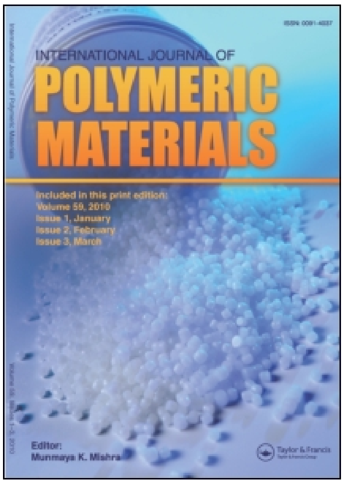

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Flame Retardation of Engineering Thermoplastics

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INTRODUCTION

Engineering thermoplastics (ETP) are polymeric materials which can be melt-processed into shaped articles for prolonged use in structural applications over a wide temperature range, under mechanical stresses and in moderate to severe chemical and physical environments. In comparison with conventional structural materials such as wood, metals, ceramics and silicon-based glass, engineering thermoplastics offer many advantages: (a) range of color and clarity; (b) flexibility; (c) range from lubricity to adhesion; (d) low-cost fabrication and decoration; (e) high thermal and electrical insulation; (f) high strength to weight ratio; (g) ease of modification of their properties using reinforcing agents, fillers and chemical additives; (h) resistance to inorganic corrosion; (i) impact resistance; (j) abrasion resistance; and, (k) energy absorption of foam.[1,2] Typical engineering thermoplastics are aliphatic polyamides, polyesters, polyacetals, aromatic polysulfides, polystyrene, polymethacrylates, polyvinyl chloride, polyethylene, polypropylene, polycarbonates, polysulfones, aromatic polyethers, poly-p-xylylene and poly(4-methylpentane-1).

Because of the above mentioned superior properties of ETP, they are constantly replacing conventional structural materials in most applications. Many of these applications call for new properties of which flame resistance is the most important. In this respect, an ultimate goal will be a complete elimination of fire hazards. However, this goal is almost impossible to realize with organic polymeric materials such as ETP.[3] Thus, with our present technology, a more realistic goal will be to reduce the flammability of ETP, that is, rendering them flame-retardant rather than flame-proof. In this communication, advances in the techniques and approaches to flame-retarding ETP are discussed and the evaluation of the flame-retardation of selected polymers are reported. Before discussing this, some general flammability concepts will be reviewed.

BASIC CONCEPTS IN POLYMER FLAME RETARDATION

The performance of any polymer in the presence of a flame has been suggested to depend on its behavior in the pre- and post-ignition processes, as well as the nature and ignitability of its degradation products. Most factors influencing the polymer flammability also dictate its thermal and thermal oxidative stabilities,[4–6] hence, one should attempt to correlate the thermal and thermal oxidative characteristics of a polymer with its flammability. Before one can predict the general flammability characteristics of a polymer, a knowledge of its performance in some or all of the following processes should be available: heating, transitions, degradation, decomposition, oxidation, ignition, combustion and flame propagation. These processes have been discussed by a few authors.[3–6] Flame retarding additives are used and intended to modify some or all of the above mentioned processes, as well as smoke generation. In this communication, the heating, transition, degradation and decomposition processes will be collectively discussed under fuel generation. Discussion of the ignition process will include oxidation. The combustion and propagation processes will be discussed as flame reproduction.

Fuel generation

For a polymer to provide fuels it must be allowed to generate volatile molecules, through degradation and/or decomposition. This can be affected by heating, but the energy input will depend to a great extent on the polymer structure. A flame retardant will be expected to slow the fuel generation by modifying the thermal properties of the polymer and/or its degradation mechanism.[5,6]

Ignition

In order to achieve ignition, the gas phase should contain a sufficient concentration of easily oxidizable flammable volatiles as well as accessible oxygen. Flame retardants will manifest their effect through diluting the fuels and/or depleting the available oxygen in the gas phase and thus minimizing possible exothermic reactions.[4,5]

Flame reproduction

After a polymer is ignited, a fully developed thermal oxiditive process, i.e., combustion, must be developed in order for it to continue burning. A positive net heat of combustion (heat generated upon combustion—heat necessary to generate more fuels) will encourage burning and flame propagation. An effective flame retardant may be expected to disrupt (a) the constant supply of fuel precursors, (b) the flow of combustible vapours, (c) the constant supply of oxygen, (d) the course for obtaining a positive net heat of combustion and (e) the mass and heat transport between the condensed and gas phases.[4–6]

TYPES OF FLAME RETARDANTS AND THEIR MECHANISMS

A very large number of flame retardants have been claimed effective for ETP in the last decade. Most of these flame retardants contain one or more of the following elements: Chlorine, bromine, nitrogen, sulfur, phosphorus, boron, antimony, tin, zinc, copper and iron.[4–15] Though the mode of action of flame retardants have been the subject of many investigations, most available information is still empirical. The possible modes of action of different groups of flame retardants, having common structural or mechanistic features, will be discussed below.

Antimony compounds

Of the great number of antimony compounds which have been claimed as flame retardants for ETP, antimony oxide (Sb_2O_3) is most important.[4–12,16,17] Normally, the antimony compounds are used in conjunction with halogen compounds and in particular chlorine-bearing systems. Antimony compounds were shown to be useful flame retardants for polyesters[18] and polyolefins.[18] Effective flame retardants based on Sb and Cl have been studied by many authors.[7,20] Their mechansim of action was suggested to be based on the formation of the volatile $SbCl_3$ (b.p. 223°C). The $SbCl_3$ was thought to act as a flame quencher of the flammable gases and/or as a dehydration agent, depending on the nature of the polymeric substrate.[7] To act as a flame quencher (or cooler), $SbCl_3$ was proposed to decompose in the combustion zone giving a fine fog of antimony oxide dust which would perform as a flame retardant partly through the so-called dust or wall effect.[21] Energy used for the formation and heating of the dust particles will deplete the combustion energy. In the presence of high concentrations of dust particles a negative net heat of combustion will be realized and the flame will fail to propagate. Furthermore, on the surface of the dust particles, active free radicals will be transformed into less active ones[13]:

$$H\cdot + O_2 \xrightarrow[\text{wall}]{} H\dot{O}_2$$

$$\text{and not} \quad H\cdot + O_2 \longrightarrow HO\cdot + O\cdot$$

Two other mechanisms are possible for the action of the Sb-halogen system: (a) SbX_3 may function as a scavenger for free radical intermediates such as $H\cdot$ or $\dot{O}H$, or (b) the dense SbX_3 vapors may act as a barrier between the gas and condensed phases through a physical blanketing effect.

Considering the above-suggested mechanisms, one may be led to believe that Sb-halogen additives function in the flame zone exclusively.[21a] However, the fact that these additives also increase char formation implies that they also have some effect on the condensed phase. Furthermore, the observed effect of the type of oxidant on these flame retardants does not necessarily indicate that their action is restricted to the gas phase. This is because it was demonstrated that the oxidative degradation in the condensed phase of some polymers, e.g., polypropylene, greatly influences the combustion chemistry.[21b,21c]

Phosphorus compounds

Most of the phosphorus flame retardants belong to the following groups of phosphorus compounds in addition to phosphorus itself (with or without caprolactam[21d]). For a more effective performance, red phosphorus was mixed with trioxane to prevent its ignition during its incorporation in thermoplastics.[21e]

Phosphines	PR_3	Phosphonates	$P(O)R(OR')_2$
Phosphine Oxides	$P(O)R_3$	Phosphites	$P(OR)_3$
Phosphonium Salts	PR_4X	Phosphates	$P(O)(OR)_3$
Phosphinates	$P(O)R_2(OR')$		

These compounds may contain nitrogen, halogen or sulfur in their R and R′ groups.

Flame retardants containing only phosphorus as the active species are likely to manifest their action through the formation of a barrier between the condensed and gas phase. This is likely to be a solid three-dimensional polymer based on metaphosphoric acid.[6,20] Polyphosphoric acid is also likely to form and act as a liquid barrier. In the presence of polyphosphoric acid or its cross-linked derivative, polymeric substrates containing (OH) and/or -NH- groups (polyesters and polyurethanes) are likely to form char in the presence of a flame.[22] It was also suggested that polyphosphoric acid is likely to redirect the solid-phase oxidation mechanism toward a complete oxidation of carbon to CO_2, as a glow-proofing agent (incomplete combustion of carbon to CO and CO_2 is responsible for the afterglow[22]).

Flame retardants containing both phosphorus and halogens are suggested to (a) have a synergistic effect on polyolefins, polyacrylates and polyurethanes (with Br and Cl), (b) show no synergistic effect with polyacrylonitrile and not even an additive effect, and (c) exhibit an additive effect with polyesters.[22] In the case of polyacrylonitrile, it is likely that phosphorus flame retardants catalyze charring through ladder polymer formation and halogens tend to decrease the catalytic effect of phosphorus. With polyesters, phosphorus may act on the condensed phase, independent of the halogens which trap free radicals in the gas phase. In cases where phosphorus-halogen synergism was observed, it was suggested that (a) volatile phosphorus halides or oxyhalides are formed and act as effective free radical traps similar to halide radicals, and/or (b) the phosphorus compounds facilitate the release of halogen to the flame zone.[22]

The synergism of the phosphorus-halogen system was suggested to exist in polyurethanes[22a] and polyesters.[9,22b] These synergists are suggested to act as free radical quenchers in the gas phase.[22c,22f] On the other hand, Weil has argued with convincing evidence against this proposed synergism.[21a]

The phosphorus-nitrogen synergism which was reported to exist in cellulosics[22g,22h] was suggested to be associated with increased phosphorylation of polymer hydroxyl groups.[22i,22j] The efficiency of these synergists depends on the chemical structure of the nitrogen compounds.[22k] In ETP, the phosphorus-nitrogen synergism was reported to exist in certain polyurethanes[22l,22m] and polyesters.[23]

Halogen compounds

The role of halogen compounds as flame retardants for polymers including ETP has been investigated and reviewed by many authors.[5,7,13,24–26] The most acceptable mechanism for their action is the liberation of a halogen radical ($X^{\cdot}$) which extracts hydrogen from the hydrocarbon substrate to form hydrogen halide. This will then react with the highly active $\dot{O}H$ radical to regenerate the less active $X^{\cdot}$ radical. The removal of the $\dot{O}H$ radicals from the gas phase is thus considered responsible for "cooling the flame" and hence, flame retardancy. In order to form an $X^{\cdot}$ radical, the carbon-halogen bond ought to cleave homolytically under the flame conditions. Thus, the weaker this bond is, the more effective the flame retardancy will become, e.g., bromo-compounds are more effective flame retardants than chloro-compounds, which in turn, are more effective than fluoro-compounds.

The synergism of halogens and either phosphorus or antimony compounds have been discussed earlier in the text.

In spite of the efficiency of halogen compounds as flame retardants for many ETP's, low and medium loading of halogen compounds in nylon 6 were claimed to increase its flammability.[27] This may be attributed to the degradative effect of the acidic degradation products of the halogenated flame retardants. These acidic products were shown to catalyze the depolymerization of nylon 6 and form combustible low molecular weight species.[28,29] The exhaustion of the halogenated moieties in the condensed phase will prevent halogen species from performing as flame retardants in the gas phase.

"Drippers"

These are flame retardants which render polymers artificially self-extinguishing through dripping of their burning melt, during and subsequent to the specimen ignition. Dripping was suggested to carry away the flame front and fuel, thus causing the depletion of the energy necessary for flame propagation at the burning site.[30,31] Douglas[30] was the first to describe thiourea and a number of ammonium salts as flame retardant drippers for nylon 66. He demonstrated that these chemicals lower the melting temperature and melt viscosity of nylon 66 which causes its melt to drip upon burning. Douglas's proposed mechanism was later verified by Kruse,[32] who reported that thiourea-containing nylons cannot be flame retarded effectively if their melt dripping becomes mechanically impossible.

The data in the previous paragraphs may give the impression that dripping is the sole mechanism of flame retardation for "drippers". However, it is felt that dripping caused by many flame retardants contributes significantly but not exclusively to their "effectiveness".

Free radical initiator—halogen systems

Combinations of halogen compounds and free radical initiators have been described by Eichhorn[33] and others[34,35] as synergistic flame retardants for polyolefins such as polystyrene. Eichhorn[33] attributed the synergism in these systems to (a) a catalyzed low temperature decomposition of halo-compounds into flame retarding species in the presence of a free radical initiator; (b) simultaneous catalyzed decomposition of the halogen compounds and polymer; and (c) delayed residence of the halogen species in the combustion zone, as a result of their gas phase interaction with the volatile pyrolysis products of the polymer. However, in recent studies[31a] of the flame retardation of polystyrene and polypropylene with peroxide-halogens combinations, it was demonstrated that the dripping of the molten polymer is a significant element in the self-extinguishing mechanism. Thus, in the presence of these flame retardants, the polymer undergoes excessive depolymerization to form a low melting, low viscosity substrate. This will drip and carry the flame away from the combustion site.

Metallic compounds or complexes, other than antimony

Nylon 66 was claimed to become flame retardant by incorporating a halide of Zn, Cd, Pb or rare metal earths.[36] Smaller quantities of any of these halides were claimed effective in the presence of other metallic species such as Sn or Cu oxides.[36] These flame retardants were suggested to affect the dehydrogenation and char formation when present in burning nylon 66.[36] The char acts as a solid barrier between the gas and condensed phase and allows self-extinguishing of the molten nylon 66.[36]

Metal ammine complexes such as $Co(NH_3)_6Cl_3$ were claimed as effective flame retardants for polyurethanes, but a mechanism for their action was not proposed.[37] A number of metal naphthenates were also claimed as flame retardants for polyolefins, such as polystyrene.[38]

In comparing Sb_2O_3-halogens with hydrated SnO_2-halogens as flame retardant synergists for some polyolefins, Touval[38a] suggested that: (a) the SnO_2 is as effective as the Sb_2O_3 system; (b) in both cases the metal compounds react with the halo-compounds to form flame-quenching products; and (c) the water of hydration is necessary for the activation and hence, the effectiveness of SnO_2 synergism with halogen compounds.

A number of halogenated boron compounds have been claimed as effective flame retardants for polyamides, but no mechanism was reported.[38b] However, one may propose that upon igniting a polymer containing these compounds, boron halides will be formed. Being strong Lewis acids, the boron halides may either (a) degrade the polyamide and render it flame retardant through a dripping mechanism, or (b) cross-link the polymer and encourage char formation.

Organometallic compounds such as ferrocenes were described as flame retardants for halogen-containing polymers such as polyvinyl chloride or polypropylene with 10% chloroparaffins.[38c,38d] For PVC, it was suggested that ferrocenes encourage char formation through catalyzing the Diels–Alder reaction of the conjugated diene resulting from the dehydrohalogenation of the polymer.[21a]

The acetylacetonates of a number of transition metals (e.g., Mn, Cu, Co, and Cr) were reported as flame retardants for polystyrene in the presence of chloro-compounds.[38e] No mechanism was proposed for these systems.

Sulfur and its compounds

Sulfur itself was described as a flame retardant for polystyrene.[38f] Synergistic flame retardant systems for polystyrene were reported to consist of certain disulfides and sulfenamides and halogens.[38g,38h] Similar to thiourea, as mentioned previously in the text, no explicit mechanism was suggested for these sulfur systems. Though part of their flame retardant effect may be attributed to their effect as drippers, the sulfur moieties may also produce free radical scavengers and/or non-combustible gases. In a study by Jolles,[38i] he claims that brominated aromatic sulfides, used as flame retardants for polyurethanes, are oxidized to sulfones resulting in a facile release of halogen.

Microencapsulated flame retardants

Microencapsulation provides means of packaging, separating and storing materials on a microscopic scale for later release under controlled conditions.[39,40] Microencapsulation in the area of flame retardants have become a fast growing technology.[41,43] Encapsulated flame retardants are expected to remain in the polymer matrix to be released only when the polymer is subjected to flame. The microencapsulation technique may be used for the incorporation of flame retardants which are toxic or skin irritants. The capsules are activated by (a) using a coating which melts or decomposes at a given temperature, and (b) using a flame retardant whose boiling point is such that it will burst the capsule at a given temperature.[43a] A self-extinguishing polystyrene composition was made using microencapsulated flame abating compounds, e.g., halogen-containing phosphates.[44] A number of reports on the use of microencapsulated flame retardants and their mode of action are now available.[44,45]

Reactive additives

These are flame retardant compounds which are capable of being incorporated permanently in the polymer during or after its formation. Polyesters were shown to become flame retardant by adding halogenated diacids or diols to the regular monomers prior to their polymerization.[46–55] Phosphorus-bearing monomers were also used for flame retarding polyesters.[56,57] Halogen-containing polycarbonates and polyester-carbonates were reported to be flame retardant.[58,59] Flame retardant polyurethanes were made from aromatic phosphorus[60–62] and/or halogen-containing monomers or pre-polymers.[63–72] Flame resistant polyurethane foams were made from monomers containing semicarbazide groups.[73,74] Fire resistant polyurethanes were formed from the reaction product of $SbCl_3$ with a polyether, polyol or polyester polyols containing a quaternary nitrogen and halogen in their chain.[74] Bromination of ABS resulted in a flame retardant resin.[75] A reaction product of β-hydroxychloroethyl methacrylate and P_2O_5 when reacted with toluene diisocyanate in the presence of methyl methacrylate and an organic peroxide, formed a nonflammable polyurethane.[76] Methacrylic resins were rendered flame resistant by incorporating a 1-dialkylphosphonoethyl methacrylate as a comonomer in the polymer chain in addition to organic bromo-compounds.[77] Alternatively, a halogen-containing comonomer and/or phosphorus compound were used to obtain flame retardant methyl methacrylate polymers.[78]

Polystyrene was flame retarded by incorporating comonomer units of vinyl bromide in the polymer chain.[79]

TYPICAL FLAME RETARDANT POLYMERS

Considering the enormous literature now available on flame retardants, it was decided to consider only the most recent literature to describe typical flame retardant polymers. Upon studying these systems, one must not ignore the fact that each group of polymers is unique regarding their response to flame retardants. In fact, the individual polymers within a group of similar materials may respond differently to various flame retardants. Groups of polymers which seem to respond similarly to flame retardants will be discussed below.

Polyolefins

Of the commercial polyolefins, polyethylene, polypropylene and polyisobutylene as well as any of their copolymers are most important and their flame retardation will be considered under polyolefins. The most effective and commonly used flame retardant is Sb_2O_3—halo-organic compounds.[80–84] Flame retardant polyethylene was made using Sb_2O_3 plus chlorinated polyethylene.[83a] A number of polyolefins were made flame retardant by phosphorus-halogen flame retardant systems.[85–87] Tin oxides plus halogen compounds[88,89] and the less effective organotin polymers[90] were claimed as flame retardants for polyolefins. Other flame retardants for polyolefins, which are considered less effective than the above mentioned systems, include (a) $R_3PO + (NH_4)_3PO_4$,[91] (b) H_2SO_4 + dicyandiamine + urea + guanidene,[92] (c) brominated terphenyl[93] and other halogen compounds,[94] (d) sodium salt of antimonic acid,[95] (e) epibromohydrin polymer,[96] (f) chlorinated polyisobutylene,[97] (g) phosphorus-halogen systems plus a free radical initiator.[98] Most of these flame retardants are likely to manifest their action through the formation of free radical scavengers (hydrogen halides and metal halides) or non-combustible gases (e.g., NH_3) in the gas phase.[99,100] Tin or phosphorus are commonly suggested to operate in the condensed phase through the formation of char. However, in the presence of a relatively inert polyolefin substrate and/or volatile phosphorus compound, the effect of this flame retardant on the gas phase should not be excluded.

Polyesters

The flame retardation of polyethylene terephthalate and other thermoplastic moulding polyester resins will be discussed collectively in this section. Halogen[94a,101–103] and phosphorus[104–108] compounds or combinations[109–112] of both are the most commonly used flame retardants for polyesters. The combination of halogen and phosphorus compounds were claimed to be more effective than either compound alone. This may be attributed to P-halogen synergism,[10,113] in spite of the controversy regarding this synergism.[21a]

Combinations of halogen compounds with oxides of Sb, Sn, Fe, Zn, Cu and Ti were used as flame retardants for polyesters.[85,114,115] No special mechanism was proposed for these systems. Recently, a flame retardant system was claimed to consist of a char former and a precursor for a flame coolant.[116,117] Starch, casein or pentaerythritol were used as the carbon source for the char formation, while phosphates and insoluble nitrogen-phosphorus polymers were used as the precursor of $H_3PO^4{}_4$ which acts as a dehydrating agent. As a source of non-flammable gases, melamine in combination with halogen moieties were used. Under these conditions, the flame retardants perform in both the gas and condensed phases.

A system based on polyamides and phosphorus compounds, e.g., triphenylphosphine oxide—nylon 6, was reported as a flame retardant for polyesters.[118] The presence of synergism in this system may not be excluded.[114] When triphenylphosphine oxide was used alone in polyesters, it was proposed to volatilize and manifest a flame retardant effect in the gas phase.[119] Tetrabromo bis-phenol diacetate and tetrabromophthalic anhydride with or without Sb_2O_3 were claimed as very effective flame retardants for poly(tetramethylene terephthalate).[120] A few other less important flame retardants were claimed, e.g., boron compounds with or without halogen[115,121] poly-epibromohydrin[121a] and urea condensates with amino-compounds.[120a] Partially halogenated polyesters were made flame retardant using zinc borate and hydrated alumina.[122] Hydrated alumina may act as a flame retardant by releasing water vapor into the gas phase.

Polystyrenes

This section pertains to polymers and copolymers based on substituted and unsubstituted styrene monomers. The ease of generation of combustible monomers upon heating these polymers makes their flame retardation rather difficult. Halogens with or without antimony compounds,[123-125] and combinations of halogen and phosphorus compounds are claimed as effective flame retardants for polystyrenes.[126-128] Other systems which are considered less effective flame retardants include red phosphorus,[129] halogen-oxyalkylated amines,[130] halo-compounds[131,132] and halogen-free radical initiators.[133] The latter system was described earlier in the text as an effective "dripper".

Terpolymers of acrylonitrile, butadiene and styrene (ABS)

Mixtures of aromatic halogen compounds and Sb_2O_3 were used for flame retarding ABS.[134-136] Combinations of aliphatic halogens (e.g., dechlorane and polyvinyl chloride) and Sb_2O_3 were described by Deanin as very effective flame retardants for ABS.[137] Other systems such as aliphatic halogen-compounds,[138-140] PVC[141] and organic phosphorus compounds[142,143] were also claimed as flame retardants for ABS. Blends of ABS and aromatic polysulfones were described as flame retardant systems.[144]

Polycarbonates

Chlorine-bearing polycarbonate was flame retarded using alkali earth carbonates[145] and other salts.[146] Though halogen compounds alone were described as flame retardants for polycarbonates,[147,148] combinations of these compounds and phosphorus esters are likely to be more effective systems.[149] Halogenated organic silanes were claimed as new flame retardants for polycarbonates,[150] though one may not expect their performance to exceed those of simple halo-compounds.

Aliphatic polyamides

In this section nylons 6, 66, 610, 12 and their copolyamides are considered collectively as aliphatic polyamides. A brief description of their flame retardation is outlined below. Extensive discussions of this subject can be found in a few recent reviews.[5,6,27]

Most of the effective flame retardants for polyamides contain halogen and metallic moieties. The latter can be Sb_2O_3[151–153] and ZnO,[153,154] Fe_2O_3[154] and certain other compounds of group V-B elements.[155,156] Mixtures of substituted phosphine oxides and different metal oxides, e.g., SnO_2, SnO, ZnO, Fe_2O_3 or Sb_2O_3 were described as potent flame retardants for polyamides.[157,158] The reaction product of phosphorus pentoxide and urea was reported as a FR for polyamides.[159] Other claimed retardants include organotin halides,[160] phosphorus and derivatives,[161] tin halides,[160] melamine,[162] melam,[162] brominated biphenyls[163] and other triazene and halo-compounds.[164] However, the efficiency of halogen compounds or melamine alone is questionable. This is because both are likely to cause a severe degradation of the polyamide chain to combustible monomers or similar species. Prior to or during ignition, the thermal degradation of the polyamides will be accelerated by the hydrogen halides produced by the halo-compounds and the amine groups of melamine.

Hydrated alumina and hydrated $CaSO_4$, which are capable of generating non-combustible water vapor at high temperatures were described as FR for polyamides.[164a] The energy loss due to the evaporation of water and the diluent effect of H_2O vapor in the gas phase may be responsible for the observed flame retardancy.

A number of sulfur and nitrogen compounds, e.g., Thiourea, were described as flame-retardants for polyamides[30] and were discussed earlier in the text as "drippers".

Polyurethanes

Discussion in this section will be limited to flame retardant thermoplastic polyurethanes. The majority of polyurethane flame retardants are based on phosphorus. These include (a) phosphates and halogenated phosphates,[165] (b) halogenated phosphate esters,[166] (c) aminomethane phosphonates,[167] (d) ammonium polyphosphate,[168] (e) ethane-diphosphonate,[169] and (f) trimethyl-ϵ-caprolactam phosphonate.[161] A very effective flame retardant for polyurethanes was described as a mixture of SbOCl and hexamine cobalt trichloride.[170] A number of other systems which may be considered as less effective flame retardants for polyurethanes include halogen compounds[94c] and organo-silicon polymers.[105]

Acrylic polymers

Similar to polystyrenes, some of the acrylic polymers such as methacrylate polymers and copolymers undergo facile thermal depolymerization. This will result in the formation of highly combustible monomers which complicate the flame retardation of these polymers. Though different classes of flame retardants were claimed effective for acrylic polymers, phosphorus-based ones are rather common. These include phosphonates,[171] bromophosphate esters,[172] and mixtures of organic phosphates with bivalent sulfur compounds.[173] Tin compounds such as $SnCl_4$, $SnBr_4$ and certain organotin compounds represent another class of important flame retardants for polyacrylates.[35,174] Upon evaluating the polyacrylates flame retardants, one must not overlook the fact that these flame retardants are capable of generating strong Lewis acids which may catalyze the decomposition of the ester moieties into combustible fractions.

Polyvinyl chloride and copolymers

These polymers contain appreciable amounts of halogens. Halogen moieties are commonly used to flame retard polyolefins effectively in the presence of certain metal compounds. Hence it is not surprising to find that some of the effective flame retardants for halogenated polymers are metallic compounds, e.g., Sb_2O_3,[175–179] Sb_2O_3—$CaCO_3$.[180] Other very effective flame retardants are phosphorus-based systems and include sulfides with organic phosphates,[173] red phosphorus[181] and organic phosphates.[182,183] In addition, borates,[121] bromo-compounds[184] and ferrocenes[21a,38c,38d] were described as flame retardants for polyvinyl chloride.

Polyphenylethers

The high aromatic content of these polymers is responsible for their favorable interaction with different flame retardants. Red phosphorus,[129] with or without halogenated aromatic compounds,[185] and a mixture of Sb_2O_3 and hexabromobenzene[186] are described as effective flame retardants for these polymers.

Polyoxymethylene

The facile thermal depolymerization of this polymer to combustibles such as formaldehyde, complicates its flame retardation. Chain-end stabilization should be considered a major pre-requisite for the polymer flame retardation. This may be achieved by the end-group capping or by a chain stabilizer as part of the polymer backbone.[187]

Phosphorus-based systems were described as flame retardants for thermally-stabilized polyoxymethylene. These flame retardants include (a) organic halogen-compounds and phosphine oxides;[87c] (b) mono- and di-ammonium phosphates;[188] (c) halogenated phosphonates;[189] (d) the phosphates of amines, ammonia or amidine and optionally a triazene which may act as a formaldehyde scavenger.[190]

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