EUROPEAN JOURNAL OF BIOMEDICAL AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 3
Issue: 8
108-116
Year: 2016

A SHORT REVIEW ON FIRE RETARDANT POLYMERIC MATERIALS

[1]*Trinath Biswal, [2]Munmun Priyadarsini and [3]P.K. Sahoo

[1,2]Department of Chemistry, VSSUT, Burla-768018.
[3]Department of Chemistry Utkal University Bhubaneswar-751001, India.

Corresponding Author: Dr. Trinath Biswal
Department of Chemistry, VSSUT, Burla-768018.

Article Received on 22/05/2016 **Article Revised on 13/06/2016** **Article Accepted on 04/07/2016**

ABSTRACT
The objective of this review work is to make interest in the field of fire retardant polymer based materials and nanomaterial as the demand of improved safety in domestic, public and industrial situation required by fire-safety standard and more accessible to the material science community, chemists, physicists and engineer. We particularly focus on some of the polymer composites and Nano composites i.e. polymer material focus with specific finely dispersed Nano filler which will undoubtedly gave the way for future materials combining physiochemical and thermo-mechanical performances with enhanced flame retardant behaviour. We generally focused here the fire retardant property of polymeric material like wood-plastic composite, poly- vinyl acetate composite, mineral flame retardant, halogenated flame retardant, phosphorous based flame retardant , nitrogen based flame retardant and silicon based flame retardant along with some Nanomaterial particles like, nano clays, carbon nano particle etc.

KEYWORDS: fire retardants, polymer nanocomposites, fire retardacny, carbon nano tube, nano clays.

INTRODUCTION

Fire has long been a major hazard in our daily lives. From the fire protection engineering point of view, most the fire hazards could be controlled when we consider all contribution factors, such as ignitability, flame velocity, materials flammability and fire suppression.[1,2,3] In our day to day life the polymer materials are mostly used due to their excellent properties like low molecular weight and easy to processing. However the polymeric material is known for their relatively high flammability, which is most often accompanied by simultaneous production of toxic gases and smoke during combustion. Hence improving the fire retardant behaviour of the polymeric materials and composite is a major challenge for extending their use in most of applications both in industry and domestic. The scientific and technical literature contains very diverse and efficient strategies for improving polymer fire retardant, which mostly depends upon the nature and chemical structure of the polymer and polymer composite. Concerned, it decomposition mode and the required level of fire safety and also global performance of polymeric material and composites. To control polymer fires, flame retardant technology is becoming increasingly important In general, flame retardant additives are used to limit the fire risk. Those additives are incorporated in the polymer matrix to increase the time to ignition, improve self-extinguishing properties, decrease the heat release rate and prevent the formation of flammable drops. Although flame retardants may differ from one another, three general flame retardancy mechanisms are applicable: gas phase flame retardants, endothermic flame retardant and char-forming flame retardants.[4,5,6]

I. Gas phase flame retardants (i.e., halogen, phosphorus): This is the chemical mechanism in the gas phase. These materials reduce the heat released in the gas phase from combustion by scavenging free radicals.
II. Endothermic flame retardants (i.e., metal hydroxides, carbonates): This is the physical mechanism in the gas phase. When on fire, these materials release a large amount of non- flammable gases (H2O, CO2), which dilute flammable gas and decease the temperature.
III. Char-forming flame retardants (i.e., intumescents, nanocomposites): This is the condensed phase mechanism. These materials operate by preventing fuel release through binding up fuel as non-pyrolyzable carbon (char) and providing thermal insulation for underlying polymer through the formation of char protection layers.

The most successful fire retardant compound for poly vinyl acetate (PVAc) is those that react chemically with the substrate and act in the condensed phase. Compound that form part of a composite should ideally exhibited much functional ability. Example of such fire retardants

are magnesium hydroxide [Mg (OH)2] and zinc borate (2 ZnO. 3 B2O3. 3 H2O). Fire retardant changes the decomposition path of polymer during heating, so as to reduce the concentration of the combustible volatile material and to promote char formation. The char may be in tumescent, offering heat and fire resistance until it reaches a critical temperature above which it burns.[7,] The use of in tumescent char system is a improvement for building infrastructure protection where emulsion polymer has been applied in coating, paints and sealants. On heating expose of these types of materials, activation and formation of an in tumescent char occurs. That provides an insulating barrier between the fire and underlying substrate. An in tumescent char normally results from an increase in significant volume or thickness of a foam–like layer. Fire protection by coating that procees via intumescences increase the path for heat transfer and increase the thermal gradient from the charred surface to the substance polymer.[8]

Wood–plastic composite (WPC) are a new class of material that means the best feature of wood and plastic, Good reactor to fire properties are necessary for many possible applications of WPC.[9] These properties are important especially for application to residential construction, transportation and furniture industries. For much application in these fields, the fire performance of the materials has to be known.[10]

In this review, the main aim is to present the keys for understanding the fire behaviour in polymeric materials and composites.

Combustion of Polymers

The chemical structure of the polymer indicates that it mainly made up from carbon and hydrogen for which are highly combustible.[11]

The combustion reaction involves two factors one combustible (reducing agent) and another one combustive (oxidising agent). The whole process usually starts with an increase in the temperature of the polymeric material due to a heat source. To such an extent that it reduces polymer bond scission. The volatile fraction of the polymer fragment diffuses into the air and creates a combustible gaseous mixture. The gaseous mixture ignites when auto ignition temperature is reached. Alternatively the fuel can also ignite at a lower temperature (flash point) upon reaction with external source of intense energy (spark, flame etc.).

The life span of the combustion cycle depends on the quantity of heat liberated due to the combustion of the fuel. When the amount of heat liberated reaches to a certain minimum level, then a complete new decomposition reaction are produced in the solid phase and therefore more combustible materials are produced. This type of combustion is called fire triangle.

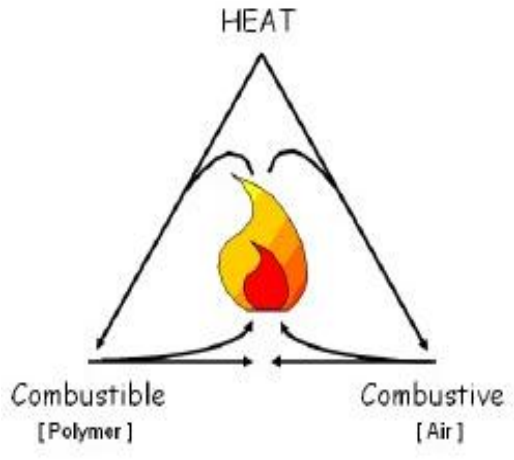

Figure 1: Principle of the combustion cycle

The thermal decomposition of polymeric material is an endothermic process, which requires an input of energy. The energy provided to the system must be higher than the binding energy between the covalently linked atoms (200 to 400 KJ for most of the C-C bond of polymer). The decomposition mechanism is highly dependent on the weakest bond and also presence or absence of oxygen in solid and gas phase. Hence thermal decomposition is the combination of effect of heat and oxygen. Hence it can be distinguished as oxidising thermal degradation.[12]

Non oxidizing

Thermal degradation is generally initiated by chain scissions under the simple effect of temperature (Pyrolysis). This scission involves different degree of material depolymerisation. The initial scission depends on several factors.

i- The presence of oxygen atoms in chain and catalyst residue. ii- Former residue of oxidation. iii- Chemical defect in polymer chain and the existence weak bonds along with chain, particularly at the end, which instates unzipping reactions.

Again chain scission can occurs in two ways.

By formation of free radicals

R1-CH2-CH2-R2→ R1-CH2 + R2-CH2

In this case the reaction does not stop at this stage because these radicals stand a chain, which occur both oxidising and on-oxidising condition.

By the migration of hydrogen atoms and the formation of two stable molecules are of which a reactive C-C double bond has. R-CH2-CH2-CH2-R2 →R1-CH2=CH2 +R2-CH3

In the oxidising thermal degradation, the polymer reacts with oxygen in air or oxygen and generated a variety of low molecular weight products (carboxylic acid, alcohol,

ketone, aldehyde etc.,). Thus degradation also releases some reactive species like, H^+,OH^-, particularly in polyolefin's.

Oxidation can lead to cross linking through recombination reaction of the micro molecular radicals. The propagation rate of the degradation process is controlled by the wrenching reaction of hydrogen atoms from the polymer chain. The oxidation stability of the polymer depends on the C-C bond energy.

Some of the researcher suggested that at combustion temperature above 300°C, polymer degradation takes place via non oxidising thermal decomposition. Under these conditions, the rate of pyrolysis is much faster than the diffusion of oxygen in solid phase. Hence the oxidation, therefore, only occurs in the gaseous phase due to presence of low molecular weight compound produced by thermal decomposition.[13,14] The decomposition gases generated by pyrolysis first mixed with oxygen by both convention and diffusion into the layer close to the surface, create free radical and then ignites. This ignition can be triggered by an external flame (Flash-ignition) or self-induced (self-ignition) when the temperature is sufficiently high. The combustion of the gases increases the polymer temperature and thus supports the pyrolysis and the production of new combustible gases. Combustion thus continues even in the absence of an external heat source. Flame propagation is also affected by physical factor more specifically thermal transfers. Conductive transfer is important in the initial phase of fire development when the height of the flame remains limited to a few terms of centimeter During these different stages, the development of considerable material heterogeneity can be highlighted particularly during combustion. Therefore , a gradient structure tends to form inside the material arising from interaction with atmospheric oxygen coupled with the outward diffusion of reactive species and also concomitant polymer chain break down within the material.[15] Several zones inside the material can be interfiled. The gaseous decomposition product first tend to be located in the cavity of the under layer and after wards migrate through surface when combustion takes place. The under layer is in direct contact with the thermal decomposition zone of the polymer and lives on the top of the layer in which the polymer remain intact even if it may undergo phase transitions. In addition, there is energy balance established between the heat transitions occurring in the homogeneous structure.

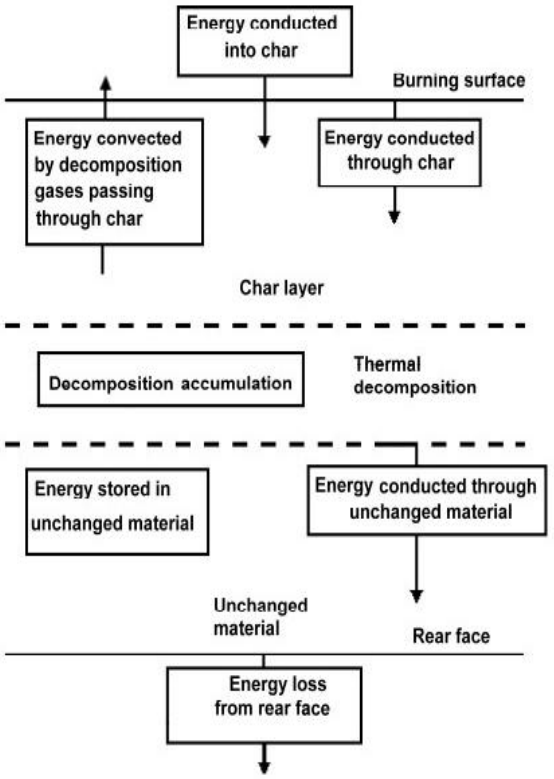

Figure 2: Identification of thermal transfers during combustion

Fire Retardant Methods

The main mode of action of fire retardant system is reported and it is mainly of two types.[16, 17] Fire retardant system can act physically (by covering the formation of protective layer or fuel dilution). They can interfere with the various process involved in polymer combustion (heating, pyrolysis, ignition, propagation of thermal decomposition)

Physical action

This method is based upon decreasing temperature induction by some flame retardant additives by heat consumption (endothermic reaction). In this method the reaction medium is cooled below the polymer temperature. Hence we can take hydrated trialuminium or magnesium hydroxide as suitable flame retardant, because it starts liberating water vapour at approximately 200 and 300° C respectively.

When the flame retardant material decomposes, it produces gasses (CO_2, H_2O,NH_3 etc.), which mixed with combustible gasses and diluted. So limiting the concentration of reagent and the possibility of ignition. In addition to this effect, some fire retardant additives have capacity of formation of a protective solid or gaseous layer between the gaseous phase where combustion occurs and the solid phase where thermal degradation takes place. Such protective layer will cause the transfer of maters, combustible gases and oxygen. As result this amount of production of decomposition gases decreases significantly causing the physical separation of

fuel gases from oxygen and prevent the combustion process.

Chemical action

This method is in general target at interfering with free radical reaction which take place during the burning of gaseous phases and protect the internal material from heating char creation (solid phase). This process occurs either in gaseous phase or in the condensed phase. The free radical mechanism of combustion process can be stopped by the incorporation of flame retardant additive (specially releases of radical (Cl^{-},Br^{-}) in the gaseous phase. These radical reacts with highly reactive species (such as H· and OH·) and forms less reactive or even inert molecule. This modification of the combustion reaction pathway is the cause of decrease in temperature and therefore a reduction of fuel is produced.[18,19]

In the condensed phase two types of chemical reaction triggered by flame retardants are possible.

- The flame retardants accelerate the rupture of the polymer chain. In this case the polymer drips and moves away from the flame action zone.
- In the second case the flame retardant forms a carbonized (expanded) on vitreous layer at the surface of the polymer chains. This char or vitrified layer acts as a physical insulating layer between gas phase and condensed phase. Depending upon the mode of function flame retardants are classified into following two categories.

Additive flame retardant

These are generally incorporated during the transformation process and do not react at this stage with the polymer but only at higher temperature at the start of the fire they usually act as mineral fuels ,hybrids on organic compounds which can include macromolecule.

Reactive flame retardant

Like additive flame retardants these are usually introduced into the polymer chain during synthesis or in a post reaction process (i.e. via chemical grafting). Such flame retardants are integrated in polymer chain.

Laboratory Method of Testing of flammability

The flammability of polymer can be characterized by their ignitability, flame spread rate and heat release. Depending on the targeted application of the polymeric material, one or more of these flammability criteria needed to be measured by appropriate flammability test. There are a number of small, intermediate or full-scale flammability tests are now adopted in industrial or academic laboratory for either screening material during product development or testing manufactured product.[20,21]

The most commonly used flammability laboratory testing methods are as follows.

Limited oxygen index(LIO)

This test was first proposed in 1966 by Ferimone and Mantin[22] and is used to indicate the relative flammability of material.[23] The LIO test is now subjected to an international standard (ISO 4589). The value of the LIO is defined as the mineral oxygen concentrated [O2] in oxygen-nitrogen mixture [O2/N2] that either maintains flame combustion of material for 3 minutes or consume a length of 5cm. of the sample , with the sample placed in a vertical position (two of the test sample is inflamed with a burner).

The LIO is expressed as

LIO =100[O2]/{[O2]+[N2]}

According to the measurement of TSO 4589, the LIO is measured on (80 x 10 x 4 mm) specimens placed vertically at the certain of glass chimney (fig 3). The mixture of gases flows up stream through this chimney and is homogenized by being posed through layer of glass beads. After 30 second purge of the column, the top of spectrum is ignited like a candle.

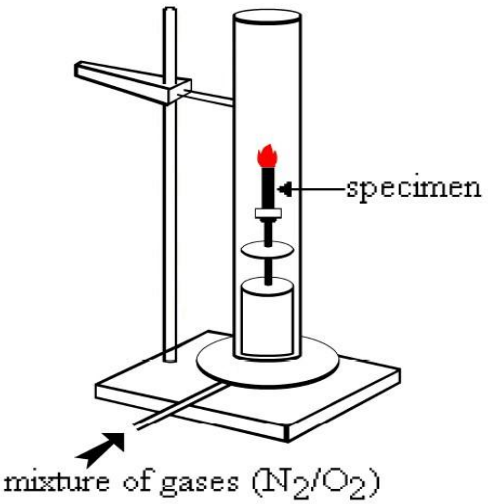

Figure 3: Experimental set-up for LOI measurement

If the air contains 21% oxygen, material with an LIO below 21 are classified as combustible, whereas those with an LIO above 21 are classified as" self extinguishing ", because their combustion sustained at ambient temperature without an external energy contribution. The higher is the LIO, the better is the flame retardant property.

Now days this test is considered to be relatively not acceptable because of the development and more standardization (elaborated table-1) Listed flash -ignition temperature, self-ignition temperature and % of LIO of different polymers.)

Table 1: Flash-ignition temperature, self-ignition temperature and correlated LOI values for selected representative polymers

Polymer	Flash-ignition temperature (°C)	Self-ignition temperature (°C)	LOI (%)
polyethylene	340	350	18
polypropylene	320	350	18
polystyrene	350	490	18
Poly(vinyl chloride)	390	450	42
Poly(tetrafluoroethylene)	560	580	95
Acrylonitrile-butadiene-styrene terpolymer	390	480	19
Poly(methyl methacrylate)	300	430	18
Poly (acrylonitrile)	480	560	27
Polyamide 6	420	450	25
Polymaide 66	490	530	24

UL94V

This test has been appeared by the "underwriter laboratory "as the flammability of the plastic material for paint in devices and appliances , it included a range of flammability test(small and large flame vertical test, horizontal test for bulk and foamed material, radical panel flame spread test). The most commonly used test is UL94V for bulk measuring the ignitability and flame spread of vertical bulk material exposed to a small flame.

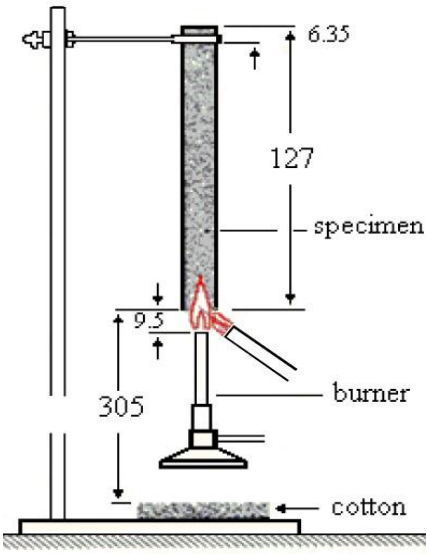

Figure 4: Experimental set-up for the UL94V flammability test

The burner is controlled to produce a blue flame with a 20m high cone and a power of 50W was supplied. The flame is applied to the bottom of the spectrum at the top of the burner which has to be located at 10 mm from the bottom edge of the specimen. The flame is laid for 10seconds and then removed. The after flame time i.e. the time required for the flame to extinguish (t1) is noted. After extinction, the flame is applied for another 10 seconds. Then after flame time (t2) is noted. Together with the afterglow time (t3) i.e. the time required for fire glow to disappear is noted. During the application of the flame, the distance between the burner and specimen must remain constant. If drops fall, the burner must be flitted through a maximum angle of 45°c slightly isolated from the specimen flame. During the conduct of test, presence of burning drops, causing a piece of cotton located under the sample to ignite must be noted.

The specimen V0,V1,V2 classified listed in (**Table- 2).**

Table 2: Classification of materials for the UL 94 V flammability test

Fire classification	
UL94 V_0	t_1 and t_2 less than 10 sec for each specimen $t_1 + t_2$ less than 50 sec for the 5 specimens $t_2 + t_3$ less than 30 sec for each specimen No afterflame or afterglow up to the holding clamp No burning drops
UL94 V_1	t_1 and t_2 less than 30 sec for each specimen $t_1 + t_2$ less than 250 sec for the 5 specimens $t_2 + t_3$ less than 60 sec for each specimen No afterflame or afterglow up to the holding clamp No burning drops
UL94 V_2	t_1 and t_2 less than 30 sec for each specimen $t_1 + t_2$ less than 250 sec for the 5 specimens $t_2 + t_3$ less than 60 sec for each specimen No afterflame or afterglow up to the holding clamp Burning drops allowed

Cone Calorimeter

The cone calorimeter is one of the most effective polymer fire behaviour test. The principle of cone calorimeter experiment is based on the measurement of the decreasing oxygen concentration in combustion gasses of a sample subjected to a given heat flux (generally 10 to 100 KW/m^2). The experimental set up of cone calorimeter standardized in the United States.(Fig-5).

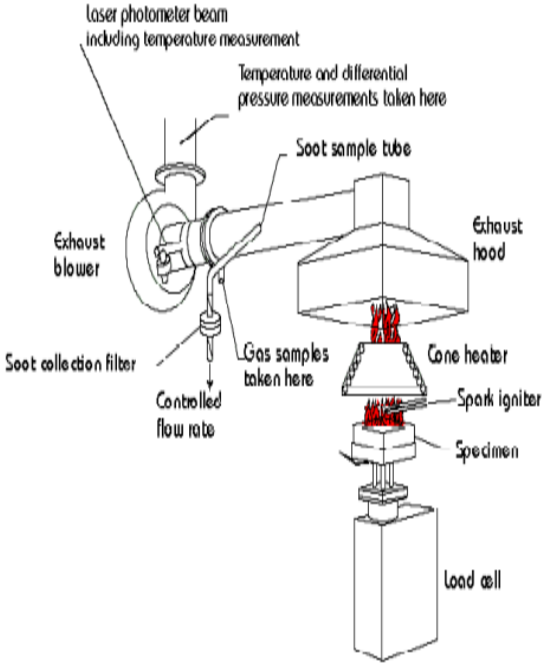

Figure 5: Experimental set-up for a cone calorimetry measurement

The sample (100 x 100 x 4 mm) is placed in a load to evaluate the evolution of mass loss during the experiment. A conical radiant electrical heater uniformly irradiated the sample from above. The combustion is triggered by an electric spark.

The so produced combustion gases pass through the heating cone and captured by means of an exhaust dues system with a centrifugal fan and hood. The gas flow, O2, CO and CO2 concentrations and smoke density is measured in the exhaust dust.

The measurement of the gas flows, O2 concentration are used to calculate the quantity of heat released per unit of time and surface area. The HRR (heat release rate) is expressed in Kw/m^2. The evaluation of the HRR over time, in particular the value of its peak or maximum HRR is usually taken into account in order to evaluate the fire properties. The calculation is based on Huggett's observation, that most of the organic material releases a quantity of heat practically, proportional to the quantity of oxygen consumed while burning. The proportionality factor is constant from one material to another material and is equal to 13.1KJ/g consumed oxygen.[24,25,26] Integration of the HRR vs. time curve gives the total heat release (THR) expressed in KJ/m^2. In addition , the cone calorimeter test also example characterization of the time to time to ignite (TTI), time of combustion or extinction (TOE), mass loss during combustion, quantities of CO and CO2 and total smoke released (TSR).

Undoubtedly, the cone calorimeter test provides more detailed fire characteristics. The heat released rate (HRR) is certainly the most widely used parameters for evaluating the properties of the polymers and polymer composite.

In many cases, flame retardant formulation lead to a significant reduction in HRR values and an increase in the combustion time but must offer without any change in the total heat released. This can more the less be considered as an enhancement of the polymer's flame retardant behaviour, since it enables the same amount of heat to be released over a longer period of time. Consequently it limits the development of fire and the risk of flash-over i.e. an extremely, even explosive, rate of fire spread over the entire area.[27,28,29]

Flame Retardant Additives

1. Phosphorous based Fame additive

The presence of polymers is much essential in everyday life. The range of phosphorous based flame retardant product is extremely wide, including phosphorous, phosphonate, phosphonite, phosphine oxide, phosphate, red phosphorous. These phosphorus based flame retardant agents can be used as additive or incorporated into the polymer chain during its synthesis and are known to be active in the condensed or vapour phase. The integration of the phosphorous and phosphonated material into organic polymer can also enhances the flame retardant properties.[30,31,32] Several condensed phase mechanism are proposed to be responsible for the characteristics photolytic properties.[33,34] The main component of flame resistance is the formation of an in tumescent char.

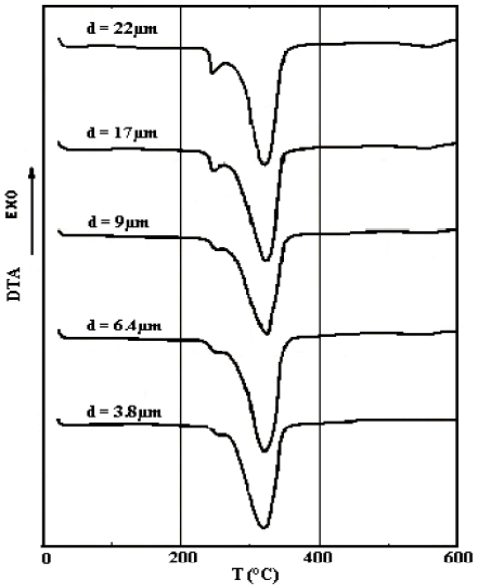

Figure 6: Effect of mean Aluminium Tri-Hydroxide (ATH) particle size on DTA, (Heating rate: 20 c/min)

Intumescence is the swelling of a material into a thick, robust, multi cellular foam upon exposure to heat. Upon its formation the char function as physical barrier

properties the underlying material from further degradation. Poly (vinyl alcohol) PVA on treatment with phosphoric acid generates phosphoesters and that when heated undergoes degradation with subsequent cross linking of the polymer leading to the formation of intumescence char.[35,36] Studies of PVA with and without the addition of phosphorous additive revealed improvement in the LIO (limiting oxygen index) of the phosphorylated sample. This result means that higher levels of oxygen are required to support the combustion of PVA in the presence of the phosphorous additive.

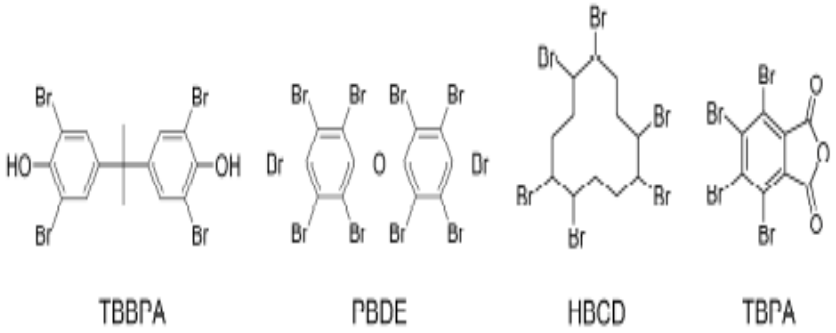

Figure 7: Chemical structure of classical halogenated flame retardant products

Thermo gravimetric analysis (TGA) showed the formation of a residue whose mass increases with increasing phosphorous contained.

In the condensed phase, the phosphorous based flame retardants are particularly effective with polymer containing oxygen.[37,38,39] (polyester, plyamidees cellulose etc.) With most of them thermal decomposition leads to the production of phosphoric acid, which condensed readily to produce pyrophosphate structures and liberate water.

2. Nitrogen-based flame retardants

Melamine is a thermally stable crystalline product characterized by a melting point as high as 345 °C that contains 67 wt% nitrogen atoms. Melamine sublimates at about 350 °C. Upon sublimation, a significant amount of energy is absorbed, decreasing the temperature. At high temperature, melamine decomposes with the elimination of ammonia, which dilutes oxygen and combustible gases and leads to the formation of thermally stable condensates, known as melam, melem and melon (Fig. 8).[40,41] These reactions compete with melamine volatilization and are more pronounced if melamine volatilization is impeded, e.g. by the formation of a protective layer. The formation of melam, melem and melon generates residues in the condensed phase and results in endothermic processes, also effective for flame retardancy. In addition, melamine can form thermally stable salts with strong acids: melamine cyanurate, melamine phosphate, and melamine pyrophosphate. Melamine and melamine salts are characterized by various flame retardant mechanisms. Upon heating, melamine-based salts dissociate and the re-formed melamine volatilizes, like neat melamine, but a large proportion of the melamine undergoes more progressive condensation than in the case of pure melamine.[42,43] The action of salts in the condensed phase is therefore significantly higher. The thermal decomposition of melamine phosphate which leads to the formation of melamine polyphosphate, with the release of melamine and phosphoric acid. The phosphoric acid released is known to phosphorylate .Many polymers and produce flame retardant effects similar to phosphorus-based flame retardant additives. The thermal decomposition of melamine polyphosphate leads to the formation of melam ultraphosphate and ammonium polyphosphate, with the release of melamine. However, the melamine in the gaseous phase competes with the formation of its condensation products, such as melam ultraphosphate. The condensation of melamine is thus accompanied by the formation of polyphosphoric structures. Ammonium polyphosphate can also be formed from melamine polyphosphate. In addition, ammonium polyphosphate tends to dissociate and release ammonia above 300°C and the free condensed hydroxyl groups give cross linked structures (ultra phosphate) with water elimination. The hydrolysis of the melam ultraphosphate generates a melam phosphate derivative or melam polyphosphate. Above 410 °C, the thermal degradation of the ultraphosphate is limited and is followed around 650 °C by the formation of a relatively stable residue. The melamine pyrophosphate evolves to melamine during thermal decomposition but its thermal performances are different from those of melamine and its other salts. The formation of carbonaceous structures is more significant here and its action mode is similar to that of ammonium polyphosphate.[44,45]

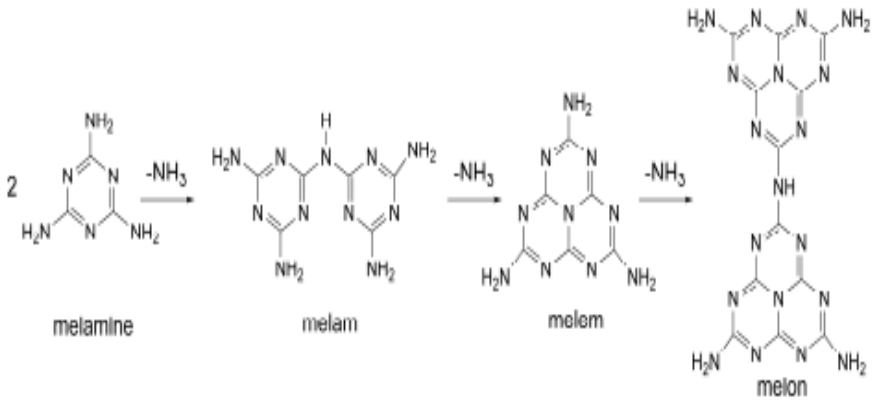

Figure: 8 Thermal decomposition of melamine and related products5.3 Silicon-based flame retardants

The addition of a relatively low amount of silicon-based compounds (silicones, silicas, organosilanes, silsesquioxanes and silicates) to polymers has been reported to substantially improve their flame retardancy. They can be used as fillers incorporated in the polymer, as copolymers or as the main form of polymer matrix. It should be mentioned that the flame retardancy of silicones has been reviewed by Kashiwagi and Gilman.[46,47]

6 CONCLUSIONS

This review has shown that a broad range of flame retardant systems have either already been studied or are currently under development to ensure greater safety in a world where plastic materials are being increasingly used in transportation and buildings, and where fire prevention remains a major issue.

While some systems, such as halogenated compounds, are in the process of being banned due to health and environmental concerns, other systems such as the use of relatively low amounts of nanoparticles or the synergistic effects of flame retardants from various families show very promising results. Among non-halogenated fire retardant additives, phosphorus and nitrogen-based compounds have proved to be very powerful solutions, especially in matrices containing oxygen or nitrogen atoms in their backbone, while silicon-based additives also appear to provide efficient solutions. We have demonstrated that the flammability of plastic materials remains a very complex scientific problem for which no single solution can be found, especially with regard to the extensive diversification of polymer matrices available.

REFERENCES

1. Bellucci F, Camino G, Nicolais L, Flammability of Polymer Composites. Wiley Encyclopedia of Composites, John Wiley & Sons, Inc., New Jersey, United States, 2012.
2. Bourbigot S, Bras ML, Flammability Handbook: Fire Retardant Plastics. Hanser Publications, Munich, Germany, 2003.
3. Morgan AB, Gilman JW. An overview of flame retardancy of polymeric materials: application, technology, and future directions. Fire an, 2013.
4. Camino G, Mattezzoli A, Braglia H., De. Lassano H., Zammarano M. "Effect of hydroxides and hydroxyl carbonate stractue on fine retardant effectiveness and mechanical protenties in ethylene viryl acetate copolymer 3rd polymer Degradation and stability, 74: 457–464.
5. Marosi G.J, "Fine retadancy of polymers, challenges a new concepts. "Express polymer Letter, 2007; 1: 545.
6. Costal L., Avantaneo M, Bracco P, Brunlla V, char formation of polyvinyl polymers "Ploymer degradation and stability, 2002; 77: 503-510.
7. Fu. M, Qu. B synergistic flame retardant mechanism of fumed silica in ethylene vinyl acetate/meagnesium hydroxide blends "polymer Degradation stability", 2004; 85: 633–639.
8. G.Pal, H. Macskasy, plastics: There behaviour in fines, Elsevier, New York, 1991.
9. A. Tkac, J.Polym. chem. Ed, 1981; 19: 1475.
10. A.M. Calenaft, K.Maries, plast. Polym, 1974; 42: 247.
11. J. Troitzsch, international plastics flammability handbook 2nd Edition, Hariser publishers, Munich, 1990.
12. A.R. Honnocks, D. Prico, Fine retardant materials, CRC press, Boston, 2001.
13. C.P Ferimone, F.J Mantin, Mod. Plast, 1966; 44: 141.
14. G. camino, L. Costa, E. Casorati, G. Bertelli, R. Locatelli, J.Appl. Polymer Sei. 1988; 35: 1863.
15. C. Huggelt, fire matter, 1980; 4: 61.
16. P.K. Sahoo, R. Samal "Fire retardancy and biodegradability of Poly (Methyl Methacrylate/Montmorillonite nanocomposite" J. of Polymer Degradation & Stability, 2007; 92: 1700-1707.
17. P. K Sahoo, R Samal, P.K Rana Synthesis of Poly(Butyl acrylate)/Sodium silicate nonocomposite Fire Retadant "European polymer Journal', 2008; 44: 3522-3528.

18. P.K. Sahoo, R.Samal Biodegradable Flame retardant Poly(Butyl acrylate)/Silicate nanocomposites by Emulsifier-Free Emulsion technique"IJCT", 2010; 17: 139-144.
19. Bourbigat. S, Duquesne.8, Fine Retadant polymers: Recent development and opportunities J.Mater. Chem, 2007; 17: 2283–2300.
20. Ma. H. Tong, L.Xu, Z.Frang, Jin.Y, Lu.F., A Novel intumescent flame Retadant: synthesis and Application in ABS copolymer, polym. Deg. Stab, 2007; 92: 720–726.
21. Bras M.L, Bourbigat. S, Delponte. C, Slat.C, Tallec. Y.L,: New In tumescent formulations of fine-retadant polypropylene – Discussion of the free Radical Mechanism of the formation of carbonaceous protective material during the thermo-oxidative treatment of the additives : F.re and mater, 1996; 20: 191–203.
22. Camino. G, Martinasso. G., Costa. L, Gobetto. R,: Thermal degradation of penta enythritol Diphosphate, Model compound for fine Retadant Intumescent systems part –II. Intumescence step "Polym. Deg. Stab, 1990; 28: 17–38.
23. Irigaki. N, Tomiha.K, Katsuura. K: Thermal degradation of phophorylated poly (vinyl alcohol) polymer, 1974; 15: 335–338.
24. Laszkiewicz. B,: Thermal behaviour of poly (vinyl alcohol) modified with phosphorous acid J.Appl. polym Sci., 1971; 15: 437–443.
25. E.D. weid, Encyclopedia of polymer science and Technology, Wiley Interscience, New York, 1986; 11.
26. A.M. Aronson, phosphorous chemistry, Acs symposium, 1992; 486: 218.
27. V. Babushok, W.Tsang, combust Flame, 2000; 124: 488.
28. G. Camino, Polym, Degrad. Stab, 1984; 12: 213.
29. H. Piechota, Kunststoffnundschau, 1965; 12: 191.
30. A. Granzow, Acc. Chem.. Res. 1978; II: 177.
31. A. Gnanzow and J.F. Cannelongo J.Appl. Polym. Sci., 1976; 20: 689.
32. E.N.Petens J. Appl. Polym. Sci, 1979; 24.
33. W.Qiang, L.Jianping, Q.Baojun, Polym. Ent., 2003; 52: 1326.
34. Y. F. Shih, Y. T. wang, R. J. Jeng, K. M. Wei poly degrad. Stab, 2004; 86: 339.
35. S. V. Levchik, L. Costa and G. Camino poly, Degrad. Stab, 1996; 43: 43
36. S. Duquesne, M.Le. Brass, S. Bourbigot, R. Delobel, G. Camino, B. Eling, C. Lindsay, T. Roeis, H, Vezon, J. Appl. polym Sci, 2001; 82: 3262.
37. G. Camino, N. Grassie, I. C. Meneill, J. Poly. Sci, polym. Chem., Ed. 1978; 16: 95.
38. S.V. Levchik, D. Weil, polym. Int., 2005; 54; II.
39. K.H. Pawlowski, B. Schartel, polym. Int, 2007; 56: 1404.
40. E.A. Murashko, G.F. Levchik, S.V. Levchik, D.A. Bright, S. Dasheviky J. Appl. Sci, 1999; 72: 1863.
41. S.V. Levchik, E.D. Weil, J.Fine Sci., 2005; 24: 345.
42. G.A. Wang, W.M. Cheng, Y.I. Tu, C.e Wang, C.Y. chem, bek polym. Degrad. Stab, 2006; 91: 2683.
43. J.R. Ebdon, D. Price, B.J. Hunt, P. Josoph, F.Gao, G.J. Milnes, L.K. Cunliffe, polym. Degrad. Stab, 2000; 69: 267
44. D. Price, L.K. Cunloffe, K.J. Bullet, T.R. Hull, G.J. Milnes, J.R. Ebdon, B.J. Hunt, P. Joseph, polym. Degrad. Stab, 2007; 12: 1101.
45. L. Costa, G. Camino, D. Luda, P. Cortemiglia, fire and polymers, Acs symposium, Washington DC, 1990; 425: 211.
46. T. Kashiwagi, J.W. Gilman, Fire retadancy of polymeric materials, Marcel Dekken Inc. New York A.F, Grand and C.A Wilkie Editors, 2000; 10: 35.
47. M Sahoo, P K Sahoo, T Biswal, R Samal Synthesis and characterization of Poly(Vinyl Acetate/MMT) Nanocomposite Flame Retadant, 2015; 2: 479-493.