The Pharma Innovation

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A review of non-halogenated flame retardant

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Abstract
Recent patent and literature indicate a growing interest in non-halogenated flame retardants are on the fast growing track due to the environmental consideration, although sometimes efficiency, lower density & good light stability are the significant factors. Patent published on the flame retardancy of polycarbonate & its blends significantly exceed the number of patent on the flame retardancy of any other polymer. Bridged aromatic phosphates have found broad applications because of there good thermal stability, high efficiency & low volatility.
Flame retardant has very important role to play in today's science and technological field and considering the importance various researcher have studied various aspect and application areas for the same. Similarly various innovative molecules have been invented and tried various researchers but this is not the end of the research.
This review summarizes main advances published over the period of last 20 years, outlining the work carried out on synthesis of non-halogenated flame retardant compounds and application of it. Another actively reported group of compounds are the metal salt of phosphorous compounds which have been found to be particularly effective in poly butylene terepthalate & polycarbonate. These products are synergistic with a number of phosphorous & nitrogen containing compounds which seems to be a very efficient and commercially useful in nylon

Keywords: Flame retardant, reduction, Organohalogens, Organophosphorus, reactive, additive, synergism, polycarbonates and polyurethanes

1. Introduction

Halogen containing flame retardant particularly based on bromine have played & continue to play a large part in flame retardancy. However, mainly because of environmental concern & end of life issue, there has been a growing interest in non-halogenated solutions. The large number of the patent and non-patent literature is focused on non-halogenated flame retardants. In this review, the more recent developments in non-halogenated flame retardants for several major group of plastic, epoxy & commercial development.

Flame retardants find an important place in the list of various additives that imparts special characters to the plastics and other consumer products to meet flammability standards for furniture, textiles, electronics, and insulation. Typically Flame retardants are chemicals used in thermoplastics, thermo sets, textiles and coatings that inhibit or resist the spread of fire.

The question of whether the halogen need replacing is still open question that is not entirely resolved on scientific background [1, 2]. Some halogen containing like tris (dibromo propyl) phosphate was banned in the late 1970.Pentabromodiphenyl ether, tetrabromo bisphenol a are recently banned in Europe & US. However all user of flame retardants want to have an alternative either to offer on the market. Thus research on halogen alternative such as phosphorous & nitrogen based is very alternative to the bromine are finding market acceptance [3].

2. Main class of flame retardants

These chemicals can be separated into several different classes are listed below

- **Halogen based Flame retardant:** This class includes organ chlorines such as chlorendic acid derivatives and chlorinated paraffin; organobromines such as decabromodiphenyl ether (decaBDE), decabromodiphenyl ethane (a replacement for deca BDE).

  Organo-halogen chemicals (including all BFRs) to be banned globally. The challenges of finding substitutes for banned halogen-containing flame retardants include:

  Lower flame retardancy: Only 10 wt% of BFRs is equivalent to about 30-50% by wt of inorganic FRs.

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High cost: Inorganic FRs is low-cost but require high loading. New HFFRs, on the other hand, are mostly costlier. The cost ratios (£) of BF-FR with phosphorous based and nonphosphorous based HFFR are about 1:6 and 1:2 respectively.

Higher thermal stability: Many HFFRs decompose at higher temperature (about 400 °C) than their halogenated counterparts (about 3300C).

Melt-dripping: Melt dripping occurs with most polymers e.g. polyethylene, polypropylene, PET, ABS and so on. Flammable drips act as secondary ignition sources. FRs should make drips non-flammable.

Deterioration in Mechanical Properties: The deterioration of mechanical properties increase proportionately with the amount of FR. Therefore, the deterioration is more with less efficient FRs [4]

- **Organophosphorus compounds**: This class includes organophosphates such as triphenyl phosphate (TPP), resorcinol bis (diphenylphosphate) (RDP), Bisphenol A diphenyl phosphate (BADP), and tricresyl phosphate (TCP); phosphonates such as dimethyl methyl phosphonate (DMMP) and phosphinates such as aluminum diethyl phosphonate [5, 6].

Phosphorus-containing flame retardants cover a wide range of inorganic and organic compounds and include both reactive products which are chemically bound into the polymer material as well as additive products which are integrated into the material by physical mixing only [7]. They have a broad range of applications, and a good fire safety performance. The most important phosphorus-containing flame retardants are phosphate esters, phosphonates and phosphinate.

Phosphorus-containing flame retardants are widely used in standard and engineering plastics, polyurethane foams, thermosets, coatings, and textiles. Phosphate esters are mainly used as flame retardant plasticizers in polyvinylchloride (PVC, alkyl/aryl phosphates) and engineering plastics, particularly in polyphenylene oxide/high impact polystyrene (PPO/HIPS), polycarbonate/ acrylonitrile butadiene styrene (PC/ABS) blends and polycarbonate (PC, e.g. triphenylphosphate, resocinol-and bisphenol A-bis-(diphenyl) phosphate). The latter are widely used in IT housings requiring high fire safety levels. Other applications include phenolic resins and coatings. Phosphates, phosphonates and phosphinates are used as reactive phosphorus containing flame retardants in flexible polyurethane foams for automotive and building applications. Additive organic phosphinates are a new class of flame retardants for use in engineering plastics, particularly in polyamides. Specific reactive phosphorus flame retardants are used in polyester fibres and for wash resistant flame retardant textile finishes. Other reactive organophosphorus compounds can be used in epoxy resins in printed circuit boards.

Flame retardant grades based on red phosphorus are mainly used in glass fibre reinforced polyamide 6 and 66. Further applications are in polyethylene and ethylene vinyl acetate (EVA), polyurethane foam, and thermosettings resins (unsaturated polyesters and epoxies). Ammonium polyphosphate grades are primarily used in intumescent coatings. They are also found in rigid and flexible polyurethane foams and polyolefins (injection moulded), in formulations for unsaturated polyesters, phenolics, epoxies and coatings for textiles.

- **In organic flame retardants:** The most common inorganic flame retardants are the hydroxides or aluminium and magnesium, huntite and Hydromagnesite [8, 9, 10, 11, 12]. Aluminium trihydroxide (ATH) is by far the most widely used flame retardant. It is very inexpensive, but usually requires higher loadings in polymers of up to more than 65%. Its mode of action is based on the release of water (Endothermic process) which cools the polymer and dilutes the flame zone. Magnesium hydroxide (MDH) is used in polymers which have higher processing temperatures, because it is stable up to temperatures of around 310 °C versus ATH which decomposes around 210 °C.

Aluminum hydroxide flame retardants (white powder) for processing temperatures up to about 210 °C, for wire and cable, electronic and electrical components based on thermosets resins, building materials, mass transportation, paints and varnishes, paper and plaster with organic binder.

Magnesium hydroxide flame retardants (white powder) for processing temperatures up to about 310 °C for wire and cable, electronic and electrical components based on polyamide resins, building materials.

There are other minerals that show flame retarding effects and are used in commercial applications. Most of them are used as synergists i.e. they enhance the performance of other flame retardants or they are used for specific effects like the suppression of smoke formation, increasing char formation etc. For example, borates are used as mixtures of boric acids and borax as flame retardants for cellulose (cotton) and of zinc borate for PVC and other plastics like polyolefins, Elastomer, polyamides, or epoxy resins. In halogen-containing systems, zinc borate is used in conjunction with antimony oxide (mainly to reduce cost), while in halogen-free systems it is normally used in conjunction with ATH, MDH or red phosphorus. In some particular applications zinc borate can be used alone. Boron containing compounds act by stepwise release of water and formation of a glassy coating which protects the surface.

Zinc compounds were initially developed as smoke suppressants for PVC (Zinc hydroxystannate). Later it was found that they also act as flame retardants in certain plastics mainly by promoting char formation.

Other inorganic fillers like talcum or chalk (calcium carbonate) are sometimes called flame retardants, their mode of action is simply by dilution, i.e. they they reduce the amount of polymer and hence the fire load.

- **Nitrogen based Flame Retardants**

Nitrogen compounds are a small but rapidly growing group of flame retardants (FR) which are in the focus of public interest concerning environmentally friendly flame retardants. Today their main applications are melamine for polyurethane flexible foams, melamine cyanurate in nylons, melamine phosphates in polyolefins, melamine and melamine phosphates or dicyandiamide in intumescent paints, guanidine phosphates for textiles and guanidine sulfamate for wallpapers. Their main common advantages are their low toxicity, their solid state and, in case of fire, the absence of dioxin and halogen acids as well as their low evolution of smoke. Their efficiency lies between that of halogen compounds and that of aluminum trihydrate and magnesium hydroxide. The

metallic hydroxides split off water and are environmentally friendly, but their low activity requires high concentrations which change the mechanical properties of the matrix that they are applied to. In contrast to many halogen compounds, flame retardants based on nitrogen do not interfere with the set of stabilizers added to every plastic material. Recyclability has become important as many plastics are recycled. Flame retarded materials based on nitrogen compounds are suitable for recycling as the nitrogen flame retardants have high decomposition temperatures. In the field of cable jacketing they evolve less corrosive gases during combustion and do not damage the electrical installations. Flame retardants based on nitrogen are environmentally friendly because they do not add any new element to those already present in the polymers such as polyurethanes, nylons and ABS. In regard to waste disposal they are comparable with fertilizers as they possess the same elements of importance, namely nitrogen and phosphorous. In comparison with metallic hydroxides they are more efficient and deteriorate the mechanical

- **Silicon based flame retardants:** Silicon-based materials are potential flame retardants as they produce protective surface coatings during a fire, caused by a low rate of heat released. Low levels of silicone in certain organic polymer systems have been reported to improve their LOI and UL-94 performance. Some compounded silicone (polydimethylsiloxane-type) contains dry powders with a variety of organic plastics. Particularly in PS, they showed that an additive level, as low as 1 to 3%, reduces the rate of heat released by 30 to 50%. They reported similar improvements in HIPS, PP, PS-blends EVA.
These compounds can either be physically mixed with the base material (additive flame retardants) or chemically bonded to it (reactive flame retardants).Despite restrictions on further production in some countries, consumer products previously treated with banned retardants are still in use and continue to release toxic chemicals into the environment, and the worldwide use of organohalogens retardants continues to increase [13].

- **Intumescent Flame retardants:** Intumescences is the result of a combination of charring and foaming at the surface of the burning polymer, which protects the underlying material from the action of the heat or flame. Intumescent FRs (IFRs) is often used for applications requiring high levels of flame retardancy. They are highly efficient and low toxic. They provide very robust fire safety and flame resistance performance. The carbon agent forms multicellular charred layers, the char may be soft or hard [14]. Soft char IFRs: composed of a carbon source pentaerythritol (PER), acid source (ammonium polyphosphate) and a gas-blowing additive (melamine) harder char IFRs: composed of sodium silicates and graphite. These are suitable for use in plastic pipe firestops as well as exterior steel fireproofing. PER is quite costly. A possible substitute is green carbon agent is chitosan (CS), obtained by the alkaline deacetylation of abundantly naturally occurring chitin. A good synergistic effect observed when chitosan/urea compound based phosphonic acid melamine salt (HUMCS), was added to an IFR system for polypropylene (PP) [14]. A reactive, intumescent, HFFRs 2-({9-[(4, 6-diamino-1, 3, 5-triazin-

2-yl) amino]-3,9-dioxido-2,4,8,10-tetraoxa-3,9-diphosphaspiro [5.5] undecan-3-yl}oxy) ethyl methacrylate (EADP), synthesized from phosphorus oxychloride, pentaerythritol, hydroxyethyl methacrylate, and melamine. EADP (Figure 2) exhibited excellent thermal stability and char-forming ability without affecting tensile strength of polypropylene [15].

Rigid polyurethane foam (RPUF) is very flammable and releases toxic gases while burning. Traditional IFRs are mixtures, and are not compatible with the RPUF matrix [16]. A phosphorousnitrogen (P-N) containing IFR, toluidine spirocyclic pentaerythritol bisphosphonate (TSPB), (Figure 3) exhibited better compatibility with RPUF and lesser negative influence on the mechanical properties of TSPB-RPUF forming compact and smooth char [17]. Waterborne polyurethane (WPU) has good applicability including fabric coating as against conventional solvent borne polyurethanes. Octahydro-2, 7-di (N, N-dimethylamino)-1, 6, 3, 8, 2, 7-dioxadiazadiphosphecine (ODDP) (Figure 4), with bi-phosphonyl in a cyclic compound, was synthesized. ODDP reacted phosphorus-nitrogen synergistic HFFR waterborne PU (DPWPU) has excellent flame retardancy due to the presence of ODDP. The LOI value of DPWPU is 30.6% with UL-94, V-0 classification obtained at 15 wt % ODDP [18].

- **Nanocomposites:** Nanocomposites is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometres, or structures having nanoscale repeat distances between the different phases that make up the material. Polymer layered-silicate nanocomposites (PLSNs) with silicate enhance mechanical properties, increase heat-distortion temperatures, improve thermal stability, decrease gas/vapour permeability and reduce flammability [19]. The use of P–N flame-retardant with montmorillonite (MMT) as a flame-retardant synergist for flame-resistant thermoplastics such as PP, PA6, and PA66 has been reported [20]. Chemically, montmorillonite is hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca) 0.33 (Al, Mg) 2 (Si4O10) (OH) 2 •nH2O. Montmorillonites swell or expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. By exchanging sodium cations for organic cations the surface energy of MMT decreases and the interlayer spacing expands. The resulting material is called organoclay [21]. Thermoplastic poly (ester ether) elastomers (TPEEs) are easily ignited and rapidly burned. TPEE nanocomposites with phosphorus-nitrogen (P-N) flame retardants and organic montmorillonite (o-MMT) were prepared by melt blending. A significant fire-retardant effect was induced in TPEE and rendered a V-0 classification in the UL 94 test [22]. Organically treated layered silicates (clays), carbon nano-tubes/nano-fibres, or other submicron particles at low loading (1-10 wt%) are used for polymer nanocomposites. The polymer nanocomposites greatly lower the base flammability of a material. Recent research has suggested that combining nanoparticles with traditional fire retardants (e.g. intumescent) or with surface treatment (e.g. plasma treatment) effectively decreases flammability [23]. When polymer nanocomposite is used, very little additive is needed (no great cost increase) and polymer
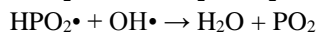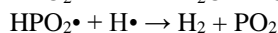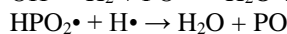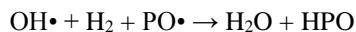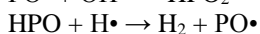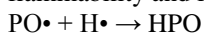
dripping/flow while burning is reduced. The composite may have multifunctional performance (ex: electrical conductivity from carbon nanotubes) and a balance between flammability and mechanical properties may be maintained. However, careful design and analysis is required for set up of a polymer nanocomposite structure. Many aspects of nanocomposite technology (long-term ageing, environmental hazards, conservation of fire safety principles etc.) are not known.

- **Synergist:** The most widely used antimony synergist is antimony trioxide, antimony pentoxide & Sodium antimonate

- **Antimony Trioxide:** Approximately 20,000 metric tons of [1309-64-4] (commonly referred to as antimony oxide), Sb_2O_3, was used in the United States in 1990 to impart flame retardancy to plastics. Although antimony trioxide is found in nature, it is too impure to be used. Flame-retardant grades of antimony oxides are manufactured from either antimony metal or the sulfide ore by oxidation in air at 600-800 °C.

- **Antimony Pentoxide:** The second most widely used antimony synergist is antimony pentoxide [1313-60-9], Sb_2O_5, produced by the oxidation of the trioxide using either a peroxide or nitric acid. Antimony pentoxide is available as a nonpigmenting colloidal suspension in either water or organic media or as an agglomerated powder.

- **Sodium Antimonate:** Sodium antimonate [15593-75-6], Na_3SbO_4, another antimony synergist of commercial importance, has an antimony content of 61-63 wt % and a bulk density of 39.4-46.4 kg/m^3. It is made by oxidizing antimony trioxide using sodium nitrate and caustic.

3. Mechanism
Since the understanding of flame retardancy mechanisms of flame retardants containing phosphorus tends to be oversimplified, in this subsection some details are underlined. Some general points about fire retardancy mechanisms will be clarified in advance, with the following subsection concentrating on more specific results and conclusions with respect to the tasks and materials investigated.

In a very similar way to the flame retardants containing halogen; those containing phosphorus can act in the gas phase [11, 24]. In this case hydrogen and hydroxy radicals are replaced by less effective radicals or are rendered harmless by radical recombination in the gas phase. Some key reactions, of the hundreds possible, are proposed to be the most important (Equation 1). Branching and chain reactions of the oxidation of hydrocarbons in the gas phase are slowed down or interrupted, which is called flame inhibition, and reduces the production of heat. The efficiency of P in the gas phase is reported to be similar or even superior to hydrogen halides like HBr [24] Although detailed investigations of the flame zone, such as identifying the intermediate products and monitoring concentrations of the different products, are rather rare [25, 26, 27] the main principle seems to be understood. It is believed that the PO-radical plays the major role. Furthermore, the resulting flame retardancy effects are obvious, including a clearly decreased heat release due to a reduced heat release rate (HRR)/mass loss rate value during flammability and fire tests.

$$PO\bullet + H\bullet \rightarrow HPO$$
$$PO\bullet + OH\bullet \rightarrow HPO_2$$
$$HPO + H\bullet \rightarrow H_2 + PO\bullet$$
$$OH\bullet + H_2 + PO\bullet \rightarrow H_2O + HPO$$
$$HPO_2\bullet + H\bullet \rightarrow H_2O + PO$$
$$HPO_2\bullet + H\bullet \rightarrow H_2 + PO_2$$
$$HPO_2\bullet + OH\bullet \rightarrow H_2O + PO_2$$

4. Application of Flame retardants
Polycarbonates and Their Blends:
At least in the last decade, patents published on the flame retardancy of polycarbonates (PCs) and their blends significantly exceed the number of patents on flame retardancy of any other polymers. Bridged aromatic diphenyl phosphates, especially resorcinol bis (diphenyl phosphate) and bisphenol A bis (diphenyl phosphate) have found broad application because of their good thermal stability, high efficiency and low volatility.

Aromatic phosphates are rarely used in plain PC because of partial loss of clarity, tendency to stress-cracking, and somewhat reduced hydrolytic stability, but are broadly used in PC/ABS. Bridged aromatic diphenyl phosphates seem to be finding much broader application than monophosphates because of good thermal stability and low volatility. Resorcinol bis (diphenyl phosphate) available from Supresta LLC under the trade name Fyrolflex RDP

Gajiwala et al. [28] synthesized and characterized the two thermally stable polymers containing a polybenzimidazole and a ladder polymer structure are described. The polybenzimidazole polymer was synthesized by condensing tetra amino phenazine with terephthaldehyde in dimethyl acetamide solvent.

Chen et al. [29] synthesized a novel silicone and phosphate modified acryl ate (DGTH) and characterized by 1H NMR and FTIR. Zuo et al. [30] synthesized a novel phosphorus-containing triazine oligomers poly (2-morpholinyl-4-pentaerythritol phosphate-1, 3, 5-triazine) (PMPT) as a kind of tri-component intumescent flame retardant (IFR).

Rakotomalala et al. (2010) [31] synthesized the latest advancements in phosphorus containing flame retardants for electrical and electronic (EE) applications and compare them with commercially available ones. The mechanism of degradation and flame retardancy of phosphorus flame retardants in epoxy resins will also be discussed.

Adivarekar et al. (2013) [32] synthesized halogen free ecofriendly phosphorous based flame retardant for polypropylene.

Polyesters and Nylons
Non-halogenated systems are of interest for polyesters and nylons and a few have recently been introduced to the market, whereas nonhalogen phosphorus-based additives, thermosol finish, or co-reactant systems have been in use for many years in PET textiles [33]. The requirements for polyesters and nylons are stringent because of high processing temperatures, sensitivity to degradation caused by possible acids and the need for long-term dimensional stability, and avoidance of exudation ('blooming'). These various requirements have eliminated most of the known phosphorus-based flame retardants apart from thermally very stable materials. In late 70s and early 80s, various metal salts of dialkylphosphinates were prepared at and tested in PET by Pennwalt [34]. Later, Ticona and Clariant [36-38] following up this invention as well as earlier work by Hoechst [35] tested a variety of dialkylphosphinates; zinc, aluminum, or calcium salts in glass-filled nylons and polybutylene terephthalate (PBT). They found that the Al or Ca salts of ethylmethylphosphinic

Acid.

Thach-Mien et al. [39] developed an environmentally friendly halogen-free phosphorus–nitrogen bond flame retardant for cotton fabrics A novel flame retardant diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3) containing phosphorous and nitrogen was prepared.

Thach-Mien et al. [40] synthesized a new charring agent, a derivative of cyanuric chloride, mono-substituted, dimethyl (4,6-dichloro-1, 3, 5-triazin-2- yloxy) methyl phosphonate (CN), was synthesized in good yield and characterized. Its flame retardant and thermo gravimetric properties were compared to those of the di-substituted compound, tetra methyl (6-chloro-1, 3, 5-triazine-2, 4-diyl) bis (oxy) bis (methylene) diphosphonate (CN-1).

Epoxy resins

There are a few ways to incorporate phosphorus-containing species into the epoxy resin network, some of which are finding commercial application [41]. Since the P–H bond can add to the epoxy group, this reaction can be used to attach hydrogen phosphonates or phosphinates to an epoxy resin. The only example of a commercially available reactant of this type is the DOPO mentioned previously. It is sold in Japan, China, and Europe and is recommended to be a part of the curing system for halogen-free flame-retardant epoxies [42]. However, it has a drawback related to its monofunctionality and can only be used in conjunction with other curing agents.

By reacting DOPO with quinone, a phenolic difunctional product can be made. This product is available in Japan from Sanko. It can be incorporated in an epoxy resin through a chain-extension process similar to tetrabromobisphenol A. Although it provides good physical properties and the required level of flame retardancy, it is not finding broad application because of its price.

Phosphine oxide structures have been proposed to impart flame retardancy to curing agents, because phosphine oxides are thermally and hydrolytically very stable. Many studies have been reported in the literature concerning the curing of epoxy resins with bis (aminophenyl)-methylphosphine oxide, as well as thermal and combustion performance of the fire-retardant epoxies [43-49].

Because of the strong nucleophilic character of the amino groups, it cures epoxy at the relatively low temperature of 150°C. Recently, Great Lakes patented a broad range of OH functional triphenyl or diphenylalkyl phosphine oxides [50]; however, probably for price reasons, they seem to be concentrating on the mixture of tri-, di- and mono-functional 4-hydroxyphenyphosphine oxides [51].

Ru-Jong et al. [52] synthesized Flame retardant epoxy polymers based on all phosphorus-containing epoxy resin, bis (3-t-butyl-4-glycidyloxyphenyl-2, 4-di-t-butylphenyl) resorcinol diphosphate, and subsequently cured with non-phosphorus containing amines, and/or novel phosphorus containing aromatic or polyoxy alkylene amines.

Zhang et al. [53] synthesized a novel bisphenol 1, 4'-bis{4-[(4-hydroxy) phenyliminomethylidene] phenoxy} benzene (BHPB), which contains azomethine moiety and flexible aromatic ether linkage, was synthesized and introduced into the curing system composed of diglycidyl ether of bisphenol A (DGEBA) and diamine.

Huang et al. [54] prepared flame-resistant novel halogen-free epoxy hybrid hexakis (methoxy methyl) melamine (HMMM), a phosphorous containing epoxy resin (EPN-D) with 9, 10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO)

group and phenol formaldehyde novolac (n-PF). All the cured EPND/ HMMM/n-PF hybrid resins achieved the UL 94 V-0 grade with high limited oxygen indices (LOI>45.7). It is found that phosphorous and nitrogen elements in the cured EPN-D/HMMM/n-PF hybrid resins had a positive synergistic effect. Gérard et al. [55] prepared the flame retardant epoxy-based thermosets. The incorporation of additives in these polymers, including synergism effects. Reactive flame-retardantswhich are incorporated in the polymer backbone-are reported and the use of fire-retardant epoxy coatings for materials protection is also considered.

Tomuta et al. [56] synthesized Dihydrazides of different structure. And tested as curing agents for DGEBA epoxy coatings. By calorimetric studies their latent characteristics were proved and the kinetics of the curing studied.

Gouri et al. [57] synthesized phosphazene compound like Cyclotriphosphazene containing the epoxy group hexaglycidyl cyclotriphosphazene (HGCP). This reactive monomer that is inherently flamed retarding contain P and N, can be used on their own as composite material precursor or added to current bulk commercial polymer diglycidylether of bisphenol A (DGEBA) to enhance flame retardancy. The thermal stability and flame retardancy of HGCP thermosets with MDA curing agent and its blend as flame retardant with DGEBA were checked by the UL-94 vertical test.

Meenakshi et al. [58] developed and characterized triphenyl phosphine oxide based phosphorus tetraglycidyl epoxy nanocomposites denoted as 'C' and to find out its suitability for use in high performance applications. Rane et al [59] are synthesized phosphorous containing amine, tripropyldiamine phosphine oxide and hybrid monomer 4-(N-pthalimidophenyl) glycidyl ether & characterized by FTIR, NMR & elemental analysis.

Polyurethane (Pu) Foams An oligomeric ethyl phosphate additive containing 19% phosphorus has been introduced by Supresta LLC as Fyrol PNX. It is an Oligomeric additive [91, 92] with a repeating unit of the structure.

Because PNX is halogen-free, it is especially of interest in Europe, particularly with respect to the automotive industry and their low fogging/volatile organic content (VOC) emission requirements. In the MVSS 302 test, this oligomer is on average 40-50% more efficient than the chloroalkyl phosphates. In terms of VOC, PNX compares well with other flame retardants used in the automotive industry, but it becomes especially advantageous because the low use level also helps to maintain low VOC.

Yang Cao et al. [60] are synthesized four excellent halogen-free biphosphonate flame retardants (EBDMP, EBDEP, MBDMP, MBDEP). They are synthesized through polycondensation and Arbuzov rearrangement reactions without using any solvents. The products were characterized by ESI-MS, FT-IR and 1H NMR. The application of EBDEP in polyurethane soft foam was studied and the results illustrated its excellent flame-proofing properties

5. Conclusion

The scientific and public debate on flame retardants has led to some regulatory restrictions on mostly halogenated flame retardants (e.g. RoHS and WEEE directives, REACH in Europe) as well as the evaluation of alternatives. The researcher confirmed that, viable alternative flame retardants are available, HFFRs have similar fire performance and technical application capabilities as BFRs. In general, halogen

free systems produce less smoke and less toxic components in smoke. Flame retardants manufacturers try to develop new and better products as well as supply their customers with all necessary information.

From the commercial standpoint, phosphorous flame retardants are in active state of development driven by their good performance & also by environmental & regulatory problem with the brominated flame retardants. Reactive polymeric phosphorous base flame retardants are under active development in epoxy printed wiring board to replace TBBA. On the scientific side, enough mechanism of action research has been carried out to show that while non-halogenated flame retardant like phosphorous flame retardant can have an important mode of action as char former or char enhancer in the condensed phase, there is increasing recognition that vapor phase action can be significant as the existence of these two different modes of action suggest many synergistic combination. Base on the literature review, various scholars have studied flame retardant subject and tried to introduce various new products with special applications.

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