Importance of Intumescence in Polymers Fire Retardancy

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Review Article

Importance of Intumescence in Polymers Fire Retardancy

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This paper presents a review of works concerning the combustion of polymers with various intumescent systems. In this review intumescent systems are considered which undergo charring and foaming upon thermal degradation, forming a blown protective cellular char. The reasons are discussed of action of various additives in intumescent systems. The bibliography includes 38 references.

Keywords: Intumescence; Polymer; Flame retardancy; Combustion; Char; Synergy; Additives

INTRODUCTION

Intumescent technology has recently found a place in polymer science as a method of providing flame retardancy to polymer formulations. Intumescent systems interrupt the self-sustained combustion of the polymer at its earliest stage, *i.e.*, the thermal degradation with the evolution of gaseous fuels.

The intumescence process results from a combination of char-ring and foaming of the surface of the burning polymer (observed between

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280°C and 430°C under air using the polypropylene/ammonium polyphosphate/pentaerythritol (PP/APP/PER) model system [1]). The resulting foamed cellular charred layer which density decreases with temperature [2] protects the underlying material from the action of the heat flux or of the flame.

CHEMISTRY OF INTUMESCENCE

Generally, intumescent formulations contain three active additives: an acid source (precursor for catalytic acidic species), a carbonific (or polyhydric) compounds and a spumific (blowing) agent. In a first stage ($T < 280°C$), the reaction of the acidic species with the carbonisation agent takes place with the formation of ester mixtures [3].

The carbonisation process takes then place at about 280°C (*via* both Friedel–Craft reactions and a free radical process [4]). In a second step, the spumific agent decomposes to yield gaseous products which cause the char to swell ($280 \leq T < 350°$). This intumescent material decomposes then at highest temperatures and looses its foamed character at about 430°C (temperature ranges are characteristic of the extensively studied PP/APP/PER system).

The carbonaceous material formed from the additives, plays two different chemical roles in the fire retardancy process:

– It contains free radical species which react with the gaseous free radical products formed during the degradation of the polymer. These species may also play a part in termination steps in the free radical reaction scheme of the pyrolysis of the polymer and of the degradation of the protective material in the condensed phase,

– It is a support for acidic catalytic species which react with the oxidised products formed during the thermo-oxidative degradation of the material.

The material resulting from the degradation of an intumescent formulation is a heterogeneous material. It is composed of "trapped" gaseous products in a phosphocarbonaceous cellular material, *i.e.*, the condensed phase.

This condensed phase is a mixture of solid phases and of liquid phases (acidic tars) possessing the dynamic properties of interest which allows the trapping of the gaseous and liquid products resulting from the degradation of the polymer. The carbonaceous fraction of the condensed phase consists of polyaromatic species which are organised in stacks characteristic of a pre-graphitization stage.

The phosphocarbonaceous material is, then, a multi-phase material composed of crystalline macromolecular polyaromatic stacks bridged by polymer links and phosphate (poly-, di- or orthophosphate) groups, crystalline additive particles and an amorphous phase which encapsulates the crystalline domains. This amorphous phase is composed of small polyaromatic molecules, easily hydrolysed phosphate species, alkyl chains formed *via* the degradation of the additive system and fragments of the polymer chain. It governs the protective behaviour of the coating: this phase has to be voluminous enough to perfectly coat the crystalline domains and has to show an adequate rigidity/ viscosity which yields the dynamic properties of interest (it avoids dripping and accommodates stress induced by solid particles and pressure).

PROTECTION *VIA* INTUMESCENCE

The proposed protection mechanism is based on the charred layer acting as a physical barrier which slows down heat and mass transfer between the gas and the condensed phases. The limiting effect for fuel evolution is proved by the presence of the polymer chains in the intumescent material. Moreover, the layer inhibits the evolution of volatile fuels *via* an "encapsulation" process related to its dynamic properties. Finally, it limits the diffusion of oxygen to the polymer bulk.

The stability of the intumescent material limits consequently the formation of fuels and leads to self-extinction in standard conditions. Oxygen consumption calorimetry in a cone calorimeter confirms that the low rate of the degradation is related to the presence of a surface intumescent material (typical example presented in Fig. 1 [5]).
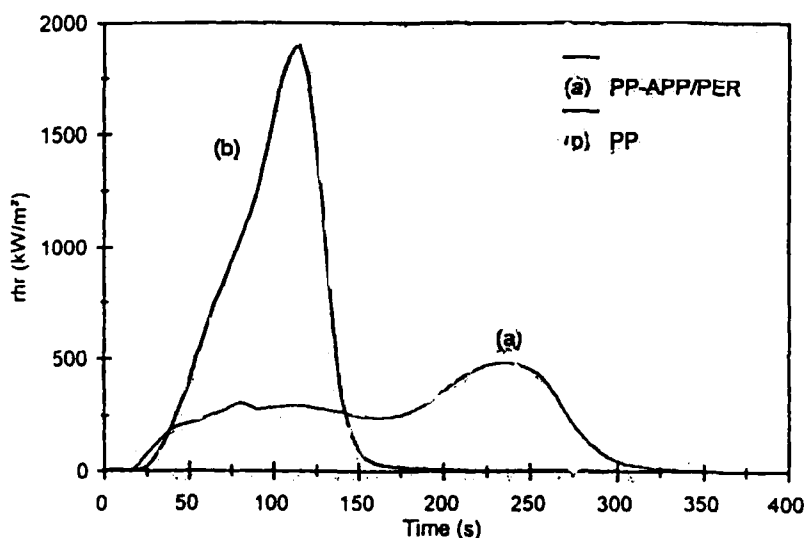
FIGURE 1   Rates of heat release (rhr) of PP and PP–APP/PER under a heat flux of 50 kW/m².

INTUMESCENT ADDITIVES

In spite of the considerable number of intumescent systems developed in the past 15 years [6–8], they all seem to be based on the application of 3 basic ingredients: a "catalyst", a charring agent and a blowing agent.

The "catalyst" is usually a P derivative, in most cases ammonium polyphosphate (APP). The function of the APP is to catalyse the dehydration, which means that it is not supposed to be a main actual reactant in the system, but to catalyse reactions of other ingredients. The relatively large amounts of APP applied, i.e., in the range of 10–20% of the weight of the composition, are not compatible with the definition of a catalyst. It is therefore possible that the APP has an additional role in the system, and serves as an ingredient in the char structure. It is also possible that the low effectivity (EFF) of the APP is caused by volatilisation of phosphorus oxides formed in the pyrolysis. The fire retardancy (FR) EFF of APP [9–11] is low (0.31). The EFF of APP, however, increases greatly upon the addition of co-additives. Depending on the chemical composition of these commercially available additives, which include the char formers and the

blowing agents, which are considered as synergists, EFF values of up to 3.5 were obtained [9]. These values are much higher than the general value of 1.3 given by van Krevelen for P in PP, which does not include intumescent systems [12]. The synergistic effectivities [9–11] (SE) i.e., the ratio of the EFF of the FR agent together with the synergist to that of the agent alone, obtained in the intumescent systems, increase from values of 5.5 and 3.0 for APP + PER and APP + melamine (ML) to values of 9.7 and 11.3, for other co-additives (Tab. I).

TABLE I   FR Effectivity (EFF) and Synergistic Effectivity (SE) of intumescent and other systems

Polymer	FR	Synerg.	EFF	SE	Ref.
PP	APP		0.31		[9, 10]
PP	APP	PER	1.7	5.5	"
PP	APP	ML	0.92	3.0	"
PP	APP	PER + ML	2.4	7.7	"
PP	APP (EDAP)		2.1	6.8	"
PP	APP	Spinflam MF82	3.0	9.7	"
PP	APP	THEIC	2.8	9.0	"
PP	APP	Exolit IFR 23P	3.5	11.3	"
PP	APP	PER + Cat.A	3.13	10.1	[3]
LRAM3.5 (EBM)	APP	PER	1.76		[13]
"	APP	Zeolite 4A	3.16	10.2	"
Cotton	Pyrovatex		4.0		[14]
Cotton	Pyrovatex	TMM	7.0	1.75	"
PP	Arom.Br		0.45		[12]
PP	Arom.Br	Sb_2O_3	1.0	2.2	"
PP	Aliph.Br		0.6		"
PP	Aliph.Br	Sb_2O_3	2.6	4.3	"
PP	NH_4Br		1.24		[15]
ABS	Dechlorane[†] Sb_2O_3		0.8		[16]
ABS	"	Br-epoxy	1.35	1.67	"
PC : PET/ 2 : 1	TPP		13.3		[17]
"	BrPC		1.7		"
"	BrPC	TPP		1.38	"
"	Br : P/7 : 3			1.57	"
PAN	APP		1.62		[18]
"	HBCD		1.21		"
"	HBCD + APP			1.55	"

Additives: LRAM3.5-ethylene/butyl acrylate/maleic anhydride terpolymer, EBM-ethylene/butyl acrylate/maleic anhydride terpolymer, TMM-trimethylol melamine, PC-polycarbonate, PET-poly (ethyleneterephthalate), TPP-triphenyl phosphate, BrPC-brominated polycarbonate, PAN-poly (acrylonitrile), HBCD-hexabromcyclododecane.

P=N SYNERGISM

Synergism, as currently used in FR terminology is a poorly defined term. Strictly speaking, it refers to the combined effect of two or more additives, which is greater than that predicted on the basis of the additivity of the effect of the components. The term SE is meant to serve as a general tool for the characterisation and comparison of synergistic systems.

In Table I values of EFF and SE computed from literature data on a number of FR synergistic systems, are presented. An EFF of 4.0 and an SE of 1.75 are obtained for P in cotton treated with Pyrovatex (dialkyl phospho-propionamide) and TMM at a 2% P and 5% N level [14]. Although the ingredients of this system P, N and a polyhydric alcohol-cotton resemble an intumescent system, the SE is much lower. A similar result is also obtained when treating cotton with ammonium sulfamate and urea [19].

The P—N synergism in the phosphorylation of cellulose is manifested by an increased rate of phosphorylation and yield of P, by an increased FR effect and improved physical properties. The magnitude of the effect varies from one N compound to another. Usually amine and amide derivatives are effective whereas nitriles are antagonistic, allegedly due to their volatility [14].

The P—N bonds can also participate in the formation of the crosslinked networks, in which the P will be fixed and its volatilisation hindered [42].

Based on element analysis and infrared XPS spectra, Weil *et al.*, confirmed recently the existence of P—N species along with phosphoric or polyphosphoric acids on the surface of char from burning an intumescent sample composed of ethylene/vinyl acetate, melamine pyrophosphate and XPM-1000 [5, 5, 5′, 5′, 5″, 5″-hexamethyltris(1,3,2-dioxaphosphorinanemethane)amine 2, 2′,2″-trioxide] [21].

HALOGEN – ANTIMONY SYNERGISM

Data on the SE of aromatic and aliphatic bromine derivatives with antimony trioxide, computed from Ref. [12] show SE values of 2.2 and 4.3, respectively. Similarly, for aliphatic chlorine derivatives with

antimony trioxide a SE value of 2.2 is computed for polystyrene (Tab. I).

The halogen – antimony synergism appears to depend both on condensed phase as well as vapor phase activities. It is believed that first some hydrogen halide is released from the halogen compound due to interaction with antimony trioxide or with the polymer. The HX reacts with the Sb_2O_3 producing either SbX_3 or $SbOX$ [22]. $SbOCl$ was found to decompose in several endothermic stages: at 245–280°C to $Sb_4O_5X_2$; at 410–475°C to Sb_3O_4X; above 685°C solid Sb_2O_3 is reformed. During the transformations gaseous SbX_3 is evolved and released to the gas phase, whereas $SbOX$, which is a strong Lewis acid, operates in the condensed phase, facilitating the dissociation of the C—X bonds [23].

The main effect of Sb_2O_3 is, however, in the gas phase. The antimony halides, after reaching the gas phase, react with atomic hydrogen producing HX, SbX, SbX_2 and Sb. The Sb reacts with atomic oxygen, water and hydroxyl radicals, producing SbOH and HX. A fine dispersion of solid SbO and Sb is also produced in the flame and catalyses the H recombination. In addition it is believed that the antimony halides delay the escape of halogen from the flame, and thus increase its concentration, and at the same time it also dilutes the flame.

BROMINE – CHLORINE SYNERGISM

The synergistic interaction between bromine and chlorine derivatives is discussed in several papers [24, 16]. Cleave reported on such an effect in mixtures of chloroparafins with pentabromotoluene [24] in the presence of Sb_2O_3. Recently, Markezich reported on results obtained on ABS, high impact polystyrene (HIPS) and PP [25]. In most cases the maximum effect is found with a Br/Cl ratio of 1:1 and with 10–12% of the total weight of the sample being chlorine and bromine. When using Dechlorane Plus and brominated epoxy resin (51% Br) with ABS in the presence of 5% Sb_2O_3, the FR EFF was calculated as 0.80. The SE obtained was 1.67. (Tab. I). This synergism is in addition to the halogen – antimony synergism and is effective only in the presence of antimony trioxide. The synergistic effect increases with the amount of antimony and reaches a maximum at 6% trioxide.

BROMINE – PHOSPHORUS SYNERGISM

There are several reports in the literature on P—Br synergism. Of particular interest is the case of PAN treated with varying ratios of APP and HBCD [18]. As seen in Table I, a SE value of 1.55 was calculated in this case. It was shown that the system acts *via* an intumescent mechanism. The bromine compound was shown by LOI and NOI tests not to operate in the gas phase but rather as a blowing agent to foam the char.

Similar SE values are computed from data in Ref. [17] for PC/PET blend treated with varying ratios of TPP and brominated PC. A SE value of 1.38 is found. When a brominated phosphate with the ratio of bromine to phosphorus of 7:3 is added to the same blend, the SE value is 1.58. There are some indications, though no clear evidence, that in these cases too bromine may serve, at least partly, as a blowing agent instead or together with the radical trapping activity in the gas phase. The Br—P SE values are considerably lower than the bromine – antimony values as well as the intumescent values, pointing to the possibility of a different mechanism.

It has recently been suggested that P compounds may replace antimony as a halogen synergist [26]. In the case of oxygen containing polymers, such as Nylon 6 and PET a strong synergism was shown: In the case of PET the total amount of additives (Br-based and P-based) decreased by over 90% compared to Br-based and Sb additive. A similar synergistic activity of Br and P was obtained for PBT, PP, PS, HIPS and ABS. A decrease in the amount of total additive of 40% was obtained for PE [26].

ROLE OF AMMONIUM POLYPHOSPHATES
IN POLYMER FIRE RETARDANCY

The synergistic effectivity of the PP-APP system is much higher than of any other synergism (Tab. I). A series of processes is occurring during the combustion of the system: decomposition of APP with release of ammonia and water, phosphorylation of the PER and of thermo-oxidised PP, dehydration, dephosphorylation, crosslinking, carbonisation and formation of char structure. The blowing agent vaporises and decomposes to incombustible gases.

Moreover, Brauman [27], studying pyrolysis of char forming composition of poly(ethylene terephthalate) with APP, suggested that APP does not only create a protective layer but also takes a part in chemical reactions in the condensed phase.

All these processes occur in a very short time with various reaction rates. The ratios of the rates, which determine the sequence of the reactions and their timing, has a dominant effect on the properties of the final char and on the flaming behaviour.

A comparison of the thermal behaviour of additive systems [28] containing different phosphate species shows that comparatively low LOI values may be related to the formation of phosphorus oxides which evolve in the conditions of a fire and, so, to the decrease of the phosphate species amount in the char.

However addition of low amounts of zeolites limits the formation of condensed polyphosphate species and increases the content of acidic orthophosphate and diphosphate species in the intumescent material [13, 29].

So far as inorganic phosphates are concerned, they are often less thermostable than some organic phosphorus-containing products that were researched [30].

A new method of synthesis of binary metal–ammonium polyphosphates $Me(NH_4)_nP_4O_{13}$, linear triphosphates $Me(NH_4)_nP_3O_{10}$ and linear tetraphosphates $Me(NH_4)_nP_4O_{13}$ was developed [31]. These phosphates are more thermally stable than ammonium polyphosphate, but similar to APP they evolve polyphosphoric acid during thermal decomposition and show fire retardant activity in aliphatic nylons [32].

As it is seen from the thermal analysis, is, binary metal–ammonium phosphates (BMAP) destabilise PA-6 (Nylon-6). Similarly, BMAPs begin to degrade at lower temperature when they are mixed with PA-6. Polyphosphoric acid evolved from BMAPs catalyses the thermal decomposition of the polymer. In spite of differences in combustion and thermal decomposition performances, BMAPs show chemical reactions (similar to APP) with PA-6 which provide intumescent char on the surface of the burning polymer.

Phospham is a cyclomatrix inorganic polymer of high thermal stability. The structure of phospham is not established and seems to be dependent on the method of preparation, however the chemical analysis usually shows the following formula $(PN_2H)_x$. Its fire retardant efficiency in aliphatic polyamides (PA-4.6) was studied by

E. Weil and N. Patel [33]. Also phospham is an efficient fire retardant additive to PA-6 as it is shown by LOI measurements (Tab. II).

The highest increment of LOI is observed at 10 wt.% phospham, whereas at further loading LOI grows more slowly. The char is observed on top of the burning specimens with phospham. As Table II shows PA-6 is involved in the charring in the presence of phospham. For example, the formulation with 10 wt.% of phospham gives 17.5% of char.

It is shown [30] that phospham is an efficient fire retardant additive to PA-6 because it promotes charring of the polymer. In spite of its high thermal stability, phospham reacts with the polyamide producing phosphonitriles and phosphoamines which decompose at higher temperature and give char. Free radical mechanism is suggested to contribute to the charring.

Whereas the role of the polyhydric alcohol as a charring agent is clearly defined, the function of the melamine appears to be more diverse: (a) endothermic action due to the volatilisation from the solid state and to decomposition in the flame, (b) it may facilitate the phosphorylation, (c) it is believed to serve as a blowing agent in the intumescent formulation as a part of the volatiles emitted during pyrolysis, which include water, CO, CO_2, ammonia and hydrocarbons, all serving to foam the char.

Investigations of intumescent compositions were focused mainly on the APP with pentaerythritol (PER) and melamine (ML) in PP and other polymeric matrices. Studying the intumescent additive APP–PER (1.5:1 wt./wt.) in various matrices: PP, PE and PS, Gnedin et al. [34] using IR spectroscopy have shown that char chemical structure practically does not depend on the matrix type and that the contents of C and P atoms in the char residue corresponds to those of the pure intumescent additive. Moreover, Delobel et al. [28],

TABLE II   Oxygen index and char yield measured in combustion of PA-6 fire retarded by phospham

Phospham, wt.%	LOI, vol.%	Charyield, wt.%
–	25.2	–
10	29.2	17.5
20	31.6	23.5
30	34.8	32.2

studying PP formulations with APP–PER additive using [31] P MAS–NMR spectroscopy, have shown that formation of higher polyphosphate chains occurs during intumescence and that a relatively sharp increase in the amount of orthophosphates species is found in the char residue. The same behaviour is observed for PP formulations with diammonium pyrophosphate and PER additive but, instead of orthophosphates, pyrophosphate species are detected. Recently Bourbigot et al. [35] investigated using XPS structure of the bulk and surface of the char, produced during the thermal treatment of APP–PER system. The authors verified that the P/C ratio increases at high temperatures (500°C) on the char surface, whereas in the bulk this ratio decreases. Furthermore, they showed that the O/C ratio follows a similar trend. They proposed a migration of phosphonates to the surface, followed by oxidation.

These authors [36] have shown that the combination of zeolites with the APP/PER or the diammonium pyrophosphate/PER systems leads to a substantial improvement of the fire-retardant properties (Tab. III) in various polymeric matrices.

The curves of the variations of the rate of heat release (RHR) versus time (typical examples in Fig. 2) show a significant decrease of the RHR maximum values of the flame retardant polymers in comparison to the pure polymer [37]. In the case of the intumescent formulations, the rate of heat release (RHR) decreases strongly after the ignition.

The toxicity of gaseous products evolving during combustion is an essential parameter which can be estimated using a cone calorimeter. During the first 250s the formulation with zeolite yields less smoke

TABLE III   FR performance of intumescent formulations with and without zeolite

System	LOI (vol.%)	UL-94 rating	System	LOI (vol.%)	UL-94 rating
PP–APP/PER	30	VO	PP–APP/PER/13X	45	VO
LDPE–APP/PER	24	VO	LDPE–APP/PER/4A	26	VO
[a]PP–PY/PER	32	VO	PP–PY/PER/13X	52	VO
PS–APP/PER	29	VO	PS–APP/PER/4A	43	VO
[b]LRAM3.5–APP/PER	29	VO	LRAM3.5–APP/PER/4A	39	VO

The additives' loading is kept constant at 30 wt.-% and the synergistic effect exhibits a maximum at 1 or 1.5 wt.-% zeolite loading.
[a] PY-diammonium diphosphate,
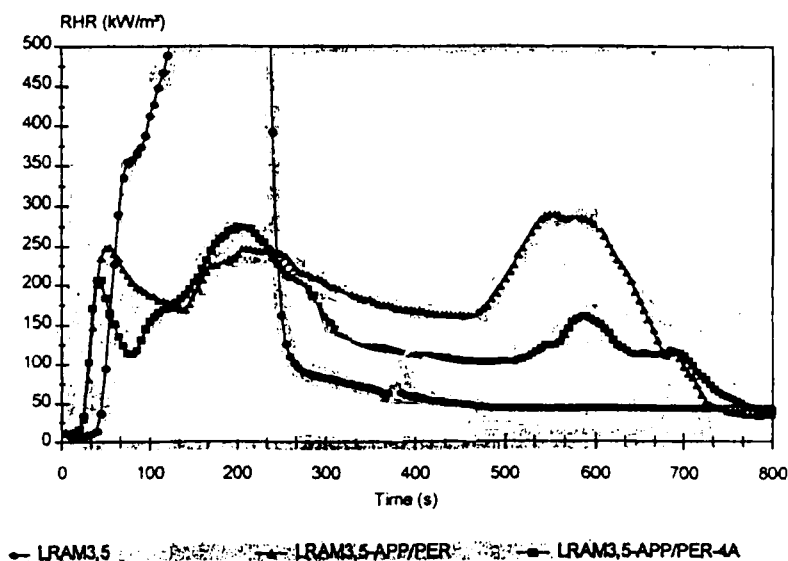[b] LRAM3.5-ethylene-butylacrylate-maleic anhydride terpolymer.

RHR (kW/m²)

FIGURE 2 Rate of heat release vs. time of the systems LRAM3.5, LRAM3.5-APP/ PER and LRAM3.5-APP/PER-4A (heat flux = 50 kW/m²).

than the formulation without zeolite and than the virgin polymer (Fig. 3), which is very important for safety.

Certain authors [36] supposed that intumescent systems develop a phosphocarbonaceous structure which is thermally stabilised by the zeolite. The zeolite particles may block polyethylenic links in the form of organic phosphates and/or aluminophosphates and therefore limit the depolymerisation, i.e., the evolution of small flammable molecules able to fuel the fire.

Moreover, it is shown that the zeolite allows the formation of a more "coherent" structure and therefore orients differently the structure of the materials. The formation of a "coherent" macro-molecular network and the participation of polyethylenic links seem therefore to be favourable for obtaining the fire-retardancy of interest. Indeed the development in the intumescent shield of a structure consisting in polyaromatic species creates a rigid material (case of the LRAM3.5-APP/PER formulation). On the other hand, the stabilisation of polyethylenic links in the intumescent structure capable of bridging polyaromatic species via alumino-and/or silicophosphate groups and/or because of the paramagnetic character of the
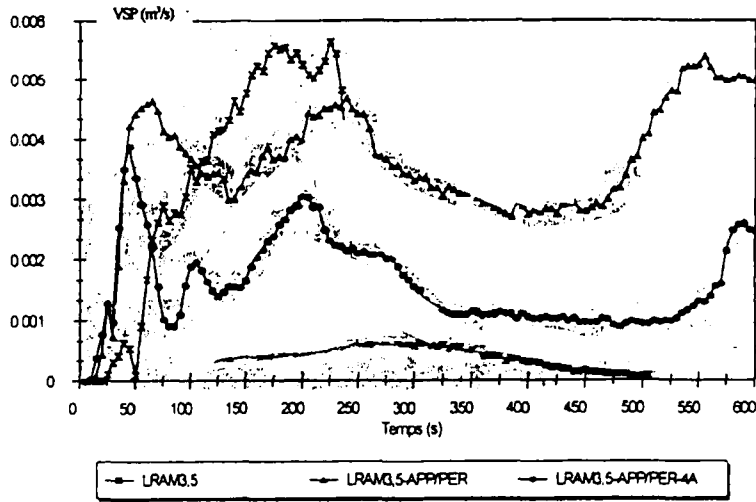
FIGURE 3 Volume of smoke production (VSP) *vs.* time of the systems LRAM3.5, LRAM3.5-APP/PER and LRAM3.5-APP/PER-4A (heat flux = 50 kW/m^2).

intumescent structure may provide the mechanical properties of interest of the intumescent coating. They provide flexibility to the carbonaceous shield which allows this shield under the conditions of fire, to suppress the creation and propagation of cracks through which oxygen diffuses to the polymeric matrix and through which small molecules may be released as fuel.

Polymers may be used in additive mixtures as carbonisation agents. In particular, PA-6/APP additive mixture, blended with thermoplastics, leads to FR properties of interest, by developing an intumescent shield which may, at least partially, limit mass and heat transfer [4].

A group of authors [38] deals with the association of ammonium polyphosphate as acid source and PA-6 as carbonisation agent used directly as fire retardant intumescent additive in an ethylene vinyl acetate 8% copolymer (EVA8) matrix. The addition of APP in EVA8 leads to a blowing up and a weak carbonisation (LOI : 24 vol.%, UL94 : no rating, with 40 wt.% loading). Fire retardancy of interest is obtained (LOI : 31 vol.%, UL94 : V-O rating) with the formulation EVA8/APP/PA-6 (ratio APP/PA-6 = 5:1 wt/wt and 40 wt.% of APP/PA-6 loading in the EVA8 matrix). Illustrative measurements of the
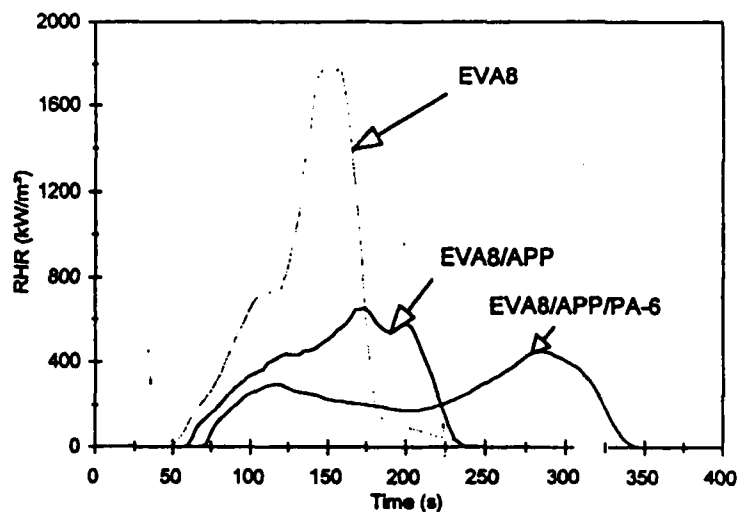
FIGURE 4   Comparison between RHR curves of EVA8 and FR systems (3 mm thick).

rate of heat release [RHR, kW/m^2] of the EVA8 and the EVA8/APP and EVA8/APP/PA-6 systems are shown in Figure 4.

The addition of PA-6 to the EVA8/APP system leads to a significant decrease of the peak of rate of heat release and thus has the advantage of delaying the ignition of the specimen and slowing down its degradation by increasing the stability of the coating. This resistance is explained by the formation of a second shield which acts as a relay of the shield formed from EVA8/APP. This second shield results from a reaction between APP and PA-6, leading to a protective ablation phenomenon. The heat transfer study shows that this protection is efficient enough to limit the degradation to the surface of EVA8/APP/PA-6.

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