

Comprehensive study of the degradation of an intumescent EVA-based material during combustion

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In this work, we have studied the evolution of an flame retardant intumescent EVA-based material during combustion. The formulation uses an original concept of the laboratory, i.e., use of char forming polymer (here the polyamide-6) as carbonisation agent associated to a carbonisation catalyst in an intumescent formulation. The fire behavior was modelled using the cone calorimeter and we have explained the evolution of the rate of heat release curve in terms of chemistry of the system using FTIR and solid state NMR. © 1999 Kluwer Academic Publishers

1. Introduction

Polyethylenic polymers are used in many fields such as housing materials, transport or electrical engineering applications. Due to their chemical constitution, these polymers are easily flammable and so, flame retardancy becomes an important requirement for many of them. This can be obtained by several ways, one of these being incorporation of additives. Up to now, halogen compounds were widely used for this purpose, but the corrosiveness, the toxicity of their combustion products and the smoke production have attracted much attention. As a result, certain sectors of industry, notably those concerned with aerospace, microelectronics, cable and wire manufacture, are particularly interested into alternative halogen-free fire retardants [1–4].

A solution for limiting the burning mechanism can consist in developing on the outer surface of the polymer a glassy [5] or an expanded shield [6, 7] which may at least partially, limit the transfer of fuel to the gas phase, the transfer of heat from the flame to the condensed phase and eventually oxygen diffusion in the condensed phase. In particular, fire retardant intumescent materials are halogen-free and form on heating foamed cellular charred layers on the surface, which protects the underlying material from the action of the heat flux or of a flame (Fig. 1).

Generally, intumescent formulations contain three active ingredients [6, 7]: an acid source (phosphate, borate, . . .), a carbonisation compound (polyols, . . .) and a blowing agent (melamine, isocyanurat, . . .). First, the acid source breaks down to yield a mineral acid.

Then, it takes a part in the dehydration of the carbonific to yield the carbon char and finally, the blowing agent decomposes to yield gaseous products. These latter cause the char to swell and hence provide the insulating material which then decomposes under the action of the outer heat flux.

The carbonisation agents commonly used in intumescent formulations for thermoplastics are polyols such as pentaerythritol, mannitol or sorbitol [9, 10]. However, exudation, reactivity during processing and water solubility are problems associated with these additives [11]. Moreover, these additives are not compatible with the polymeric matrix, and the mechanical properties of the formulations are then very poor.

The Laboratory develops FR intumescent formulations for polyolefins using char forming polymers (polyamide-6, polyurethane, . . .) as carbonisation agent [12–16]. The advantage is to obtain flame-retarded polymers with improved mechanical properties in comparison with polymers loaded with classical FR formulations, and to avoid the problems of exudation and water solubility.

In particular, intumescent mixtures of the additives ammonium polyphosphate (APP) and polyamide-6 (PA-6) have been developed for use in polypropylene [9], ethylene propylene rubber, ethylene-vinyl acetate copolymers [12] and other polyolefins. Unfortunately, the two additives are not compatible when mixed and then master batches of the additives blends may not be used as obtained for industrial applications. The solution consists in processing the blend using

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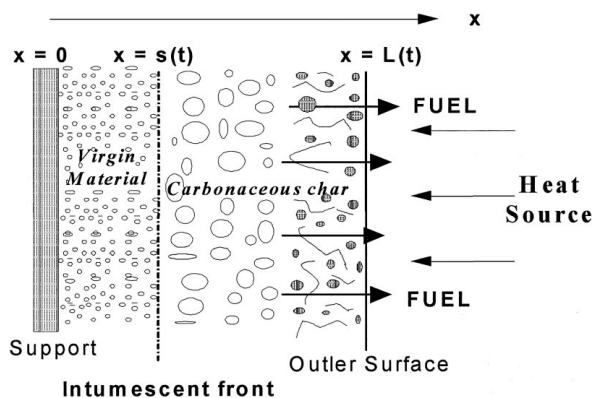


Figure 1 One-dimensional model of the intumescence in the condition of fire [8].

a compatibilizer (ethylene-vinyl acetate copolymer, functionalised terpolymers of ethylene, siloxane-based resins) which maximises the interfacial bonding and so prevents the reject of the mineral additive throughout the polymer matrix [12]. Among these agents, ethylene-vinyl acetate copolymer has been selected, it increases the “compatibility” of APP and PA-6 and in addition acts as a synergistic FR agent [9].

The association of ammonium polyphosphate as the acid source and polyamide-6 as the carbonisation agent has been used directly as fire retardant intumescent additive in an ethylene vinyl acetate 8 wt % copolymer matrix (EVA). Insertion of this additive system in EVA leads to a significant improvement of the fire performances of the material [13, 14]. Fig. 2 shows that interesting results are obtained in EVA with the intumescent APP/PA-6 system at 30 and 40 wt % loading. The optimal Limiting Oxygen Index (LOI) [17] ratio APP/PA-6 is 5 wt %/wt % and UL-94 V-0 rating (vertical flame test) [18] is achieved [19].

The cone calorimeter allows to simulate the conditions of fire in a small bench scale and to measure in particular, the heat release during combustion using oxygen consumption calorimetry [20–22]. Indeed, it has now been established that the property which most critically defines a fire is the heat release [23–28], because two conditions are necessary for a fire to propagate from the product first ignited to another one, in the surroundings. First, sufficient energy, as heat, needs to be released to cause secondary ignition. Secondly, the

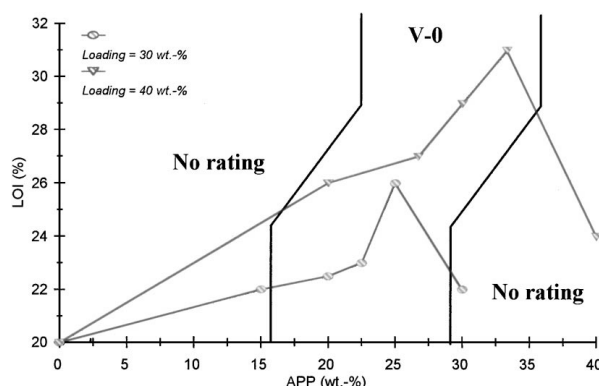


Figure 2 LOI values and UL-94 rating vs. APP and APP/PA-6 loading in EVA-APP/PA-6 intumescent formulations [19].

heat release needs to occur sufficiently fast so that the heat is not quenched in the “cold” air surrounding the latter product.

The rate of heat release (RHR) curves of EVA-APP/PA-6 and EVA, measured using the cone calorimeter, shows the efficiency of the intumescent system APP/PA-6 in the case of a large fire (Fig. 3). The virgin polymer has a RHR maximum at about 1800 kW/m² whereas this of the EVA-APP/PA-6 formulation is only about 400 kW/m².

In order to understand the fire behaviour of the EVA-APP/PA-6 formulation, the aim of this work deals with the chemical characterisation of the intumescent materials formed during combustion in the conditions of the cone calorimeter. The study is led using FTIR and solid state NMR of carbon and phosphorus.

2. Experimental

2.1. Materials

The following products were used: ethylene-vinyl acetate 8% copolymer (EVA8, Lactene 1005 VN3, melt index: 0.4 g/10 mn as pellets supplied by Elf Atochem), polyamide-6 (PA-6, as pellets supplied by Rhône-Poulenc), and ammonium polyphosphate (APP, (NH₄PO₃)_n, n = 700, Hostafam AP422, soluble fraction in H₂O < 1 wt %, supplied by Clariant).

Materials were mixed at 235 °C using the Brabender Laboratory Mixer measuring head (type 350/EH, roller blades, checking of the mixing conditions using the data processing torque rheometer system Brabender Plastimeter PL2000, constant shear rate: 50 rpm). Sheets were then obtained using a Darragon press at 220 °C with a pressure of 10⁶ Pa.

2.2. Oxygen consumption calorimetry

The Stanton Redcroft Cone Calorimeter was used for measurements on samples following the procedure defined in ASTM 1354-90. Rate of Heat Release (RHR) measurement is based on oxygen consumption calorimetry [20]. The standard procedure used [22] involves exposing specimens measuring 100 × 100 mm and 3 mm thick in horizontal orientation to an external heat flux of 50 kW/m² representing generalised fire [23]. The external heat flux is shut down at different characteristic times, the sample is removed from the cone calorimeter and quenched in the air before spectrochemical analyses.

2.3. FTIR

Infra-red spectra were recorded in the spectral zone 400–4000 cm⁻¹ using an Nicolet Impact 400D spectrometer. Samples were grinded and mixed with KBr pelletising.

2.4. Solid state NMR

¹³C NMR measurements were performed on a Bruker ASX100 at 25.2 MHz (2.35 T) with magic angle spinning (MAS), high power ¹H decoupling (DD) and

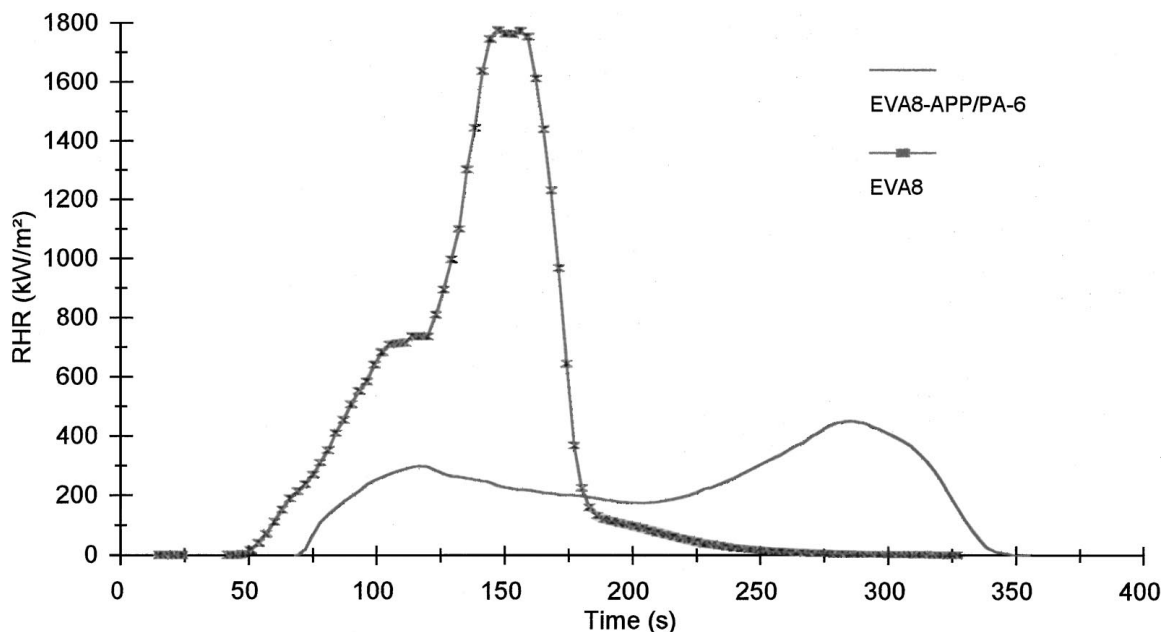


Figure 3 RHR curves (heat flux = 50 kW/m²) of the virgin EVA and of the formulation EVA-APP/PA-6 [19].

¹H-¹³C cross polarisation (CP) using a 7 mm probe. The contact time was 1 ms. A repetition time of 10 s was used for all samples. The reference used was tetramethylsilane and the spinning speed was 5000 Hz.

³¹P NMR measurements were performed at 40.5 MHz with magic-angle spinning (MAS), with or without high power ¹H dipolar decoupling (DD) and a repetition time of 450 s (because of the long spin-lattice relaxation time). All spectra were acquired as a result of 500 scans. The reference used was 85% H₃PO₄ in aqueous solution.

3. Results and discussion

The RHR curve of the formulation EVA-APP/PA-6 allows to determine several characteristic times (Fig. 4). The first event to notice is the heating of the polymer ($t = 30$ and 50 s). The ignition of the material occurs at about 75 s. One can also remark the particular shape of the RHR curve (wavy curve) of the intumescent polymer. It can be assigned according previous studies [29, 30] to the development of intumescence up to 110 s (RHR increases strongly and then the slope of the

RHR curve decreases). Then the RHR is reduced and a plateau is reached in which the RHR is suppressed significantly ($110 < t < 200$ s). It corresponds to a stable efficient protective shield. Finally ($t > 200$ s), there is degradation of the protective coating which forms a stable carbonaceous residue ($t = 350$ s). In order to understand what are the species formed as a function of time during combustion, the external heat flux is shut down at the different characteristic times defined Fig. 4. Then the samples so obtained, are analysed by FTIR and solid state NMR.

FTIR spectra as a function of time ($110 \text{ s} < t < 350 \text{ s}$) are presented Fig. 5 and the assignment of the main bands Table I. Bands at 2800 and 2900 cm⁻¹ are observed till 300 s. They can be assigned to CH₂ groups in polyethylenic chains. This result suggests that polymer fragments are kept in the intumescent structure.

At every time, the spectra present broad bands between 1100 and 1300 cm⁻¹ assigned according to MacKee *et al.* [31], to P-O-C bonds in “phosphate-carbon” complexes and/or P-O in a vitreous structure.

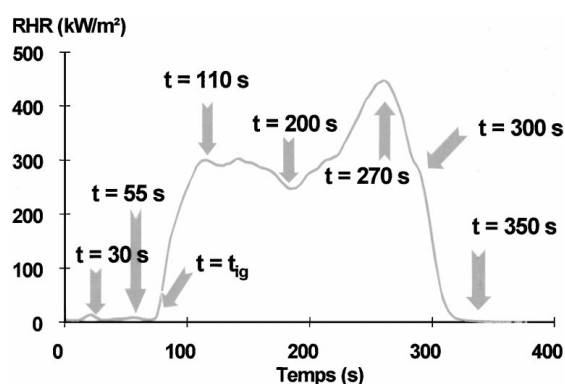


Figure 4 RHR values vs. time of the formulation EVA-APP/PA-6 and determination of the characteristic times.

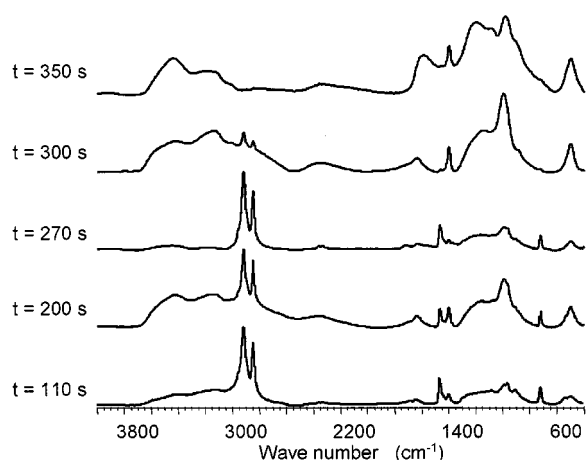
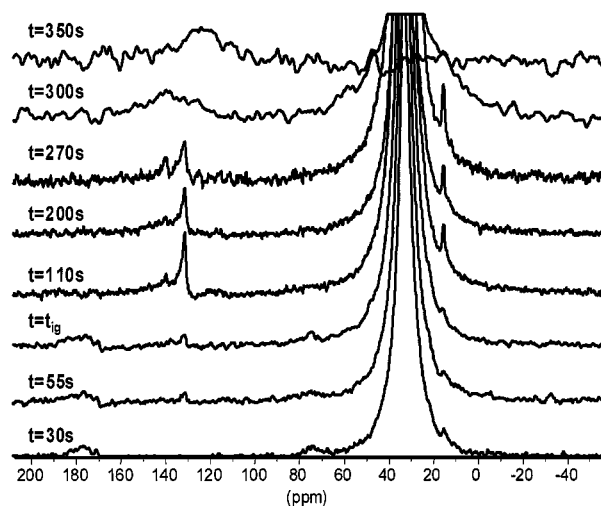


Figure 5 FTIR spectra as a function of characteristic times of EVA-APP/PA-6.

TABLE I Assignment of the band of the FTIR spectra

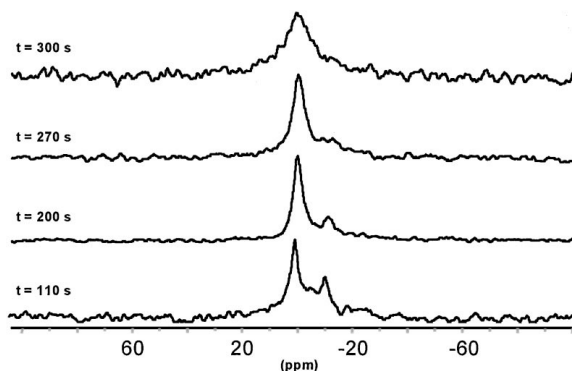
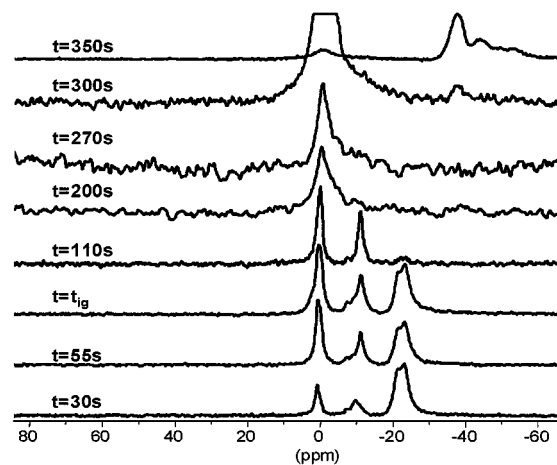
Wavenumber (cm ⁻¹)	Assignment	Reference
700–800	Deformation vibration of CH ₂ and/or C–C aromatic and/or P–O	[32, 33]
850–1000	ν_{as} of P–O in P–O–P	[32]
950–1050	ν_{sym} of PO ₂ and PO ₃ in complexes Phosphate-Carbon	[32, 33]
1100–1120	ν_{sym} of P–O	[32, 33]
1100–1300	Stretching mode of P–O–C in complexes Phosphate-Carbon and/or P–O in a vitreous structure	[31, 42, 43]
1225–1250	Stretching mode in P=O	[32, 33]
1400–1450	NH ₄ ⁺	[32, 33]
1500–1550	Symmetrical deformation of CH ₂ , CH ₃	[32, 33]
1625–1670	Stretching mode of P(O)–OH	[32, 33]
2300–2500	Stretching mode of P–OH	[32, 33]
(In overlap)		
2650–2800	Stretching mode of P–OH	[32, 33]
(In overlap)		
2820–2850	Symmetrical stretching mode of de CH ₂	[32, 33]
2900–2930	Asymmetrical stretching mode of de CH ₂	[32, 33]
3050–3250	NH ₄ ⁺	[32, 33]
3210–3500	OH	[32, 33]

Figure 6 CP-DD-MAS NMR ¹³C spectra as a function of characteristic times of EVAAPP/PA-6.

The additional broad bands about 1000 cm⁻¹ can be assigned to modes of symmetrical vibrations of PO₂ and PO₃ [32, 33]. The spectra suggests therefore the formation of a phosphocarbonaceous structure.

CP-DD-MAS NMR ¹³C confirms the assumptions deduced from the FTIR study (Fig. 6). Bands at 32 ppm can be assigned to polyethylenic chains [34] and are observed up to 300 s. Nevertheless at 300 s, the band at 32 ppm is not well resolved. It can be assigned to aliphatic group issue from the degradation of polymer chains.

From 30 s, it is to notice the appearance of a band at 14 ppm (not observed on the spectrum of the sole polymer) which can be assigned to methyl group on aliphatic chains [35, 36]. It means therefore that there is scission of the polyethylenic chains leading to the for-

Figure 7 MAS NMR ³¹P spectra as a function of characteristic times of EVA-APP/PA-6.Figure 8 DD-MAS NMR ³¹P spectra as a function of characteristic times of EVA-APP/PA-6.

mation of shorter chains. When heating EVA degrades and acetic acid is evolved which implies the formation of end chains methyl groups.

At 55 s and at the ignition, a band at around 130 ppm is observed which can be assigned to aromatic species [37, 38]. The carbonisation of the material begins therefore during heating of the material. Between 110 and 270 s, the appearance of a band around 140 ppm of weak intensity suggests the condensation of aromatic species to polyaromatic species [35, 37, 38]. At 300 s, a broad band centred at 140 ppm is observed which implies the presence of several non-magnetically equivalent carbons [35]. As discussed before in a previous work [39], this peak may be assigned to several types of aromatic and polyaromatic species which can be partially oxidised. Finally at 350 s, the spectrum of the residue presents a weak signal to noise. Only one band of weak intensity (broad band centred around 125 ppm) assigned to polyaromatic species is observed. The coating is then degraded when the combustion stops.

FTIR suggests the formation of a phosphocarbonaceous structure. To examine and to confirm it, NMR ³¹P is a powerful tool. Spectra made without and with dipolar decoupling are presented respectively Figs 7 and 8.

During the heating of the material and till the ignition, the characteristic bands of APP (–22 and –24 ppm) are observed. One can observed that it already degrades and reacts during heating. Indeed all spectra show a band

centred at 0 ppm which can be assigned to orthophosphate linked to aliphatic groups and/or orthophosphoric acid [40, 41].

After the ignition, an additional band can be observed at about -13 ppm till 270 s (weak intensity at this last time). This band can be assigned to pyrophosphate species and/or to diphenyl- or triphenylorthophosphate groups [34]. It should be noted that the spectrum at 110 s recorded with DD has a better signal to noise ratio than this one without DD. It means that there are heteronuclear interactions phosphorus-proton. The opposite is observed at 200 and 270 s. It can be proposed that at 110 s the observed species are mainly pyrophosphates and/or orthophosphates linked to uncondensed aromatic groups. Then the aromatic species condense and the material is composed by a phosphocarbonaceous structure bridged by orthophosphate species.

These assignments can explain the evolution of the FTIR spectra. Indeed the intensity of the broad band ($1100\text{--}1300\text{ cm}^{-1}$) decreases till 270 s, then increases till 350 s. It can be therefore assigned to P–O group in a vitreous structure. It suggests the formation of phosphocarbonaceous structure which provides a “coherent phosphorus-carbon” structure. Then at 270 s, this structure degrades to form a vitreous coating of phosphoric acid and/or polyphosphoric acid (a band of weak intensity is observed at -36 ppm (Fig. 8) assigned to a polyphosphoric acid [36]).

From this study, we can propose a mechanism of action of the flame retardant system in the conditions of the cone calorimeter.

In a first step, the polymer melts and APP degrades and can catalyse the formation of the carbonisation of the material. The intumescence develops after ignition. There is the formation of a phosphocarbonaceous structure which can trap the polymer chains and the protection is effective till 200 s. The RHR values remain low. Then the intumescent shield degrades and a part of the polyethylenic chains trapped in the structure can be evolved. So, the flame is fed in “fuel” and the RHR values increase. Beyond 300 s, there are no longer polymer chains and the combustion is stopped. The RHR values become null.

From these considerations, it can be proposed a mechanism of action of the FR intumescent system in the conditions of the cone calorimeter. In a first step, intumescence develops. There is the formation of a phosphocarbonaceous structure which can trap the polymer chains. In the second step, this structure degrades and the polymer chains are evolved. Finally, a carbonaceous residue is formed, there are no longer polymer chains that is to say, there is no longer fuel, and the combustion stops.

4. Conclusion

In this work, we have studied the evolution of an flame retardant intumescent material during combustion. The formulation uses an original concept of the laboratory, i.e., use of char forming polymer as carbonisation agent in an intumescent formulation. The fire behavior was modelled using the cone calorimeter and we have ex-

plained the evolution of the rate of heat release curve in terms of chemistry.

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