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Combustion of char-forming polymeric systems

A V Antonov, I S Reshetnikov, N A Khalturinskij

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Abstract. Chemical reactions occurring in the combustion and decomposition of char-forming polymeric systems and the effects of the nature of the polymer and additives on the reaction pathways are discussed. The thermal characteristics of the chars formed upon combustion are considered. The bibliography includes 86 references.

I. Introduction

The lowering of ignitability and flammability of polymers and the creation of fire retarding materials is an urgent problem which demands immediate solution. Regulation concerning the prohibition or limited use of flammable polymeric materials in industrial and civil engineering, construction of means of transportation (aircraft, automobiles, railway cars, ships), electrical and electronic engineering and production of special-purpose materials have been passed in many countries.

This circumstance has given a strong impetus to the studies aimed at elaboration and practical application of fire retarding polymeric materials. In the coming years, many commodities prepared on the basis of polymeric materials will be manufactured only in a fireproof form.

The production of fire retarding polymeric materials is following three main directions, *viz*., synthesis of fire retarding polymeric materials, chemical and physical modification of polymers and the use of fire retardants.

The first trend, which holds especially great promise, consists in the synthesis of polymers of two types, *viz*., polymers yielding incombustible gases upon decomposition and highly thermostable rigid-chain polymers. The first group of compounds includes fluorine- or nitrogen-containing polymers (*e.g*., fluoroplastics, nitroso and triazine elastomers)[1] and organoelement polymers (*e.g*., polyphosphazenes, polysiloxanes and polycarboranes).[2–4] The second group comprises polymers containing heterocyclic fragments, such as polysulfones (arylox, bakelite, radel, udel, *etc*.), polyphenylene sulfides, liquid-crystalline polyesters (vectra, econol, *etc*.), polyamides (phenilon, kevlar, polymers containing mesogenic groups), polyimides (kapton, epilex, ultem, torlon, *etc*.) and polyheterocycles, such as polypyrazoles, polyoxazoles, polybenzoimidazoles, polybenzooxazoles, polyquinoxalines and polyimidazobenzophenanthrolines (the BBB polymer).[5] Rigid-chain polymers combine low flammability and high thermostability with other valuable properties, *e.g.,* high chemical and radiation stability, high durability and dielectric characteristics.

Studies[6–8] of effects of the chemical structure and conditions of preparation of polymers on their flammability and thermal characteristics have demonstrated a good correlation between the yields of non-volatile residues formed upon decomposition of the polymers and their flammability (oxygen index, OI). The yields of carbonised products depend on the chemical structures of polymers.[6,7] The smaller the number of flexible 'hinge' groups in the polymer molecule the higher the char yield. It is of note that the flammability of poly(ester imides) depends on the method used for their synthesis.[8] It was shown also that the thermal stability of a polymer is determined by the nature of its end groups and the presence of admixtures.

Unfortunately, the high cost of organoelement and high-performance polymers restricts the fields of application of materials based on them. Today, the production of low-cost polymers which employs less power-consuming synthetic procedures and less expensive monomers seems to have especially great potential.

Chemical and physical modification of polymers is the second trend in the production of fire retarding polymeric materials. In order to decrease the flammability of carbochain polymers, carbochain monomers are copolymerised with halogen- or phosphorus-containing monomers. In addition, chemical modification of synthetic polymeric products can be achieved by treating them with various reagents: this can be effected, *e.g*., by bromination, chlorination, phosphorylation[9–12] and polymer-analogous transformations aimed at incorporating halogen- and phosphorus-containing groups into polymers and copolymers.[13–15] This approach was used to obtain brominated polystyrene[16] and polyphenylene oxides,[17] copolymers of vinyl acetate, ethylene and derivatives of halogen-containing acids[18] and phosphorus-containing epoxy resins (PER).[19]

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Physical modification of polymers is based on the treatment of the polymer surface with various types of energy (plasma, thermal and laser beams, UV or IR irradiation, *etc*.). Using this approach, one can obtain fire retarding polymeric materials based on various polymers.[20] Unfortunately, modification very often induces significant changes in the properties of the polymers and cannot be used to decrease the flammability of industrial polymers.

The third approach to the preparation of fire retarding polymeric materials, which employs fire retardants, is the most popular and efficient way.

Polybrominated biphenyls and diphenyl oxides are the most widespread compounds endowed with the ability to decrease the flammability of industrial plastic materials. However, there is evidence that combustion and thermal degradation of polymeric materials based on them is accompanied by the formation of highly toxic products.[21–23] Thus, the need arose for fire retarding materials devoid of low-molecular-weight polybrominated compounds. High-molecular-weight bromine-containing fire retardants meet this demand. It was established [16, 17, 23] that thermal degradation of brominated polyphenylene oxides and polystyrene was not accompanied by the formation of highly toxic products either in the presence or in the absence of plastic materials. Fire retarding styrene-based plastics have been developed which contain high-molecular-weight fire retardants, their properties are comparable with those of styrene-based materials containing low-molecular-weight fire retardants.[24]

II. Intumescent systems

The problem of formation of toxic compounds in the combustion of polymeric materials is completely eliminated if intumescent systems (IS) devoid of polybrominated diphenyls or diphenyl oxides are used. An IS represents a mixture of compounds which form foamed cokes on the polymer surface upon heating and thus prevent combustion. The fire-resistance due to foamed coke layers is associated with thermal insulation and barrier properties in mass transfer.[25, 26]

The superficial foamed coke layer is formed as a result of complex physical and chemical processes, each contributing to the decrease in the polymer flammability. The factors affecting the flammability of IS-containing polymers can be classified as follows:

1. Reversal of the route of the polymer thermal degradation towards the formation of foamed cokes and incombustible volatile products.

2. A change in the heat balance of combustion due to the thermal effects of chemical reactions occurring on intumescence and dilution of fuels with incombustible gaseous products.

3. Thermal insulation of the polymer surface from reverse heat flows.

4. Prevention of fuel diffusion into the combustion zone.

5. Prevention of oxygen diffusion from the environment to the polymer surface.

The first two factors exert their influence on combustion through chemical reactions between individual components of the polymeric composition, while the rest are closely connected with the physical structure of the foamed coke.

III. Types of intumescent systems

1. The use of intumescent systems for decreasing the flammability of carbochain polymers

The following compounds can be used as IS components:[27, 28] inorganic acids (in free form or as derivatives which generate acids on heating), polyhydroxy derivatives, nitrogen and halogen derivatives.

This classification is arbitrary, since any component may contain several functions. The presence of a nitrogen- or a halogen-containing compound is not always necessary. It is believed that acids favour carbonisation of polyhydroxy derivatives (carbon source) due to dehydration, whereas nitrogen- or halogen-derivatives (foaming agents) facilitate intumescence of the system due to intense degradation associated with evolution of large quantities of gaseous compounds.

IS that are to be used in polymeric materials should meet the following requirements :[29]

1. IS must be resistant to temperatures above 200 °C, which are often used in polymer processing.

2. Thermal degradation of polymers must not interfere with the foaming reaction.

3. IS should produce a protective foamed coke layer over the whole polymer surface despite the dilution of the additive with the polymer.

4. IS should not induce any significant changes in the physical and mechanical properties of the polymer or interact with other additives (pigments, stabilisers, *etc*.).

5. The mineral acid formed upon heating of the corresponding derivative used as IS should be high-boiling and should not be a strong oxidant.

Phosphoric acid derivatives (amides, esters, imides) meet these requirements most completely. Of these, high-molecular-weight ammonium polyphosphate (APP), $-[P(ONH_4)(O)O]_n-$, where $n = 20-3000$, is the most popular fire retardant.[30]

The IS containing APP used for decreasing the flammability of carbochain polymers are listed in Table 1. Several other compounds tested as fire retardants for various polymers are listed in Table 2.

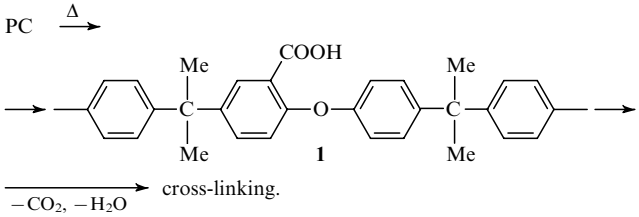
These data suggest that efficient reduction of flammability demands a high degree of polymer filling, which inevitably increases its cost, deteriorates its physical and mechanical properties and impedes its processing.

The mechanisms of action of IS systems are different and depend on the structure of the polymer and the additives. The polymer can take part in the formation of the carbonised layer on the surface of the burning material, but the foamed coke layer can be also formed in the absence of the polymer.

2. The use of intumescent fire retardants for the preparation of polymeric materials based on polycondensation polymers

Polycarbonates are widely employed in electrical engineering, instrument making and automobile construction. These compounds are endowed with valuable and unique properties, such as higher thermal stability and lower flammability compared with polyalkenes and styrene-based plastic materials. Many branches of industry have a great demand for fire retarding polymeric materials based on polycarbonates (PC). The flammability of PC can be lowered if alkali metal salts of organic acids are used as additives. The preparation of materials with OI above 35% demands only small quantities of the additive ($\leqslant 3\%$).

The mechanism of action of these additives has been studied.[48, 49] It is known that thermal degradation of polycarbonates occurs through two main routes. The first route consists in isomerisation followed by the formation of aryloxybenzoic acids **1**. Further thermal conversions of the thermal degradation products yield ethers, xanthones and cross-linked structures:



The second route involves intramolecular transfer reactions, resulting in cyclic oligomers of type **2**. The reaction of product **2** with water and subsequent elimination of CO_2 yield phenols:

Table 1. APP-based intumescent systems.

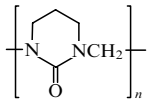
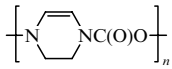
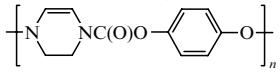
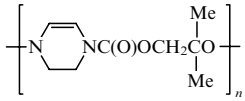
Polymer	Additive	Mass ratio APP : additive	APP content in the polymer (%)	OI	Ref.
Polypropylene	a condensation product of substituted ureas with formaldehyde	2 : 1	25 – 30	34 – 35	30 – 33
	ethylenebis[tris(2-cyanoethyl)]phosphonium bromide	2 : 1	30	30	34
		3 : 1	20	26.5	35
		3 : 1	20	25	35
		3 : 1	20	26.5	36
		3 : 1	20	25.5	36
		3 : 1	20	23.5	36
	a condensation product of aromatic diisocyanates with pentaerythritol and melamine	–	24	37	32
	pentaerythritol phosphate	7 : 3	30	26	37
	pentaerythritol phosphate, melamine	6 : 3 : 1	30	38	37
	pentaerythritol, guanidinium carbonate	6 : 3 : 1	30	36	37
Shock-resistant polystyrene	ethylenebis[tris(2-cyanoethyl)]phosphonium bromide	1 : 1	30	30	34
Polystyrene	a condensation product of aromatic diisocyanates with pentaerythritol and melamine	–	24	37	38
Polyacrylonitrile	hexabromocyclododecane	1 : 1	20	28 – 30	39

Table 2. Fire retardants as additives to polyalkenes.

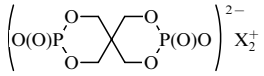
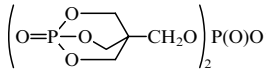
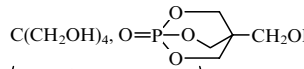
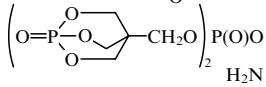
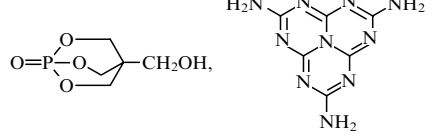
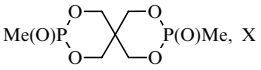
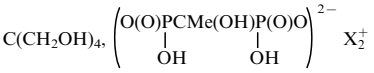
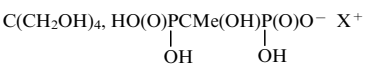
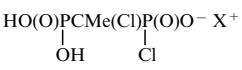
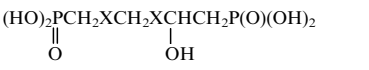
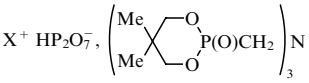
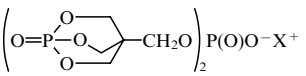
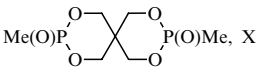
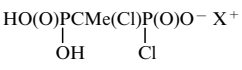
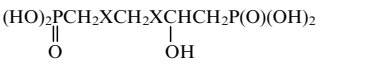
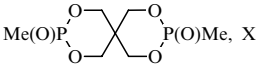
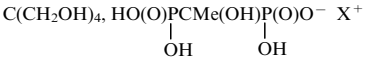
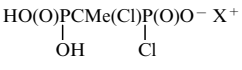
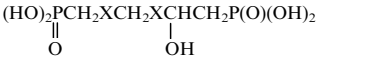
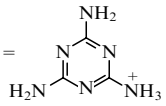
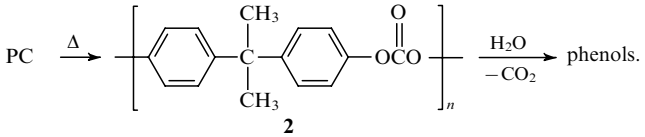
Polymer	IS [a]	IS content in the polymer (%)	OI	Ref.
Polypropylene	a condensation product of P_2O_5 with pentaerythritol and melamine	30	32	40
		30	28.5	41
		30	33	41
	a mixture of piperazine pyrophosphate and melamine phosphate	30	36 – 38	42
	condensation products of triglyceryl isocyanurate with *ortho*-(poly)phosphoric acid	20	24 – 25	43, 44
		30	33	37
		30	32.5	37
		30	34.5	37

Table 2 (continued).

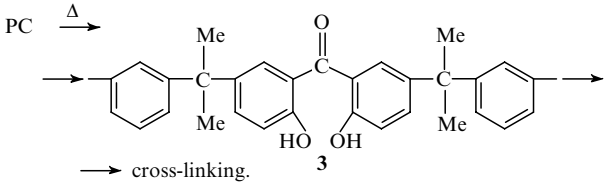
Polymer	IS [a]	IS content in the polymer (%)	OI	Ref.
Polypropylene	$X^+HPO_4^-$, $C(CH_2OH)_4$	30	32.5	37
		30	24	45
		30	31	45
		30	30	45
		30	21	45
		30	28	45
A copolymer of ethylene with propylene	a mixture of piperazine pyrophosphate and melamine phosphate	30	28 – 30	46
A copolymer of ethylene with vinyl acetate		35	27	47
Polystyrene		30	25 – 26	41
		30	25	45
		30	23	45
		30	22	45
Polyethylene		30	23	45
		30	30	45
		30	22	45
		30	25	45

[a] Designation: X^+ = 

PC  phenols.

2

It has been found that the high efficacy of alkali metal salts of organic acids is determined by the fact that they accelerate thermal degradation of PC. This results in the increase in the amount of the char formed and evolution of CO_2 as one of the polymer decomposition products at lower temperatures. In addition, decomposition of PC in the presence of organic acid salts is accompanied by the Fries rearrangement (migration of acyl groups of phenol esters to the *o*-position of the benzene ring), eventually resulting in the formation of cross-linked structures of the type **3**:



3

→ cross-linking.

Thermal decomposition of polycarbonates occurring along this route leads to the formation of a solid foamed coke layer on the polymer surface, which prevents further spreading of the flame. It was found [49] that foamed coke is made up of the polymer degradation products, *i.e.*, PC takes an active part in its formation, whereas the additive catalyses this process but is not directly involved in it.

It is known that the main drawback of PC is a drastic decrease in their impact strength at low temperatures.[50] Polymeric materials based on PC and an acrylonitrile–butadiene–styrene copolymer (ABS) and polyethylene terephthalate (PETP) are free from such defect. Some aromatic sulfonates as well as phosphorus- and bromine-containing compounds were tested as fire retardants for PETP–PC [51] and ABS–PC mixtures.[49, 52] It was found that aromatic sulfonates become less efficient after addition of ABS to PC.[49] The decrease in the fire retarding efficacy with the change in the composition of the polymeric matrix is due to the lowering (by 50 °C) of the temperature at which decomposition of PC containing ABS begins. As a result, the fire retardant does not affect the composition of PC pyrolysis products and the antipyrogenous effect of aromatic sulfonates on the PC–ABS mixture is not manifested.

Thus, IS prepared from aromatic sulfonates exert rather specific selective action and even minor alterations in the composition of the polymeric mixture may significantly decrease their efficiency.

Phosphorus-containing fire retardants can be recommended for the preparation of polymeric high-resistant materials based on a PC–ABS mixture. Although these compounds are less efficient than the bromine-containing ones, the materials based on them possess better mechanical properties.[39] The bromine- and phosphorus-containing fire retardant is especially efficient in PC–PETP and PC–ABS mixtures.[51, 52]

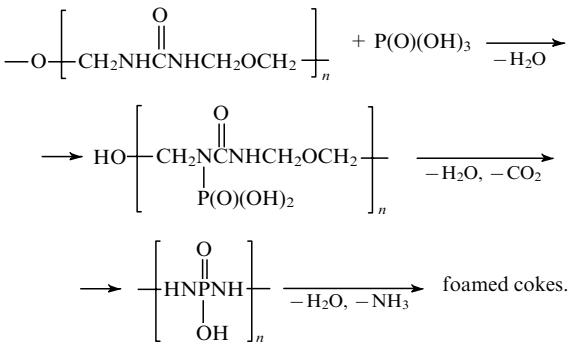
The combustion of systems prepared from polyurethane and ammonium polyphosphate [53] or polyamide and ammonium polyphosphate [54] yields foamed cokes, predominantly due to the reaction of the polymer with the additive resulting in the formation of cross-linked products. Recently it was shown [55] that certain melamine salts are efficient as fire retardants for polycapramide, because these compounds also favour the formation of cross-linked products in the reaction of the additive with the polymer. The reactions resulting in the formation of foamed cokes have been considered.

Phosphoric acid is known to be an efficient fire retardant for cellulose.[56] Phosphoric acid reacts with the polymer, which alters the mechanism of thermal degradation of cellulose towards char formation; therefore, this system can be related to IS.[57]

By virtue of their stability, adhesiveness, dielectric properties, thermal stability and technological efficiency, epoxy resins (ER) and phenol–formaldehyde resins (PFR) are widely employed as binding agents in preparation of reinforced plastic materials in many branches of technics. Fire retardants affecting the mechanism of their thermal degradation are the most efficient for these polymers. Thus the efficiency of some transition metal salts (*e.g.*, cobalt acetate) is due to their catalytic effect on dehydration and dehydrogenation of ER and PFR.[58, 59] This significantly increases the char yield, while the yield of volatile flammable products formed in thermal degradation of ER decreases in the presence of organophosphorus compounds [19] and certain phosphines.[60]

The effects of the composition of ER on the mechanism of thermal degradation and the composition of the pyrolysis products responsible for the flammability of ER have been discussed.[61] It was shown that enhanced char formation is the determining factor in this process.

Chemical reactions occurring in the presence of phosphoric acid used as IS for carbamide–formaldehyde resin (CFR) have been discussed in detail.[62] It was shown that in the course of thermal conversions phosphoric acid reacts with the amide groups of CFR to give *N*-phosphorylated products, which lose water, ammonia and carbon dioxide and eventually turn into foamed cokes



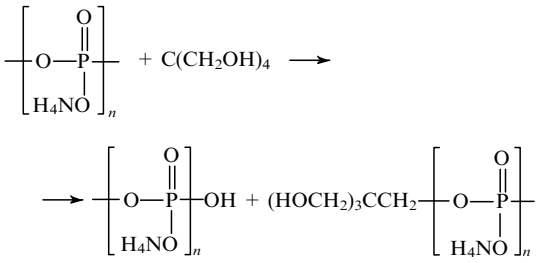
A viscous melt of poly(amidophosphates) favours the formation of a swollen carbonised layer and suppresses thermal oxidation of foamed cokes, which enhances the fire-proof effect.

Phosphorus-containing compounds, like phosphoric acid, react with functional groups of the polymer to yield foamed cokes which protect the polymer surface from the heat flow. It is the formation of foamed cokes that is responsible for the significant lowering of the flammability of the polymers to which a fire retardant has been added.

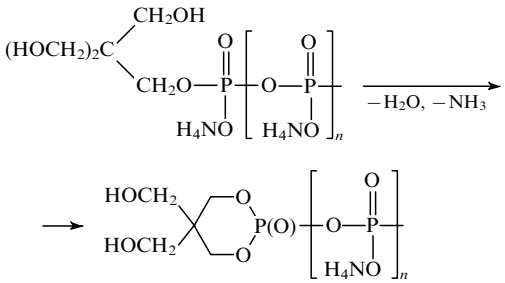
IV. Chemical reactions occurring in the intumescence

Chemical reactions occurring in the intumescence are most extensively studied for IS consisting of ammonium polyphosphate and pentaerythritol. The sequence of chemical and physical processes has been established: decomposition of ammonium polyphosphate at 215 °C, esterification of the alcoholic groups of pentaerythritol with liberation of H_2O, which results in the increase in the bulk of IS, solidification of the swollen carbon–phosphorus residue at 360 °C.[30]

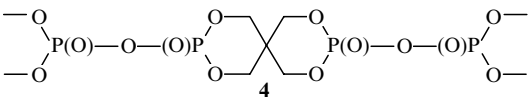
Studies using thermogravimetric analysis (TGA), thermovolumetric analysis and ^{31}P NMR spectroscopy have shown [63–69] that pentaerythritol is phosphorylated with APP at 210 °C with the scission of the main polyphosphate chain of APP and the formation of the $-[P(O)OCH_2]-$ phosphate groups. This reaction does not yield volatile products.



This is followed by the formation of cyclic esters of polyphosphoric acid with elimination of ammonia and water.

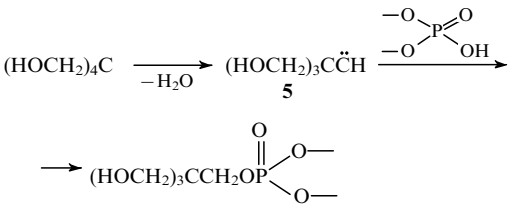


Repetition of these reactions gives the structures of type **4**.

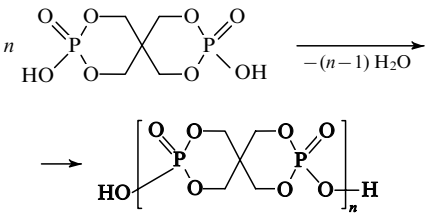


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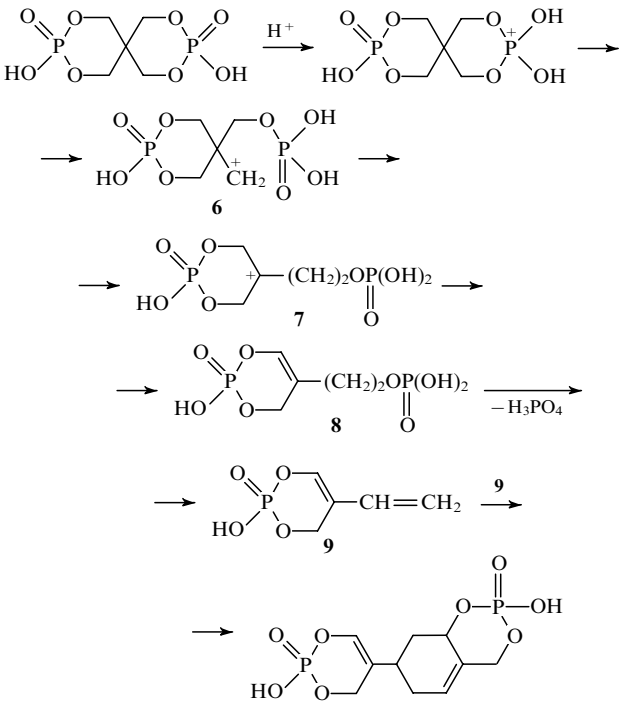
The fact that the APP – pentaerythritol pyrolysis products are paramagnetic has led the authors to suppose that their formation occurs *via* an intermediate carbene **5**.[69]



An alternative hypothesis suggests[63] that esterification of APP is preceded by the formation of a carbenium ion. The formation of cyclic structures as intermediates in thermal conversions of APP – pentaerythritol mixtures has made it possible to use bisphosphate of pentaerythritol as a model compound for investigation of a intumescence mechanism.[63,64] It was shown that condensation with elimination of water and formation of structures of type **4** is the first step in the degradation of this bisphosphate.

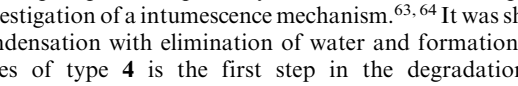


An analysis of ^{31}P and ^{13}C NMR spectra made it possible to propose the following mechanism for char formation. Its first step is the formation of the carbenium ion **6** owing to protonation and cleavage of the C–O bond. This ion can be rearranged into a stable tertiary carbocation **7**; deprotonation of the latter leads to the formation of the double bond. Subsequent pyrolysis of the ester **8** can occur with the elimination of phosphoric acid resulting in diene derivatives **9** which enter into the Diels – Alder reaction to give polycyclic compounds of the type **10**.



Repetition of these reactions yields conjugated aromatic structures.[70] The reactions can be accompanied by condensation of phosphoric acids and polymerisation; therefore, the reaction products possess irregular structures. Intumescence occurs within a narrow temperature range (300 – 350 °C) and results in the formation of a bulky carbonaceous residue containing admixtures of phosphoric acid.

The lack of a sufficient body of evidence does not allow any valid conclusion on the possibility of the interaction of polymers with IS. It was found[63–68] that polypropylene (PP) has virtually no effect on the mechanisms of intumescence. In turn, IS do not influence the composition of products formed upon polymer decomposition. Experiments with TGA in air have shown[38,71] that the contribution of the polymer to char formation is insignificant. Presumably phosphoric acid reacts with alcohols formed in the oxidation of PP with atmospheric oxygen. Enhanced paramagnetic properties of the residue obtained upon pyrolysis of the polymeric composition in comparison with pure IS are attributed to the reaction of free radicals formed upon thermal degradation of the polymer with IS (APP + pentaerythritol).[69]



5

This assumption was supported by the finding that the mass of the char residue diminishes in the presence of free radicals.

An analysis of the chemical composition of the chars formed upon thermal degradation of PP, polyethylene (PE) and polystyrene (PS) with IS (APP + pentaerythritol) has shown[39] that the chars formed at any temperature and with any polymer or without it are made up of identical chemical structures, which represent a combination of fragments containing quaternary carbon atoms with irregular aromatic and phosphorus – oxygen units.

However, there is conclusive evidence[72] that the chemical structure of a comonomer and its content in the polymer strongly affect the interaction of IS based on APP and pentaerythritol with ethylene copolymers. It was found that butyl acrylate – ethylene and maleic anhydride – ethylene copolymers markedly increase the efficiency of IS due to their interaction in the condensed phase. It was also shown that aluminosilicate zeolites also significantly increase the efficiency of IS.[72]

Reactions of ammonium polyphosphate with polyols (pentaerythritol, starch, polyvinyl alcohol, glycerol) have been studied in the search for the optimum ratio of reaction components to be used for the filling of polymers in order to decrease their flammability.[45]

Irrespective of the polyol/APP ratio, all the systems examined displayed exothermic peaks of various intensities in the DPA curves. Presumably, this was due to the reaction of the polyol with APP with elimination of ammonia and water in this temperature range. The magnitude of the thermal effect was estimated on the assumption that the maximum thermal effect corresponds to the most complete reaction. It was established[45] that all the systems under study were characterised by identical mass loss and had identical masses of char residues, but differed in thermal effects.

The optimum APP/polyol ratio for all the systems tested was 7 : 3 (mass %) as can be judged from the identical mass loss in the reaction. However, no strict correlation between the char yield, mass loss upon esterification and maximum thermal effect was found for systems containing methylphosphonic acid and pentaerythritol.[45]

V. Heat-insulating characteristics of foamed cokes formed upon combustion and thermal degradation of polymeric systems containing intumescent fire retardants

The efficiency of IS is determined primarily by heat-insulating characteristics of foamed cokes formed in the combustion of

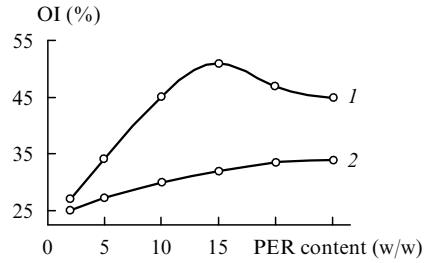


Figure 1. The OI values for specimens burnt under ordinary conditions (*1*) and for specimens from which 'char caps' were removed during combustion (*2*).[19]

polymers. The role of 'char caps' in the lowering of flammability has been established [19] by comparing OI of specimens burnt by routine methods with those where the foamed coke layer formed in the course of combustion was continuously removed (Fig. 1). The considerable difference in the characteristic curves and much greater values of OI in the former case (Fig. 1, curve *1*) suggest that the presence of foamed cokes is the main factor decreasing flammability. Measurements of hydrodynamic resistances have shown [73] that foamed cokes cannot prevent the diffusion of degradation products to the combustion zone. It was concluded [73] that heat-insulating properties of 'char caps' play the crucial role in flammability reduction. These results are in good agreement with the finding [74] that the foamed coke layer is permeable by low-molecular-weight liquids. However, the results of microstructural analysis of foamed cokes formed in the combustion of IS-containing PP compositions by scanning electron microscopy led the authors to conclusion [62] that diffusion of degradation products through the foamed coke layer plays an important role in combustion. The compositions with low OI displayed multiple fissures and breaks in the carbon structure, whereas foamed cokes formed from the compositions with high OI had closed pores.

Evidently, heat-insulating characteristics (HIC) of foamed cokes are responsible for the high efficiency of IS in PP. Model studies of forced combustion, [36, 75] where a polymer sample with a thermocouple inserted at a definite distance from its surface was flame-burnt, have demonstrated that the foamed coke layer formed significantly lowers the polymer temperature. Under these conditions, the rate of the polymer temperature changes, *i.e.*, HIC, of the foamed coke correlated with the OI. No such correlation was found for PP charged with various fillers (10% – 30%) in addition to IS.[30]

The HIC of foamed cokes formed from different compositions and polymeric matrices but containing the same amounts of IS have been investigated.[76] A great variety of compositions allowed the authors to establish a relationship between the flammability of polymer material and thermal characteristics of foamed cokes in a broad range of OI values. Thus it was found that a satisfactory correlation between OI and HIC was observed only for relatively low (< 25) OI values. In addition, it was shown that the flammability of IS-containing polymeric systems is determined not only by the HIC of 'char caps' but also by the rate of foamed coke layer formation.

Most authors believe that HIC of foamed cokes play the major role in flammability reduction, although no satisfactory correlation between these parameters has been found so far.

Various factors determining the HIC of foamed cokes formed upon combustion have been investigated.[62, 77] A unit used in these studies allows the registration of the light flux and the response in the sample's rear (Fig. 2*a*). The sample to be tested, which represents a disc (~ 1 mm thick) 10 mm in diameter (Fig. 2*b*) is mounted on a thin metal stage. The sample surface is irradiated with the light generated by a carbon dioxide laser. Part of the radiant flux is diverted to an ILD-24M irradiation meter by means of a semitransmitting mirror made of a chalcogenide glass. A

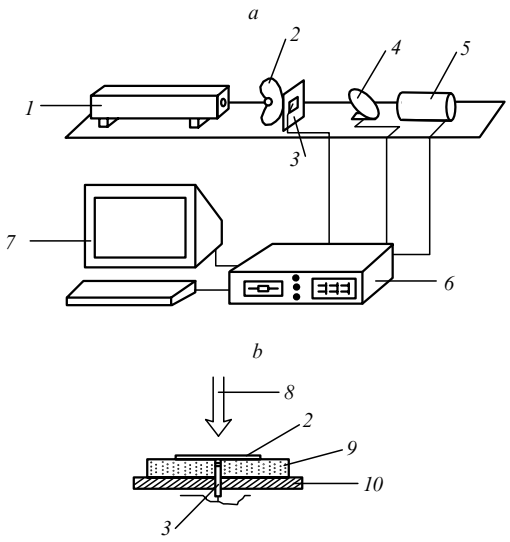


Figure 2. A schematic representation of a unit (*a*) and a stage (*b*) for studying heat-insulating characteristics of various materials; (*1*) carbon dioxide laser; (*2*) sample; (*3*) a thermocouple; (*4*) chalcogenide glass; (*5*) radiation meter; (*6*) interface; (*7*) computer; (*8*) the radiant flux; (*9*) asbestos support; (*10*) base.

chromel-copel thermocouple (0.08 mm thick) is placed on the sample's rear. Having passed through the mirror, the radiant flux reaches the sample and warms it up. The signal of the thermocouple response is passed to a computer. The experiments were carried out with both continuous and pulsating radiant fluxes (in the latter case, the ratio of the pulse length to the pause was equal to two) and ignition of the sample did not occur.

Figure 3 shows the temperature *vs* time curves for the combustion of PS, PP and PE containing IS prepared from APP and pentaerythritol.[39] Complete burn-out of polymers containing no fire retardants normally takes 15 s at temperatures $\leqslant 800$ K and does not depend on their chemical nature. Comparison of experimental curves points to significant differences in the properties of foamed cokes at the moment of their formation. The shape of these curves is of complex type; each portion of the curve corresponds to a definite state of the system. A drastic increase in the temperature in the initial moment corresponds to the heating of the composition prior to foamed coke layer formation. Subsequent decline (curves *2* and *3*) or a bend (curve *1*) correspond to the formation and growth of the foamed coke layer on the polymer surface. The plateau corresponds to the intumescence of the sample in bulk and is associated with heat absorption upon intense degradation. A slow increase in temperature up to the steady-state level in the terminal steps indicates that the intumescence process is completed and the whole mass of the sample has been converted into foamed coke. The shape of the curve for the composition prepared from PE (curve *1*) suggests that the

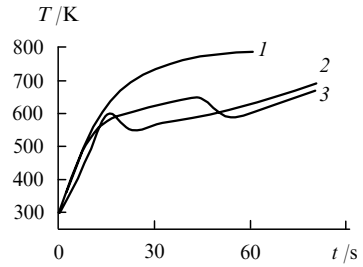


Figure 3. Heat-insulating characteristics of foamed cokes prepared from IS-containing polymeric compositions based on APP and pentaerythritol; (*1*) PE; (*2*) PP; (*3*) PS.

formation of foamed coke occurs at an extremely slow rate and it has low HIC. A small bend on the curve for the compositions prepared from PS (curve *3*) points to a relatively high rate of foamed coke formation, which is followed by a decrease in the rate of warm-up for a short period. The shapes of the curves for the compositions prepared from PP and PS (curves *2* and *3*) indicate that the formation of, and accumulation of, the foamed coke occur much faster than in the case of the compositions based on PE. These foamed cokes have enhanced HIC, but their shapes and the positions of their extrema point to differences in the kinetics of their intumescence. The sharp maximum on the curve for the composition based on PP (curve *2*) suggests that the activation energy of the intumescence reaction is low, while the rate of intumescence and the HIC of foamed cokes formed even at insignificant heat fluxes are high. The maximum on the curve for the composition derived from PS (curve *3*) points to the higher rate of intumescence and formation of foamed coke at higher temperature in comparison with the composition prepared from PP. In the final step, the rates at which the temperature changes occur and their limiting values for the compositions prepared from PP and PS coincide (curves *2* and *3*), which testifies to identical properties of the 'char caps' formed. The differences in the HIC of 'char caps' at the moment of their formation and the similarity of their HIC in the case of IS-containing PS and PP compositions can be attributed to the differences in their internal structure, which is schematically presented in Fig. 4. In both cases, 'char caps' represent thick walls with large cavities inside. The walls of the 'caps' have porous structures, which differ in pore size and in wall thickness. The foamed coke formed from the composition based on PP has smaller pores and thinner walls; the air fraction (v/v) is greater (Fig. 4*a*).

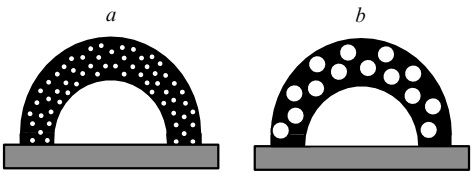


Figure 4. A schematic representation of foamed cokes formed under the action of a heat flux; (*a*) a composition prepared from PP; (*b*) a composition prepared from PS.[39]

Investigations into the effects of phosphorus-containing fire retardants based on methylphosphonic acid on the flammability of PE, PP and PS have demonstrated [47] that in the case of PE and PP the fire retardants prepared from the adduct of melamine–formaldehyde resin and methylphosphonic acid (MFMA), from the adduct of methylphosphonic acid and melamine (DPM-3) combined with pentaerythritol and from methylphosphonic diamide (MPD) are more efficient than halogen-containing fire retardants currently used.

The temperature *vs* time curves for the combustion of PP and PE containing MFMA as the fire retardant are shown in Fig. 5. Comparison of these curves suggests that MFMA strongly affects the properties of foamed cokes at the moment of their formation. In the case of a PP composition, foamed cokes are formed at a faster rate and have enhanced HIC. Therefore, MFMA can be regarded as a typical IS, although its efficiency and the HIC of the foamed cokes formed are inferior to those of compositions based on APP.

Figure 6 shows the temperature *vs* time curves for the combustion of PP, PS and PE containing a 4:1 DPM-3–pentaerythritol mixture.[47] Comparison of these curves points to a strong effect of the polymeric matrix on the properties of foamed cokes at the moment of their formation. In the case of PS compositions, the foamed cokes are formed at slow rates and have low HIC. The foamed cokes formed at a fast rate in the

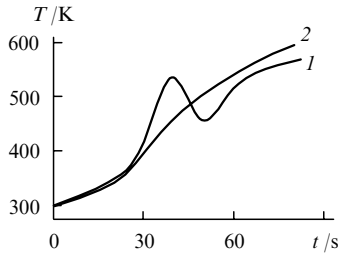


Figure 5. Heat-insulating characteristics of fire retardant-containing compositions prepared from the adduct of melamine–formaldehyde resin with MFMA; (*1*) PE + MFMA; (*2*) PP + MFMA.[47]

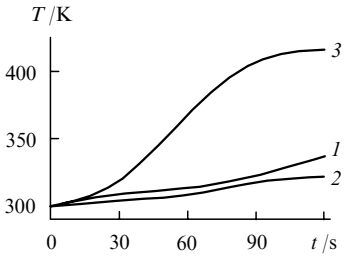


Figure 6. Heat-insulating characteristics of fire retardant-containing polymeric compositions prepared from the adduct of methylphosphonic acid with DPM-3;[47] (*1*) PS + DPM-3; (*2*) PE + DPM-3; (*3*) PP + DPM-3.

combustion of PP and PE compositions have high HIC. The HIC of foamed cokes show a good correlation with the efficiency of the fire resistant agent. For PP, the efficiency of DPM-3 is close to that of APP, whereas for PE, DPM-3 is more efficient than APP.

The temperature *vs* time curves for the combustion of PP, PS and PE containing MPD are shown in Fig. 7.[78] As can be seen, the presence of a polymer significantly lowers the rate of foamed cokes formation. It is of note that the chars formed in the decomposition of compounds prepared from PE and PS have very low HIC, whereas the chars formed in the combustion of compositions derived from PP have high HIC.

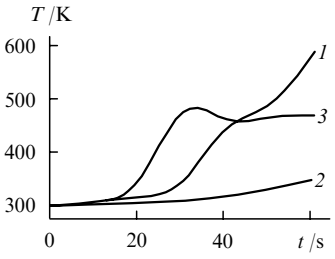


Figure 7. Heat-insulating characteristics of fire retardant-containing compositions prepared from MPD; (*1*) PS + MPD; (*2*) PE + MPD; (*3*) PP + MPD.

The plateau (Fig. 7) corresponding to the intumescence of the bulk of the sample is very low. It may thus be assumed that the amount of the char formed is insufficient for long-term protection of the polymer. Thus, the mechanism of action of MPD as the fire resistant agent is based primarily on the reversal of the destructive processes occurring in PE, which results in smaller quantities of volatile flammable products. Although MPD favours char formation in polymers, it is not the main factor responsible for the flammability reduction, since the char formed cannot protect the polymer in the course of combustion.

MPD has a limited use because fire retarding polymeric compositions containing this fire retardant are difficult to process: phase separation occurs in moulding and casting. One of the clues to the solution of this problem is microencapsulation of the fire retardant prior to its introduction into the system. Besides, the choice of an appropriate shell may not only facilitate compatibility of the fire retardant with the polymeric matrix, but also increase its efficiency.

The effects of various types of shells on HIC and flammability of polymeric materials prepared from PP and PE have been studied.[77] The following polymeric shells were employed for microencapsulation: high-density PE, polyvinyltriethoxysilane and an aromatic polyamide based on terephthalic acid and *m*-phenylenediamine. It was shown that the chemical nature of the polymeric shell strongly affects the flammability and HIC of polymeric compositions based on PE and PP.

The temperature *vs* time curves for the combustion of PP containing non-encapsulated MPD and MPD encapsulated in PE and polyvinyltriethoxysilane are shown in Fig. 8. As can be seen, the shell strongly affects the physical structure of the char at the moment of its formation. As was noted above, the formation of char in the combustion of PP containing MPD occurs at a very slow rate (Fig. 8, curve *2*). The polyethylene film does not influence the combustible and protective properties of the chars formed upon combustion (Fig. 8, curve *3*). Char formation accompanying the decomposition of MPD-containing compositions enclosed in polyvinyltriethoxysilane occurs much faster and the chars formed possess enhanced HIC (Fig. 8, curve *1*).

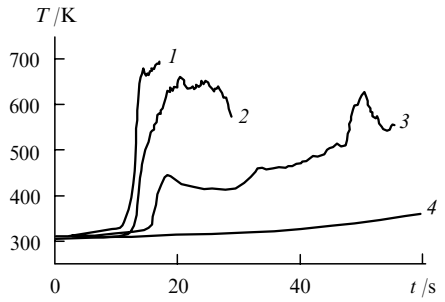


Figure 8. Heat-insulating characteristics of fire retardant-containing compositions prepared from MPD encapsulated in polymeric films:[77] (*1*) PP; (*2*) PP + MPD; (*3*) PP + MPD encapsulated in PE; (*4*) PP + MPD encapsulated in polyvinyltriethoxysilane.

Thus, the efficiency of IS (OI of the polymeric compositions) correlates well with the HIC of foamed cokes formed upon combustion. The higher the HIC of the chars formed the greater the efficiency of IS in these compositions.

VI. Conclusion

The major effect of fire retardants used for decreasing the flammability of polymers consists predominantly in increasing the char yields in the combustion and thermooxidative degradation of polymeric materials. The additives favouring char formation upon the interaction of polymeric components on heating are successfully employed for the preparation of fire retarding polymeric materials. The studies[79–84] published in 1996–1998 have demonstrated that metals and metal-containing materials are best suited for this purpose. This trend of research holds especially great promise, for some metal-containing additives are able to catalyse chemical cross-linking reactions in polymers containing functional groups.[85, 86] Their addition not only affects the yields of chars and the kinetics of their formation but also changes their physical structure.

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