*Macromol. Symp.* **2003**, *198,* 435-447

# Effect of Fillers on Fire Retardancy of Intumescent Polypropylene Blends

*X. Almeras,*[1] *M. Le Bras,**[1] *F. Poutch,*[2] *S. Bourbigot,*[3] *G. Marosi,*[4] *P. Anna*[4]

[1]Laboratoire PERF UPRES EA 1040, ENSC-Lille, BP 108, 59652 Villeneuve d'Ascq Cedex France
E-mail: Michel.Le-Bras@ensc-lille.fr
[2]CREPIM Bruay la Buissière, France
[3]ENSAIT, Gemtex, Roubaix, France
[4]Technical University of Budapest, Hungary

**Summary:** Addition of Ammonium Polyphosphate/Polyamide-6 system is known to provide flame retardancy in many polymers blends via an intumescent process. Particulate fillers (talc and calcium carbonate) are used in large quantities in PP. Combination of fillers in PP can modify the properties of the polymeric matrix.
This study investigates the effect of fillers (talc and calcium carbonate) on the fire performance of the Polypropylene/Ammonium polyphosphate/Polyamide-6 blend. It is shown that the fire performance strongly depends on the nature of the filler used. Talc increases and calcium carbonate decreases in the fire performance of the blend.

**Keywords:** ammonium polyphosphate, cone calorimetry, intumescence, polyamide-6, polypropylene, talc and $CaCO_3$

## Introduction

Polypropylene (PP) is representing a big part of polymer worldwide consumption just after polyvinyl chloride and polyethylene. Addition of low cost fillers such as calcium carbonate or talc, was historically justified by cost reduction but more and more improvement of performance becomes the main driver. The low cost material have numerous advantages like a high modulus, excellent chemical resistance and easy process conversion. This explains why the polymer has grow significantly in automotive or appliances.[1]

Moreover, for safety reasons, applications of polyolefinic materials in common transport, materials require fire retardant properties. One way to increase the fire properties is to develop intumescent systems.

Intumescent technology[2],[3] has found a place in polymer science as a method of providing flame retardancy to polymeric materials.[4],[5] On heating, fire retardant (FR) intumescent materials form a foamed cellular charred layer on their surfaces, which protects the underlying materials from the action of heat flux and flame. The proposed mechanism is based on the

DOI: 10.1002/masy.200350837

charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phase.[6] Generally, intumescent formulations contain three ingredients: an acidic source, a carbonisation agent and a blowing agent.

It was shown that incorporating ammonium polyphosphate (APP) in polyamide 6 (PA-6) provides fire properties of interest.[7]-[8] However, the compatibility of the APP/PA6 blends obtained by direct mixing of APP in melted PA-6, is low : a migration of the mineral salt [9] occurs during solidification of the melt. In this case, the use of an interfacial agent is required. Ethylene-vinyl-acetate (EVA) copolymers, which are known to be very efficient interfacial agents[10]-[11] have thus been used as compatibilisers in the intumescent PP/APP/PA6 system. That has been revealed using calorimetry by oxygen consumption that fire properties of interest were obtained by using $EVA_{24}$ as interfacial agent in the PP/APP/PA-6 intumescent system.[12] Moreover, some authors have shown that fillers, particularly glass fibres, have a great influence on the fire properties and lead to an increase in the fire performance.[13]

In this study, the effect of talc and calcium carbonate on the fire properties are investigated and compared with the PP/PA-6/APP/$EVA_{24}$ system without fillers.

## Experimental

### Materials

Raw materials were polypropylene (homopolymer grade 3120 MN 1 MFI 8 (230°C, 2.16kg), as pellets supplied by Appryl), PA-6 (as pellets supplied by Nyltech), APP (AP 462: $(NH_4PO_3)_n$, $n \approx 700$, powder supplied by Clariant), $EVA_{24}$ supplied as pellets by Elf-Atochem (EVATANE grades). Polypropylene talc (PPTALC, MFI Polyfort FPP 20 T as pellets supplied by Schulman S.A. hereafter called talcom).

Two fillers were added into the polypropylene : Talc (mean size of particles 15 μm supplied by Suommen takki) and Calcium carbonate (mean size particles 2.5 μm supplied by Omnia).

### Processing and Formulations

The fillers (talc and $CaCO_3$ without sizing agent) were added to PP using a Brabender DSK 42/7 intermeshing counter-rotating twin-screw extruder at 190°C and 150 rpm to obtain a composite with mineral loading of 20 wt-%. Then the PP composites were mixed with PA-6, APP, and $EVA_{24}$ using a Brabender Mixer measuring head (type 350/EH, roller blades) at 230°C and 50 rpm. We have checked the mixing conditions using the data processing torque rheometer system Brabender Plasticorder PL2000. Sheets ($100 \times 100 \times 3\ mm^3$) were then obtained using a Darragon pressing machine at 200°C and at a pressure of $10^6$ Pa. The different processed blends mixed are listed in Table 1.

Table 1. Composition of the PP based blends.

| PP (wt-%) | PA-6 (wt-%) | APP (wt-%) | Talc (wt-%) | $CaCO_3$ (wt-%) | $EVA_{24}$ (wt-%) | Samples label |
|---|---|---|---|---|---|---|
| 60 | 8.75 | 26.25 | | | 5 | Reference |
| 48 | 8.75 | 26.25 | 12 | | 5 | PPtalcom |
| 48 | 8.75 | 26.25 | 12 | | 5 | PPtalc |
| 48 | 8.75 | 26.25 | | 12 | 5 | PPcarb |

**Fire Testing**

Limiting Oxygen Index (LOI) was measured using a Stanton Redcroft instrument on sheets ($100x10x3$ $mm^3$) according to ASTM 2863.[14] UL-94 tests were carried out on $127x12.7x3$ $mm^3$ sheets according to the UL-94 testing.[15]

Samples are exposed to a Stanton Redcroft Cone Calorimeter according to ASTM 1356-90 and ISO 5660 at an external heat flux of 50 $kW/m^2$ which corresponds to the heat evolved during a fire.[16] Conventional data (Rate Heat Release (R.H.R.), Total Heat Emitted (T.H.E.), $CO/CO_2$ evolutions and residual mass) were computed using a software developed in our laboratory. For experiments performed at 50 $kW/m^2$, RHR and THE values were reproducible to within ±10% and weight loss, CO, $CO_2$ were reproducible to within ±15%. The data presented in the following are averages from at least 3 experiments.

**Thermal Analysis**

Thermogravimetric analyses were carried out at heating rate 10°C/min in a flowing synthetic air (Air Liquid grade; flow rate = $5.10^{-7}$ $Nm^3/s$) using a SETARAM MTB 10-8 thermobalance. In each case, samples were 10 mg and were positioned in open vitrous silica pans. The precision on temperature measurements is ± 1.5°C in the range 50°C-850°C.

The curves of weight difference between the experimental and theoretical TG curves are computed as follows : $\Delta(T)$ : curve of weight difference : $\Delta(T) = M_{exp}(T) - M_{th}(T)$. with:

$M_{th}(T)=(0.60-X)M_{poly}(T)+XM_{fill}(T)+0.2625M_{APP}(T)+0.0875M_{PA-6}(T)+0.05M_{EVA}(T)$.

Where $M_{poly}(T)$, $M_{APP}(T)$, $M_{PA\text{-}6}(T)$, $M_{fill}(T)$, $M_{EVA}(T)$ and $M_{exp}(T)$ are respectively the polymer weight, APP, PA-6, the fillers and of the blends given by their TG curves.

The $\Delta(T)$ curves allow to point out an eventual increase or decrease in the thermal stability of the polymeric matrix related to the presence of one or every additives.[17]

## Results

### Fire Testing

LOI values and UL-94 rating of the different blends are given in the Table 2.

Table 2. LOI values and UL-94 ratings of the intumescent blends versus the fillers grade.

| Blends | LOI (vol %) | UL-94 rating |
|---|---|---|
| PP/PA-6/APP/$EVA_{24}$ | 32 | V0 |
| PPcarb/PA-6/APP/$EVA_{24}$ | 29 | V1 |
| PPtalc/PA-6/APP/$EVA_{24}$ | 31 | V0 |
| PPtalcom/PA-6/APP/$EVA_{24}$ | 32 | V0 |

Incorporating talc has no effect on the LOI nor on the UL-94 rating whereas with $CaCO_3$, the LOI value is lower than those obtained with talc or without fillers. Moreover, a V1 rating is obtained with $CaCO_3$ whereas a V0 rating is achieved with the other formulations. Using $CaCO_3$ leads to a decrease of the fire performance of the blend.

The R.H.R. curves of the formulations are presented on Fig. 1.

Incorporating APP with PA6[12] in PP and PP/fillers blends leads to the development of an intumescent structure in the cone calorimeter conditions. Whatever the blend, two peaks are observed separated by a plateau value of R.H.R. According to other studies,[6] the first peak may be assigned to the development of the intumescent protective structure. The formation of a stable efficient protective shield may explain the plateau value where the R.H.R is roughly constant. The second peak is assigned to the degradation of this protective layer.

Incorporating calcium carbonate in the blend increases the first RHR peak from 200 kW/m$^2$ without fillers to 350 kW/m$^2$ and decreases the time needed for the complete degradation of the polymeric material.

Adding talc decreases the first peak of RHR but no significant difference of the time to destruction and of the second RHR peak value is observed. However, it seems that the best results are obtained using the commercial PPtalc matrix. The stability of the shield is about 420 seconds whereas it is 350 seconds for the other blends.

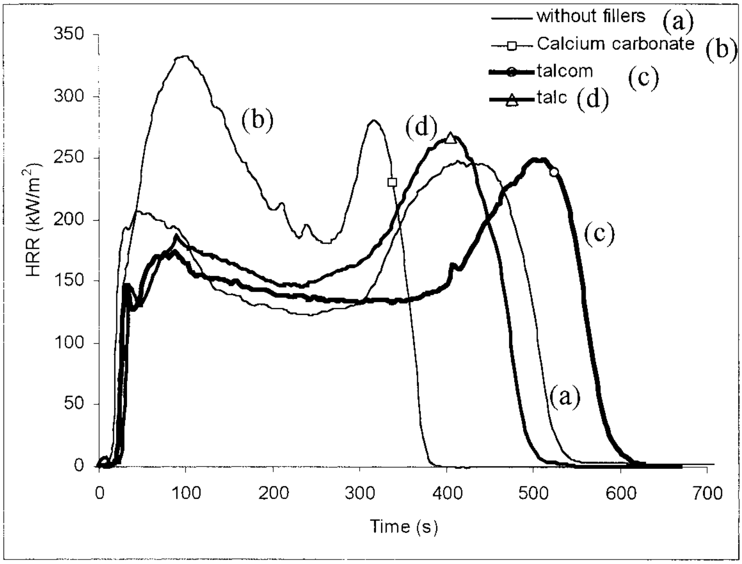

Fig. 1. R.H.R. versus time for PP/APP/PA6/EVA$_{24}$ formulations at an heat flux of 50 kW/m$^2$.

The curve of the total heat evolved during the test are plotted on Fig. 2.

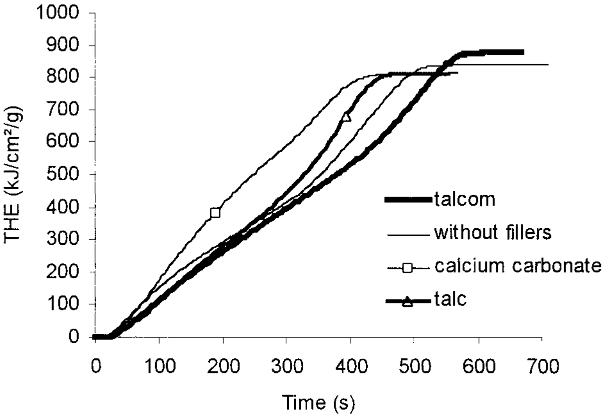

Fig. 2. THE versus time for PPfillers/APP/PA6/EVA$_{24}$ formulations at an external heat flux of 50 kW/m$^2$.

Incorporating fillers does not lead to a decrease in the final THE value. However, the time to heat release depends upon the fillers and is highly decreased using $CaCO_3$. The final THE is the same whatever the blend.

$CO_2$ and CO emissions curves are plotted on Fig. 3 and Fig. 4.

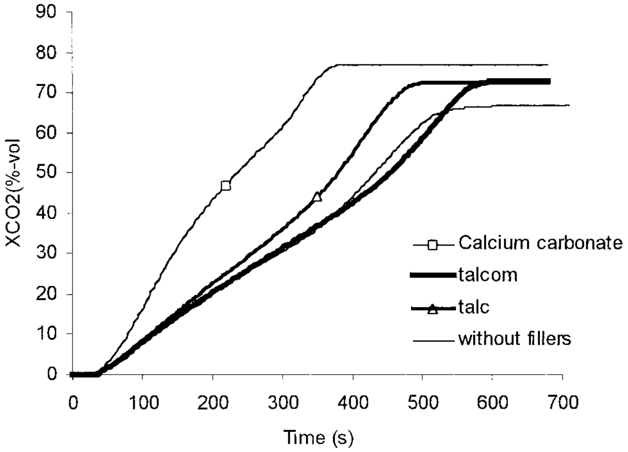

Fig. 3. $CO_2$ emission versus time for PP/APP/PA6/EVA$_{24}$ formulations under an external heat flux of 50 kW/m$^2$.

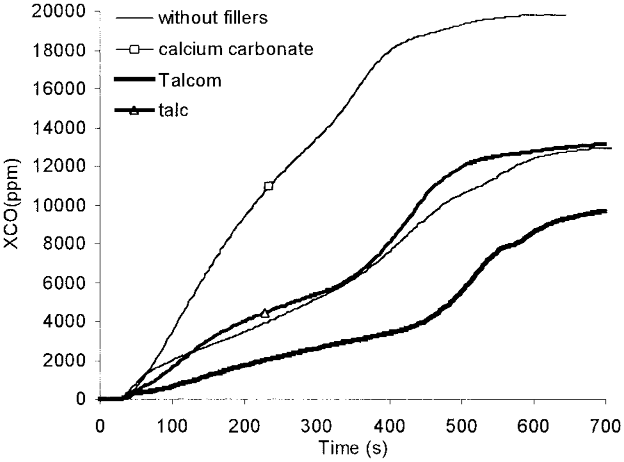

Fig. 4. CO emission versus time for PP/APP/PA6/EVA$_{24}$ formulations under an external heat flux of 50 kW/m$^2$.

Incorporating fillers lead to an increase in the final among of evolved $CO_2$. Adding talc allows to increase the delay of the CO and $CO_2$ emission compared to the blend with $CaCO_3$. This delay particularly increases with the commercial product and the amount of CO evolved decreases. Moreover, the amount of $CO_2$ evolved does not increase. So, a part of the carbonaceous residue is preserved. Nevertheless, the efficiency of talc is reduced when the blend extruded in our lab is considered. Using $CaCO_3$ induces a decrease in the delay to obtain the maximum value. This could be interpreted as a destabilisation of the protective shield.

An increase in the amount of the evolved CO for the blend with $CaCO_3$ is noted Fig. 4, compared to the other blend. This is probably due to the degradation of $CaCO_3$. This hypothesis will be discussed in the following.

The residual weight curves for the blends versus time are plotted on Fig. 5.

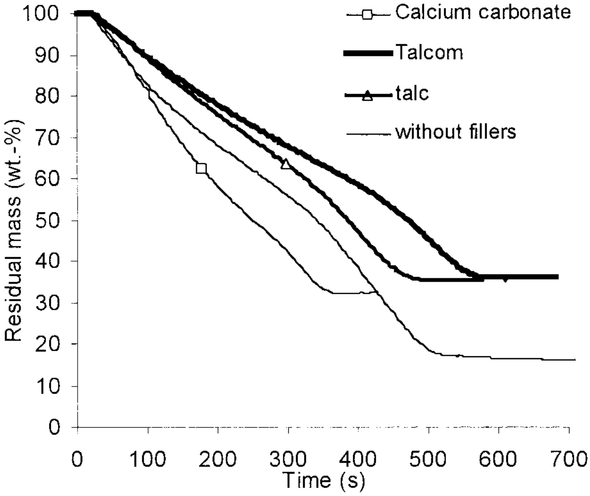

Fig. 5. Evolution of the residual mass for $PP/APP/PA6/EVA_{24}$ formulations versus time under an heat flux of 50 $kW/m^2$.

Incorporating talc enables to obtain a final residual weight greater than without. Moreover, as previously observed, using talc enables to get a higher stability of the material which is maximal using the commercial product.

Using $CaCO_3$ leads to a loss of the thermal/fire stability in the cone calorimeter condition. The amount of residual weight obtained is about 35 wt-% with talc and 30 wt-% with calcium carbonate whereas it is only 17 wt-% without. As there is 13 wt-% of fillers, with talc in the cone calorimeter conditions, some materials are preserved.

The curves of the thermo-oxidative degradation of the blends with their fillers and their derivatives are plotted Figure 6 and Figure 7.

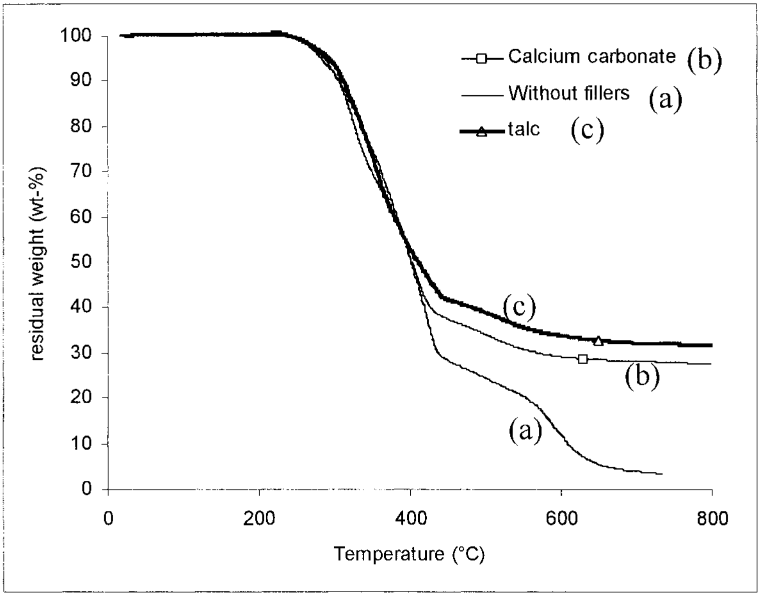

Fig. 6. TG curves under air of the PP/APP/PA-6/EVA$_{24}$ intumescent blend (heating rate: 10°C/min).

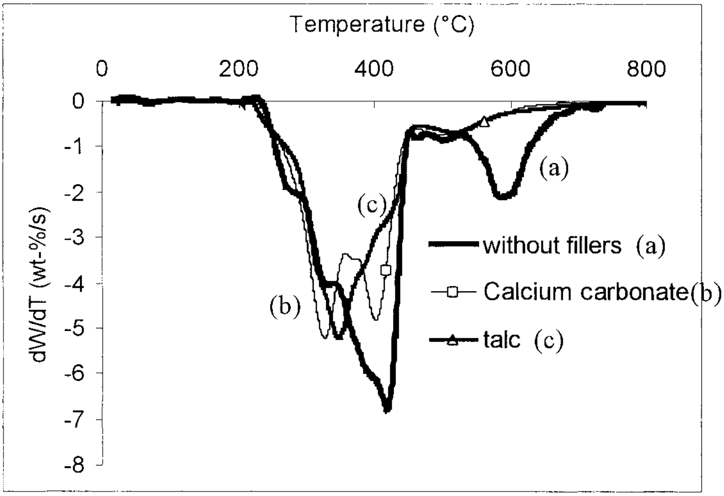

Fig. 7. DTG curves under air of the PP/APP/PA-6/EVA$_{24}$ intumescent blend (heating rate: 10°C/min).

TG and DTG curves of the PP/PA-6/APP/EVA$_{24}$ blend (Figure 6 and Figure 7) show four significant changes in the slopes, which prove that its degradations is at least a four main steps process. Previous studies show that the carbonization process of the system occurs via 4 steps.[17] From 230°C the additives react and form phosphate esters. Between 280°C and 350°C, the development of intumescence occurs and between 350°C and 430°C, the intumescent coating degrades. At higher temperatures, there are structural changes leading to the formation of a new carbonaceous species (established in the temperature range 430°C < T < 560°C) up to 430°C which may be interpreted as above. Then a plateau is observed between 430-560°C. This plateau may be assigned to a particular protective "carbon". Finally, the curve decreases at higher temperature. There is modification of the carbonaceous structure which is no longer protective and the formation of a "high temperature" residue (about 4 wt.-% at 800°C).

TG and DTG curves of the PPtalc/PA-6/APP/EVA$_{24}$ blend (Figure 6 and Figure 7) are similar to the curves of the blend without fillers until 560°C. Beyond 560 °C, a high temperature residue (about 32 wt-%) is obtained.

TG and DTG curves of the PPcarb/PA-6/APP/EVA$_{24}$ blend (Figure 6 and Figure 7) shows three significant changes in the slopes, which prove that its degradations is at least a three steps process. The first one begins at about 250°C until 430°C. Then, the material shows a low rate degradation between 430°C and 560°C, and finally a high temperature residue (about 28 wt-%) is formed.

The $\Delta T$ curves are presented Figure 8. Under the conditions of thermo-oxidative degradation, it is observed that the protection by the intumescence phenomenon is a several steps' process.

In the case of PP/PA-6/APP/EVA$_{24}$, the curve of weight loss difference shows that interactions between the additive and the polymeric matrix occur. The formation of the intumescent coating occurs from 210°C which implies a comparatively more important stability of the system (experimental curve>simulated curve) from 350°C up to 500°C. In this region (210<T<500°C), a first coating is formed with a maximum of protection at 380°C. Above this temperature, the shield looses partially its efficiency. Above 420°C, a second protective process is observed which leads to the formation of a second shield. This latter acts as a relay of the first one. Finally from 560°C, we can assume degradation of the material (fast decrease of weight difference) and the formation of a residue.

In the case of PP/talc/PA-6/APP/EVA$_{24}$, the curve of mass difference has the same shape as PP/PA-6/APP/EVA$_{24}$ up to 450°C which may be interpreted as above. Then a plateau is observed between 450-550°C. This plateau may be assigned to a particular protective "carbon".

Finally the curve increases until 630°C, a second protective process is observed which leads to the formation of a second shield. Then a plateau is observed at high temperature.

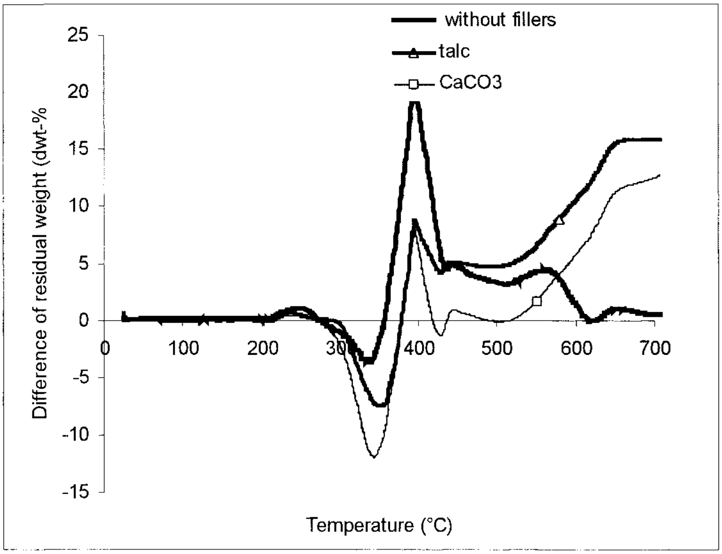

Fig. 8. Difference between experimental and theoretical TG curves of PP/PA-6/APP/$EVA_{24}$, PPtalc/PA-6/APP/$EVA_{24}$ and PPcarb/PA-6/APP/$EVA_{24}$ systems (under air flow).

In the case of PP/$CaCO_3$/PA-6/APP/$EVA_{24}$, the mass difference curve has the same shape as PP/PA-6/APP/$EVA_{24}$ up to 410°C which may be interpreted as above. Then the difference between experimental residual weight and computed residual weight is null until 560°C. There is no efficient shield which is formed as in the case of other blends. Over 560°C, the curve of mass difference increases.

The comparison between the curves of mass difference shows interesting results ; particularly over 560°C. The curves of filled systems with fillers increase whereas the curve of the blend decreases. This implies that interactions and reactions between polymer, and additives are larger with fillers. So, they may allow to form a structure which may block polymer links (or its degradation products) within the coating and therefore, to decrease the degradation rate of the system. These results are to be compared with the one observed in the case of APP/PER-Zeolite systems.[19]-[20] In these systems, zeolite is a synergistic agent which strongly enhances fire proofing performances. This acts by improving the "quality" of intumescent coating and by "trapping" polymer links (via the formation of stable aluminosilicophosphate esters) into the structure which provides interesting mechanical properties to the shield. In our case, formations of calcium phosphate and magnesium phosphate are suspected.

Considering possible formation of magnesium phosphate and calcium phosphate, if only fillers and APP interact, the maximum residual weight is about 17 wt-% and 13.4 wt-% for talc and calcium carbonate. But, 32 wt-% and 28 wt-% with talc and calcium carbonate result from a thermo-oxidative degradation. This proves that a part of carbon is preserved at high temperature by the formation of a protective ceramic shield.

Another point could be pointed out. As observed by TGA, the use of $CaCO_3$ reduces the delay of stabilisation.

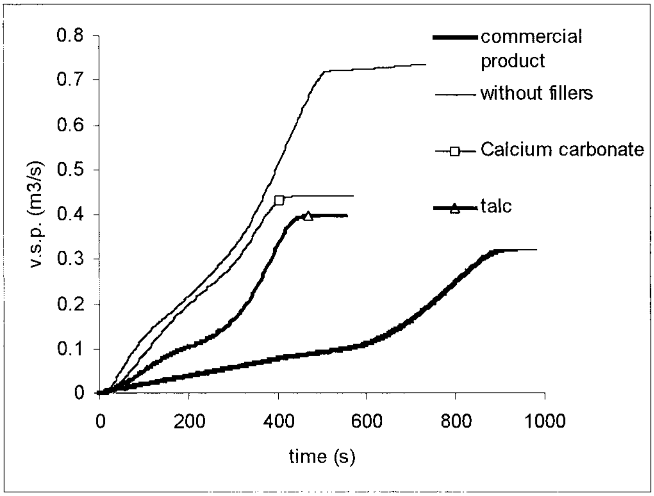

Fig. 9. Volume of Smoke Production (V.S.P.) emission versus time for PP/APP/PA6/$EVA_{24}$ formulations under an external heat flux of 50 kW/$m^2$.

Incorporating the fillers enable to reduce the amount of V.S.P. (Figure 9) increasing the conversion for a high temperature residue. Moreover, using talc enables to get a higher stability of the material which is maximal using the commercial product. Considering the amount of V.S.P. evolved without fillers, this is due to the combustion of a part of polymer.

## Discussion

PP/APP/PA6/$EVA_{24}$ formulation presents enhanced fire performance in comparison with virgin PP. This improvement can be assigned to the formation of a carbonaceous shield during the combustion that slows down the degradation of formulations and that enables to form a stable residue.[12] With fillers, a similar behaviour is observed. The fire behaviour strongly depends on the nature of fillers. It was first shown by Bertelli and al[21] that fillers, in particular hydrated silica or alumina decrease fire retardancy of PP based on intumescent systems with APP. Contrary to these results, Levchik and al[22] observed an increase in the fire properties with talc and calcium carbonate in PA-6/APP system.

Incorporating talc enables to get enhanced fire properties (decrease in the first RHR peak, increase of the residual weight). On the contrary, using calcium carbonate leads to a decrease in the fire performances. Moreover, a protective material does not form in the 420-520°C range and the residual weight obtained (31 wt-%) is lower than with talc (36 wt-%) whereas fillers were added in same quantities.

First, the results obtained with calcium carbonate could be explained by its basic properties. To obtain an intumescent behaviour, three ingredients are needed [12] : a carbonific or char former, an acidic species promoter and a « spumific » or gas-generating and inflating agent. The basic calcium carbonate reacts with APP to give calcium phosphate stable until 1400°C[23] and as a consequence forbids the formation of phosphoric acid and the intumescent char could not be formed as confirmed by visual observation during the cone calorimeter experiment. With $CaCO_3$, the samples do not blow up such as with talc or without fillers. The surface of the sample has the same colour at the end but, whereas with talc, the thickness of the sample increase from 3 mm to 15 mm in the middle whereas it is 3 mm for the burning sample with $CaCO_3$.

Many differences were observed when talc was added in our lab and with a commercial product. Many reasons could explain this phenomenon : first, the structure (cristallinity, cohesion of the blend)[1] strongly depends on the morphology and on the dimensions of the talc particles. As the composition of the intumescent blends are the same, the PP and talc characteristics are suspected to play a great part in the fire properties. Absence of information about the characteristic of the commercial PPtalc do not allow any discussion about this part.

## Conclusion

This work shows the importance of the nature of fillers on the fire properties of an intumescent composite materials. In fact, whereas, it decreases with calcium carbonate, the fire behaviour is preserved or increased with talc. Moreover, the residual weight increases at the end because of the development of a ceramic at the surface To follow this work, an investigation on the blend composition would be undertaken after the process and after the burning of the sample.

To conclude the PPtalc/PA-6/APP/$EVA_{24}$ blend shows very good fire performance : LOI > 30 vol-%, $R.H.R._{max} < 250$ kW/m$^2$, a low level of CO, $CO_2$ and smoke emission which could allow to use it for some application.

## Acknowledgement

This work has been financially supported by the Commission of the European Communities through contract N° G5RD-CT-1999-00120.

[1] Shields TJ, Zhang J. In: Karger-Kocsis J, Editor. Polypropylene an A-Z Reference. Dordrecht (Netherlands): Klumer Academic Pub., 1999:247.
[2] Tramm, H.L., US Patent No. 2106938, 1938
[3] Vandersall, H.L., J. Fire and Flammability, 2, 1971, 97
[4] Montaudo, G., Scamporino, E. & Vitalini, D., J. Polym. Sci., Polym. Chem., 21 (1983), 3361
[5] Camino, G., Actes du Premier Colloque Francophone sur l'Ignifugation des Polymères, ed. J. Martel, Saint Denis, France, 1985 p36
[6] Bourbigot S, Le Bras M, Delobel R. J Fire Sci 1995;13:3
[7] Bourbigot S, Le Bras M, Siat C. In: Lewin M, Editor. Recent advances in Flame Retardancy of Polymeric Materials. Norwalk (USA): BCC Pub., 1997;7:146.
[8] Bourbigot S, Le Bras M. In: Troitzsch J, Bourbigot S, Le Bras M, Editors. International Plastics Flammability Handbook. New-York : Hanser Pub., 2000, Chapter 5, under press.
[9] Le Bras M, Bourbigot S, Felix E, Pouille F, Siat C, Traisnel M. Polymer 2000;41:5283.
[10] Davis RD, Jarrett WL, Mathias LJ. Polymer 2001;42:2621.
[11] Liu NC, Baker WE. Adv Polym Tech 1992;11: 249.
[12] Almeras X, Dabrowski F, Le Bras M, Poutch F, Bourbigot S, Marosi G, Anna P, Polym Deg Stab (accepted).
[13] Dabrowski F, Le Bras M, Delobel R, Le Maguer D, Bardollet P and Aymami J, Flame retardant 2002, p 127
[14] Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics ASTM D2863/77 : American Society for Testings and Materials: Philadelphia, PA, 1977.
[15] Tests for flammability of plastics materials for part devices and appliances, Underwriters Laboratories, ANSI//ASTM D-635/77: Northbrook, IL, 1977.
[16] Babrauskas V. Fire and Mat 1984;8(2):81.
[17] Delobel, R., Le Bras, M., Ouassou N. and Alistiqsa, F., J. Fire Sc., 1990, 8(2):85.
[18] Bourbigot S, Le Bras M, Bréant P, Trémillon JM. Polym Deg Stab 1996;53:275.
[19] Bourbigot, S., Le Bras, M., Delobel, R., Décressain, R. and Amoureux, J.P. J. Chem. Soc, Faraday Trans, 1996 92(1):149
[20] Bourbigot, S., Le Bras, M., Delobel, R., Bréant, P. and Trémillon, J.M.. J. Chem. Soc, Faraday Trans, 1996, 92(18):3435.
[21] Bertelli G, Camino G, Marchetti E, Costa L, Casorati E and Locatelli R, Polym Deg Stab, 1989, 25, 277
[22] Levchik G.F., Levchik S.V., and Lesnikovich, Polym Deg Stab, 1996, 54, 361
[23] Van Wazer, In Interscience publishers, INC, New York, Phosphorus and its compounds, Vol I, 1958, p 528-529