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J.-P Gibert, J. Lopez-Cuesta, A Crespy, Anne Bergeret. Study of the degradation of fire-retarded PP/PE copolymers using DTA/TGA coupled with FTIR. *Polymer Degradation and Stability*, 2000, 67 (3), pp.437-447. 10.1016/S0141-3910(99)00142-1 . hal-03254691

**HAL Id: hal-03254691**

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Submitted on 9 Jun 2021

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# Study of the degradation of fire-retarded PP/PE copolymers using DTA/TGA coupled with FTIR

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## Abstract

A PP/PE copolymer was successively flame retarded using  $\text{Mg}(\text{OH})_2$ , then using brominated trimethylphenyl indane associated with  $\text{Sb}_2\text{O}_3$  (Br/Sb), and finally using blends of equal weights of this last combination with  $\text{Mg}(\text{OH})_2$  or talc-containing non-hydrated fillers. Decompositions of pure and additive-containing copolymer were studied by DTA/TGA coupled with FTIR. A good correlation exists between the maxima of Gram–Schmidt curves and the derivatives of TGA curves. The coupling of techniques shows that the incorporation of the Br/Sb flame retardant limits strong exothermic phenomena due to sample ignition. In the case of  $\text{Mg}(\text{OH})_2$  associated with Br/Sb, the decomposition of the hydrated mineral occurs at a lower temperature than the reaction between brominated trimethylphenyl indane and  $\text{Sb}_2\text{O}_3$ . This delays the action of Br/Sb flame retardant towards higher temperatures, improving the thermal stability of the polymer. A good agreement is also found between DTA/TGA-FTIR conclusions and fire resistance tests carried out on standardized samples. When magnesium hydroxide is replaced by the fillers, the interest in using a pure talc, which appeared in fire resistance tests, is not strongly confirmed by DTA/TGA-FTIR. This discrepancy may be ascribed to the reduced influence of mass diffusion phenomena due to the small weight of the sample used in thermal analysis experiments.

## 1. Introduction

Several kinds of flame retardants are commonly used to improve the flame resistance of polypropylene and its copolymers. The brominated flame retardants are very effective due to their influence on flame chemistry [1]. Nevertheless their decomposition products are thought to cause environmental concerns. Despite the development of new generations of brominated compounds [2], the risk of release of corrosive vapours is always present and limits the use of this category of flame retardant, in electronics and other fields. The use of mineral fillers depends mainly on their ability to decompose endothermically by discharging gases, particularly water vapour. Nevertheless, the temperature range of the filler decomposition is not always compatible with those of processing or thermal decomposition of a given polymer. Consequently, the choice of hydrated fillers is limited, moreover, the high loadings necessary to meet flame

resistance requirements lead to changes in mechanical properties. However, mineral fillers may confer fire resistance by other means: leading to a lowering of radiative and convective heat transfer and of transfer of volatile compounds from the melted solid towards the gaseous phase [3].

In previous work, we tried to associate flame retardants made up of compounds of brominated trimethylphenyl indane/ $\text{Sb}_2\text{O}_3$  (20% wt) with  $\text{Mg}(\text{OH})_2$  [4] or talc (20% wt) [5] to obtain a good compromise between flame resistance and mechanical properties in a PP/PE copolymer. Concerning fire resistance properties, it appeared that talcs and particularly  $\text{Mg}(\text{OH})_2$  could significantly delay the ignition of these samples. Moreover, V0 class can be reached in the case of  $\text{Mg}(\text{OH})_2$  and in the case of the finest and purest talcs.

Differential thermal and thermogravimetric analysis were performed in addition to fire tests to investigate the behaviour of mixed compositions and particularly to ascertain the role of fillers and their possible interactions with the brominated trimethylphenyl indane/ $\text{Sb}_2\text{O}_3$  flame retardant. However, due to the complexity of DTA/TGA spectra, many interpretations seemed tenta-

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tive. In consequence, the use of a coupling between these techniques and infrared spectroscopy was expected to provide more information and remove doubts about these interpretations. This coupling was first carried out on pure copolymer and then on copolymers filled with  $\text{Mg}(\text{OH})_2$ , and then with the brominated trimethylphenyl indane/ $\text{Sb}_2\text{O}_3$ , and finally on mixed compositions of this last blend with  $\text{Mg}(\text{OH})_2$  and talc-containing fillers. DTA/TGA curves were recorded and completed with the derivative of TGA curve (called DTG). Recording of on line IR spectra was completed by the plotting of Gram Schmidt curves, which provide information about the evolution of gases evolving from heated samples.

## 2. Experimental

### 2.1. Materials

The PP/PE copolymer studied was supplied by Appryl, Lavera, France (3150 MN 5). Its main characteristics are: Young's Modulus = 1300 MPa, yield tensile stress = 26 MPa, notched Charpy impact resistance at 23°C = 7 kJ/m<sup>2</sup>, melt index = 12 g/min.

Brominated flame retardant was made up of 75% brominated trimethylphenyl indane (FR 1808, 73% bromine in weight, Dead Sea Bromine Group, Beer Sheva, Israel) and 25% antimony trioxide (Antiox BS RG, La Compagnie Chimique et Métallurgique, Campine, Belgium). The median sizes of antimony trioxide and magnesium hydroxide (Dead Sea Bromine Group, Beer Sheva, Israel) are respectively 2.3 and 1.5 microns. Their surface areas are, respectively, 2 and 6.5 m<sup>2</sup>/g. Magnesium hydroxide was treated by fatty acids (2% wt) prior to incorporation.

Two fillers A and B, containing various amounts of talc and carbonates (Tals de Luzenac, Toulouse, France) were used: A is a quite pure talc (97% wt). B is made up of dolomite (Ca and Mg carbonate, 70% wt) and talc (25% wt). Their median diameters are, respectively, 2.3 and 7.1 microns and their specific surface areas are respectively 10.0 and 5.5 m<sup>2</sup>/g.

Compounds were prepared at temperatures near 200°C using a Clextral BC 21 twin screw extruder. Their compositions are presented in Table 1. Dumbbell specimens were produced at temperatures near 260°C using

an Otto 95 Sandretto injection moulding procedure. Samples used in DTA/TGA-FTIR experiments (around 50 mg) were cut from above moulded specimens.

### 2.2. DTA/TGA-FTIR coupling

A differential thermal analysis instrument was combined with a thermogravimetric apparatus SETARAM TGDTA92 (Lyon, France). Standard platinum crucibles were used, and measurements were carried out in a dynamic air or argon atmosphere (gas carrier) at a heating rate of 5°C/min up to 650°C with samples weights around 50 mg.

The FTIR instrument is a Bruker IFS 66 (Karlsruhe, Germany). The gaseous compounds are removed by the gas carrier of the DTA/TGA apparatus through a heatable transfer line (200°C) to a heated gas cell (200°C) of 22 ml. This cell is heated to prevent gas condensation on the outer (KBr) and the inner (ZnSe) windows. An IR beam goes through the gas cell so that the gaseous compounds are analyzed by transmission. The detector is a liquid nitrogen cooled MCT (Hg-Cd-Te, 4800–600 cm<sup>-1</sup>) detector. Carrier gases used are transparent to the IR beam.

Each IR spectrum is an average of 8 spectra measured at a resolution of 8 cm<sup>-1</sup>. Spectra are calculated from the algorithms working directly on the interferometric data. The Gram-Schmidt orthogonalization technique, initially developed in the chromatographic area, was recently applied to the analysis of polymer degradation by TGA coupled with FTIR [6–8]. It can be carried out on the whole range of spectra or only on a range corresponding to a specific evolving gas, which allows a quantitative analysis of these gases to be performed. In this study, the evolution of water vapor, carbon dioxide gas (CO<sub>2</sub>) and combustible gases were determined. The combustible gases were assumed to be aliphatic or unsaturated alkanes. Therefore, the Gram-Schmidt orthogonalization technique was applied in the range 4040–3400 cm<sup>-1</sup> for the water vapor, 2410–2220 cm<sup>-1</sup> for the CO<sub>2</sub> gas and 3120–2755 cm<sup>-1</sup> for the combustible gases. Each range above corresponds respectively to the bending vibrations of the O–H bond for the water vapor, of the C=O bond for CO<sub>2</sub> and of the C–C or C=C bonds for combustible gases. The deformation vibrations of these bonds were not taken into account because they overlap one another.

Table 1  
Flame retardant compositions of the PP/PE copolymer

	PP/PE	Mg(OH) <sub>2</sub>	FR 1808	Sb <sub>2</sub> O <sub>3</sub>	Filler A	Filler B
PP/PE + Mg(OH) <sub>2</sub>	36	64	0	0	0	0
PP/PE + FR/Sb	60	0	30	10	0	0
PP/PE + FR/Sb + Mg(OH) <sub>2</sub>	60	20	15	5	0	0
PP/PE + FR/Sb + Filler A	60	0	15	5	20	0
PP/PE + FR/Sb + Filler B	60	0	15	5	0	20

### 2.3. Fire tests

DTA/TGA-FTIR experiments were compared with the fire tests previously carried out: UL 94 tests and determination of ignition times (AFNOR NF P 92-505). In this last test  $70 \times 70 \times 4$  mm<sup>3</sup> samples are exposed to a 500 W radiator. Samples are placed on a grid located 30 mm under the bottom of the epiradiator. Results concerning the use of talc-based fillers are given in Ref. [5]. Results concerning Mg(OH)<sub>2</sub> in a similar PP/PE copolymer are given in Ref. [4].

## 3. Results and discussion

### 3.1. Decomposition of PP/PE copolymer

Decomposition of PP/PE copolymer was carried out under air and argon. Fig. 1 shows the heat flow and the sample temperature curves of PP/PE copolymer heated under air or argon. Fig. 2 presents the weight loss and DTG (TGA and derivative of TGA) curves. Fusion of PP crystallites appears on both heat flow curves at 160°C. The presence of oxygen is responsible for an exothermic peak of thermooxidation appearing close to 240°C, followed by an endothermic one from 270°C due to the breaking of the macromolecules. Owing to the well known action of oxygen in reducing the stability of polymer bonds when temperature increases, this phenomenon occurs at a lower temperatures than with argon (from 375°C). Moreover, combustible volatile vapours accumulate despite the gas stream. This leads, in the case of air, to an ignition phenomenon which finds expression in a strong exothermic peak in the DTA curve at a temperature close to 400°C. The sudden ignition

limits the ability of the apparatus to regulate the sample temperature which rises by up to 40°C above the corresponding linear temperature programme in argon.

The IR spectrum of evolved combustible gases outlined at 427°C (Fig. 3) shows that alkenes with alkyl side chains are the main decomposition components in argon. Table 2 lists some of the several compounds found using a vapor phase FTIR library and Fig. 3 shows the good agreement between experimental data and one of the compiled IR spectra (2,3-dimethyl 1-hexene). The hit quality index is an index of accuracy between the experimental infrared spectrum and the library spectrum, based on the location and intensity of the peaks; it is calculated on a [0–1000] scale, 1000 corresponding to the best agreement.

Fig. 4 represents the Gram–Schmidt curves corresponding to combustible gases, carbon dioxide and water vapor in the case of the oxidant decomposition and only to combustible gases in the case of non-oxidant decomposition. Gram–Schmidt curves are outlined in respect to the same weight of copolymer (1 g). One can observe that maximal production of the three gases occurs at the same time. The good correlation between on-line FTIR spectroscopy and DTA/TGA analysis is highlighted by the same values of time for Gram–Schmidt and DTG maxima.

### 3.2. Decomposition of flame retarded PP/PE copolymer with Br/Sb blend and Mg(OH)<sub>2</sub>

#### 3.2.1. Comparison of the Br/Sb blend and Mg(OH)<sub>2</sub> flame retardant properties

The synergistic action of organohalogenated compounds and antimony trioxide as flame retardants is very well known and some authors [1,9,10] have pro-

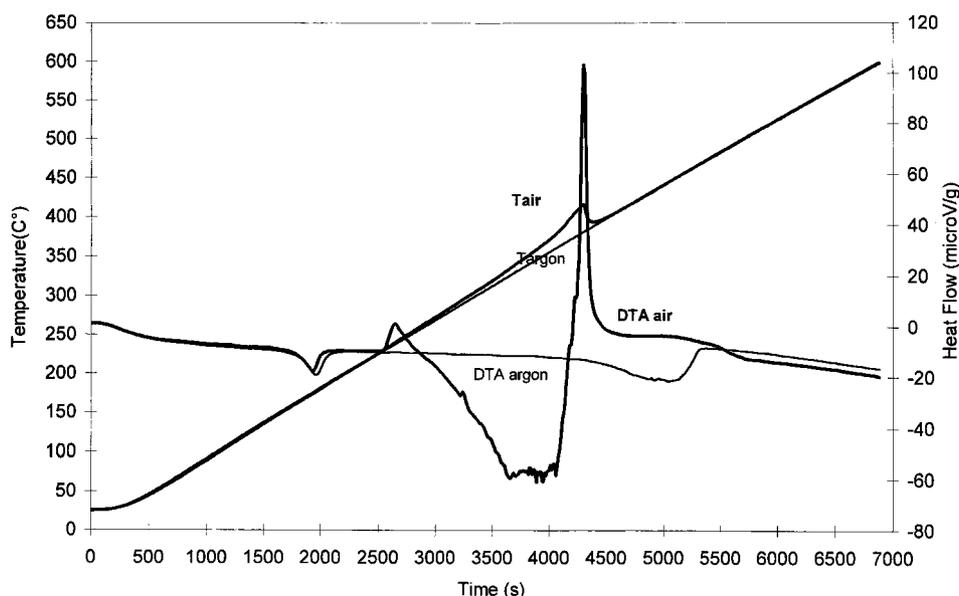


Fig. 1. DTA curve and sample temperature of PP/PE copolymer under air and argon.

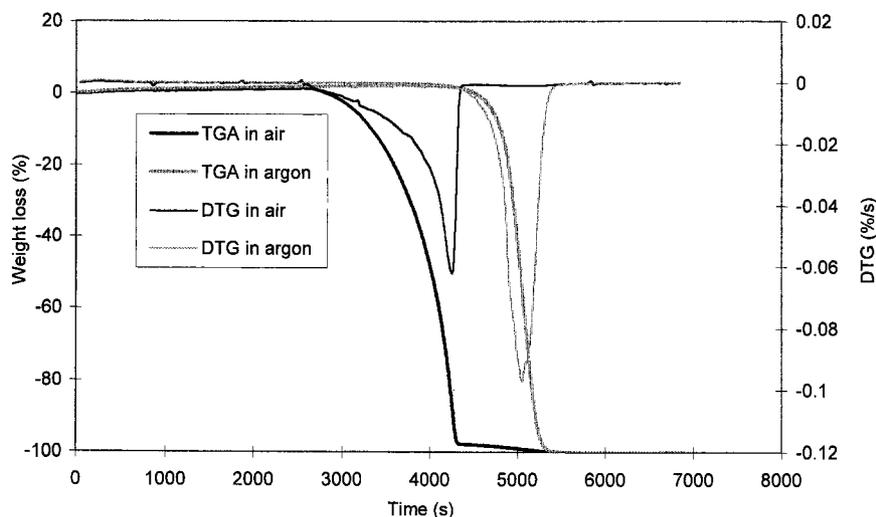


Fig. 2. TGA and DTG of PP/PE copolymer in air and argon.

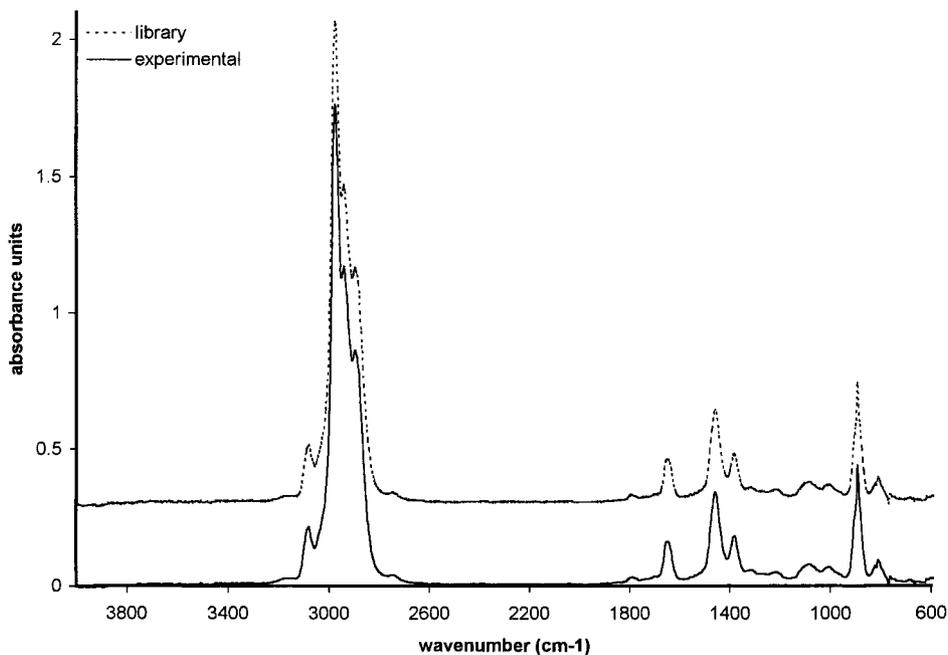


Fig. 3. IR spectrum of evolved combustible gases outlined at 427°C and comparison with a selected alkene library spectrum.

posed or reported detailed mechanisms of reaction. The interaction of both components generates free radicals able to modify the flame chemistry and particularly to react with the OH· and H· radicals, which are very active in an oxidant degradation of a polymer. The use of brominated flame retardants containing antimony trioxide also produces specific degradation products like antimony tribromide, antimony oxybromides and hydrogen bromide.

**3.2.1.1. Fire tests results.** Fire tests carried out on the PP/PE copolymer [4] showed that a 40% loading in brominated trimethylphenyl indane/Sb<sub>2</sub>O<sub>3</sub> corresponds

to a V0 class at UL 94 test. In fact, the Br/Sb flame retardant acting mainly in the gaseous phase may reduce the ignition periods to one second or less. The time of first ignition after exposure to the radiator is also increased (Table 3) in comparison with the unloaded polymer.

The action of magnesium hydroxide as flame retardant is also well known. The endothermic loss of water (30% wt) occurring close to 350°C [11,12] cools the condensed phase and dilutes the gaseous phase containing the flammable gases evolving from the polymer. High loadings (more than 60% wt in PP) are required to meet competitive behaviour with brominated flame

Table 2  
Report of IRFT spectrum search

Compound name	Hit quality	Molecular formula	Molecular weight (g/mol)	CAS registry number
2,3-dimethyl 1-hexene	830	C <sub>8</sub> H <sub>16</sub>	112.22	16746-86-4
2-ethyl 1-butene	773	C <sub>6</sub> H <sub>12</sub>	84.16	1632-16-2
2-methyl 1-pentene	682	C <sub>6</sub> H <sub>12</sub>	84.16	763-29-1
2-ethyl 1-hexene	631	C <sub>8</sub> H <sub>16</sub>	112.22	760-21-4
2-methyl 1-butene	559	C <sub>5</sub> H <sub>10</sub>	70.14	563-46-2

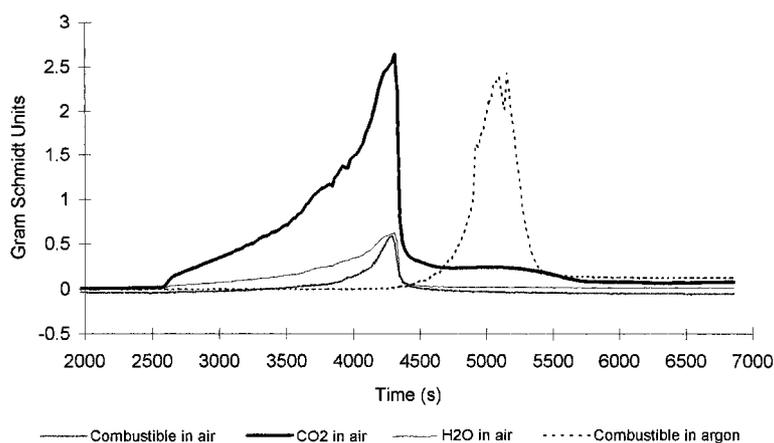


Fig. 4. Gram-Schmidt curves of evolving gases in air and argon.

retardants. Fire tests previously carried out on 64% Mg(OH)<sub>2</sub> loaded PP/PE copolymer [4] showed that ignition periods are significantly higher than with brominated flame retardants. Conversely, times of first ignition are longer (Table 3). The combination of equal weights of the two kinds of flame retardants resulted in intermediate values for ignition periods of polymer. A strong increase in first ignition time may suggest that a synergism occurs at the first stages of thermal degradation of the polymer.

**3.2.1.2. TGA spectra.** The interest of the incorporation of the above additives is illustrated by the TGA spectra (Fig. 5). Weight losses indicated on the graphic correspond to relative values plotted as for the same weight (1 g) for the different samples. Each composition containing additives delays the time for a given weight loss fraction. Time-temperature correspondences for each sample are indicated in Fig. 6.

Table 3  
Ignition time in radiator test (AFNOR NF P 92-505)

Composition	Ignition time (s)
PP/PE	43
PP/PE + Mg(OH) <sub>2</sub>	58
PP/PE + FR/Sb	49
PP/PE + FR/Sb + Mg(OH) <sub>2</sub>	73
PP/PE + FR/Sb + Filler A	59
PP/PE + FR/Sb + Filler B	49

Since the composition of the brominated compound/Sb<sub>2</sub>O<sub>3</sub> mixture was optimized in order to maximize its reactivity, the loss of weight of the sample which goes together is complete. In samples containing magnesium hydroxide, the calcinated residue contains mainly magnesium oxide. The relative location of TGA curves seems to indicate that the brominated flame retardant is more efficient than magnesium hydroxide.

Moreover, some particular features appear on TGA curves. The use of differential curves (DTG, Fig. 7) allows a better understanding of the decomposition phenomena by showing two domains in the case of sample PP/PE containing the Br/Sb mixture, each one corresponding to the appearance of a DTG peak. The first part of the DTG curve (360–385°C) is delayed in comparison with that of unloaded copolymer but it has a similar slope. This evolution can be ascribed mainly to the single decomposition of the polymer. The second part of the DTG curve occurs after a slowing down of the decomposition rate due to the action of the flame retardant. A preliminary analysis of the brominated compound/Sb<sub>2</sub>O<sub>3</sub> mixture by TGA/DTA revealed that the two components react together from around 375°C, giving rise to an exothermic effect.

Concerning the Mg(OH)<sub>2</sub> filled sample, the range of filler decomposition with water vapor release (315–360°C) is clearly visible on DTG curve. This range corresponds to a lower decomposition rate than observed for higher temperatures. Beyond the release of water the decomposition rate increases until a maximum value

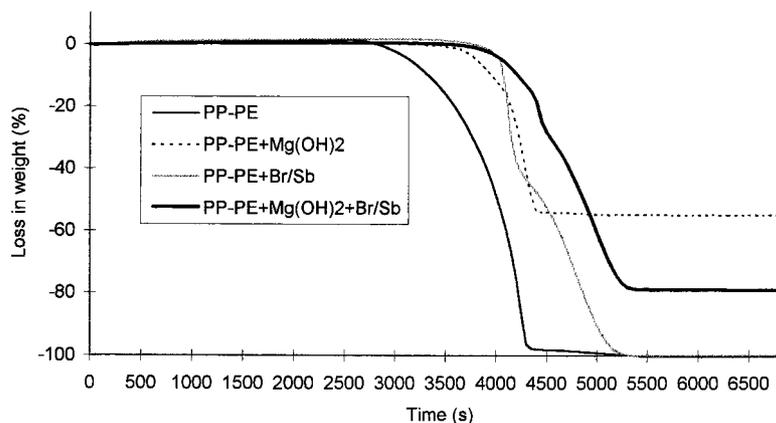


Fig. 5. TGA curves of PP/PE copolymer containing flame retardants.

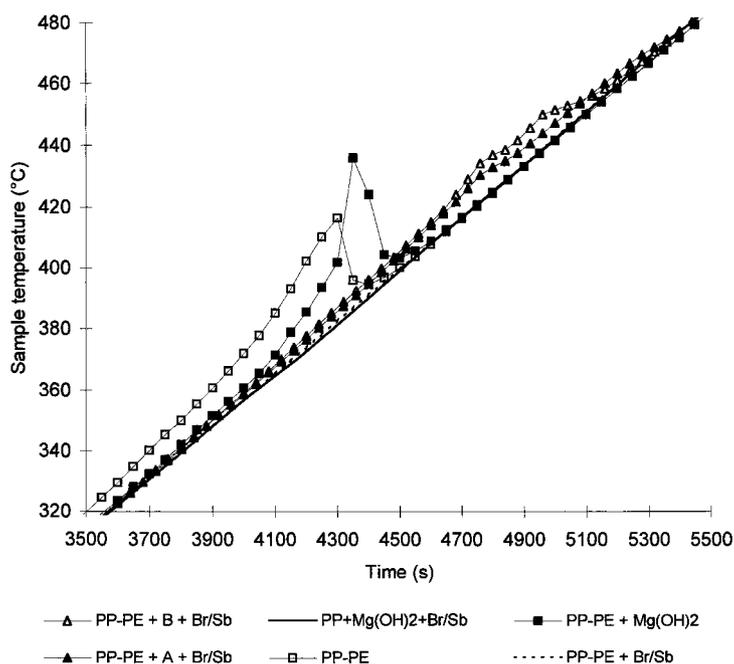


Fig. 6. Sample temperatures in DTA-DTG experiments under air atmosphere.

near 380°C. This maximum occurs later than in the case of the unloaded copolymer (365°C), nevertheless the slope of the DTG curve after water release seems higher in the case of the  $Mg(OH)_2$  filled sample.

**3.2.1.3. DTA spectra.** DTA curves of  $Mg(OH)_2$  filled and unfilled copolymer (Fig. 8) are in good accordance with TGA curves. The endothermic release of water cools the copolymer and reduces the breaking of macromolecules occurring beyond 250°C. While the endothermic effect observed on the unfilled sample is mainly due to the breaking of chains, that observed on the filled sample can also be ascribed to the endothermic release of water from magnesium hydroxide. The presence of the mineral delays the exothermic decomposition of the copolymer. Nevertheless this last phenomenon seems

stronger in the case of the filled copolymer. Moreover, we can notice that the intensity of these exothermic events causes a significant increase in sample temperatures as compared with expected (Fig. 6).

The DTA curve (Fig. 8) of the copolymer containing the brominated flame retardant shows only small heat flows in comparison with above samples. Moreover, the scale of the figure limits the resolution. The most interesting features of this curve are grouped together in the insert on Fig. 8 and correspond to the exothermic reaction between the brominated compound and the antimony trioxide (375 to 385°C) and the endothermic peak caused by the breaking of the copolymer chains (400 to 460°C). One can notice that this last phenomenon occurs in the same range as the unfilled copolymer decomposition in argon.

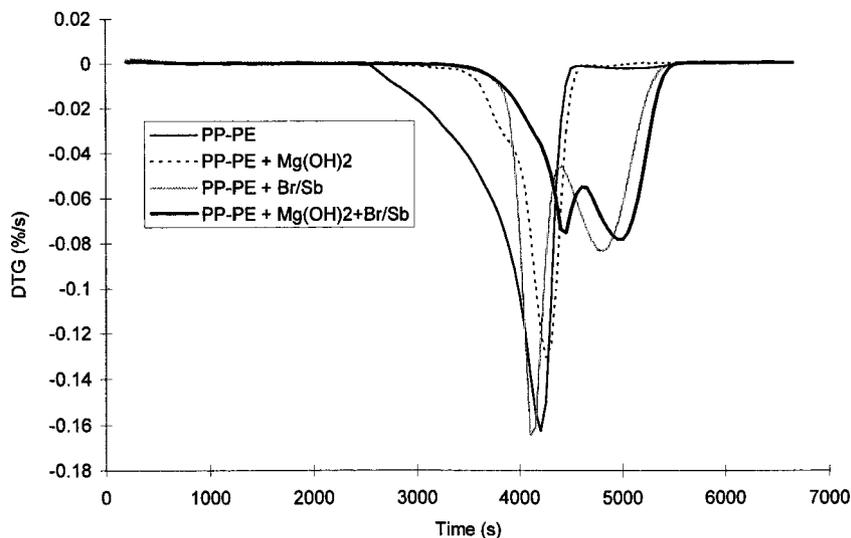


Fig. 7. DTG curves of PP/PE copolymer containing flame retardants.

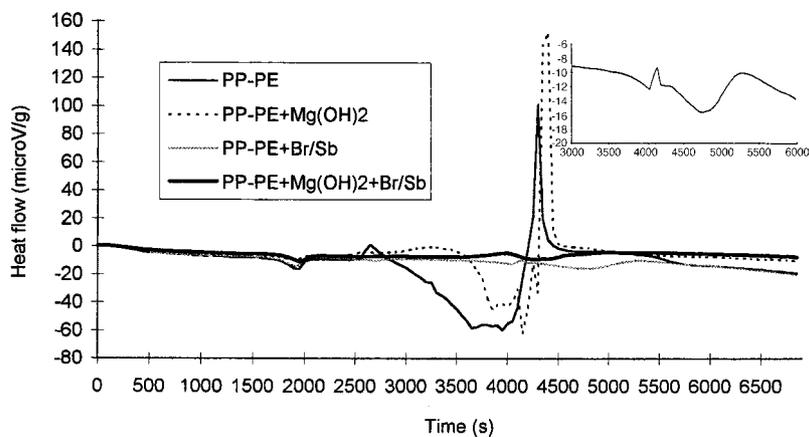


Fig. 8. DTA curves of PP/PE copolymer containing flame retardants.

3.2.1.4. Gram–Schmidt curves. The Gram–Schmidt curves corresponding to combustible gases, CO<sub>2</sub> and H<sub>2</sub>O vapors evolving from the Mg(OH)<sub>2</sub> filled and unfilled samples (Figs. 4 and 9) confirm these interpretations. The amount of the three kind of gases evolved is delayed and reduced with the introduction of the hydrated filler. For the filled sample, the decomposition of filler occurring from 315°C leads to a slowing down of the CO<sub>2</sub> release until 365°C. Up to this value the release of combustible vapors not degraded into CO<sub>2</sub> and H<sub>2</sub>O is negligible. A same maximum for the Gram–Schmidt curves is attained for 390°C in the case of the filled sample. Only a slight lag exists between the Gram–Schmidt and DTG maxima.

The effect of the brominated FR appears also on the corresponding Gram–Schmidt curves (Fig. 10). No significant amount of effluents is noted up to 350°C. In the range 350–385°C, peaks of combustible gases and water appear. However, at 385°C, the peak of combustible

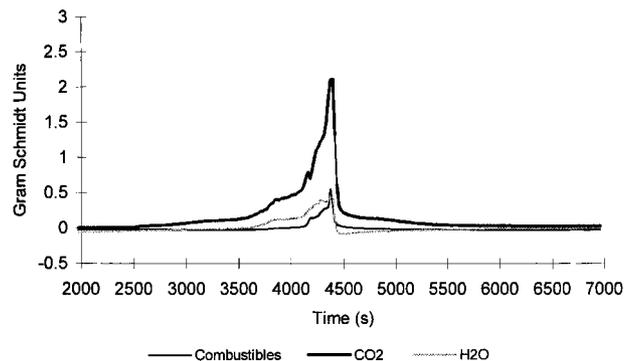


Fig. 9. Gram–Schmidt curves of PP/PE+Mg(OH)<sub>2</sub> evolving gases in air.

volatiles diminishes, the peak of water disappears. This means that the ignition phenomena are considerably limited due to the reaction between the components of the brominated FR. Beyond 385°C, the only presence of

a peak of combustible volatiles indicates the lack of ignition and a decomposition similar to this occurring in a non-oxidant atmosphere. Here, one can observe a very good agreement between the two maxima of each curve (DTG and Gram–Schmidt).

### 3.2.2. Combination of the Br/Sb blend and Mg(OH)<sub>2</sub>

The combination of the brominated flame retardant with magnesium hydroxide provides the better resistance to the thermal decomposition for the PP/PE copolymer (Fig. 5). The DTG curve (Fig. 7) also has two peaks, as in the case of the copolymer with the brominated flame retardant. This behaviour can be interpreted in the same way. Furthermore, the DTG shows the decomposition of the magnesium hydroxide at the first stages of weight loss. This decomposition begins at the same temperature (335°C) as in the Mg(OH)<sub>2</sub> filled copolymer, but the release of water seems to occur in a larger range (until 385°C instead of 360°C).

One can also notice that the two DTG peaks are shifted towards high temperatures. The difference can be estimated at 25°C. This seems to indicate complex “relay effects” corresponding to a synergism between the brominated FR and Mg(OH)<sub>2</sub>. However, the DTA curve corresponding to this mixed composition (Fig. 8) appears difficult to interpret, due to the relatively low intensity and overlapping of the thermal phenomena.

Gram–Schmidt curves (Fig. 11) account for the interpretation of TGA curves. The first release is water vapor corresponding to the decomposition of Mg(OH)<sub>2</sub> in the same range as indicated on the DTG curve. This peak and that of water produced by a limited ignition of the sample overlap each other. The first maximum on the DTG curve corresponds to peaks for all the effluents at 400°C, the second maximum at 450°C corresponds to the highest peak in the Gram–Schmidt figure due only to the release of combustible gases.

The interpretation of the synergism evoked above can be made on the basis of the following scenario of thermal decomposition and flame retardancy.

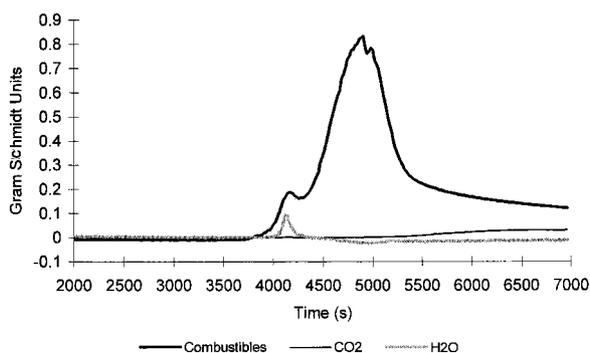


Fig. 10. Gram–Schmidt curves of PP/PE + Br/Sb evolving gases in air.

It has been shown that the brominated compound alone limits the thermal degradation of the polymers [1,9]. Consequently, at temperatures lower than that of its reaction with Sb<sub>2</sub>O<sub>3</sub>, around 375°C (see above), the decomposition of the PP/PE is slowed down due to the interactions with the decomposition products of the brominated compound. Using DTA/TGA coupled with FTIR, it is possible to detect its slow decomposition occurring even before its fusion at 250°C.

From 300°C, the decomposition of Mg(OH)<sub>2</sub> cools the sample and reduces the decomposition of the copolymer and the brominated compound. Since the release of combustible volatiles is now delayed in comparison with the sample containing the brominated compound but not the magnesium hydroxide, the synergistic action of the brominated compound with antimony trioxide is also delayed. This can explain the DTG peak shifts observed on the two corresponding curves. In consequence, the combination of Mg(OH)<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub> and the brominated compound appears to extend the thermal stability of the PP/PE copolymer.

### 3.3. Decomposition of flame retarded PP/PE copolymer with Br/Sb blend and fillers containing talc

Several authors have mentioned the influence of non-hydrated fillers, as regards flame retardant activity [3,13]. They generally tend to increase thermal conductivity but they may increase radiative heat losses of the sample when it is exposed to a heat source. Moreover, it has been shown that some mineral fillers act as diffusion barriers for the combustible volatile gases. Factors like fineness, shape (aspect ratio), filler–polymer adhesion and nucleation ability were proposed to interpret the enhancement of ignition time in the case of talc [5].

#### 3.3.1. Fire tests results

Concerning ignition time and the only two fillers tested in the present study, it was observed that a high content of calcium carbonate is far less interesting than a very pure talc (Table 3), both fillers also being tested

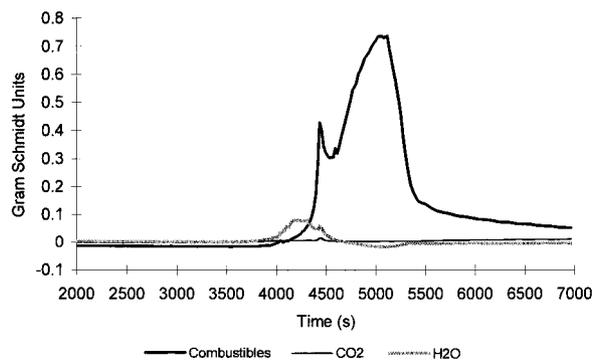


Fig. 11. Gram–Schmidt curves of PP/PE + Br/Sb + Mg(OH)<sub>2</sub> evolving gases in air.

in combination with the above brominated retardant. The same conclusion could also be deduced from UL 94 tests.

### 3.3.2. TGA and DTA spectra

The examination of the corresponding TGA and DTA curves (Figs. 12 and 13) does not show any significant differences between the two fillers. The DTG curves (Fig. 14) are made up of two peaks, similar to the above compositions containing the brominated flame retardant. However, the peak shifts towards high temperature are less marked.

The decomposition of the two filled samples begins significantly at intermediate temperatures in comparison to unfilled polymer and those containing the brominated compound. Conversely, the second DTG peak is now larger than the first one. It indicates a more important rate of decomposition in the zone of action of the components of the brominated flame retardant.

DTA curves show strong exothermic peaks in the range 420–440°C and the exothermicity seems slightly more important in the case of the filler containing CaCO<sub>3</sub>. In comparison to the unfilled sample, the range of exothermic phenomena is more extended. It seems to group together the thermooxidation of the copolymer,

the reaction between the components of the brominated flame retardant and the combustion of volatiles at high rates of decomposition.

Fig. 6 shows that the increase of sample temperature in respect to the linear progression is less and appears later than in the case of the unfilled sample.

### 3.3.3. Gram-Schmidt curves

Gram-Schmidt curves (Figs. 15 and 16) confirm the existence of a wide range of decomposition with ignition for the two samples. However, the release of gases seems to begin later when the filler is a pure fine talc. In fact, from the DTA/TGA-FTIR results it can be deduced that these mixed compositions behave like PP/PE loaded with an insufficient amount of brominated flame retardant to avoid ignition phenomena. The considerable production of combustible volatiles from 335°C entails an early action of this one.

It slows down the decomposition rate at a lower temperature than above compositions with the same composition of flame retardant (see DTG curves). The large consumption of this latter renders it not efficient enough to avoid the combustion phenomena observed in the 420–440°C range.

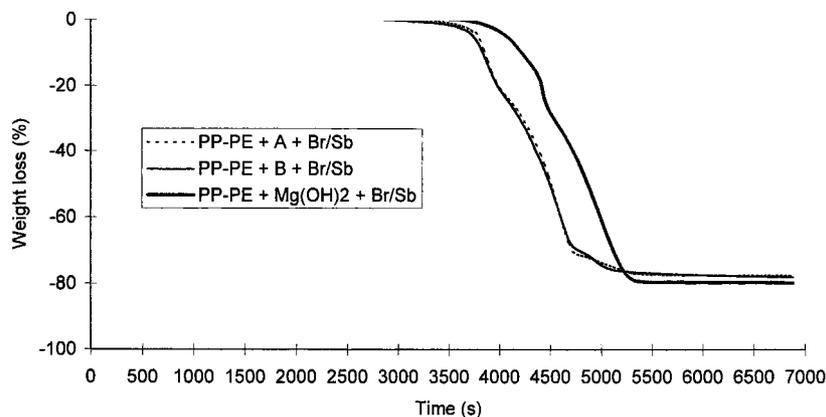


Fig. 12. TGA curves of filled PP/PE copolymer containing Br/Sb flame retardants.

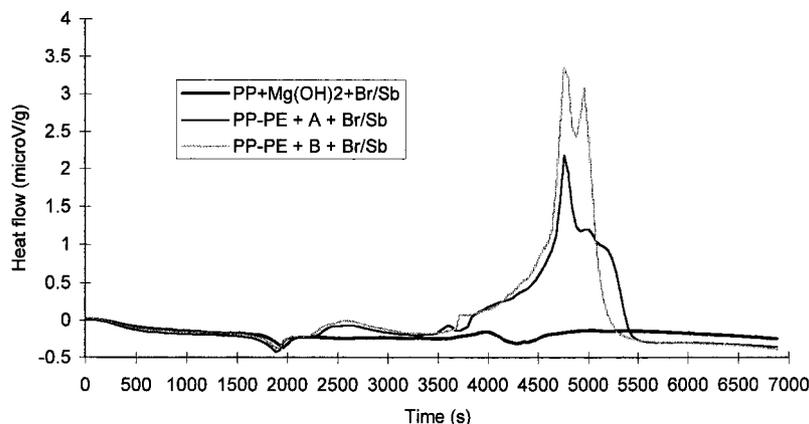


Fig. 13. DTA curves of filled PP/PE copolymer containing Br/Sb flame retardants.

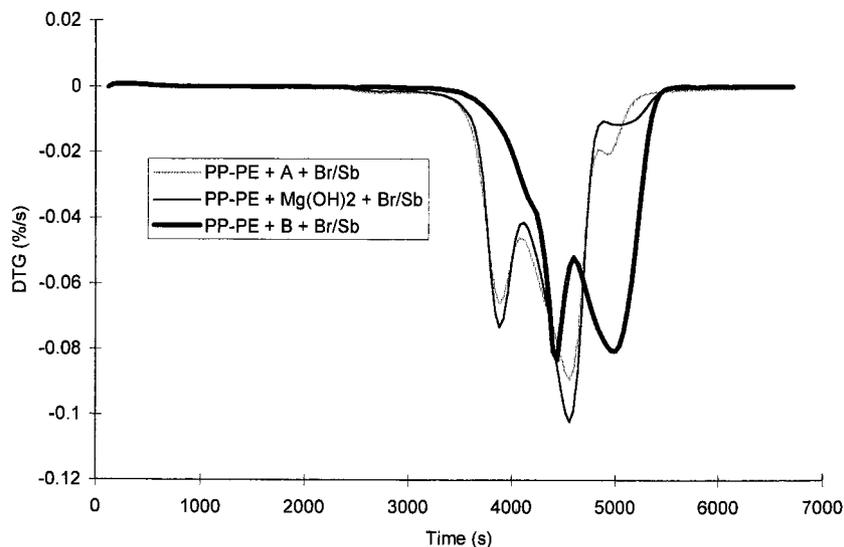


Fig. 14. DTG curves of filled PP/PE copolymer containing Br/Sb flame retardants.

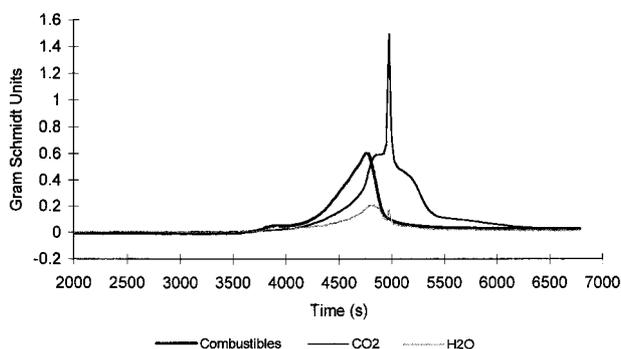


Fig. 15. Gram-Schmidt curves of PP/PE + A + Br/Sb.

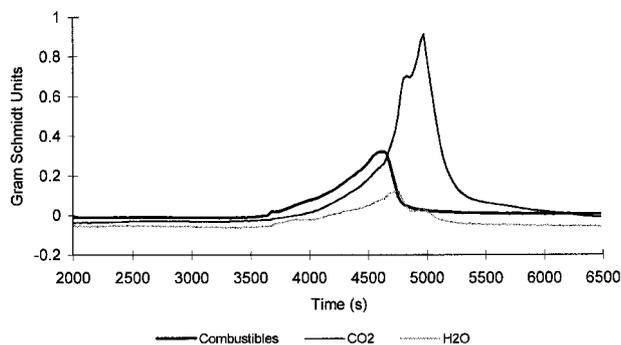


Fig. 16. Gram-Schmidt curves of PP/PE + B + Br/Sb.

Taking into account the low volume of the sample used in our experiments, fire resistance mechanisms involving the possible formation of diffusion barriers to decomposition gases in the condensed phase should not be very effective. The significant differences in fire resistance tests noticed for mixed compositions containing the two fillers may consequently be ascribed to the sample size being too small to allow such mechanisms to be clearly discerned.

#### 4. Conclusion

This study has been carried out in order firstly to appraise the connections between DTA/TGA analysis and on-line FTIR in the case of flame retardant compositions. In particular, our purpose consisted in examining whether a good agreement exists between DTA/TGA-FTIR analysis performed with low weight samples (some mg) and results gained from standardized fire resistance tests carried out with appropriate specimens (some g).

Moreover, in the case of combinations of hydrated or non-hydrated fillers in combination with a brominated flame retardant in a PP/PE copolymer, our objective was also secondly to ascertain the role of fillers as regards fire resistance.

Concerning the first point, the DTA/TGA coupling with FTIR appears to be a very useful tool, since it helps to interpret TGA and DTA curves which can be relatively complex in the case of flame retarded compositions. In addition, the comparison between DTG plots and the Gram-Schmidt curves for each kind of gas evolved is of further interest.

Then, the results obtained using this coupling of techniques allow us to complete those provided by previous studies using fire resistance tests. In that way, the synergism observed in the radiator test for the combination of  $Mg(OH)_2$  and brominated trimethylphenyl indan/ $Sb_2O_3$  blend which concerns first ignition, is also highlighted using DTA/TGA-FTIR. A decomposition scenario is proposed to interpret the behaviour of this mixed composition. This accounts for the use of such a combination for improving the fire resistance of PP/PE copolymers.

The DTA/TGA-FTIR coupling shows also the limitation of use of  $Mg(OH)_2$  as flame retardant. After the

release of water from the filler, the decomposition rate of the polymer increases dramatically, with a strong exothermic effect due to the ignition of combustible vapors. The use of  $\text{Mg}(\text{OH})_2$  alone consequently seems to be restricted to objects thick enough to allow a continuous release of water vapor during combustion.

The low volume of sample used in DTA/TGA-FTIR experiments limits the effect connected to the existence of mass or temperature gradients and mass or heat transfer. Consequently, results obtained with this coupling of techniques may differ from tests performed on larger specimens. The interest of the incorporation of fine and lamellar particles such as talc cannot be clearly discerned either in comparison with other fillers.

## References

- [1] Troitsch HJ. Flame retardants in plastics additives. In: Gaechter R, Mueller H, editors. *Plastics additives*. Hanser, 1993 [chapter 12].
- [2] Smith R, Georlette P, Finberg I, Reznick G. *Polym Degrad Stab* 1996;54:167.
- [3] Tserikidze O, Khalturinskij N. *Int J Polym Mater* 1993;20:75.
- [4] Montezin F, Lopez Cuesta J-M, Crespy A, Georlette P. *Fire and Materials* 1997;21:245.
- [5] Longerey M, Lopez Cuesta J-M, Gaudon P, Crespy A. *Polym Degrad Stab* 1999;64:489.
- [6] Mullens J, Reggers G, Ruysen M, Carleer R, Yperman J, Franco D, Van Poucke LC. *J Thermal Anal* 1997;49:1061.
- [7] Mullens J, Carleer R, Reggers G, Ruysen M, Yperman J, Van Poucke LC. *Bull Soc Chim Belg* 1992;101:267.
- [8] Pielichowski K, Hamerton I. *Polymer* 1998;39:241.
- [9] Camino G, Costa L. *Polym Degrad Stab* 1988;20:271.
- [10] Touval I. Antimony oxide. In: Milewski JV, Katz HS, editors. *Handbook of fillers for plastics*. Van Nostrand Reinhold, 1987 [chapter 5].
- [11] Hornsby PR, Watson CL. *Polym Degrad Stab* 1990;30:73.
- [12] Ashley RJ, Rothon RN. *Plast Rubber Compos Process Appl* 1991;15:19.
- [13] Rothon RN. Effects of particulate fillers on flame-retardant properties of composites. In: Rothon RN, editor. *Particulate-filled polymer composites*. Longman Scientific and Technical, 1995 [chapter 6].