

# Ecological Issue of Polymer Flame Retardancy

G. E. Zaikov, S. M. Lomakin

*Institute of the Biochemical Physics of Russian Academy of Sciences,  
119991, Kosygin 4, Russia*

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**ABSTRACT:** The use of polymer flame retardants has an important role in saving lives. The main flame retardant systems for polymers currently in use are based on halogenated, phosphorous, nitrogen, and inorganic compounds. All of these flame retardant systems basically inhibit or even suppress the combustion process by chemical or physical action in the gas or condensed phase. Conventional flame retardants, such as halogenated, phosphorous, or metallic additives, have a number of negative attributes. An ecological issue of the application of conventional flame retardants demands the search of new polymer flame retardant systems. Among the new trends of flame retardancy are intu-

mescent systems, polymer nanocomposites, preceramic additives, low-melting glasses, different types of char formers, and polymer morphology modification processing. The brief explanations on the three major types of flame retardant systems (intumescent systems, polymer nanocomposites, and polymer organic char formers) are the subject of this overview. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2449–2462, 2002

**Key words:** polymer combustion; flame retardants; intumescent systems; polymer nanocomposites, char former; preceramic additives; dioxins

## INTRODUCTION

Our environment has a mostly polymeric nature, and all polymers burn whether natural or synthetic. The use of polymer flame retardants has an important role in saving lives. There are four main families of flame-retardant chemicals:

- Inorganic flame retardants including aluminum trioxide, magnesium hydroxide, ammonium polyphosphate, and red phosphorus. This group represents about 50% by volume of the global flame retardant production.<sup>1</sup>
- Halogenated flame retardants, primarily based on chlorine and bromine. The brominated flame retardants are included in this group. This group represents about 25% by volume of the global production.<sup>1</sup>
- Organophosphorus flame retardants are primarily phosphate esters and represent about 20% by volume of the global production.<sup>1</sup> Organophosphorus flame retardants may contain bromine or chloride.
- Nitrogen-based organic flame retardants are used for a limited number of polymers.

## Mechanisms of action

Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid, or gas phase. They interfere with combustion during a particular stage of this process, e.g., during heating, decomposition, ignition, or flame spread.

Substitution of one type of flame retardant with another consequently means a change in the mechanisms of flame retardancy. Halogen-containing flame retardants act primarily by a chemical interfering with the radical chain mechanism taking place in the gas phase during combustion. High-energy OH and H radicals formed during combustion are removed by bromine released from the flame retardant. Although brominated flame retardants are a highly diverse group of compounds, the flame-retardancy mechanism is basically the same for all compounds. However, there are differences in flame-retardancy performance of the brominated compounds, as the presence of the compounds in the polymer will influence the physical properties of the polymer. In general, aliphatic bromine compounds are easier to break down and hence more effective at lower temperatures, but also less temperature resistant than aromatic retardants.

Aluminum hydroxide and other hydroxides act in a combination of various processes. When heated, the hydroxides release water vapor that cool the substrate to a temperature below that required for sustaining the combustion processes. The water vapor liberated has also a diluting effect in the gas phase and forms an oxygen-displacing protective layer. Additionally, the

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

oxide forms together with the charring products an insulating protective layer.

Phosphorus compounds mainly influence the reactions taking place in the solid phase. By thermal decomposition the flame retardants are converted to phosphorus acid, which in the condensed phase extracts water from the pyrolyzing substrate, causing it to char. However, some phosphorus compounds may, similar to halogens, act in the gas phase as well by a radical trap mechanism.

## Background

The interest in flame retarding polymers goes back to the nineteenth century with the discovery of highly flammable cellulose nitrate and celluloid. In more recent times the conventional large volume of plastics such as phenolics, rigid PVC, and melamine resins possess adequate flame retardancy. By the 1970s the major flame retardant polymers were the thermosets—namely, unsaturated polyesters and epoxy resins—which utilized reactive halogen compounds and alumina hydrate as an additive. There was also a large market for phosphate esters in plasticized PVC, cellulose acetate film, unsaturated polyesters, and modified polyphenylene oxide. Alumina trihydrate (ATH) was the largest volume flame retardant in unsaturated plastics.

Consumption of halogen-containing flame retardant additives in the 1970s was much less than the other additives. The term “halogenated flame retardants” covers a large number of different organic substances, all with chlorine or bromine in their molecular structure. Bromine and chlorine have an inhibitory effect on the formation of fire in organic materials. Flame retardants are added to plastics and textiles in order to comply with fire safety requirements. The halogenated flame retardant additives were Dechlorane Plus, a chlorinated acyclic (for polyolefins), tris-(dibromopropyl) phosphate, brominated aromatics, pentabromochlorocyclohexane, and hexabromocyclododecane (for polystyrene). The next ten years was to see a number of new brominated additives on the market. There was produced a number of chlorinated flame retardant products under the Dechlorane trade name. The products included two moles of hexachlorocyclopentadiene, and contained 78% chlorine; Dechlorane Plus, a Diels–Alder reaction product of cyclooctaliene and hexachlorocyclopentadiene with 65% chlorine; a Diels–Alder product with furan and a product containing both bromine and chlorine with 77% halogen developed for the polystyrene and acrylonitrile–butadiene–styrene (ABS) materials.<sup>1</sup>

In 1985–1986 a German study detected brominated dioxins and furans from pyrolysis of a brominated diphenyl oxide in the laboratory at 510–630°C.<sup>1</sup> The relevance of these pyrolysis studies to the real hazard

presented by these flame retardants under actual use conditions has been questioned. Germany and Holland have considered a ban or curtailed use of brominated diphenyl oxide flame retardants because of the potential formation of highly toxic and potentially carcinogenic brominated furans and dioxins during combustion. The issue spread to other parts of Europe where regulations were proposed to restrict their use.<sup>2,3</sup>

The chemical stability of the substances—particularly in the cases of PBBs and PBDEs—is also the reason why brominated flame retardants for years have been in focus in the international environmental debate. PBDEs and PBBs, which are the most stable of the described BFRs, are spread widely in the environment, are bioaccumulated and are accumulated in sediments, where they are only very slowly degraded.

## HALOGENATED DIPHENYL ETHERS AND DIOXINS

Chlorinated dibenzo-*p*-dioxins and related compounds (commonly known simply as dioxins) are contaminants present in a variety of environmental media. This class of compounds has caused great concern in the general public as well as intense interest in the scientific community. Laboratory studies suggest the probability that exposure to dioxin-like compounds may be associated with other serious health effects including cancer. Conventional laboratory studies have provided new insights into the mechanisms involved in the impact of dioxins on various cells and tissues, and ultimately, on toxicity.<sup>1</sup> Dioxins have been demonstrated to be potent modulators of cellular growth and differentiation, particularly in epithelial tissues. These data, together with the collective body of information from animal and human studies, when coupled with assumptions and inferences regarding extrapolation from experimental animals to humans and from high doses to low doses, allow a characterization of dioxin hazards.

Polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) are chemically classified as halogenated aromatic hydrocarbons. The chlorinated and brominated dibenzodioxins and dibenzofurans are tricyclic aromatic compounds with similar physical and chemical properties, and both classes are similar structurally. Certain of the PCBs (the so-called coplanar or mono-*ortho* coplanar congeners) are also structurally and conformationally similar. The most widely studied of these compounds is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). This compound, often called simply dioxin, represents the reference compound for this class of compounds. The structure of TCDD and several related compounds is shown in Figure 1.

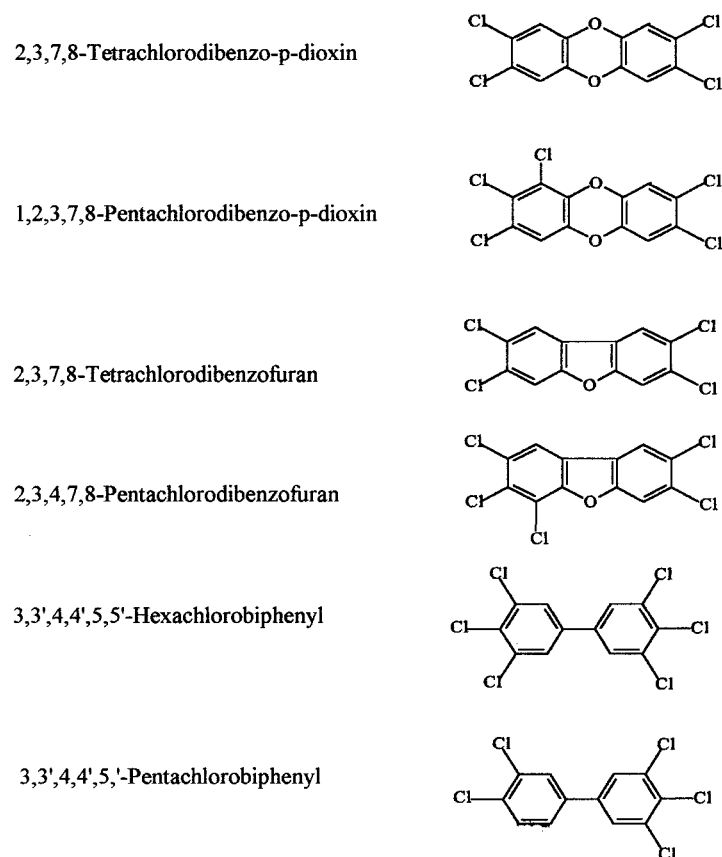


Figure 1 The structures of dioxin and similar compounds.

These compounds are assigned individual toxicity equivalence factor (TEF) values as defined by international convention [U.S. Environmental Protection Agency (EPA), 1989]. Results of *in vitro* and *in vivo* laboratory studies contribute to the assignment of a relative toxicity value. TEFs are estimates of the toxicity of dioxin-like compounds relative to the toxicity of TCDD, which is assigned a TEF of 1.0. All chlorinated dibenzodioxins (CDDs) and chlorinated dibenzofurans (CDFs) with chlorines substituted in the 2, 3, 7, and 8 positions are assigned TEF values.<sup>1</sup> Additionally, the analogous brominated dioxins and furans (BDDs and BDFs) and certain polychlorinated biphenyls have recently been identified as having dioxin-like toxicity, and thus are also included in the definition of dioxin-like compounds. Generally accepted TEF values for chlorinated dibenzodioxins and dibenzofurans are shown in Table I.<sup>4</sup>

A recent World Health Organization/International Program on Chemical Safety meeting held in the Netherlands in December 1993 considered the need to derive internationally acceptable interim TEFs for the dioxin-like PCBs. Recommendations arising from that meeting of experts suggest that in general only a few of the dioxin-like PCBs are likely to be significant contributors to general population exposures to dioxin-like compounds.<sup>5</sup> Dioxin-like PCBs may be respon-

sible for approximately one-fourth to one-half of the total toxicity equivalence associated with general population environmental exposures to this class of related compounds.

TABLE I  
TEFs for CDDs and CDFs<sup>5</sup>

Compound	TEF
Mono-, di-, and Tri-CDDs	0
2,3,7,8-TCDD	1
Other TCDDs	0
2,3,7,8-PeCDD	0.5
Other PeCDDs	0
2,3,7,8-HxCDD	0.1
Other HxCDDs	0
2,3,7,8-HpCDD	0.01
Other HpCDDs	0
Mono-, Di-, and Tri-CDFs	0
2,3,7,8-TCDF	0.1
Other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
Other PeCDFs	0
2,3,7,8-HxCDF	0.1
Other HxCDFs	0
2,3,7,8-HpCDF	0.01
Other HpCDFs	0
OCDF	0.001

There are 75 individual compounds comprising the CDDs, depending on the positioning of the chlorine(s), and 135 different CDFs. These are called individual congeners. Likewise, there are 75 different positional congeners of BDDs and 135 different congeners of BDFs. Only 7 of the 75 congeners of CDDs or of BDDs are thought to have dioxin-like toxicity; these are ones with chlorine/bromine substitutions in, at least, the 2, 3, 7, and 8 positions. Only 10 of the 135 possible congeners of CDFs or of BDFs are thought to have dioxin-like toxicity; these also are ones with substitutions in the 2, 3, 7, and 8 positions. While this suggests 34 individual CDDs, CDFs, BDDs, or BDFs with dioxin-like toxicity, inclusion of the mixed chloro/bromo congeners substantially increases the number of possible congeners with dioxin-like activity. There are 209 PCB congeners. Only 13 of the 209 congeners are thought to have dioxin-like toxicity; these are PCBs with 4 or more chlorines with just 1 or no substitution in the *ortho* position. These compounds are sometimes referred to as coplanar, meaning that they can assume a flat configuration with rings in the same plane.

Similarly configured polybrominated biphenyls are likely to have similar properties; however, the database on these compounds with regard to dioxin-like activity has been less extensively evaluated. Mixed chlorinated and brominated congeners also exist, increasing the number of compounds considered dioxin-like. The physical/chemical properties of each congener vary according to the degree and position of chlorine and/or bromine substitution. Very little is known about occurrence and toxicity of the mixed (chlorinated and brominated) dioxin, furan, and biphenyl congeners.

In general, these compounds have very low water solubility, high octanol-water partition coefficients, and low vapor pressure, and tend to bioaccumulate.

Although these compounds are released from a variety of sources, the congener profiles of CDDs and CDFs found in sediments have been linked to combustion sources.<sup>1</sup>

The Hazards Substance Ordinance in Germany specifies the maximum level of chlorinated dibenzodioxins and furans that can be present in materials marketed in Germany. This has been extended to the brominated compounds. The two largest volume flame retardants decabromodiphenyl oxide and tetrabromo bis-phenol A are said to meet these requirements.<sup>2,3</sup>

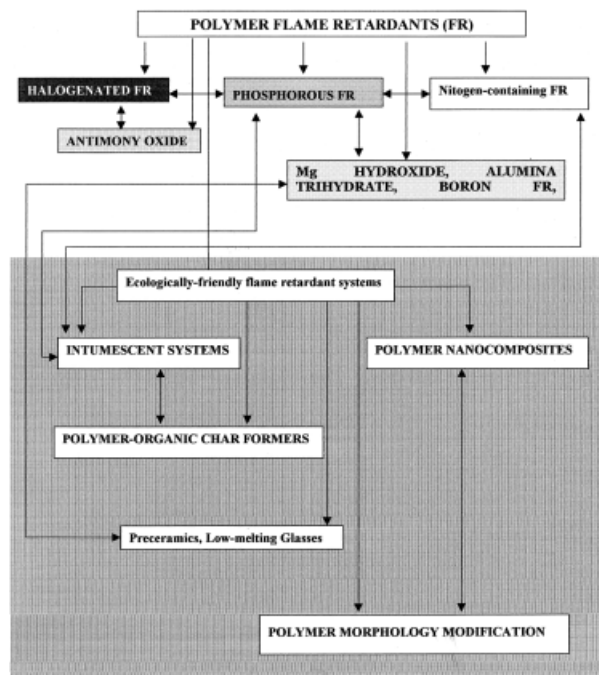
The International Program for Chemical Safety (IPCS) of the World Health Organization has made several recommendations. Polybrominated diphenyls production (France) and use should be limited because of the concern over high persistency, bioaccumulation, and potential adverse effects at low levels. There is limited toxicity data on deca- and octabromo-

diphenyls. Commercial use should cease unless safety is demonstrated. For the polybrominated diphenyl oxides, a Task Group felt that polybrominated dibenzofurans, and to a lesser extent the dioxins, may be formed. For decabromodiphenyl oxide, appropriate industrial hygiene measures need to be taken and environmental exposure minimized by eluent and emission control. Controlled incineration procedures should be instituted. For octabromodiphenyl oxide, the hexa- and lower isomers should be minimized. There is considerable concern over persistence in the environment and the accumulation in organisms, especially for pentabromodiphenyl oxide.

There are no regulations proposed or in effect anywhere around the world banning the use of brominated flame retardants. The proposed European Union (EU) Directive on the brominated diphenyl oxides is withdrawn. Deca- and tetrabromo bis-phenol A as well as other brominated flame retardants meet the requirements of the German Ordinance regulating dioxin and furan content of products sold in Germany.<sup>6</sup>

The European search for a replacement for decabromodiphenyl oxide in HIPS has led to consideration of other bromoaromatics such as Saytex 8010 from Albemarle and a heat-stable chlorinated paraffin from ATOCH EM. The former product is more costly, and the latter, if sufficiently heat stable, lowers the heat distortion under load (HDUL) significantly. Neither approach has been fully accepted. In September 1994, the U.S. EPA released a final draft of exposure and risk assessment of dioxins and like compounds.<sup>5</sup> This reassessment finds the risks greater than previously thought. Based on this reassessment, a picture emerges that tetrachlorodiphenyl dioxins and related compounds are potent toxicants in animals with the potential to produce a spectrum of effects. Some of these effects may be occurring in humans at very low levels and some may be resulting in adverse impacts on human health. The EPA also concluded that dioxin should remain classified as a probable human carcinogen.<sup>5</sup>

Polymer producers have been seeking nonhalogen flame retardants and the search has been successful in several polymer systems. Nonhalogen flame retardant polycarbonate/ABS blends are now commercial. They contain triphenyl phosphate or resorcinol diphosphate (RI)P as the flame retardant. Modified polyphenylene oxide (GE's Noryl) has used phosphate esters as the flame retardant for the past 15–20 years and the industry recently switched from the alkylated triphenyl phosphate to RDP. Red phosphorus is used with glass-reinforced nylon 6,6 in Europe and melamine cyanurate is used in unfilled nylon. Magnesium hydroxide is being used commercially in polyethylene wire and cable. The nonhalogen solutions present other problems such as poor properties (plasticizers lower heat distortion temperature), difficult process-



**Figure 2** Block scheme of polymer flame retardant systems.

ing (high loadings of ATH and magnesium hydroxide), corrosion (red phosphorus), and handling problems (red phosphorus).

In the present publication we have tried to present a basic trends in the flame retardant hierarchy.

### FLAME RETARDANT SYSTEMS

The main flame retardant systems for polymers currently in use are based on halogenated, phosphorous, nitrogen, and inorganic compounds (Fig. 2). All of these flame retardant systems basically inhibit or even suppress the combustion process by chemical or physical action in the gas or condensed phase. To be effective, the flame retardants must decompose near the decomposition temperature of the polymer in order to do the appropriate chemistry as the polymer decomposes, yet be stable at processing temperatures. Conventional flame retardants, such as halogenated, phosphorous, or metallic additives, have a number of negative attributes. An ecological issue of its application demands the search of new polymer flame retardant systems. Among the new trends of flame retardancy the use of intumescent systems, polymer nanocomposites, preceramic additives, low-melting glasses, different types of char formers, and polymer morphology modification are salient.<sup>1</sup> However, the close interactions between the different flame retardant types in order to achieve a synergistic behavior should be assumed. The block scheme of polymer flame retardant systems is given in Figure 2.

Brief explanations of the three major types of flame retardant systems (intumescent systems, polymer nanocomposites, and polymer organic char former) are presented below.

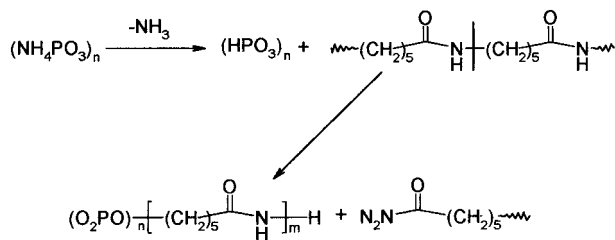
### Intumescent additives

The intumescent behavior resulting from a combination of charring and foaming of the surface of the burning polymers is being widely developed for fire retardancy because it is characterized by a low environmental impact.

Among alternative candidates, intumescent materials have received considerable attention because they provide fire protection with minimum of overall fire hazard.<sup>7</sup> Since the first intumescent coating material was patented in 1938,<sup>8</sup> the mechanism of an intumescent flame retardant refers to the forming of a foam that acts as an insulating barrier between the fire and substrate. In particular, such an intumescence depends significantly on the ratio of C, N, and P atoms in a compound.<sup>7,9</sup> Although intumescent coatings are capable of exhibiting good fire protection for the substrate, they have several disadvantages such as water solubility, brushing problem, and relatively high cost.<sup>10</sup> The fire retardation of plastic materials is generally achieved by incorporating fire-retardant additives into the plastic during processing.<sup>11,12</sup> Since the processing requires that the additives withstand up to above 200°C, the intumescent systems without sufficient thermal stability cannot be incorporated into various plastics. A phosphate–pentaerythritol system was investigated and developed as the intumescent materials.<sup>7</sup> For example, a systematic study on a mixture of ammonium polyphosphate and pentaerythritol has shown that intumescence occurs on flaming.<sup>13,14</sup> Thus, new intumescent materials with appropriate thermal stability have been synthesized for better fire retardancy.<sup>15</sup>

The most important inorganic nitrogen–phosphorus compound used as an intumescent flame retardant is ammonium polyphosphate, which is applied in intumescent coatings and in rigid polyurethane foams. The most important organic nitrogen compounds used as a flame retardants are melamine and its derivatives, which are added to intumescent varnishes or paints. Melamine is incorporated into flexible polyurethane cellular plastics, and melamine cyanurate is applied to unreinforced nylons. Guanidine sulfamate is need as a flame retardant for PVC wall coverings in Japan. Guanidine phosphate is added as a flame retardant to textile fibers, and mixtures based on melamine phosphate are used as flame retardants to polyolefins or glass-reinforced nylons.

All the above-mentioned compounds: ammonium polyphosphate, melamine, guanidine, and their salts



Scheme 1 Reaction of APP with nylon 6.

are characterized by an apparently acceptable environmental impact.

Mechanistic studies in nylon 6 with added ammonium polyphosphate (APP), ammonium pentaborate (APB), melamine, and its salts were carried out using combustion and thermal decomposition approaches.<sup>16,17</sup> It was shown that APP interacts with nylon 6, producing alkylpolyphosphoric ester, which is a precursor of the intumescent char. On the surface of burning polymer, APB forms an inorganic glassy layer protecting the char from oxidation and hindering the diffusion of combustible gases. Melamine and its salts induce scission of H—C—C(O) bonds in nylon 6, which leads to increased crosslinking and charring of the polymer.<sup>17</sup> APP added at 10–30% wt to nylon 6 is ineffective in the low molecular weight polymer since oxygen index (LOI) remains on the level of 23–24,<sup>18</sup> corresponding to nonfire-retarded nylon 6. However, APP becomes very effective at loadings of 40 and 50% where the LOI increased to 41 and 50, respectively.

A condensed phase fire retardant mechanism is proposed for APP in nylon 6.<sup>18</sup> In fact, an intumescent layer is formed on the surface of burning nylon 6/APP formulations, which tends to increasing content of APP.

Thermal analysis has shown that APP destabilizes nylon 6, since the thermal decomposition is observed at a temperature 70°C lower than that the pure nylon 6.<sup>18</sup> However, the intumescent layer effectively protects the underlying polymer from the heat flux and therefore in the configuration of the linear pyrolysis experiments the formulation nylon 6/APP (40%) decomposes more slowly than pure polymer.<sup>18</sup> These experiments prove the fire retardant action of the intumescent char. The mechanistic studies of the thermal decomposition in the system nylon 6/APP show that APP catalyses the degradation of the polymer and interacts with it, forming essentially 5-amidopentyl polyphosphate (see Scheme 1).

On further heating, 5-amidopentyl polyphosphate again liberates polyphosphoric acid and produces the char. The intumescent shielding layer on the surface of the polymer is composed of the foamed polyphosphoric acid, which is reinforced with the char.<sup>18</sup>

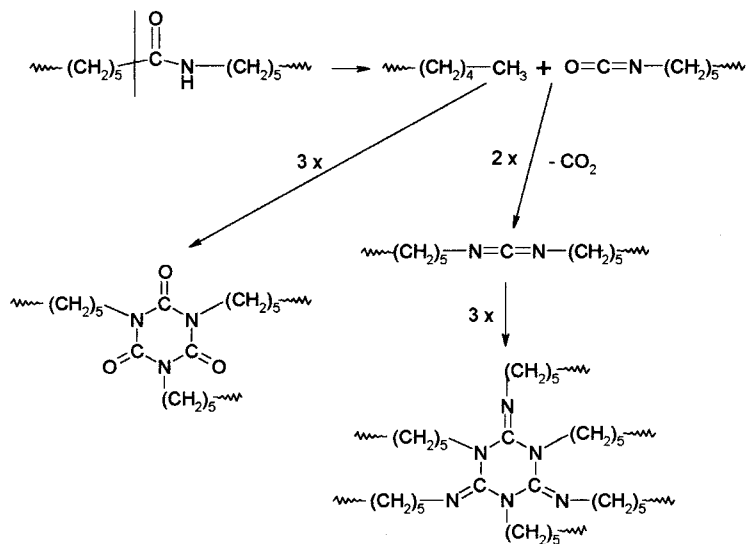
The effectiveness of ammonium pentaborate  $\text{NH}_4\text{BO}_5$  (APB) in the high molecular weight nylon 6

( $M_n = 35,000$ ) is similar to that of APP as measured by oxygen index.<sup>19</sup> In contrast to APP, APB does not give an intumescent layer. Instead, a brown-black glassy-like compact layer is formed. As thermal analysis has shown, APB destabilizes nylon 6 since the latter decomposes at 50°C lower. It is likely that freed boric acid catalyses the thermolysis of the nylon. In contrast to APP, no other chemical interaction of nylon 6 and APB was found. In fact, the residue obtained in nitrogen in thermogravimetry for the formulations nylon 6/APB corresponds to that calculated on the basis of individual contributions of nylon 6 and APB to the residue.<sup>19</sup> It is likely that accumulated on the surface of burning polymer is a molten glassy layer of boric acid/boric anhydride that protects the char from oxidation. This layer reinforced by the char creates a barrier against diffusion of the volatile fuel from the polymer to the flame, which decreases combustibility of nylon 6.<sup>19</sup>

A systematic mechanistic study of halogen-free fire retardant nylon 6, via the combustion performance and thermal decomposition behavior of nonreinforced nylon 6 with added melamine, melamine cyanurate, melamine oxalate, melamine phthalate, melamine pyrophosphate, or dimelamine phosphate has been reported.<sup>20</sup> Melamine, melamine cyanurate, melamine oxalate, and melamine phthalate promote melt dripping of nylon 6, which increases as the additive concentration increases. These formulations self-extinguish very quickly in air and their LOI increases with increasing concentration (Table II).<sup>20</sup> The melt dripping effect is very strong in the case of melamine phthalate, where a small amount of the additive (3–10%) leads to large increases in LOI (34–53). The combustion behavior of melamine pyrophosphate and dimelamine phosphate are different from melamine and the other melamine salts (Table II). The former are ineffective at low concentrations 15% and become effective at a loading of 20–30% because the intumescent char is formed on the surface of burning specimens. The mechanism of the fire retardant action of both melamine pyrophosphate and dimelamine phosphate is similar to the APP, since melamine, by analogy with

TABLE II  
Oxygen Indices for High Molecular Weight Nylon 6  
with Added Melamine or Its Salts  
(LOI for Pure Nylon 6 = 24)<sup>20</sup>

Additive concentration (% wt)						
	3	5	10	15	20	30
Melamine	—	29	31	33	38	39
Dimelamine phosphate	—	23	24	25	26	30
Melamine pyrophosphate	—	24	25	25	30	32
Melamine oxalate	—	28	29	—	33	—
Melamine cyanurate	—	35	37	39	40	40
Melamine phthalate	34	48	53	—	—	—



Scheme 2 Mechanism of thermal decomposition of nylon 6 in the presence of melamine.<sup>23</sup>

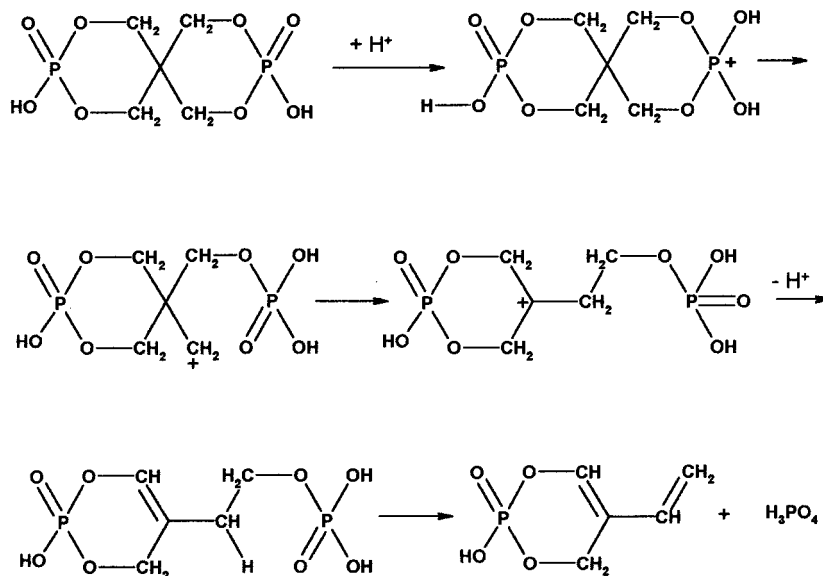
ammonia volatilizes, whereas the remaining phosphoric acids produce esters with nylon 6, which are precursors of the char.<sup>21</sup> Some part of the freed melamine condenses, forming probably melem and melon.<sup>22</sup> Melamine partially evaporates from the composition nylon-6/melamine (30%), whereas the other part condenses, giving 8% of solid residue at 450°C. However, similar behavior with more thermostable residue is shown by melamine cyanurate. Melamine pyrophosphate, like dimelamine phosphate,<sup>21</sup> gives about 15% of thermostable char. It is likely that accumulated on the surface of the burning polymer is a glassy layer of molten boric acid boric anhydride that protects the char from oxidation. The glass, reinforced by the char, creates a barrier against diffusion of the volatile fuel from the polymer to the flame, which decreases combustibility of nylon 6.<sup>19</sup>

As infrared characterization of solid residue and high boiling products has shown,<sup>21</sup> carbodiimide functionalities are formed at the thermal decomposition of nylon 6 with melamine and its salts. An unusual mechanism of chain scission of nylon 6 through CH<sub>2</sub>—C(O) bonds,<sup>23</sup> is likely to become operative in the presence of melamines (Scheme 2). The resultant isocyanurate chain ends undergo dimerization to carbodiimide or trimerization to N-alkylisocyanurate. Carbodiimide can also trimerize to N-alkylisotriazine. These secondary reactions increase the thermal stability of the solid residue and increase the yield of the char.

In order to understand better the chemical reactions that are responsible for the intumescent behavior of APP–PER (pentaerythritol) mixtures, as model examples, a study of the thermal degradation of pentaerythritol diphosphate (PEDP) was undertaken.<sup>24</sup> PEDP is a model compound for structures identified in ammo-

niun polyphosphate–pentaerythritol mixtures heated below 250°C. Using thermogravimetric analysis (TGA) have been identified five major degradation steps between room temperature and 950°C, and volatile products are evolved in each step. The formation of the foam reaches a maximum at 325°C, corresponding to the second step of degradation; foam formation decreases at higher temperatures. There are no differences in the TGA or differential scanning calorimetry (DSC) curves in nitrogen or air up to 500°C. Above this temperature, thermal oxidation leads to almost complete volatilization in a single step, which is essentially completed at 750°C. The elucidation of the chemical reactions that occur upon degradation is easier if each step is studied separately. The separation of the steps is accomplished by heating to a temperature at which one step goes to completion, and the following reaction occurs at a negligible rate.<sup>24</sup> The chemical reactions which occur in the first two steps lead to the initial formation of a char-like structure which will undergo subsequent graphitization.

The first reaction is the elimination of water with the condensation of OH groups. This overlaps with the elimination of organics when as little as 28% of the possible water has been evolved. This involves essentially complete scission of the phosphate ester bonds and results in a mixture of polyphosphates and a carbonaceous char. Three mechanisms have been proposed in the literature for this reaction<sup>25,26</sup>: a free-radical mechanism, a carbonium ion mechanism, and a cyclic *cis*-elimination mechanism. The free-radical mechanism was eliminated due to the lack of an effect of free-radical inhibitors on the rate of pyrolysis.<sup>26</sup> The carbonium ion mechanism is supported by acid catalysis and kinetic behavior, and may compete with the elimination mechanism.<sup>25,26</sup> The carbonium ion mech-

Scheme 3 Ester pyrolysis mechanism.<sup>25</sup>

anism should occur exclusively if there is no hydrogen atom on the  $\beta$ -carbon atom, as in PEDP, which is necessary for the cyclic transition state of the elimination mechanism. The olefin is generated from the thermodynamically most stable carbonium ion. Hydride migration or skeletal rearrangement may take place to give a more stable ion of a carbonium ion of high reactivity is produced. After ring opening in the ionic ester pyrolysis mechanism, a second ester pyrolysis reaction occurs, which could also take place by the *cis*-elimination mechanism, as shown in Scheme 3. The formation of char can occur either by free-radical- or acid-catalyzed polymerization reactions from the compounds produced in the pyrolysis. For example, the Diels–Alder reaction followed by ester pyrolysis and sigmatropic (1,5) shifts leads to an aromatized structure; this is shown in Scheme 5.<sup>25</sup> Repetition of these steps can eventually build up the carbonaceous char that is observed. The reaction pattern shown in Schemes 4 and 5 should help provide the structures observed by spectroscopy in the foamed char.<sup>25</sup> These reactions probably occur in an irregular sequence and in competition with other processes; the final products are obtained by some random combination of polymerization, Diels–Alder condensation, aromatization, etc. Ester pyrolysis supplies the chemical structures that build up the charred material through relatively simple reactions.<sup>25</sup>

The intumescent behavior resulting from a combination of charring and foaming of the surface of the burning polymers is being widely developed for fire retardance because it is characterized by a low environmental impact. However, the fire retardant effectiveness of intumescent systems is difficult to predict because the relationship between the occurrence of the

intumescence process and the fire protecting properties of the resulting foamed char is not yet understood.

### Polymer–organic char former

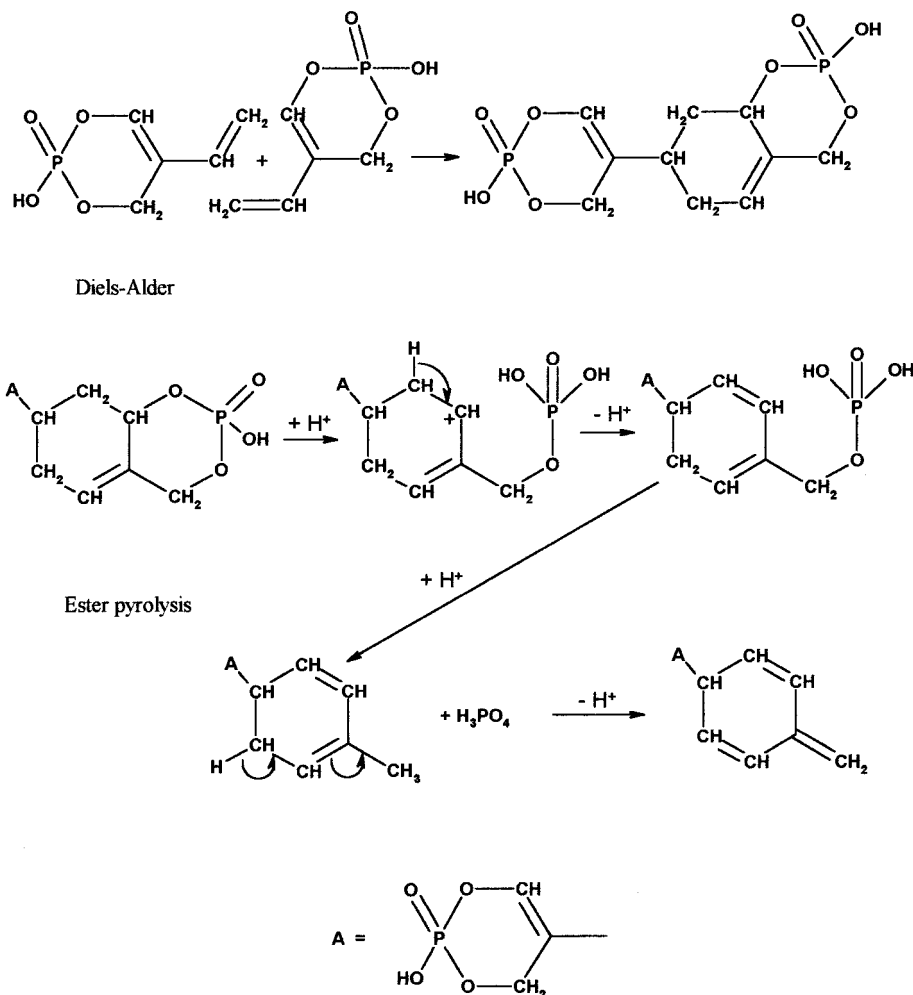
There is a strong correlation between char yield and fire resistance. This follows because char is formed at the expense of combustible gases and because the presence of a char inhibits further flame spread by acting as a thermal barrier around the unburned material. Polymeric additives (polyvinyl alcohol systems) that promote the formation of char in the polyvinyl alcohol–nylon 6,6 system have been studied.<sup>27</sup> These polymeric additives usually produce a highly conjugated system—aromatic structures that char during thermal degradation and/or transform into crosslinking agents at high temperatures (see Scheme 6).

Scission of several carbon–carbon bonds leads to the formation of carbonyl ends. For example, aldehyde ends arise from the reaction.

The identification of a low concentration of benzene among the volatile products of PVA has been taken to indicate the onset of a crosslinking reaction proceeding by a Diels–Alder addition mechanism.<sup>28</sup> Clearly benzenoid structures are ultimately formed in the solid residue, and the infrared (IR) spectrum of the residue also indicated the development of aromatic structures.

Acid-catalyzed dehydration promotes the formation of conjugated sequences of double bonds (a) and Diels–Alder addition of conjugated and isolated double bonds in different chains may result in intermolecular crosslinking producing structures, which form graphite or carbonization (b) (see Scheme 7).



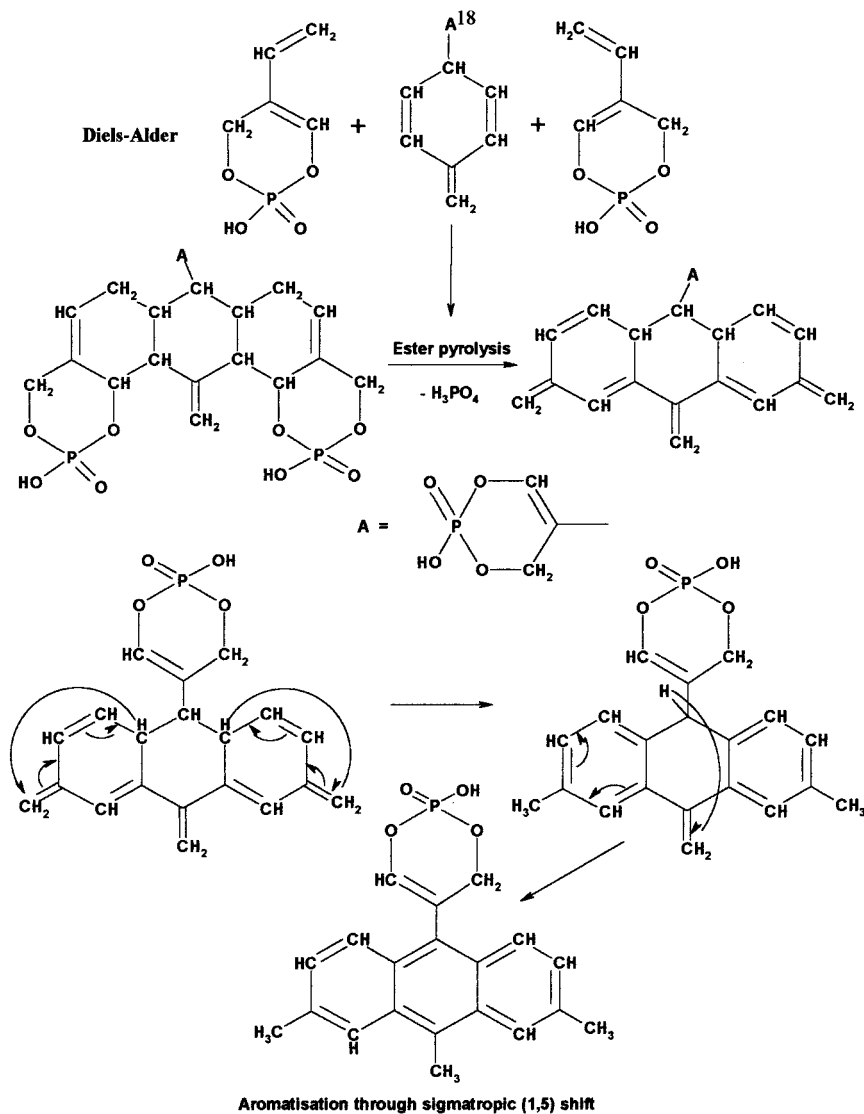
Scheme 4 Acid-catalyzed char formation.<sup>25</sup>

In contrast to PVA, nylon 6,6, which was subjected to temperatures above 300°C in an inert atmosphere, was completely decomposed. The wide range of degradation products, which included several simple hydrocarbons, cyclopentanone, water, CO, CO<sub>2</sub>, and NH<sub>3</sub>, suggested that the degradation mechanism must have been highly complex. Further research has led to a generally accepted degradation mechanism for aliphatic polyamides.<sup>29</sup>

The idea of introducing PVA into nylon 6,6 composition was based on the possibility of high-temperature acid-catalyzed dehydration.<sup>30</sup> This reaction can be provided by the acid products of nylon 6,6 degradation hydrolysis, which would promote the formation of intermolecular crosslinking and char. Such a system has been called "synergetic carbonization" because the char yield and flame suppression parameters of the polymer blend of poly(vinyl alcohol) and nylon 6,6 are significantly better than pure poly(vinyl alcohol) and nylon 6,6 polymers.<sup>31</sup>

An additional improvement to the flame-resistant properties of the poly(vinyl alcohol)-nylon 6,6 system

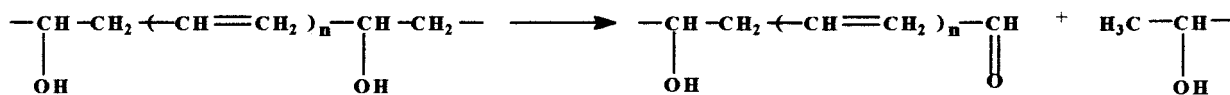
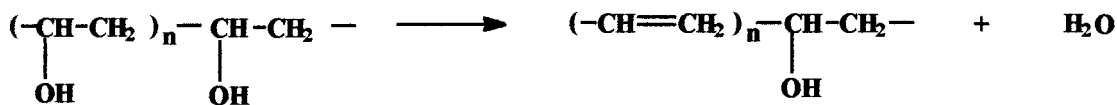
was suggested by means of substitution of pure poly(vinyl alcohol) by poly(vinyl alcohol) oxidized with potassium permanganate (PVA-ox).<sup>31</sup> Early it was reported that the oxidation of PVA by in alkaline solutions occurs through formation of two intermediate complexes. The final step of this process was attributed to the formation of poly(vinyl ketone) as a final product of oxidation of the substrate.<sup>32</sup> The fire retardancy approach was made on the basis of fire behavior of the PVA-ox samples. It was experimentally shown, using the Cone Calorimeter tests, that there was a dramatic decrease of the rate of the heat release and significant increase in ignition time for the oxidized PVA in comparison with the original PVA (Table III). One reason for this phenomenon may be explained by the ability for PVA oxidized by KMnO<sub>4</sub>—(polyvinyl ketone structures) to act as a neutral and/or monobasic bidentate ligand.<sup>33</sup> The experimental results of others (IR and electronic spectra) provide strong evidence of coordination of the ligand (some metal ions Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>) through the monobasic bidentate mode.<sup>34</sup> Based on the above, the

Scheme 5 Free-radical char formation.<sup>25</sup>

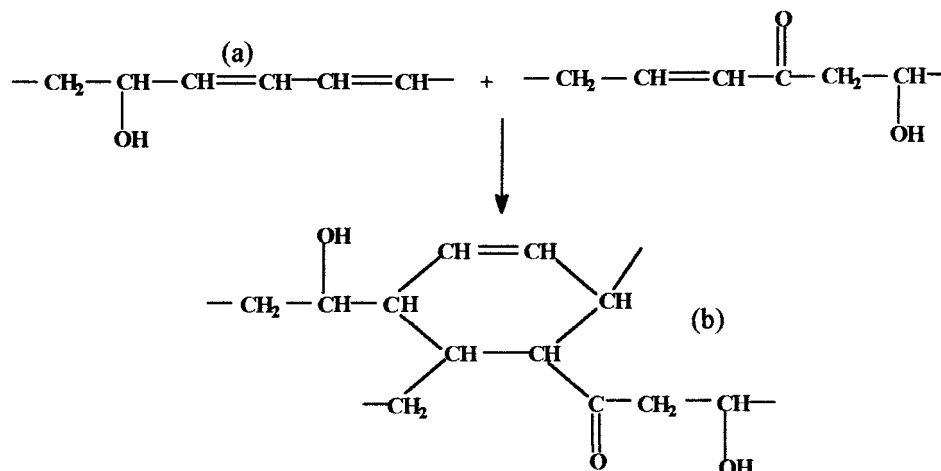
structure in Scheme 8 can be proposed for the polymeric complexes.

Cone Calorimeter combustion tests for PVA and PVA oxidized by KMnO<sub>4</sub> (Table III) clearly indicated

the substantial improvement of fire-resistance characteristics for PVA oxidized by KMnO<sub>4</sub> in comparison with PVA. PVA oxidized by KMnO<sub>4</sub> gives about half the peak of heat release rate (peak RHR kW/m<sup>2</sup>),



Scheme 6



Scheme 7

when compared with pure PVA. Even at  $50 \text{ kW/m}^2$ , the yield of char residue for PVA oxidized by  $\text{KMnO}_4$  was 9.1%.<sup>31</sup>

The result of elemental analysis of PVA oxidized by  $\text{KMnO}_4$  indicates the presence of 1.5% of Mn remaining in this polymeric structure.<sup>31</sup> It has been suggested that the catalytical amount of chelated Mn structure incorporated in the polymer can provide a rapid high-temperature process of carbonization followed by formation of char.<sup>31</sup>

The sample with PVA oxidized by  $\text{KMnO}_4$  displayed even better flame retardant properties due to the catalytical effect of Mn-chelate fragments on the formation of char (Table III). However, the less satisfactory correlation is given in the determination of total heat release data (Table III).<sup>31</sup> Although the Cone measurements indicated a decrease of total heat release for nylon 6,6-PVA and nylon 6,6-PVA oxidized by  $\text{KMnO}_4$  in comparison with pure PVA, the sample of nylon 6,6 with PVA oxidized by  $\text{KMnO}_4$  showed a higher value of total heat release than nylon 6,6 with PVA (Table III). This fact has been qualitatively explained by the influence of a catalytical amount of chelated Mn structure incorporated in polymer on the smoldering of the polymer samples.

The flame-out time for nylon 6,6 with PVA oxidized by  $\text{KMnO}_4$  is larger than the flame-out times of nylon

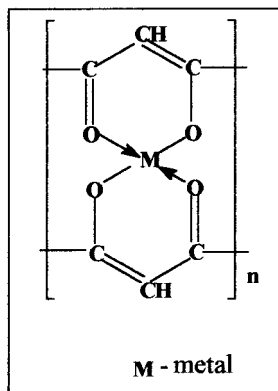
6,6-PVA and nylon 6,6 (Table IV). The values of average heat of combustion indicate the exothermal process of smoldering provided by chelated Mn structures (Table IV). The approximately equal amount of char yield for nylon 6,6-PVA and nylon 6,6-PVA oxidized by  $\text{KMnO}_4$  has been found.<sup>31</sup>

Polymer-organic char former (PVA system) incorporated in nylon 6,6 reduced the peak rate of heat release from  $1124.6 \text{ kW/m}^2$  (for nylon 6,6) and  $777.9 \text{ kW/m}^2$  (for PVA) to  $476.7 \text{ kW/m}^2$ , and increased the char yield from 1.4% (for nylon 6,6) to 8.7% due to a "synergistic" carbonization effect. (Cone Calorimeter was operated at  $50 \text{ kW/m}^2$  incident flux.)

Cone Calorimeter data of nylon 6,6 composition with PVA oxidized by  $\text{KMnO}_4$  (Mn-chelate complexes show the improvement of peak rate of heat release from  $476.7 \text{ kW/m}^2$  (composition of nylon 6,6 with PVA, 80:20 wt %) to  $305.3 \text{ kW/m}^2$  (composition of nylon 6,6 with PVA oxidized by  $\text{KMnO}_4$ , 80:20 wt %).<sup>31</sup> On the other hand, the exothermal process of smoldering for composition of nylon 6,6 with PVA oxidized by  $\text{KMnO}_4$  has been noted.<sup>31</sup> This reaction has been evidently provided by chelated Mn structures, which increases the total heat release of nylon 6,6/PVA oxidized by  $\text{KMnO}_4$  blend in comparison with the nylon 6,6/PVA blend.

TABLE III  
Cone Calorimeter Data of Nylon 6,6/PVA<sup>31</sup>

Material, heat flux ( $\text{kW/m}^2$ )	Char yield (% wt)	Ignition time (s)	Peak RHR ( $\text{kW/m}^2$ )	Total heat release ( $\text{MJ/m}^2$ )
PVA, 20	8.8	39	255.5	159.6
PVA, 35	3.9	52	540.3	111.3
PVA, 50	2.4	41	777.9	115.7
PVA-ox $\text{KMnO}_4$ , 20	30.8	1127	127.6	36.9
PVA-ox $\text{KMnO}_4$ , 35	12.7	774	194.0	103.4
PVA-ox $\text{KMnO}_4$ , 50	9.1	18	305.3	119.8



Scheme 8

### Polymer nanocomposites

Polymer-layered silicate (clay) nanocomposites are materials with unique properties when compared with conventional filled polymers. Polymer nanocomposites, especially polymer-layered silicates, represent a radical alternative to conventionally filled polymers.

Solventless, melt intercalation of high molecular weight polymers is a new approach to synthesize polymer-layered silicate nanocomposite. This method is quite general and is broadly applicable to a range of commodity polymers from nonpolar polystyrene to strongly polar nylon. Polymer nanocomposites are thus processable using current technologies and easily scaled to manufacturing quantities. In general, two types of structures are possible: intercalated and disordered or delaminated with random orientation throughout the polymer matrix. Due to their nanometer size dispersion, the nanocomposites exhibit improved properties when compared to the pure polymers or conventional composites. The improved properties include increased modulus, decreased gas permeability, increased solvent resistance, and decreased flammability. For example, the mechanical properties of a nylon 6 layered-silicate nanocomposite, with a silicate mass fraction of only 5%, show excellent improvement over those for the pure nylon 6.<sup>35</sup> The nanocomposite exhibits a 40% higher tensile strength,

TABLE IV  
Cone Calorimeter Data of the Heat of Combustion and the Flame-Out Time for Nylon 6,6 Compositions at a Heat Flux of 50 kW/m<sup>2</sup>

Composition	Flame-out time (s)	Average heat of combustion (MJ/kg)
Nylon 6,6	512	31.5
Nylon 6,6-PVA (80:20, wt %)	429	25.1
Nylon 6,6/PVA-oxidized by KMnO <sub>4</sub> (80:20, wt %)	747	29.5

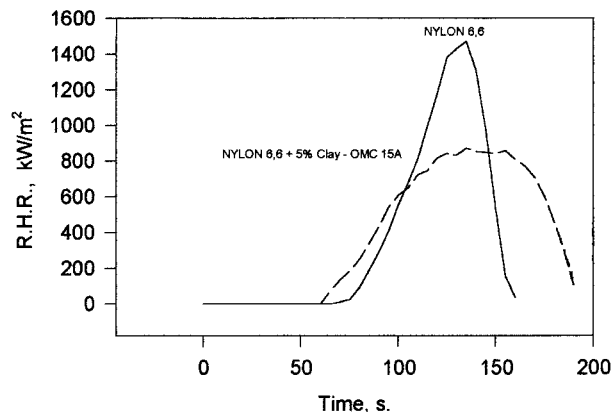


Figure 3 Rate of heat release vs time for nylon 6,6 and nylon 6,6 nanocomposite at heat flux of 35 kW/m<sup>2</sup>.

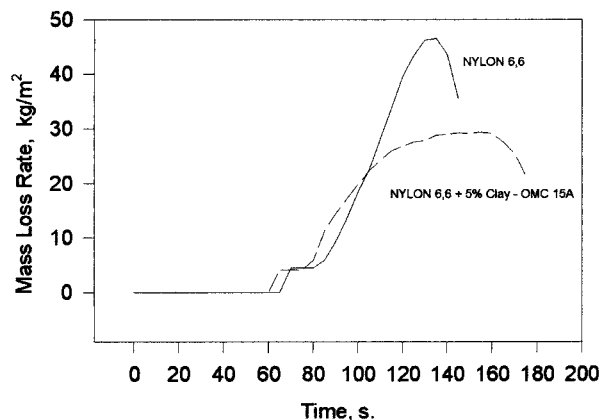
68% greater tensile modulus, 60% higher flexural strength, and a 126% increased flexural modulus.<sup>35</sup>

In the polymer industry there exists a need for new, more effective, and environmentally friendly flame resistance polymers. Recent data on the combustion of polymer nanocomposites indicate that they could be employed for this purpose.<sup>36</sup>

There are several proposed mechanisms as to how the layered silicate affects the flame retardant properties of polymers.<sup>36</sup> The first is increased char layer, which forms when nanocomposites are exposed to flame. This layer is thought to inhibit oxygen transport to the flame front, as well as gaseous-fuel transport from the polymer and therefore reduce the heat release rate of the burning surface. At higher temperatures, the inorganic additive has the ability to act as a radical scavenger due to adsorption to Lewis acid sites. This may interrupt the burning cycle as radical species are needed to break polymer chains into fuel fragments. The disordered nanocomposites also inhibit oxygen and combustible "fuel" species transfer by increasing the path length of these species to the flame front. The path length is dramatically increased due to the surface area of the silicates (approximately 700 m<sup>2</sup>/g for Na<sup>+</sup> montmorillonite). There is also a high possibility of alumina-silicate solid phase catalysis of polymer decomposition, which can dramatically change the overall scheme of thermal degradation process kinetics.

Combustibility of some polymer nanocomposite materials was studied using Cone calorimeter<sup>37,38</sup> under irradiation of 35 kW/m<sup>2</sup>, which is equivalent to that typical of a small fire.<sup>39</sup> Rate of heat released (RHR), which is one of the most important parameters associated with the flammability and combustion of a material, such as those illustrated in Figure 3, can be evaluated during this test.<sup>37,38</sup>

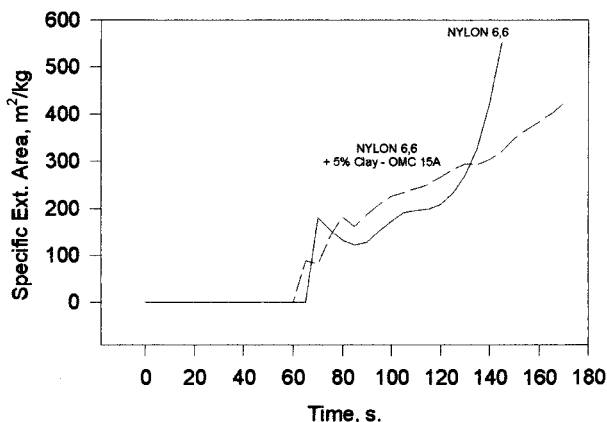
The plots (Figs. 3–5) compare the results obtained for nylon 6,6 as such and an intercalated nylon 6,6 hybrid produced by using a Carver press to mix nylon



**Figure 4** Mass loss rate vs time for nylon 6,6 and nylon 6,6 nanocomposite at heat flux of  $35 \text{ kW/m}^2$

6.6 with 5% by weight Cloisite 15A (montmorillonite modified by ion exchange with dimethyl-dithallow ammonium from Southern Clay Products, Inc.) in inert nitrogen atmosphere at  $260^\circ\text{C}$  for 30 min. It can be seen that the RHR displays a lower maximum peak in the case of the nanocomposite (Fig. 3), whereas the quantity of heat released (the area under the RHR curve) is about the same for both products, suggesting that their thermal degradation mechanism is the same.<sup>38</sup> The release of heat by the nanocomposite over a longer period, however, points to its slower degradation. Figures 4 and 5 on mass loss and specific extinction area illustrate the advantages of nanocomposite over initial nylon 6,6 fire behavior.

During the combustion test of the nanocomposite specimen, a carbon layer formed on its surface from the start, grew over time, and resisted the heat. Formation of a carbonized layer on the surface of the polymer is a feature of all nanocomposites studied so far: the pattern illustrated in Figure 6 has been reported for other nanocomposites based on polystyrene (PS), polyethanol (PE), and polypropylene (PP).<sup>38</sup> X-ray diffraction (XRD) and transmission electron mi-



**Figure 5** Specific extinction area (smoke) vs time for nylon 6,6 and nylon 6,6 nanocomposite at heat flux of  $35 \text{ kW/m}^2$ .



**Figure 6** The TEM image of a carbon residue obtained by combustion of a nylon 6.6 nanocomposite.<sup>38</sup>

croscopy (TEM) examination of this residue has revealed an intercalated nanocomposite structure.<sup>38</sup> The TEM image<sup>38</sup> of a carbon residue obtained by combustion of a nylon 6.6 nanocomposite in Figure 6 shows the intercalation of silicate layers (dark zones) with “carbon” layers (light zones). It should be emphasized that this intercalated structure was derived from the combustion of a delaminated hybrid. It is clear that the disordered structure collapsed during the combustion and was replaced by a self-assembled, ordered structure.

## References

- Lomakin, S. M.; Zaikov, G. E. *Ecological Aspects of Flame Retardancy*; VSP International Science Publishers: Zeist, Holland, 1999; p 170.
- Beck H.; Dross A.; Ende, M.; et al. *Ergebnisse von Ruckstand-untersuchungen auf polychlorierte Dibenzofurane und Dibenzodioxine in Frauenmilch aus der Bundesrepublik Deutschland*, Vol. 34; *Bundesgesundheitsblatt*, 1991; pp 564–568.
- Theelen, R. M. C. In *Biological Basis for Risk Assessment of Dioxin and Related Compounds*. Banbury Report No. 35; Gallo, M., Scheuplein, R., Van der Heijden, K., Eds.; Cold Spring Harbor Laboratory Press: Plainview, NY, 1991.
- Ahlborg U. G.; Becking, G. C.; Birnbaum, L. S.; et al. *Chemosphere* 1994, 8(6), 1067.
- U.S. Environmental Protection Agency. *Estimating Exposure to Dioxin-Like Compounds*, EPA/600/6-88/005 Ca, Cb, Cc, Washington DC, 1994.
- Green, J. J. *Fire Sci* 1996, 4, 26–442.
- Anderson, C. E., Jr.; Dziuk, J., Jr.; Mallow, W. A.; Buckmaster, J. *J Fire Sci* 1985, 3, 151.
- Tramm, H.; Clar, C.; Kuhnel, P.; Schuff, W. U.S. Pat. 2 106 938, 1938.
- Kay, M.; Price, A. F.; Lavery, I. J. *Fire Retard Chem* 1979, 6, 69.
- Cagliostro, D. E.; Riccitiello, S. R.; Clark, K. J.; Shimizu, A. B. *J Fire Flam* 1975, 6, 205.
- Delobel, R.; Le Bras, M.; Quassou, N.; Alistigsa, F. *J Fire Sci* 1990, 8, 85.
- Camino, G.; Costa, L.; Trossarelli, L. *Polym Deg Stab* 1984, 7, 25.
- Camino, G.; Martinasso, G.; Costa, L.; Cobetto, R. *Polym Deg Sta* 1990, 28, 17.
- Levchik, S. V.; Costa, L.; Camino, G. *Polym Deg Stab* 1992, 36, 31.
- Heinrich, H. *Deutsch. Pat. DE 4 015 490A1*, 1991.

16. Levchik, S. V.; Camino, G.; Costa, L.; Levchik, G. F. *Fire Mater* 19, 1995, 1–8.
17. Levchik, S. V.; Levchik, G. F.; Balabanovich, A. I.; Camino, G.; Costa, L. *Polym Degrad Stab* 1996, 54, 205–215.
18. Levchik, S. V.; Costa, L.; Camino, G. *Polym Degrad Stab* 1992, 36, 229.
19. Levchik, S. V.; Levchik, G. F.; Selevich, A. F.; Leshnikov, A. I., *Vesti AN Belarusi, Ser Khim* 1995, 3, 34–39.
20. Levchik, S. V.; Levchik, G. F.; Camino, G.; Costa, L. *J Fire Sci* 1995, 13, 43.
21. Levchik, S. V.; Balabanovich, A. I.; Levchik, G. F.; Camino, G.; Costa, L. *Polym Degrad Stab* 1998.
22. Costa, L.; Camino, G.; Luda di Cortemiglia, M. P. In *Fire and Polymers*; Nelson, G. L., Ed.; ACS Symposium Series 425; American Chemical Society: Washington, DC, 1990; p 211.
23. Levchik, S. V.; Costa, L.; Camino, G. *Polym Degrad Stab* 1992, 43, 43–49.
24. Camino, G.; Martinasso, G.; Costa, L. *Polym Degrad Stab* 1990, 27, 285–296.
25. Camino, G.; Lomakin, S. In *Fire Retardant Materials*; Horrocks, A. R., Price, D., Eds.; CRC Press: Boca Raton, FL, 2001; Chap 10, in press.
26. Haake, P.; Diebert, C. E. *J Am Chem Soc* 1971, 93, 6931–6937.
27. Tsuchiya, Y.; Sumi, K. *J Polym Sci A1* 7, 1969, 3151.
28. Finch, C. A., Ed. In *Polyvinyl Alcohol. Properties and Applications*; John Wiley: London, 1973; p 622.
29. Achhammer, B. G.; Reinhard, F. W.; Kline, G. M. *J Appl Chem* 1951, 1, 301.
30. Lomakin, S. M.; Zaikov, G. E. *Khimicheskaya Fizika* 1995, 14, 39–47.
31. Zaikov, G. E.; Lomakin, S. M. *Plasticheskie Massy* 1996, 39, 211.
32. Hassan, R. M. *Polym Intern* 30, 1993, 5.
33. Hassan, R. M.; El-Gaiar S. A.; El-Summan, A. M. *Polym Intern* 1993, 32, 39.
34. Hassan, R. M.; Abd-Alla, M. A.; El-Gahmi, M. A. *J Mater Chem* 1992, 2, 613.
35. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigato, O. *J Mater Res* 8, 1993, 1185.
36. Giannelis, E. P. *Adv Mat* 1996, 8 (1), 29.
37. Gilman, J. W.; Kashivagi, T.; Nyden, M.; Brown, J. E. T.; Jackson, C. L.; Lomakin, S.; Giannelis, E. P.; Manias, E. In *Chemistry and Technology of Polymer Additives*; Al-Malaika, S., Golovoy, A., Wilkie, C. A., Eds.; Blackwell Science: Oxford, 1999; Chap 14.
38. Gilman, J. W.; Kashivagi, T., C. L., Giannelis, E. P., Manias, E., Lomakin, S., Lichtenhan, J. D., Jones, P. *Fire Retardancy of Polymer*; Le Bras, M., Camino, G., Bourbigot, S., Delobel, R., Eds.; The Royal Society of Chemistry: Cambridge, 1998.
39. Babrauskas, V.; Peacock, R. *Fire Safety J* 1992, 19, 255.