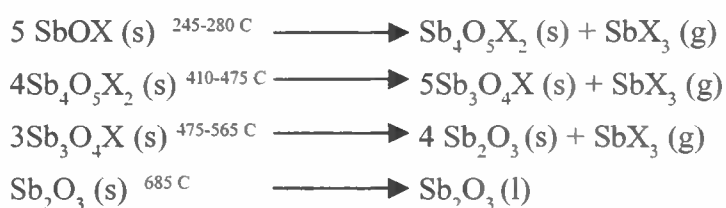
3.1.2 Chlorinated FR

Cycloaliphatic chlorine compounds obtained as Diels-Alder diadduct of hexachloro-cyclopentadiene and 1, cyclooctadiene, Dechlorane PlusÒ has been reported to be useful as FR either alone or together with synergists such as ZnO, zinc borate and iron oxide for nylons, polypropylene and various olefinic wire and cable materials. Recently, synergists used with chlorinated FR, such as Dechlorane, for different polymers have been reported in the literature. Several synergistic formulations based on combinations of zinc borate and iron oxide together with Dechlorane for Nylons, PBT, ABS, HIPS and PP has been reported in this paper.

A few reactive chlorinated FR compounds have also been reported in the literature earlier. Examples of such FR are chlorendic acid and chlorostyrene. For thermoplastics such as polyethylene (PE), polypropylene (PP) and nylon, neither chlorinated paraffins (CP) nor reactive monomers could be used because these additives affected crystall-inity of materials. Moreover, CP was not found to be thermally stable at moulding temperatures that are generally required for the processing of plastics. In such cases cycloaliphatic chlorine compounds of the type mentioned above has been reported to be useful.

3.2 Antimony FR

Antimony oxide itself has no FR activity but in combination with halogenated compounds it functions as an effective FR. The main advantage of adding antimony oxide is to reduce the amount of halogenated FR, which has been found to negatively influence the mechanical properties of the plastics. As a general rule approximately 25% bromine or 40% chlorine in the form of organohalide is required to reduce the flammability of plastics to an acceptable level. It has been shown that good FR properties of plastics could be obtained by adding only 12% of decabromodiphenyloxide in presence of 5% antimony trioxide. In general, FR plastics containing organohalogen compounds require 2-10 wt-% of antimony. Further, a molar ratio of 1:3 of antimony: halogen has been shown to yield the optimal synergistic activity. Such synergistic combinations have been found to be suitable for nylon, cotton, polyester fibres, polystyrene foam and for polyolefins.

In such FR systems, SbX_3 has been found to be the active component. At lower concentrations, oxychloride (SbOX) is the active component that has been shown to decompose in several endothermic stages at different temperatures to SbX_3 as below:

$$5\ SbOX\ (s) \xrightarrow{\ 245\text{-}280\ C\ } Sb_4O_5X_2\ (s) + SbX_3\ (g)$$

$$4Sb_4O_5X_2\ (s) \xrightarrow{\ 410\text{-}475\ C\ } 5Sb_3O_4X\ (s) + SbX_3\ (g)$$

$$3Sb_3O_4X\ (s) \xrightarrow{\ 475\text{-}565\ C\ } 4\ Sb_2O_3\ (s) + SbX_3\ (g)$$

$$Sb_2O_3\ (s) \xrightarrow{\ 685\ C\ } Sb_2O_3\ (l)$$

SbX_3 is released to the gas phase and undergoes a series of reactions with fuel generating less heat. Such reactions involve reactions with atomic hydrogen producing HX, SbX, SbX_2 and Sb. Sb reacts with atomic oxygen, water and hydroxyl radicals, producing SbOH and SbO and removes them from the flame reactions. The SbO formed also scavenges H-atoms. SbOX, which is a strong Lewis acid, operates in the condensed-phase by facilitating dissociation of C-X bonds, releasing more halogen and forming char. Char formation inhibits further degradation of polymer and also reduces the surface area. Decrease in surface area results into formation of lower amounts of volatile combustibles due to volatilisation.

A fine dispersion of solid SbO and Sb is also produced in the flame, which catalyses hydrogen radical recombination. The latter results in a lower steady-state concentration of hydrogen radicals resulting into enhanced FR effect.

The effectivity of antimony oxide has been shown to depend on several factors that can be summarised as below:

1) Degree of conversion of substrate to SbX_3 and SbOX species. This has been found to be dependent on the nature of the polymer and the strength of the C-X bonds depending on the type of halogenated compounds.

2) Flux of SbX_3 from the substrate to the flame.

3) Degree of conversion to Sb and HX.

4) Interaction of active species with H-atoms.

Presence of phosphorus compounds in such systems has been shown to behave antagonistic due to the formation of non-volatile antimony phosphate. Among the antimony compounds, only trioxide has been found to be most effective compared to tetra- and pentaoxide. For nylon 11, it has been shown that N-containing compounds

render a triple synergistic effect for FR systems comprising of brominated compounds and antimony.

According to a recent report from Danish Protection Agency, antimony trioxide has been classified to be harmful (X_n) according to EU directive and must be labelled with the risk-phrase "Possible risk of irreversible effects" (R 40) due to possible carcinogenicity. The substance is reported as teratogenic. The effects in ecotoxicological test are primarily on algae ranging from very toxic to harmful. However, toxicity on crustaceans or fish is very low.

Due to the health and price reasons, several cases of substitution of antimony oxide in PVC and also for Nylons have been reported in the literature.

3.3 Aluminium trihydrate (ATH)

ATH has been used as a flame retardant and smoke suppressant since 1960's and is available in a variety of particle sizes and particle size distribution (PSD) ranging from <1m to 80-100m. It has been shown that on thermal degradation ATH undergoes an endothermic decomposition at 200°C. Between 205 and 220, this decomposition is slow. Above 220°C, the decomposition becomes very rapid and hydroxyl groups of ATH begin to decompose endothermically. The major endothermic peak at 300°C represents the decomposition of a-trihydrate to a-monohydrate and subsequently to g-alumina. Heat of dehydroxylation has been found to be 280 cal/g (298 kJ/mol). ATH in dry form has been shown to contain 34.6% chemically bound water by weight.

Flame retardation by ATH has been shown partly to be due to the heat sink effect, as mentioned earlier, and partly due to the dilution of combustible gases by the water formed as a result of dehydroxylation. Alumina formed as a result of thermal degradation of ATH has been shown to form a heat-insulating barrier on the surface.

The only problem with ATH is that they are required at high loading levels in order to obtain equivalent flame retardancy as by other additives e.g. 100 to 225 parts per 100 parts resins (phr). Such high loadings may affect both the mechanical and the processing properties of the polymers. ATH loadings can however be reduced by selecting proper PS, surface modification and proper dispersion. ATH accepts most of the other additives such as silanes, titanates, stearates and oleates. It has been shown that modifying ATH with dimethyl phosphite FR efficiency of ATH can substantially be increased.

3.4 Magnesium based FR

Magnesium hydroxide functions both as flame retardant and smoke suppressant. It releases 30-33% water at about 325°C and about 50% loading by weight is required to obtain necessary FR properties. Heat of decomposition for Mg $(OH)_2$ is 328 cal/g. It has been reported that for polyolefins, the FR properties are affected by surface area, PS, surface activity and purity of Mg $(OH)_2$. Recommended surface area should be less than 20 m^2/g because the higher surface area decreases the melt flow of polyolefins.

In order to reduce its influence on mechanical properties of polymers, the PS should be smaller than 10m. Ultrafine Mg $(OH)_2$ grade having a median PS of 1m and where 100% of the particles are less than 6m have been found to be most suitable. Surface activity is measured in terms of free basic groups at the surface in order to assure any acid-base reaction with the polymer, which may result into high melt viscosity. Purity is important from the point of view of electrical properties and soluble salts are generally not acceptable.

For PVC, a combination of Mg (OH)$_2$ and ATH in 3:1 ratio rendered a higher degree of smoke suppression. Combinations with molybdenum compounds such as nickel molybdate, molybdenum trioxide and ammonium octyl molybdate, have also been found to be very effective as fire suppressant for PVC.

Magnesium carbonate alone has also been found effective as smoke suppressant for PVC. It releases about 60% by weight water and 25% by weight CO$_2$ at 230°C and 400°C.
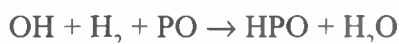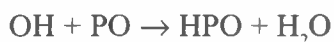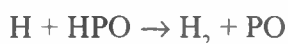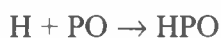
3.5 Phosphorus-containing FR

Phosphorus-containing FR includes inorganic phosphates, insoluble ammonium phosphate, organophosphates and phosphonates, bromophosphates, phosphine oxides and red phosphorus. These types of FR can be condensed- or vapour-phase active or can exhibit both types of activity simultaneously. The mechanism for flame retardancy varies with the phosphorus compound and the polymer type. However, two principal modes of reaction have been suggested: dehydration and cross linking.

During burning, Phosphorus FR produces non-volatile acids, which functions as dehydration catalysts. This, in turn dehydrates the polymer matrix forming graphite type char residue. The latter reduces the formation of flammable gases from the surface. These systems require oxygen and a source of phosphorus acids that are not volatile under the burning conditions. These agents display decreasing efficiency as FR as the oxygen content of the polymer decreases. Vapour phase activity of these agents is primarily observed for non-oxygen containing polymers. Due to their low molecular weights, they are volatile and are lost either during high temperature processing or in the early stages of combustion. Additionally, their transition to the gaseous phase can cause smoke from the burning material to contain toxic phosphorus containing compounds. In order to avoid such problems, organophosphorus functionality has been incorporated in the polymer structure.It has been shown that inclusion of phosphine oxide structure in aliphatic PA such as nylons, they show excellent thermo-oxidative stabilities, slightly lower than fully aromatic PA. It has been suggested that these polymers can either be used alone or as high molecular weight FR additive for commercially available polymers.

Cross linking, on the other hand, promotes char formation by creating a C-C network and resulting into decrease in chain cleavage. Phosphorus compounds are also used in intumescent systems and are described separately in this report.

Flame inhibition reactions similar to the halogen radical trap theory have been proposed where PO is generally the most significant species. The main reactions can be summarised as below:

$$H_3PO_4 \rightarrow HPO_2 + HPO + PO$$
$$H + PO \rightarrow HPO$$
$$H + HPO \rightarrow H_2 + PO$$
$$OH + PO \rightarrow HPO + H_2O$$
$$OH + H_2 + PO \rightarrow HPO + H_2O$$

Phosphorus has been found to be synergistic with halogen compounds. Compounds containing both phosphorus and bromine in the same molecule have been shown to be much more effective than the blends of bromine and phosphorus additives.

Some of the commonly used phosphorus derivatives are summarized below.

Red phosphorus has been reported to be most efficient FR in oxygen containing polymers such as polycarbonate, polyethylene terephthalate (PET), polyamide and filled phenolic resin. Flame retardancy takes place due to the formation of phosphorus-oxygen bonds that reduces the ester cleavage temperature for PET or PMMA by 75-100°C. The latter results into cross linking reactions resulting into polyaromatic structures, which are less volatile. Thus, addition of red phosphorus reduces the formation of flammable products and promotes the development of heat shield on the polymer surface, resulting into flame retardancy.

The drawback with red phosphorus is that they impart red colour. Working risk factors are due to its flammability and autoignition and also degradation may give toxic phosphine. Therefore, 50% concentrates of red phosphorus in polymers are commercially available to avoid these problems.

Triethyl phosphate is used alone or with bromine synergist as FR for unsaturated polyester resins. Less volatile types include trialkyl phosphates specifically, tributyl-, trioctyl- and tris-butoxyethyl phosphate. Several high phosphorus products are also commercially available, which are required at lower concentrations.

Aryl phosphates including triphenyl, isopropyl- and t-butyl-substituted triaryl and cresyl phosphates are mainly used, as FR. Phosphates of reduced volatility is also commercially available. Aryl phosphates are used as FR for phthalate plasticized PVC. It has been shown that although PVC does not require any flame retardancy, presence of dioctyl phthalate reduces the oxygen index substantially and thereby makes them flammable. It has been shown that triaryl phosphate is much more effective as FR than alkyl diaryl phosphate. However, alkyl diaryl phosphate has been shown to be more efficient plasticizer than triaryl phosphate. For polyphenylene oxides (PPO), which are usually blends or alloys of PPO and polystyrene (PS) containing 35-65% of impact PS, alkylated triaryl phosphates (15 phr) have been found to be very efficient FR. For PC/ABS blends, 13% triphenyl phosphate has been shown to be very effective.

Several halogen containing phosphates such as chloro- and bromo phosphates are also commercially available. Chloroalkyl phosphates have been found useful in flexible PU but because they are not stable to the exotherm heat during curing reactions, they render discoloration problems. Therefore, a blend of pentabromo diphenyloxide and triaryl phosphate is mainly used in flexible PU.

Brominated phosphates have been reported to be effective FR for PBT or PET and PC/ABS. It has been shown that by using such FR, good flame retardancy can be obtained without using antimony. Reactive phosphorus polyols including phosphine oxide diol and triol have also been reported to be useful as FR for PU, PET and epoxy resins.

Nitrogen containing polymers have been found to be synergistic with phosphorus compounds. For example, polymers containing amine and amide groups were synergistic whereas polymers containing nitrile groups have been found to be antagonistic.

Use of oligomeric phosphate FR for polymers has also been reported in the literature. Due to low decomposition of ammonium polyphosphate (APP), their use as FR is restricted in polyamides and therefore binary metal-ammonium phosphates (BMAPs) have been found suitable for such polymers.BMAPs of transitory metal has been found to be more effective for PA-6 than APP.

3.6 Intumescent flame-retardant systems

Almost all intumescent systems comprise, in general, of three basic components: 1) an acid source such as ammonium polyphosphate (APP), 2) a charring agent such as pentaerythrytol (PER) and 3) a nitrogen blowing agent such as melamine.

In intumescent systems a series of chemical and physical processes occur during the pyrolysis and combustion of the materials. The chemical processes are: decomposition of APP to phosphoric acid, esterification (phosphorylation) of the polyol (pentaerythritol) followed by decomposition and regeneration of the phosphoric acid. Decomposition of melamine helps blow the resulting thick char that finally insulates the substrate from the flame and oxygen. The physical processes, which controls the flame retardancy includes diffusion and transport of combustible and incombustible gases through the polymer melt to the flame zone, transfer of the molten polymer and of the flame retarding molecules to the flame, diffusion and permeation through the char barrier.

All these reactions occur in a very short period of time with various reaction rates. These reaction rates determine the properties of the final char and the flaming behaviour of the materials. By properly designing these rates using proper formulations, it is possible to obtain desired fire retardant properties for different polymeric materials.

The main function of APP is to catalyse the dehydration reaction of other components. It has been shown that in spite of the fact that APP functions only as a catalyst, it is required at rather large concentrations i.e. in the range of 10-20% of the weight of the composition. Use of APP in large concentrations may partly be explained due to its participation in the char structure and partly due to its volatilisation as phosphorus oxides during the pyrolysis of the material. It has been reported in the literature that the effectivity of APP is rather low (0.31), which can be raised to substantial values by the addition of co-additives such as pentaerythritol, melamine etc.

The function of PER as charring agent is quite well understood. However, the function of melamine has shown to be rather diverse: 1) endothermic action due to volatilisation and decomposition, 2) facilitate phosphorylation and 3) serve as a blowing agent forming water, CO, CO_2, ammonia and hydrocarbons all serving to foam the char.

From OI measurements for an intumescent system for PP containing APP, melamine and PER, it has been shown that both PER and melamine is synergist for APP. However, within a specific composition melamine and PER have been shown to be interchangeable without affecting OI of the composition. In presence of a metallic catalyst (1%), a substantial increase in OI was observed in the absence of melamine. Based on this observation several conclusions were proposed: a) melamine or other N-based blowing agents were not essential in the intumescent formulation; b) other gases present in the system performed the blowing function; c) the phosphorylation occurs directly by APP possibly via phosphoramide structures; d) the effect of the catalyst was not connected with the blowing activity.

The catalyst was suggested to have two effects: 1) facilitation or acceleration of the phosphorylation reaction and 2) stabilization of polyphosphoric acid by forming bridges or crosslinks between adjacent chains, thus hindering its dehydration to volatile oxides. This enables a fuller participation of the polyphosphoric acid in the phophorylation as well as in the char structure. It has been shown that only small concentration of catalyst is required to obtain higher values of OI. However, at higher catalyst concentration, OI-value was shown to decrease. This was assumed to be due to the fact that at higher concentration of the catalyst, more crosslinks were formed resulting into

very stable and unreactive polyphosphoric acid. This, in turn, resulted into lower OI-values. Similar effects for talc and magnesium oxide were reported in the intumescent flame retardancy of nylon, in which no melamine was used. It was shown that zeolite-4A also functioned as a very effective catalyst at 1.5% concentration for the intumescent flame retardancy of ethylene-butyl acrylate and maleic anhydride terpolymer containing APP and PER. OI increased with increasing amount of oxygen containing components of the terpolymer. The latter helped partly in the formation of char and partly in a better utilisation of APP.

In intumescent systems, char properties such as thickness of char layer, high carbon content, low penetrability, high viscosity of pyrolyzing melt, homogeneous small pores have also been reported to play an important role by increasing OI-values and thereby increasing the fire retardancy. Such effects have been shown by addition of P-derivative to a PF-char surface and by addition of boric oxide to APP.

As evident from the discussions above, formation of char as a result of fire is very important in order to reduce the flammability of materials. Char formation reduces the formation of volatile fuels as a result of polymer degradation, insulates the surface and also function as mass transfer barrier. Char enhancing systems, in general, are very useful because they usually reduce flammability without increasing soot or carbon monoxide yield.

It has been reported that a mixture of Silica gel (6%) and Potassium carbonate (4%) and Zirconium oxide-borate systems increases char yields for several polymer types. It was also shown that char yield for polymers like SBS, PP etc can be increased by blending preceramic polymers such as polycarbosilane, polysilastyrene and polysilsesquioxanes. Use of metal complexes such as zinc (Zn)-molebdenum (Mo) together with phosphate esters and ATH has been found effectively increase char yields for PVC.

It has been shown that polymer layered-silicate (PLS) nanocomposites can be used to increase the char yield and fire retardancy. PLS nanocomposites are hybrid organic polymer-inorganic materials containing layered silicates at molecular levels. Such nanocomposites are termed as intercalated or delaminated depending on the nano-morpholgy. In intercalated structures, polymer chains are inserted into the gallery space between the individual silicate layers and comprise of well ordered multi-layered structures. Delaminated structures are, however, obtained when the individual silicate layers are well dispersed in the organic polymer. It has been shown that flammability of Nylon 6, 12 and PS reduced significantly at low mass fraction of silica (2-5%). To illustrate the efficiency of nanocomposites as FR additive, it has been shown that magnitude of improvement for PS was comparable to PS containing a total mass fraction of 30% of decabromodiphenylether and Sb_2O_3. It has been shown that such additives affect condensed phase reactions. One possible explanation can be that multilayered carbonaceous silicate structure may act as an excellent insulator and mass transport barrier, slowing the escape of volatile products generated during polymer decomposition.

This shows that flame retardancy of materials can be obtained by using such nano-composites having several advantages such as: 1) use of halogens can be eliminated, 2) physical properties of materials can be greatly improved, 3) materials can be easily recycled, 4) systems do not increase the CO or soot produced during the combustion and

5) enhances the performance of char layer as an insulator and a mass transport barrier.

Graft copolymerization as a strategy has also been reported in the literature to increase the char yield for polymers such as ABS, PS, and polyamide. It has been shown, that by grafting char forming monomers such as acrylonitrile and sodium salts of polyacrylic acids, FR properties can be obtained. Such polymers can also be used as FR additives for other polymers.

Char yield for PVC has also shown to be increased by using low-valent metals based on Cu(0) and Cu(I) as reductive coupling agents. Such additives have been found useful both as smoke suppressant and fireretardant. Moreover, it has been shown that such additives are very effective in suppressing benzene production. It has been shown that each reductive coupling crosslink would halt simultaneously the growth of two polyene sequences. This, in turn, results into inhibition of dehydrochlorination and thereby slows down the polymer degradation. Since zero-valent metals cannot be blended directly with polymer due to several reasons, suitable compounds capable of decomposing at pyrolysis temperature of PVC to liberate a free metal were used. Among the various compounds, formats and oxalates have been found to be most effective. Cu(I)halides and phosphite complexes of CuCl and CuBr have also been found to be very effective as reductive coupling agents.

Thus, it is evident that in intumescent systems, performance of flame-retardants can be affected in several ways where all measures that result into enhanced char yields are specially preferable. Thus, it is obvious that there exist a number of possibilities to design optimised tailor-make formulations.

4 Evaluation of a few commercial samples

In the light of all theoretical discussions above, we decided to analyse a few commercial samples. We selected one sample of expanded polystyrene (EPS), one electrical contact and one furniture stuffing material based on Neoprene. EPS material is a very important group of material and is widely used in the buildings and other constructions as insulation material and poses a potential flammability risk. Such materials are usually flame retarded by using brominated additives. Electrical contacts are also often flame-retarded and magnesium hydroxide is most commonly used as FR additive. So far the furniture stuffing's are concerned, they are also flame retarded by using halogenated additives.

The main aim of this investigation was to determine the halogen content in the material samples, the thermal degradation behaviour, char yield and also the pyrolysis products formed as a result of thermal degradation. For our comparative studies we could only obtain a non flame-retarded sample on EPS.

Halogen contents

Since only the EPS and the stuffing sample contained halogen, we determined halogen contents only in these polymers by using Schöniger method and the results can be summarised as below:

Product name	Chlorine content (%)	Bromine content (%)
Sundolit cellplast (FR quality)	-	0.6
Stuffing material (FR quality)	2.1	-

The analysis results show that fire-retardancy has been obtained by using halogens, although halogen contents are not so high. Here, one may raise the question how non-flammable these material samples are because no quantitative fire retarding properties are measured on these samples except that they fulfil the requirements according to standards. This further reveals that these standard test methods have no meaning unless quantitative fire related properties, which have been mentioned above in this report, are measured. The chlorine content in the stuffing material may arise from the use of Neoprene polymer.

Thermal Degradation

In order investigate the thermal degradation behaviour of different polymer samples, we analysed all the samples by TGA and the results are shown in Figures 1-3. Fig 1 shows thermal degradation behaviour of fire-retarded (2) and non-fire-retarded (1) Sundolit samples.

The results show that by adding 0.6% of bromine in Sundolit, the onset temperature for thermal degradation of PS has been raised from 297.5 to 326.8 °C. Moreover, the addition of brominated FR har not contributed into any char formation. This suggests that FR properties for Sundolit are mainly obtained by partly raising the thermal degradation temperature of PS and partly by restricting the gas-phase reactions due to the presence of small amounts of bromine.

Fig 2 shows degradation behaviour of the polymer from electrical contact. Since electrical contacts are usually manufactured from polyolefins, we investigated the degradation behaviour of both high-density polyethylene (HDPE) and polypropylene (PP) and the results are summarized in Fig 4. It is evident from the figure that HDPE and PP has onset temperatures at 355.3° and 309.6°C and both the materials degrade very quickly once the degradation starts. This suggests that, in this case too the FR properties have mainly been obtained by modifying the thermal degradation behaviour of polyolefin material. We also measured the presence of a very small amount of char in this sample, which may arise from the presence of $Mg(OH)_2$, which might have been used as FR additive.

Fig 3 also reveals that the fire retardancy for stuffing material may also have been obtained by changing mainly the degradation behaviour of material besides affecting the gas-phase reactions to some extents due to the presence of chlorine atoms.

Thus, these measurements show that TGA renders very useful information so far the flame retardancy of materials are concerned. However, It would have been very interesting if we could also determine the other fire related properties such as OI, HRR etc as mentioned above in section 3.

One more aspect, which was important for our investigation, was to analyse the emission products, which are formed as a result of pyrolysis of fire retarded products in order to get an idea on the influence of such FR additives on the environment. Therefore, we analysed the pyrolysis products from the flame-retarded Sundolit sample (PS) by first pyrolysisng the sample at 550°C followed by analysis of all the gaseous products by GC/MS. The results are summarized in Fig 5. The results show that pyrolysis products mainly comprise of styrene monomer and dimers and we could also detect presence of brominated compounds at retention time 14.23 min.

All these analysis shows that only one FR-mechanism has been used in the fire-retardancy of materials. This suggests that the formulations are no way optimised from the fire retardancy point of view. Moreover, since the samples fulfils the fire retardancy requirements according to the branch standards and no quantitative fire-related properties have been reported for these samples, it is very difficult to comment how good these materials are flame-retarded.

Thus, the study shows that there exists wide opportunities for further optimisations of FR properties by utilising several FR mechanisms in the formulations at the same time. In this way it is possible to both reduce the amounts of brominated FR additives in the polymers and also to eliminate them completely. However, all these efforts requires further developmental work which includes both the testing of fire-related properties and the final polymer properties.

In order to set-up realistic goals to phase-out BFR's, the first attempt according to my opinion should be made to eliminate the use of PBB, PBDE and TBBA type of FR and replace them with less toxic FRs as proposed in this report. Further, if alternative BFRs are to be used, attempts should be made to reduce the amounts of such additives to a minimum either by using suitable synergists or by including several FR mechanisms in the formulations as mentioned above.

5 Recommendations for further work

The present investigation shows that it is almost inevitable to decrease the flammability of all the polymer materials due to their high flammability. However, in order to eliminate the environmental hazards posed by the brominated FRs, we suggest the following developmental work in continuation to this study, where we can use our expertise in this area and also use some of our halogen-free proprietary formulations to modify them further in order to make the suitable for other polymers:

1   We shall suggest to perform work in order to find other FR-systems as suggested in this report.

2   We shall suggest to concentrate our developmental work for a few polymer types which poses the major fire problems for the society e.g. polyolefin, PS, PU, ABS, PC/ABS etc.

3   Since polymer degradation mechanisms and FR mechanisms for a different additive varies, the study will include estimation of fire-related properties, physical and processability properties of polymers as suggested above.

4   Based on these results, further optimisation of formulations will also be planned based on the guidelines presented in this report.

6 Bibliographies

1 Flame Retardancy of Polymeric Materials, M Lewin and G S Kirshenbaum eds., Business Communication Co (BCC), 1990, 1997.

2 Fire and Materials II, G L Nelson Ed, ACS Symposium Ser. 599, 1995.

3 Fire & Materials, Journal

4 Polymer Degradation Stabilisation, Journal

5 J Fire Science

6 Fire Retardancy of Polymers, M Le Bras, G Camino, S Bourbigot and R Delobel eds., Royal Society of Chemistry, 1998.

7 J Applied Polymer Science.

8 Chemistry & Technology of Polymer Additives, S Al-Malaika, A Golovoy & C A Wilkie eds., Blackwell Science Ltd. 1999.

9 Flame Retardant 2000, Interscience communications, London, 2000.

10 Räddningsverket, Bromerade Flamskyddsmedel: Miljöeffekter vid brand, 1997.