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A Review Paper on Flame Retardant Polyamide 6 Composites

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Abstract: Polyamide 6 is an aliphatic polyamide which is commercially important due to its excellent physical properties such as high fatigue strength, low coefficient of friction, enhanced toughness and high resistance to chemicals. It meets great demand in various fields, e.g. transportation, textile, sports, electronics, electrical etc. But, polyamide 6 is highly flammable and shows intensive dripping when heated or ignited, which increases its fire hazard. Consequently, improving the flame retardant behavior of Polyamide 6 is a major challenge for extending its use to various applications. The addition of conventional fire retardant (FR) additives such as alumina trihydrate, magnesium hydroxide to halogen, phosphorous, nitrogen and boron based compounds is the most common approach to improve the flame retardancy of a polymer. They often require high levels of loading (40-50 %) for adequate flame retardancy that leads to additional costs, processing difficulties and deterioration of polymer mechanical properties. Also, halogen based compounds generate toxic and corrosive combustion products like dioxin which draw the concerns over their environmental impact. Recently, new formulations incorporating nanoscale fillers such as nanoclay in addition to conventional flame retardants have been reported to show enhanced barrier performance, superior mechanical, thermal and fire properties as compared to a classical flame-retarded PA6. Literature survey shows that research progress is now in the direction to understand how to select materials, formulations, processing routes to develop a very cost effective and efficient flame retardant system with overall low loading of fillers to avoid the deterioration of mechanical properties of the polymer.

Keywords: Polyamide 6, Nylon 6, Flame retardant, Flammability, Composites, Polymer.

1. Introduction

The research and development on novel polymeric materials belongs to an important field of material science. The polymeric materials are replacing the traditional inorganic engineering materials due to their wide range of useful properties and ease of processability [1]. Among the polymers, aliphatic polyamides are important engineering thermoplastics having large applications in fibre, film and plastic industries [2]. Polyamide 6 is one of the prominent member of the aliphatic polyamides which is commercially important due to its excellent physical properties such as high fatigue strength, low coefficient of friction, enhanced toughness and high resistance to chemicals [3]. It meets great demand in various fields, e.g. transportation, textile, sports, electronics, electrical, telecommunication etc. But, polyamide 6 is highly flammable and shows intensive dripping when heated or ignited, which increases its fire hazard [4]. Consequently, improving the flame retardant behavior of Polyamide 6 is a major challenge for extending its use to various applications.

The addition of conventional fire retardant (FR) additives is the most common approach to improve the flame retardancy of a polymer. These conventional flame retardants vary from hydrated fillers such as alumina trihydrate, magnesium hydroxide to halogen, phosphorous, nitrogen and boron based compounds. They interact physically and chemically with the polymer during different stages of combustion thereby reduce the flammability of the polymer. Despite the advantages of these conventional FR additives, there are many drawbacks as they often require high levels of loading (40-50 %) for adequate flame retardancy that leads to additional costs, processing difficulties and deterioration of polymer mechanical properties. Also, halogen based compounds generate toxic and corrosive combustion products like dioxin which draw the concerns over their environmental impact [5]. In the past two decades, much attention has been diverted to use nanoscale fillers as flame retarding additives in polymers because a very small amount of nanoclay can significantly enhance barrier performance, mechanical, thermal and fire properties of the polymer significantly [6, 7]. Polymer-layered silicate nanocomposites are an environment friendly alternative to the conventional filled polymers. They have distinct advantages over conventional fire retardants. In contrast to the incorporation of high levels of conventional fillers, relatively low amount up to 5 wt% of silicates are only necessary in nanocomposites to provide good flame retardancy to the polymer [8]. Research results, however, showed that addition of only clays to the polymer matrix is not sufficient for commercial applications, since they fail in important regulatory fire tests [9-11]. Therefore, in order to meet these tests, polymer/clay nanocomposites are now being used in conjunction with conventional flame retardants. This article reviews the research progress in the field of flame retardant polyamide 6 composites.

2.1. FLAME RETARDANCY

A flame retardant polymeric material means which does not persist burning or glowing, once the source of ignition is removed, even though some changes are observed in the physical and chemical characteristics. When a polymer disintegrates in thermal decomposition, different types of products are formed: (1) combustible gases, e.g. methane, ethane, and carbon monoxide; (2) non-combustible gases, e.g. carbon dioxide; (3) liquids (partially degraded polymers); (4) finely divided solid particles which may be decomposing polymer fragments or soot in the combustion gases; and (5) discrete solids (carbonaceous residue or char). The large evolution of highly combustible gases will be likely to increase the flammability of polymers. Liquid products will tend to spread heat to neighboring parts of the polymer structure. Therefore, reducing the generation of combustible gases and preventing fire spreading are the basic methods to achieve flame retardancy. Various flame retardants are used to inhibit polymer ignition or flame spread as reported by many scientists [12].

2.1.1 GENERAL APPROACHES TO OBTAIN FLAME RETARDANCY

There are various approaches such as reactive, additive and surface modification to achieve a flame retardant polymeric material. In reactive approach, a flame retardant co-monomer is added during polymerization to become integrated into the polymer structure and the synthesized polymer is inherently flame retarded. In additive approach, the flame retardant additives are added into polymer melt during mixing but do not chemically react with the polymer. In surface approach, flame retardant substances are grafted or coated on to the polymer surface which is well known as flame retardant finishing and widely used for obtaining flame retardant textiles. All the three approaches i.e. reactive, additive and surface approaches can be applied both to polymers and textiles.

2.1.2 Types of flame retardant additives

Flame retardant additives can be classified as halogen, phosphorus, nitrogen, sulfur based flame retardants, inorganic flame retardants and intumescent flame retardants. Different types of flame retardants inhibit or suppress the combustion process by physical or chemical action in the gas or condensed phase through different mechanisms.

2.1.2.1 Halogen based flame retardants

Halogen based compounds are the most familiar flame retardants in the plastic industry. These flame retardants are used primarily in polymers for the electronic and electrical equipments. They are very cost effective and require only a low loading to provide sufficient flame retardancy. The choice of a halogen based flame retardant additive depends on the type of polymer used and it includes the parameters such as thermal stability, melting and decomposition temperature. The stability of the halogen compounds follows the order: F > Cl > Br > I. Iodine compounds are very less stable to be used commercially as they release halogenated species during polymer processing. Whereas, the fluorinated compounds are more thermally stable than most of the polymers due to very strong bonding to carbon and thus, do not release halogen radicals at the decomposition temperature of the polymers. Bromine and chlorine compounds are the most commonly used halogen based flame retardants. Bromine based flame retardants are twice as effective as those based on chlorine but they are more expensive and are more susceptible to photochemical degradation. The most widely used brominated flame retardants are: polybrominated diphenylethers (PBDE), brominated polystyrene, hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA), brominated phenols etc.

Halogen-containing flame retardants work either in the vapor phase or in the condensed phase [13]. But mainly, they are believed to work through vapour phase (Scheme 1). In the vapour phase, halogenated based flame retardants function by inhibiting the branching radical reactions which takes place during the combustion. The most active chain carriers H and OH radicals formed by chain branching are removed by halogen containing flame retardants and get replaced with low energy halide radicals [14] resulting in the hindrance of combustion.

(i) H and OH radicals formation by chain branching

$$H\cdot + O_2 \rightarrow OH\cdot + O$$
$$O + H_2 \rightarrow OH\cdot + H\cdot$$

(ii) halide radicals (X·) formation by breakdown of flame retardant

$$RX \rightarrow R\cdot + X\cdot$$

(iii) formation of hydrogen halide

$$X\cdot + RH \rightarrow R\cdot + HX$$

(iv) interference of radical chain mechanism by hydrogen halide

$$HX + H\cdot \rightarrow H_2 + X\cdot$$
$$HX + OH\cdot \rightarrow H_2O + X\cdot$$

(v) regeneration of hydrogen halide

$$X\cdot + RH \rightarrow R\cdot + HX$$

Scheme 1: Vapour phase action of halogenated flame retardants.

Halogenated compounds provide inadequate flammability performance when used alone in plastics. The addition of antimony compounds greatly improves their efficiency, providing equivalent performance with lower loadings of the halogenated compounds. However, halogenated compounds as a flame retardant have been currently restricted by legal authorities due to major environmental side-effects such as bioaccumulation in the environment and human health risks as they release toxic and corrosive gases by degradation during processing, recycling, and in the case of a fire. In view of that, recent developments in flame retardants have shifted strongly towards the use of environment friendly halogen-free compounds [15].

2.1.2.2 Phosphorus based flame retardants

Phosphorus-based flame retardants have received considerable attention as halogen-free flame retardants [16]. Both inorganic and organic phosphorus compounds are extensively used for imparting flame retardancy to a range of polymers. Phosphorus flame retardants include elemental red phosphorus, water-soluble inorganic phosphates, insoluble ammonium

polyphosphate, phosphine oxides, phosphites, organophosphates & phosphonates [17]. The flame retardant mechanism of phosphorus based flame retardants depends on the nature of phosphorus compound and the chemical structure of the polymer. They are highly effective in polymers containing oxygen or nitrogen [18]. Phosphorus flame retardants containing halogens or nitrogen generally show synergistic behavior due to the formation of phosphorus halides or oxyhalides or P-N bonds on decomposition [19, 20].

Additive and reactive both types of phosphorus flame retardants are commercially available which can act both in condensed as well as in vapour phase. In condensed phase, phosphorus based flame retardants promote the char formation and form an insulating layer on surface of the polymer [21]. In gas phase, phosphorus based flame retardants dilute the flammable volatiles and replace the hydrogen & hydroxyl radicals by less effective radicals or make them harmless by radical recombination. Branching and chain reactions due to oxidation of hydrocarbons are slowed down due to quenching of radicals which results in to flame inhibition and reduces the production of heat [22].The flame inhibition reactions by phosphorus based flame retardants in vapour phase are shown in Scheme 2.

$H_3PO_4 \rightarrow HPO_2+HPO+PO$

$PO\bullet + H\bullet \rightarrow HPO$

$PO\bullet + OH\bullet \rightarrow HPO_2$

$HPO + H\bullet \rightarrow H_2 + PO\bullet$

$OH\bullet + H_2 + PO\bullet \rightarrow H_2O + HPO$

$HPO_2\bullet + H\bullet \rightarrow H_2 + PO_2$

$HPO_2\bullet + OH\bullet \rightarrow H_2O + PO_2$

$HPO_2\bullet + H\bullet \rightarrow H_2O + PO$

Scheme 2: Flame inhibition reactions by phosphorus based flame retardants.

The most commonly used phosphorus flame retardants are: red phosphorus, triphenyl phosphate, resorcinol diphosphate, ammonium polyphosphate and organic phosphinates. In the present study, ammonium polyphosphate and organic phosphinates have been used as flame retardant additives. The detailed information about these additives is given below:

(a) Ammonium polyphosphate (APP): Ammonium polyphosphate (APP) is the ammonium salt of polyphosphoric acid. It is a water insoluble, non-melting, non-hygroscopic solid having high phosphorus content. It has two main crystalline forms; crystal form I and II. Crystal form I is characterized by short, linear chain length ($n < 100$) with lower decomposition temperature, higher water solubility and more water sensitivity (hydrolysis) than crystal form II. Crystal form II has crosslinked and branched structure ($n > 1000$), exhibits very low water solubility (< 0.1 g/100 ml) and is more favored for flame retardant activities. The molecular structure of APP is shown in Fig. 1.

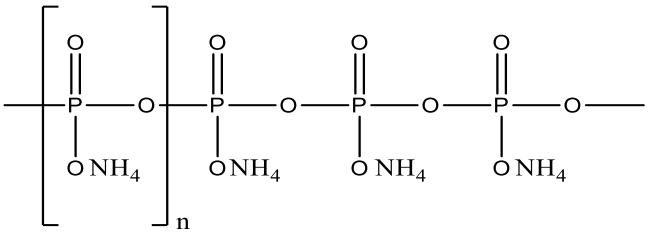
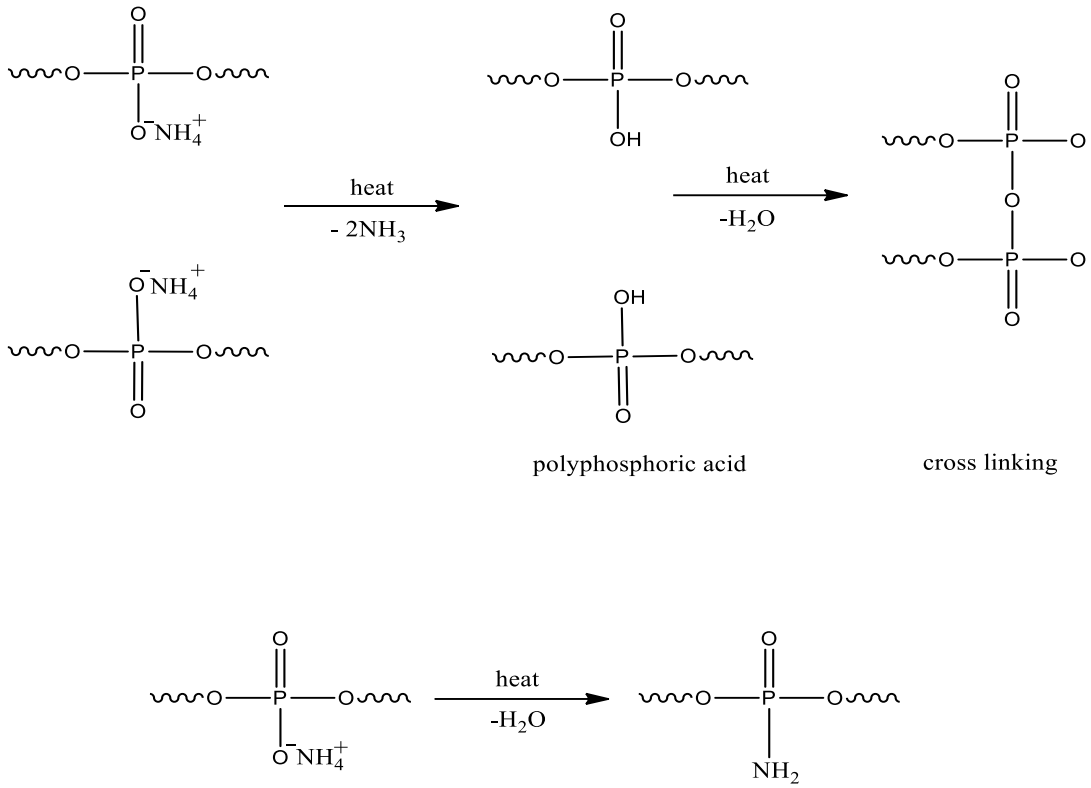


Fig. 1: Molecular structure of APP.

Short chain APPs start to decompose at temperatures above 150 °C whereas long-chain APPs decompose at temperatures above 300 °C. On thermal degradation, APP gives polyphosphoric acid, orthophosphates, phosphoric acid, ammonia and water [23, 24]. The thermal degradation of APP is shown in Scheme 3 [25].



Scheme 3: Thermal degradation of APP

Polyphosphoric acid, phosphoric acid and orthophosphates acting as an acid source catalyze the dehydration of oxygen or nitrogen-containing polymers such as polyesters [26], polyamides [27], polyurethane [28], etc., and thus, lead to polymer charring. The flame retardant effect of APP depends on the level of incorporation. At very low loading, APP is not efficient in aliphatic polyamides [29], however, its efficiency is highly increased at large concentration (> 10 % in PA66) and (> 30 % in PA6).

(b) Organic phosphinates: Organic dialkyl phosphinates developed by Clariant Company (Germany) belong to a novel class of phosphorous flame retardants. Clariant explored a wide range of aluminum, zinc, and calcium salts of dialkyl phosphinates as flame retardants [30, 31]. These are hydrophobic fine powders with very low residual solubility in water. Some of the important characteristics of dialkyl phosphinates are their good thermal stability (up to 320 °C), high phosphorus content (~17 %), low toxicity, low smoke density, high comparative tracking index and low affinity to moisture [32]. They show a strong flame retardant activity on their own and also a pronounced synergistic effect with nitrogen containing organic substances. Products based on organic phosphinic acid salts were originally developed for fibre glass reinforced polyamides (PAs). Unlike other halogen-free FRs, such as melamine cyanurate or red phosphorus, the phosphinate based systems can be used at nearly all glass levels up to 50%. The required loading depends on several parameters, such as the type of PA polymer or blend, thickness of material and fibreglass content. Similar to other phosphorus compounds, it is believed that organic phosphinates act through both condensed and vapour phase mechanism. It has been observed that the predominant mechanism depends on the type of polymer and synergistic agents.

2.1.2.3 Nitrogen based flame retardants

Nitrogen based flame retardants are considered as environment friendly because they are less toxic, do not have any extraneous impurity and are suitable for recycling [33]. The most important type of nitrogen based flame retardants are melamine and its derivatives such as melamine cyanurate, melamine phosphate, melamine pyrophosphate and melamine polyphosphate [34]. Melamine and its derivates show the flame retardant effect by acting both in condensed and gas phase [25]. They work in all stages of burning process through a range of mechanisms, including endothermic reactions, inert gas dilution or scavenging of free-radicals [35]. Melamine is a thermally stable white crystalline solid with high melting point of approximately 345 ºC [36]. It sublimes at about 350 ºC, with absorption of significant amount of heat (1965 kJ/mol), thus acts as a heat sink during burning process. The vaporized melamine acts as an inert gas and dilutes the oxygen and combustibe gases present at the point of combustion. In the condensed phase, melamine releases ammonia and get transformed into cross-linked structures known as melam, melem and melon, which promotes the char formation [37]. Melamine and its salts are characterized by various flame retardant mechanisms. The action of melamine based salts in the condensed phase is significantly higher than pure melamine [38**]**. The thermal decomposition of melamine phosphate produces melamine polyphosphate, with the release of melamine and phosphoric acid. The released phosphoric acid phosphorylates the polymer and produces similar flame retardant effects as in case of phosphorus based flame retardants. Upon heating melamine polyphosphate releases melamine and produces melam ultraphosphate & ammonium polyphosphate. The melamine released condenses to form polyphosphoric structures. Ammonium polyphosphate dissociates above 300 °C to give free hydroxyl groups with release of ammonia. The free hydroxyl groups produce crosslinked ultraphosphate structures with elimination of water to give relatively stable residue at high temperature [27].

2.1.2.4 Sulfur based flame retardants

There are only a few publications found in literature based on applications of sulfur containing flame retardants. It has been found that a very high degree of flame retardancy can be achieved by applying specific oxygenated hexavalent sulfur derivatives in combination with char forming agents for flame retarding polyamides. These compounds are less toxic, less corrosive and less expensive than halogen and phosphorus based compounds [39]. In comparison to very high loading (20-30 wt%) of conventional FRs; very low loading of ammonium sulfamate (AS) & dipentaerythritol (DP) (<5 wt%) together promotes significant improvement in flame retardancy of PA6 [40].

Ammonium sulfamate (AS) melts at 129-135 ºC. Thus, it is in melt form during processing and hence, uniformly mix with the polyamide 6. It decomposes at high temperatures and releases non-combustible gases, such as NH_3 and H_2O. Therefore, the combination of AS and polyol (carbon source) acts as an intumescent flame retardant for polyamide. It facilitates the formation of the intumescent char layer with honeycomb-like structure, which is responsible for the improved flame retardancy of PA6 [41]. However, it has been observed that AS may cause polymer matrix degradation due to high temperature (~ 220 ºC) generally involved in PA6 processing. In this temperature range, AS releases ammonia which leads to the aminolysis of PA6 during processing.

In recent researches, Guanidine Sulfamate (GS) has also been used as a flame retardant in PA6 [42]. Guanidine sulfamate shows synergistic effect with phosphorus based compounds such as melamine polyphosphate in PA6 [42]. It promotes char formation at high temperature and an intumescent structure is formed when GS and melamine polyphosphate (MPP) are combined in PA6, which results in to improved flame retardancy of PA6.

2.1.2.5 Inorganic flame retardants

The most commonly used inorganic flame retardants are metal hydroxides (especially of aluminium and magnesium), hydroxycarbonates, antimony trioxide and boron containing compounds.

(a) Metal hydroxides: Aluminum tri-hydroxide $Al(OH)_3$ and magnesium dihydroxide $Mg(OH)_2$ are two major hydrated minerals which are used as fire retardant fillers for polymers. These two minerals comprise more than 50 % by weight of the world-wide sales of flame retardants and are of high industrial importance as they are of very low cost, easily available, non toxic and environment friendly. Whereas, they require very high loading (30–60%) to obtain flame retardancy which lead to detrimental effects on the properties of polymer.

Aluminum and magnesium hydroxides function as flame retardants due to highly endothermic dehydration to metal oxides and water. This consumes energy and removes the heat from the substrate which slows down the decomposition of the substrate, and keeps it below its ignition temperature. Dehydration of aluminum tri-hydroxide starts at ~200°C having a reaction enthalpy of 1050 kJ/kg. Magnesium hydroxide has a higher dehydration temperature ~300°C and a higher reaction enthalpy of 1300 kJ/kg that makes it suitable for the polymers to be processed at higher temperatures. In addition to the condensed phase heat sink effect, the water of dehydration evolves into the flaming zone which effectively cools and dilutes the available fuel in the gas phase. This leads to reduced heat release and smoke evolution. Furthermore, the porous ceramic residues, i.e., anhydrous alumina and magnesia obtained from dehydration reactions, act as a heat barrier by forming protective layers on exposed sample surface. [43, 44**]**. ATH and MH both are used in large quantities in low smoke, halogen-free wire and cable applications.

$$2Al(OH)_3 \xrightarrow[+1050\ kJ/kg]{200\ ^\circ C} Al_2O_3 + 3H_2O$$

$$Mg(OH)_2 \xrightarrow[+1300\ kJ/kg]{300\ ^\circ C} MgO + H_2O$$

(b) Boron containing compounds: Boron based compounds are extensively used as flame retardants. The compounds which are water soluble such as borax and boric acid, are widely used with cellulosic materials. Whereas, the water insoluble and thermally more stable boron based compounds such as borates, are used to achieve flame retardant plastic materials [36, 45]. Numerous hydrated zinc borates with chemical composition $xZnO.yB_2O_3.zH2O$, have been developed to be used as fire-retardant additives in polymers. Zinc borate functions as a smoke suppressant, afterglow suppressant besides its flame retardant effect.

The most frequently used one is zinc borate with the formula $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$. The molecular structure of $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ is shown in Fig. 2 [46].

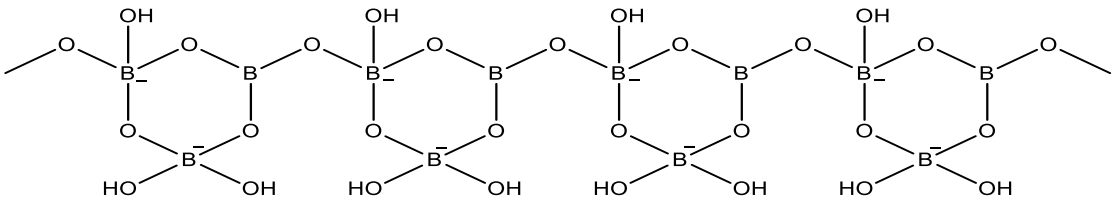


Fig. 2: Chemical structure of $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$.

It undergoes endothermic decomposition (503 kJ/kg) from 290 to 450 °C and liberates water, boric acid and boron oxide (B_2O_3).The B_2O_3 produced gets softened at 350 °C and melts above 500 °C to form a protective glassy layer on the polymer surface. In case of polymers having oxygen atoms, the presence of boric acid leads to the dehydration of polymer, resulting in to the formation of carbonized char. The liberated water serves to blow the char layer to a foam, which insulates the bulk of the polymer from the heat source and dilutes the fuel. The formation of glassy layer, increased char formation and the dilution of the gaseous breakdown products by the released water imparts flame retardancy to the polymer.

2.1.2.6 Intumescent flame retardants

Intumescent system was reported in literature in 1938. The process of “getting to a swollen state” is referred to as intumescence in flame retardant terms. Intumescent flame retardants reduce the fire risk and flame spread by formation of a swollen or foamed up insulating protective layer when exposed to heat. The amount, stability, integrity and structure of foamed

char determines the flame retardant effect of an intumescent system. A typical intumescent composition consists of three components which are an inorganic acid (catalyst), a char forming agent (carbonific) and a blowing agent (spumific). The sequential representation [47] of intumescent process is shown in Fig. 3.

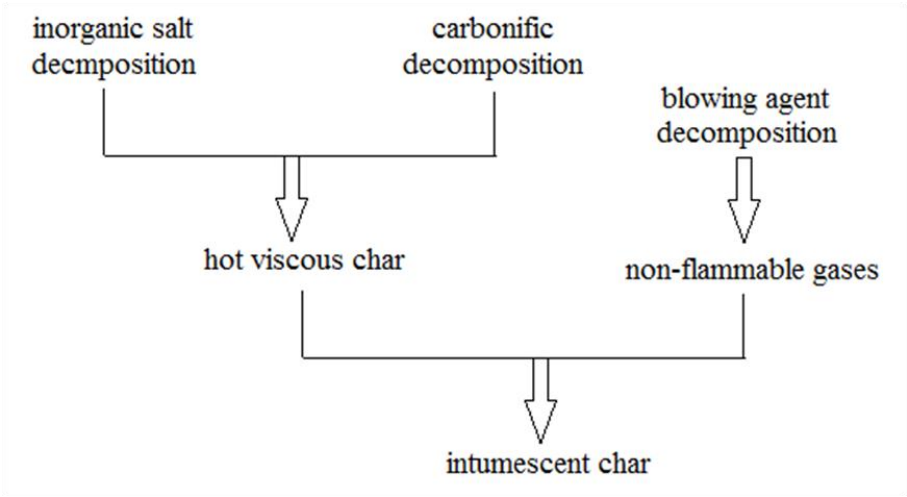
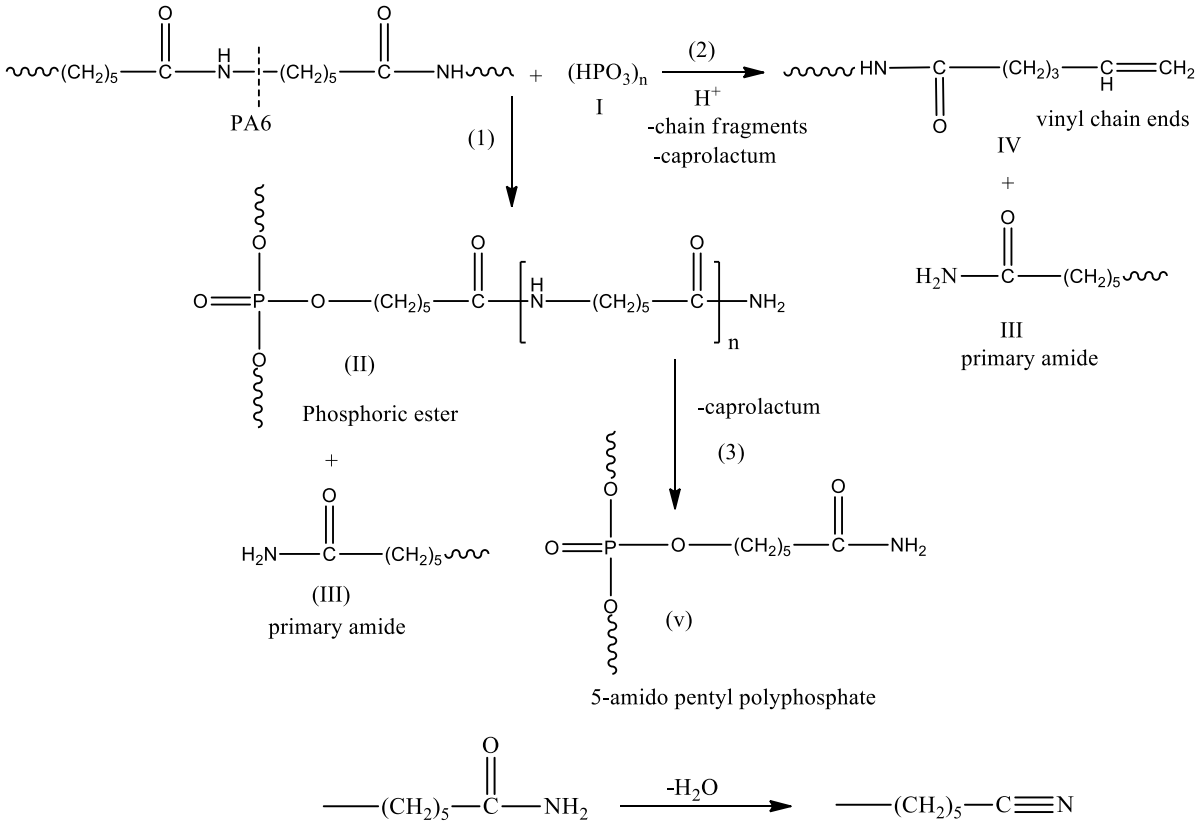
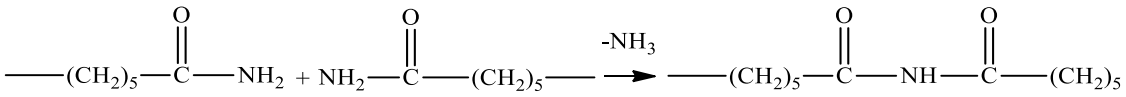


Fig. 3: **Sequence of intumescent process.**

In early 1980's, the combination of ammonium polyphosphate, dipentaerythritol, and melamine was the most commonly used intumescent flame-retardant system for polymeric materials [15]. Ammonium polyphosphate acts both as an acid source as well as a blowing agent during combustion. It shows its flame retardant effect in condensed phase by the formation of intumescent char. Polyphosphoric acid, phosphoric acid and orthophosphates produced from thermal degradation of APP act as an acid source and go through esterification reaction with char forming agent whereas released ammonia and water act as blowing source. A condensed-phase flame retardant mechanism has been proposed for APP in nylon 6 [29]. An intumescent layer is formed on the surface of burning PA6/APP formulations which becomes more effective with increasing content of APP. The thermal decomposition mechanism [29, 48] of the system PA6/APP is shown in Scheme 4.

From thermal analysis, it has been observed that APP causes destabilization of PA6, as the onset of weight loss shifts from 330 °C for pure PA6 to 260 °C for PA6/APP. The polyphosphoric acid produced from thermal degradation of APP reacts with PA6 (reaction (1)) to form phosphoric ester (II) and primary amide chain ends (III). Simultaneously, acid catalyzed scission of CH_2-NH bond of PA6 (reaction 2) produces primary amides (III) and vinyl chain ends (IV).





Scheme 4: Thermal decomposition mechanism of PA6/APP system.

Primary amide chain ends can further undergo competing reactions such as elimination of water with the formation of nitrile chain ends or condensation reactions with the elimination of ammonia. Phosphoric esters produced in (reaction (1)) undergo unzipping type process with the elimination of caprolactam and proceed until formation of 5-amido pentyl polyphosphate (V). At higher temperature (315-360 ºC), 5-amido pentyl polyphosphate dehydrates the polymer to produce char and liberates polyphosphoric acids. The intumescent layer formed on the surface is composed of foamed polyphosphoric acid reinforced with the char which protects the underlying polymer from the heat flux [29].

Exolit OP 1311 and Exolit OP 1312 are the intumescent flame retardants based on aluminum diethyl phosphinate and melamine derivatives as synergists for the use in polyamides. Exolit OP1311 consists of aluminium diethylphosphinate (Al $[(C_2H_5)_2PO_2]_3$, and melamine polyphosphate in the ratio of 2:1 [46]. Exolit OP 1312 has the similar composition as 1311 with some additional zinc borate as thermal stabilizer [49]. These products show the flame retardant effect through intumescence. The thermoplastic polymer containing Exolit OPs swells and crosslinks on exposure to flame and forms a stable char on the surface. The protective layer provides a heat insulation effect, reduces oxygen permeability and stops dripping of molten polymer [50]. Polyamide compounds flame retarded with Exolit OPs exhibit very good physical and electrical and recyclability properties. German researches have studied the mechanism of flame retardant action of aluminum diethylphosphinate in polyamide 6,6 [51]. They reported that pure phosphinate generally provides a gas phase mode of action, however on addition of melamine polyphosphate, the mode of action shifts to the condensed phase and insulated char barrier becomes more effective with the addition of zinc borate. Nitrogen synergists have been found to be highly effective with the phosphinate salts. A V-0 rating is obtained in polyamide 6 with 8 % melamine cyanurate and 8 % aluminum methyl ethyl phosphinate [52].

2.1.3 MODE OF ACTION OF FLAME RETARDANTS

A wide variety of flame retardants have been developed over the past 40 years. The flame retardant additives usually operate by mechanisms classified as “physical” and “chemical” modes of action taking place in the “condensed” or “gas” phases, to interfere with the combustion process during heating, decomposition, ignition or flame spread [53-55]. The different modes of action of flame retardant systems (Fig. 3) are described below:

Physical action

The combustion process can be retarded by physical action in various ways:

(i) By cooling: Some flame retardant additives undergo endothermic decomposition (energy absorbing process) and cool the substrate to a temperature below that required for sustaining the combustion process. Such an endothermic reaction acts as a “heat sink”. This category includes the examples of hydrated minerals such as alumina tri-hydrate and magnesium hydroxide, which undergo endothermic release of water vapor at around 200 and 300 °C, respectively.

(ii) By formation of protective char layer: Some flame retardant additives on thermal decomposition, form nonflammable protective char barrier on the surface of the polymer. The protective barrier layer restrains heat and mass transfer between the pyrolysis and flaming zones. and thus, retards the combustion process. e.g. phosphorus and boron compounds.

(iii) By dilution: The addition of inert fillers and flame retardant additives which release inert gases such as water, CO_2 and NH_3 on decomposition, dilute the fuels in solid and combustible gas mixture. This limits the amount of flammable material and increases the substrate’s fire resistance. e.g. hydrated minerals, glass fibres etc.

Chemical action

Flame retardancy through chemical action can occur in either the gaseous or the condensed phase.

(i) Gaseous phase: Gas phase active flame retardants strongly hinder the combustion process either by releasing specific radicals (e.g. Cl• and Br•) which inhibit the radical reactions by reacting with highly reactive species such as H• and OH• to form less reactive or even inert molecules or by generating significant amount of less-combustible gases. This leads to a significant reduction in the exothermicity of the reaction and therefore, cools down the system e.g. Halogenated flame retardants.

(ii) Condensed phase: In the condensed phase, the flame retardants can work by two types of chemical reactions. In one way, they react with the polymer and break down the polymer chains. Due to which, the polymer drips and deviates from the flaming zone. Alternatively, a carbonized or vitreous layer is formed by flame retardants at the surface of the polymer by dehydration, cyclization or cross-linking reactions. This layer acts as an insulating barrier and protects the polymer from heat and oxygen necessary for the combustion process. e.g. phosphorus and boron compounds.

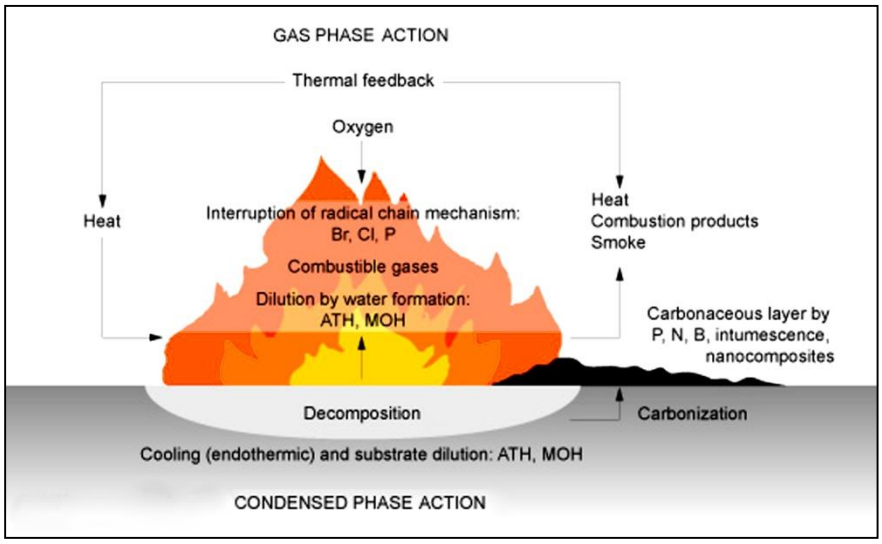


Fig. 4: Modes of action of flame retardant additives .

2.1.4 SYNERGISM AND ANTAGONISM OF FLAME RETARDANTS

The term synergism is defined as improved performance of the mixture of two or more components for a given property compared to the linear combination of performance of individual components at the same concentration. Contrary to this, a reduction in performance of combined system in comparison to simple additive of individual performance is termed as antagonism. The general concept of synergism and its use for optimization of flame retardant formulations have been reviewed extensively by [56]. Synergism can be obtained either by a combination of flame retardancy mechanisms, such as gas phase action by a halogenated flame retardant combined with condensed phase char formation by a phosphorus based flame retardant, or by a combination of flame retardant compounds reinforcing the same mechanism, e.g. combination of nanoclays and phosphorus based flame retardants, both acting by condensed phase mechanism. If synergism is observed among different flame retardants, low loading of flame retardants can be used to obtain same flame retardant effect. For this reason, to find synergism among different flame retardant additives is very important for the development of flame retardant material by additive approach [25, 57]. The same substance may show the synergistic effect with a flame retardant additive, and antagonistic effect with some different flame retardant additive. Various synergisms have been observed among different flame retardants such as antimony-halogen, nitrogen-halogen, nitrogen-phosphorus, phosphorus-phosphorus, boron-phosphorus, silicon- phosphorus, etc [25].

2.1.5 POLYMER/CLAY NANOCOMPOSITES

By definition, the word composite is generally used for any material made from the combination of more than one component. Depending on the component materials, composites develop either a continuous phase such as polymer, metal, ceramic, etc. or a dispersed phase such as carbon particles, silica powder, glass fibres, clay minerals, etc. Additionally they show properties that are effectively different from the components taken separately. Most of the commercially available composites have structural units of order of micrometer length scale and are generally developed to improve the mechanical properties of matrix material. On changing the dimensions of a structural unit from micrometer scale to nanometer scale results in to a composite material known as nanocomposite. Over the last few years, nanocomposites have received a great deal of interest due to their significant advantages over conventional composites. Various types of nano-fillers that have been studied include layered silicates [58, 59], carbon nanotubes [60-62], metal-oxide nanoparticles [63, 64], expandable graphite [65, 66], layered titanate [67], polyhedral oligomeric silsesquioxanes (POSS) [68], layered double hydroxides (LDHs) [69, 70] etc. Among these, the layered silicates are the most investigated nanofillers for the development of polymer composites [71, 72]. Polymer nanocomposites based on layered silicates are one of the most significant and important engineering materials in today's materials research, as they usually show significant improvements in mechanical, barrier and fire-retardant properties in comparison to the pure polymer. The improved properties of polymer/clay nanocomposites are due to the large surface-to-volume ratios of the nanoclay particles that lead to strong interfacial interaction with the polymer matrix, as opposed to conventional composites [58, 59]. Historically, the addition of layered silicates to polymers goes back to last 50 years. The earliest motivation for the use of nanoclay was stimulated by the work done at Toyota Central Research and Development Laboratories in the late 1980s, where the first practical application of nylon 6/MMT nanocomposite was commercialized [73]. Very small amount of MMT loading resulted in pronounced improvements of thermal and mechanical properties of nylon 6. Later on, Vaia et al [74] reported the formation of polymer/layered silicate nanocomposites by using melt mixing without the use of organic solvents which further led to motivate the interest in development of polymer layered silicates.

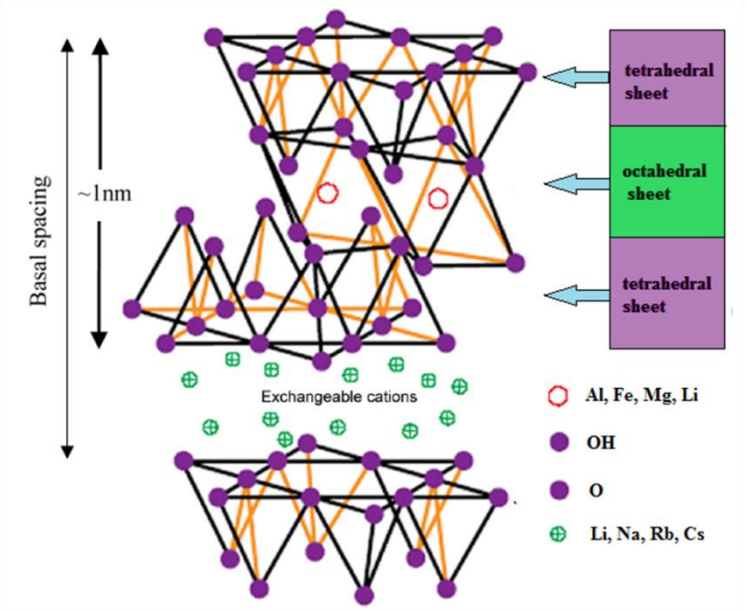


Fig. 5: Crystal structure of montmorillonite (MMT) clay.

On the basis of nature of components (polymer matrix, nanoclay and organic surfactant) and processing conditions, dispersion of clay particles results in formation of three different types of composites (Fig. 5).

(a) Conventional composites or phase separated micro-composites: In these composites, the clay is not separated in to layers but agglomerates, due to which the polymer chains can't penetrate into the galleries of clay and result in to the formation of micro-composites. In these micro-composites, silicates act as only fillers and required in large amount to attain significant improvement in the composite properties, which otherwise is attained at much lower concentration in case of nanocomposites.

(b) Intercalated nanocomposites: Intercalated nanocomposites are obtained when the insertion of a polymer chain into the layered silicate structure occurs in a regular fashion resulting in formation of alternate layers of polymer and inorganic layers with a repeat distance of only few nanometers.

(c) Exfoliated or delaminated nanocomposites: In an exfoliated nanocomposite, the clay layers are well separated from one another and irregularly dispersed within the continuous polymer matrix. This occurs when the polymer chains completely overcome the electrostatic forces of interaction between clay platelets in composites. Usually, the low clay content leads to the formation of an exfoliated nanocomposite.

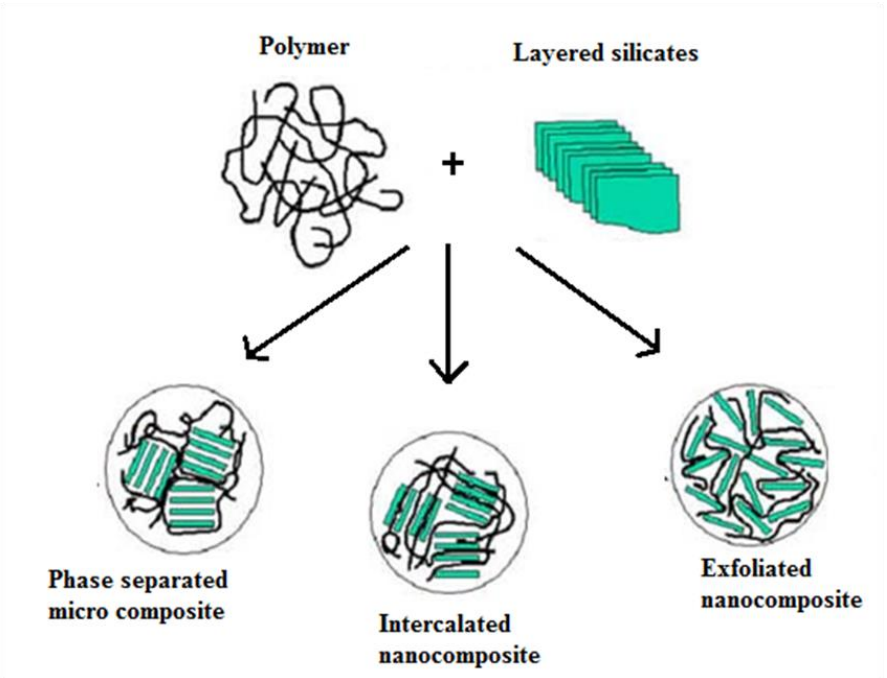


Fig. 6: Different micro-structures of polymer/clay composites.

2.1.6 RESEARCH PROGRESS

Initially, the majorities of the flame retardants were based on halogen containing additives and were found to be very efficient fire retardants in polyamide 6. Ceric B et al [75] developed flame retardant PA6 by addition of antimony oxide and stannous chloride to poly-ε-caprolactam melt. PA6 formulation containing 30 % glass fibres, 19 % of brominated epoxy oligomers (derived from tetrabromobisphenol A and epichlorohydrin and 3.7 % of antimony oxide, was reported to give V-0 rating at 1.6 mm thickness [76]. However, halogenated additves were found to have some negative aspects due to release of toxic and corrosive gases such as dioxins & furans which drew the concerns over their environmental impact. Therefore, the research

was continued to find alternative conventional non-halogenated fire retardants, which included inorganic fillers such as alumina trihydrate, magnesium hydroxide, carbonates, phosphorous, nitrogen, silicon and boron based compounds.

PA6 was successfully flame retarded to a V-0 rating at 1.6 mm thickness, using about 60 % loading of $Mg(OH)_2$, but due to high loading it was difficult to process [77]. Later on, it was observed that $Mg(OH)_2$ shows synergistic effect with phenol formaldehyde novolac resin. The V-0 rating was obtained for PA6 containing 53 wt% of $Mg(OH)_2$ and 4 wt% of novolac [78]. It was also observed that addition of antimony oxide, magnesium sulfate, and zinc borate/zinc oxide/ferric oxide/zinc molybdate/zinc stannate improved the flame retardancy of PA6 [79].

Apart from various advantages of conventional FR additives, there were many drawbacks as they generally required very high loading in order to meet required flammability standards which resulted in to an increase in product costs, processing difficulties and worsening of polymer mechanical properties. To overcome these difficulties, the research was diverted to use nanoscale fillers to develop environmentally benign and superior flame retardant polymer nanocomposites. Among all the potential nanoscale fillers, layered silicates have been most widely investigated due to their natural abundance and large aspect ratio, which is highly favorable in matrix reinforcement. The most widely used clay for the preparation of polymer nanocomposites is montmorillonite belongs to smectite group of clay minerals.

In 1976, the first PA6/clay nanocomposites were reported by Fujiwara and Sakomoto [80]. Later on, Toyota research team [81-83] reported improved methods for developing PA6/clay nanocomposites using in-situ polymerization. It was reported that PA6/clay nanocomposites exhibited improved heat distortion temperature, superior strength, modulus, gas barrier properties, and comparable impact strength as compared to pure nylon 6 [84-86]. Specifically, the improved heat distortion temperature of the PA6 nanocomposite made it suitable to be used as part of the engine, consequential weight savings in a car.

Song et al [87] reported synergistic effect on using modified montmorillonite, magnesium hydroxide (MH), and red phosphorus (RP) in PA6 leading to superior mechanical and flame retardant properties as compared to a classical flame-retarded PA6. Horrocks et al [88] observed the synergistic effects of organoclays with ammonium polyphosphate or polyphosphine oxide in flame retardancy for PA6.

Pramoda et al [89] investigated the thermal degradation behaviour of PA6/clay nanocomposites. The onset temperature of degradation was found to be 12 ºC higher for PA6-2.5 wt% clay nanocomposite in comparison to pure PA6 and remain unchanged for composites with higher clay loading up to 10 wt% clay. It was attributed to the exfoliated structure obtained for composite with 2.5 wt% loading and agglomeration observed for those with higher loading. The activation energy for degradation was higher for PA6-2.5 wt% clay nanocomposite in comparison to pure PA6 under N_2 atmosphere.

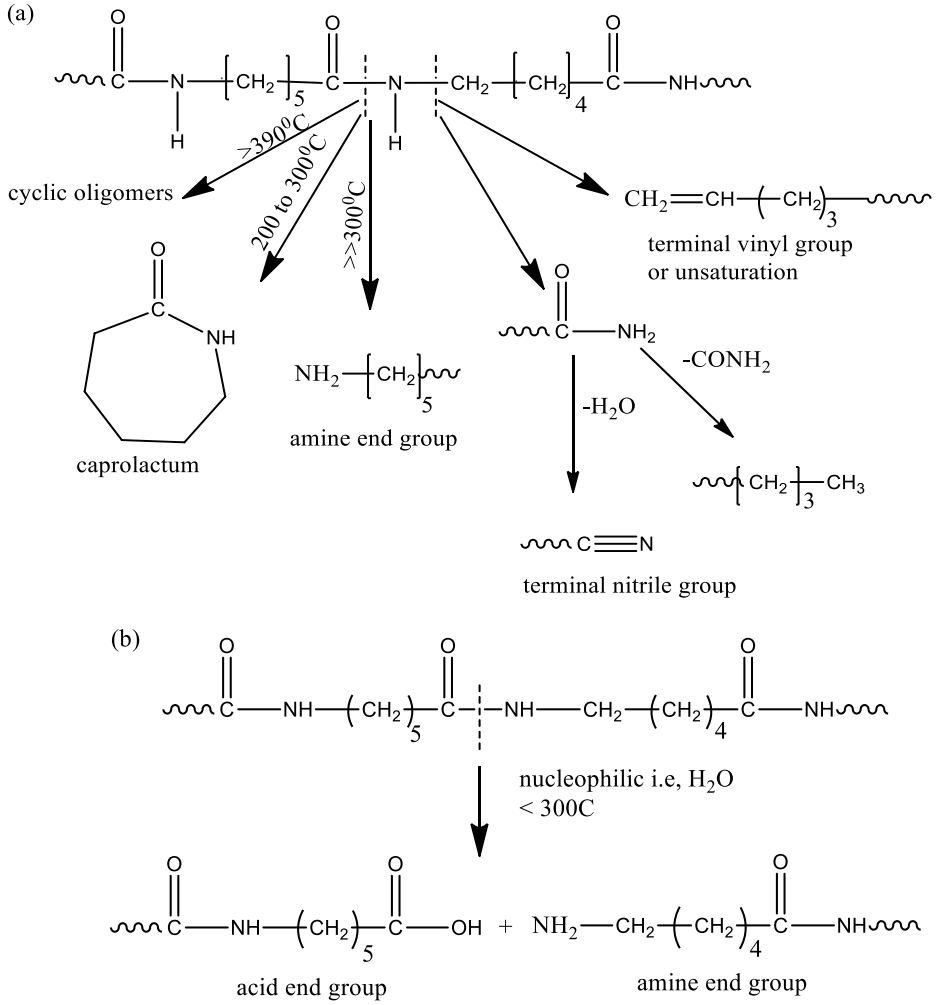
Yoon et al [90] studied the structure and crystallization of PA6/clay nanocomposite fibres. On the basis of XRD data, the α crystal form was found dominant in PA6 whereas γ crystal form was dominant in PA6/clay nanocomposite with annealing and drawing. The tensile modulus increased by 30 % for PA6/clay fibres compared with PA6 at room temperature.

A number of studies by Gilman [91], Kashiwagi [92] and Bourbigot [93] have been carried out, where PA6 is shown to produce enhanced char yield due to cross-linking or char-forming reactions in the presence of nano-dispersed clay.

Recently, extensive studies have revealed that PA6/intumescent/clay nanocomposites are very cost effective and efficient flame retardant systems. Horrocks et al [94] investigated the effect of nanoparticles in combination with intumescent flame retardants in PA6. The synergistic effect between micro-dispersed intumescent flame retardants and nanoparticles help to further enhance flame retardant performance and reduces the overall filler contents that leads to positive effects on polymer processing and properties. Levchik et al [95] reported the synergism of talc and manganese dioxide with APP in PA6 to promote charring and to enhance the insulation properties of the intumescent coating resulting in to a significant improvement in flammability performance. It was found that inert talc interacts with the APP forming inorganic glass and hence improve the shielding effect of intumescent protective char. The fire-retardant action of APP/MnO_2 mixture was twofold. It promoted the involvement of PA6 in charring and also improved the thermal insulating properties of the intumescent char by forming phosphate glasses on the surface of burning polymer.

Later on, effect of melamine and its salts on thermal decomposition of PA6 was studied by Levchik et al [96]. It was reported that melamine, melamine phthalate, melamine oxalate and melamine cyanurate facilitate thermal decomposition of PA6 leading to the evolution of oligomeric chain fragments which promote non-combustible flow dripping and help extinguishment of the flame.

Numerous studies have been reported on thermal decomposition mechanism of PA6. Straus and Wall [97] suggested hydrolytic scission of the peptide CO–NH bonds to explain the high concentration of CO_2 arising from the decomposition of the acid groups produced by the hydrolytic scission of PA6 decomposition. Kamerbeck et al [98] postulated that the thermal decomposition of PA6 involves two types of reactions: primary reactions (< 300°C) and secondary reactions, (> 300°C). They suggested that thermal decomposition begins via homolytic scisson of the N-alkylamide bond and produce primary amide, nitrile, vinyl, isocyanate and alkyl chain ends. At temperature > 300°C, the secondary reactions result into crosslinking of aliphatic nylons responsible for gelling phenomenon at high temperature. Dussel et al [99] also reported the homolytic scission of N-alkylamide or peptide bonds and found amines, amides and nitriles to be main fragments of thermal decomposition of PA6. Ohtani et al [100] found the caprolactam as a predominant volatile product from PA6, with only a small nitrile peak in their pyrolytic gas chromatography experiments. Levchik et al [48] reported that thermal degradation of PA6 occurs through competiting mechanisms (radical or molecular) and produces a mixture of caprolactum and chain fragments with nitrile and vinyl chain ends. Hornsby et al [101] suggested that in the presence of water, peptide bond hydrolysis is predominant whereas scission of N-alkylamide bonds or CH_2-CH_2 linkages at β-position to the carbonyl group is also possible at high temperature. The degradation of products thus formed could be continued by random chain scission to produce various lower molecular weight hydrocarbon fragments. Ballistreri et al [102] detected mainly cyclic oligomers of PA6 in direct chemical ionization mass spectrometry experiments. In spite of the significant number of publications, there is no generally accepted mechanism for the thermal decomposition of PA6. The contribution of each mechanism appears to depend on experimental conditions such as temperature, presence of nucleophile etc. On the basis of reported results, Davis et al [103] classified the PA6 thermal decomposition products in to three categories: (i) products produced at temperature below 300 ºC in the absence of a nucleophile (Scheme 5a); (ii) products produced at temperatures much higher than 300 ºC in the absence of a nucleophile (Scheme 5a) and (iii) products produced in the presence of a nucleophile, specifically water (Scheme 5b).



Scheme 5: (a) PA6 thermal degradation products in the absence of a nucleophile and (b) in the presence of a nucleophile.

Jang et al [104] studied the effect on degradation pathway of PA6/clay nanocomposites with increase in clay content. The main degradation pathway for PA6 was suggested as aminolysis and/or acidolysis through intrachain reaction leading to the formation of ε-caprolactum. With increase in clay content, the amount of ε-caprolactum produced was decreased and viscosity of solid residue was increased. It was suggested that in the presence of clay inter-chain reactions become significant due to trapping of polymer chains in the gallery space of clay during thermal degradation.

The researchers [105-106] reported that PA6 reinforced with 25–30 % glass requires 20 % loading of Exolit OP 1311 to reach UL 94 V-0 rating. A V-0 rating was obtained in PA6 having 8 % of melamine cyanurate and 8% of aluminum methyl ethyl phosphinate. Synergistic effects were observed between nitrogen containing additives and the phosphinate salts in PA6 [52].

Uhl et al [107] prepared expandable graphite/PA6 nanocomposites using melt blending method. Cone calorimetric data showed a significant decrease in peak heat release rate for PA6/graphite nanocomposites even larger than what observed for PA6/clay nanocompsoites. But thermo-mechanical properties were inferior for PA6/graphite nanocomposites in comparison to PA6/clay equivalents.

Li et al [108] investigated the thermal degradation behaviour of multi-walled carbon nanotubes / PA6 composites. The dispersion of amino-functionalized MWNTs in PA6 was found to be more homogeneous than purified MWNTs. The presence of MWNTs improved the thermal stability of PA6 under air but little affected under nitrogen atmosphere.

Dahiya et al [109] investigated the thermal behaviour of PA6/bentonite clay/APP composites. The thermal stability of PA6/Org-BNT/APP composite was increased by 10 ºC when 5% of APP out of 20% in PA6/APP was replaced with 5% of Org-BNT. Synergistic effect were observed in between APP and bentonite clay in terms of char yield. No effect was observed on thermal stability and char yield by reducing the particle size of APP. In a recent research [110], effect of APP in combination with zinc phosphate and zinc borate was investigated on thermal degradation and flame retardation of PA6/clay nanocomposites. Synergistic effects were observed on addition of zinc borate with AP760 in PA6/clay nanocomposites for increasing thermal stability by 38 ºC.

Lewin et al [49] developed fully flame retardant PA6 and PA66 by using only 1.5-2.5 wt % of ammonium sulfamate (AS) or diammonium imidobisulfonate (DIBS) together with 0.4-0.85 wt% of pentaerythritol or dipentaerythritol. UL-94 rating of V-0 was obtained on bars of 1/16” and 1/32” with no flaming drips and very low burning time. The tensile strength values were very high and close to the untreated polymer. Lewin et al [111] investigated the flammability behavior of sulfamate flame retarded PA6 in the presence of organo-layered silicates (OMMT). Addition of OMMT up to 1 wt% preserved the UL-94 rating (V-0) and LOI values, but on further increasing the concentration the UL-94 rating and LOI values are reduced. On addition of 5

wt% of PVP poly(vinyl pyrrolidone) to the above system resulted in partial restoration of flame retardancy. Cone-calorimeter experiments revealed reduction in HRR of PA6 on addition of OMMT. The reduction in HRR was proportional to the percentage of OMMT applied. The addition of pristine clay to ammonium sulfamate and dipentaerythritol containing PA6 fully retained the FR and mechanical properties.

Xia et al [41] studied the morphology and thermal degradation of ammonium sulfamate flame retarded PA6. LOI value of PA6 was found to increase with increase in AS content. SEM results indicated that ammonium sulfamate facilitated the formation of intumescent char layer with honeycomb-like structure which improved the flame retardancy of PA6. The activation energy for thermal degradation of PA6 was decreased on addition of AS, suggested that AS facilitated the thermal degradation of PA6.

Dahiya et al [112] extended the work of Lewin et al [40] and studied the effect of nanoclays & fumed silica at low loading (1% and 2 wt%) on AS-DP treated PA6. All PA6 samples were found to be V-2 rated. LOI values were reduced on addition of nanoparticles to ammonium sulfamate (AS) and dipentaerythritol (DP) containing PA6. Cone-calorimetric results showed the decrease in peak heat release rate on addition of nanoarticles to PA6/AS/DP flame retardant system.

Coquelle et al [113] investigated the decomposition pathway of ammonium sulfamate flame retarded PA6 fibres. The fibres containing less than 7 wt% of AS were found to be spinnable and retained the mechanical properties. Microcalorimeter results revealed that peak heat release rate was reduced by 30 % on addition of 7 wt% of AS to PA6. The results indicated that AS acts both in condensed phase and gas phase to improve the flame retardancy of PA6. AS changed the degradation pathway of PA6 leading to enhanced char formation.

Recently, Coquelle et al [42] reported the effect of guanidine sulfamate/melamine polyphosphate mixture on flame retardancy of PA6. Microcalorimeter experiments revealed a 30 % decrease in peak heat release rate on addition of only 5 wt% of GAS/MPP mixture to PA6. LOI value and UL-94 rating were improved from 28 vol% & V-2 for pure PA6 to 37 vol% & V-0 for PA6/GAS (2.5 wt%)/MPP (2.5 wt%), respectively. Analysis of gas phase and condensed phase showed that GAS and MPP modified the degradation pathway of PA6 forming polyaromatic structure at high temperature. In a recent research [114], Effect of Lithium Chloride and N-Butyl Benzene sulfonamide on processing and flammability of PA6/sulfamate/nanoclay composites have been studied. Inclusion of 2 wt% of lithium chloride (LC) & N-butyl benzene sulfonamide (NBS) each enabled to reduce the processing temperature by about 10 ^{o}C for extruding the flame retarded PA6 composite with sulfamate system.

CONCLUSIONS

Polyamide 6 meets great demand in various fields, e.g. transportation, textile, sports, electronics, electrical, telecommunication etc. But, polyamide 6 is highly flammable and shows intensive dripping when heated or ignited, which increases its fire hazard. Consequently, improving the flame retardant behavior of Polyamide 6 is a major challenge for extending its use to various applications.

Initially, the majorities of the flame retardants were based on halogen containing additives and were found to be very efficient fire retardants in polyamide 6. However, halogenated additives were found to have some negative aspects due to release of toxic and corrosive gases such as dioxins & furans which drew the concerns over their environmental impact. Therefore, the research was continued to find alternative conventional non-halogenated fire retardants, which included inorganic fillers such as alumina trihydrate, magnesium hydroxide, carbonates, phosphorous, nitrogen, silicon and boron based compounds. Apart from various advantages of conventional FR additives, there were many drawbacks as they generally required very high loading in order to meet required flammability standards which resulted in to an increase in product costs, processing difficulties and worsening of polymer mechanical properties. To overcome these difficulties, the research was diverted to use nanoscale fillers to develop environmentally benign and superior flame retardant polymer nanocomposites. Among all the potential nanoscale fillers, layered silicates have been most widely investigated due to their natural abundance and large aspect ratio, which is highly favorable in matrix reinforcement. It has been found that PA6/clay nanocomposites exhibited improved heat distortion temperature, superior strength, modulus, gas barrier properties, and comparable impact strength as compared to pure nylon 6.

Synergistic effect on using modified montmorillonite along with conventional flame retardants in PA6 lead to superior mechanical and flame retardant properties as compared to a classical flame-retarded PA6. A number of studies revealed that PA6 is shown to produce enhanced char yield due to cross-linking or char-forming reactions in the presence of nano-dispersed clay. Recently, PA6/intumescent/clay nanocomposites have been found to be very cost effective and efficient flame retardant systems. The synergistic effect between micro-dispersed intumescent flame retardants and nanoparticles help to promote charring leading to enhanced flame retardant performance and reduces the overall filler contents that leads to positive effects on polymer processing and properties.

Therefore, in present scenario, the research is progressing in finding such formulations which may lead to acceptable thermal and flammability properties with very low loading of flame retardants in order that not compromising with the mechanical properties of the Polyamide 6. It will have great potential for the uses of Polyamide 6 in the fields demanding flame retardancy along with adequate mechanical properties.

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