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Fire retardant behaviour of halogen-free calcium-based hydrated minerals

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ABSTRACT

The flame retardant effect of hydrated lime, partially and completely hydrated dolomitic limes in polyethylene and ethylene vinyl acetate copolymers was evaluated and compared to that of magnesium hydroxide and aluminium hydroxide. An important decrease of the peak of heat release rate as measured by cone calorimeter test was observed for Ca-based composites. Thermogravimetric and X-Ray Diffraction analysis indicated that the calcium hydroxide fraction plays an important role in the generation of an intumescent mineral residue during the combustion.

1. Introduction

Metallic hydroxides, such as aluminium hydroxide (ATH) or magnesium hydroxide (MDH) are the most effective halogen free flame retardants for cable applications. These fillers act as fire retardants mainly through their endothermic dehydration that occurs between 180 and 200 °C for ATH and 300–340 °C for MDH [1–5]. It was reported that hydrated minerals in general, and MDH in particular, act mainly by five mechanisms [6], i.e. endothermic decomposition, release of diluent gas (water, CO_2), char formation, solid phase diluent and the heat capacity of the mineral fraction that reduces the amount of energy available to degrade the polymer. The flame retardant action of these hydroxides is very effective up to 400 °C since their endothermic degradation leads to the generation of non-cohesive and powder like residues, mainly composed by Al_2O_3 and MgO, respectively. These non-cohesive residues are not able to ensure an efficient barrier protection against fire. Therefore, there has been much work published regarding the development of new formulations, allowing the enhancement of the efficiency of the hydrated minerals by partially substituting them with synergistic additives such as organo-modified montmorillonite (oMMT) nanoparticles [7–10], multi-walled carbon nanotubes [11], layered double hydroxide [12], delaminated talc [13], zinc borate [14,15], fumed silica [16], expandable graphite [17], zinc hydroxystannate [18] and ammonium polyphosphate [19]. Such approach led to the formation of a thermally stable structures, which then burns slowly due to the limitation of both heat transfer and diffusion of fuel and oxygen [13,20] and providing a better shielding effect. Although ATH and MDH are the most well-known fire retardant minerals, several other hydroxides and hydroxycarbonates, such as boehmite [4], hydrotalcite [4] hydromagnesite [21–23] and hydromagnesite/huntite hybrid compound (available under the trade name of Ultracarb by ELCAB) [6,24], present potential benefit in polymers since they decompose endothermically with release of carbon dioxide, water or both.

Calcium hydroxide ($Ca(OH)_2$) may be of interest for this type of application since its endothermic dehydration occurs at higher temperatures (around 400 °C). The partial substitution of hydrated minerals by calcium hydroxide seems to be an interesting way to broaden the temperature range of the FR system action and extend their efficiency over 400 °C. It is worth mentioning that the use of calcium hydroxide, as flame retardant agent, has been reported by few papers [25–27]. These studies concluded that Calcium hydroxide exhibit relatively poor flame retardant properties due to the exothermicity of the carbonation reaction that occurs during the combustion. In addition, Hornsby et al. [28] report the use of

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Calcium sulphate dehydrate ($CaSO_22H_2O$) as a low-cost material with limited flame retardant properties due to its low temperature of dehydration (60–130 °C) [27].

Calcium-magnesium hydrated based minerals, such as hydrated dolime and partially hydrated dolime, are promising fillers that combine the advantageous of the use of both calcium and magnesium hydroxide since they contain both the two hydroxides in their own structures.

The aim of this work is to evaluate the interest of the use of various calcium-based hydrated minerals as flame retardant agents for polyolefins, i.e. medium-density polyethylene (MDPE), ethylene-vinyl acetate copolymers (EVA), polypropylene (PP) and polystyrene (PS).

2. Experimental

2.1. Materials

The polymers used for the experiments are:

- Medium-density polyethylene (MDPE) 3802 was kindly supplied by Total Petrochemicals.
- Ethylene-vinyl acetate (EVA) copolymer containing 28 wt% of vinyl acetate from Arkema (Escorene UL328) was used.
- Polypropylene (PP), B 10 FB grade, from Polychim Industrie.
- Polystyrene (PS), Polystyrol VPT grade, from BASF.

Alumina tri-hydrate (Martinal® OL107) and magnesium di-hydroxide (Magnifin® H10) were provided by HUBER were used as benchmarks. Several hydrated lime samples, including partially or completely hydrated dolimes were supplied by Lhoist (31, rue de l'industrie, 1400 Nivelles – Belgium). Formula, compositions and physical properties of the fillers used in this study are summarized on Table 1.

The weight losses of the different fillers were determined by thermogravimetry under air at a heating rate of 20 °C/min. TG curves are reported in Fig. 1. Magnesium di-hydroxide and alumina tri-hydrate showed the highest weight loss, i.e. 30 wt%, and 34 wt% respectively. Their one-step endothermic decompositions correspond to water release that occurs in a temperature range from 310 °C to 430 °C in the case of MDH and from 200 °C to 320 °C for ATH.

The thermal decomposition of calcium hydroxide occurs between 370 and 690 °C and corresponds mainly to water release. Two degradation steps were observed: the first one, set between 370 and 470 °C, released 21 wt% of water while the remaining 5 wt% were released during the second step of degradation between 550 and 680 °C, corresponding to the thermal degradation of $CaCO_3$.

Completely hydrated dolime showed a weight loss of 27 wt% from 310 to 660 °C corresponding to water release (23 wt%) and CO_2 release (4.7 wt%). Water release occurred in two steps from 310 to 380 °C and from 385 to 455 °C, corresponding to the thermal decomposition of $Mg(OH)_2$ and $Ca(OH)_2$, respectively.

The thermal decomposition of partially hydrated dolime is similar to that of completely hydrated dolime except that the

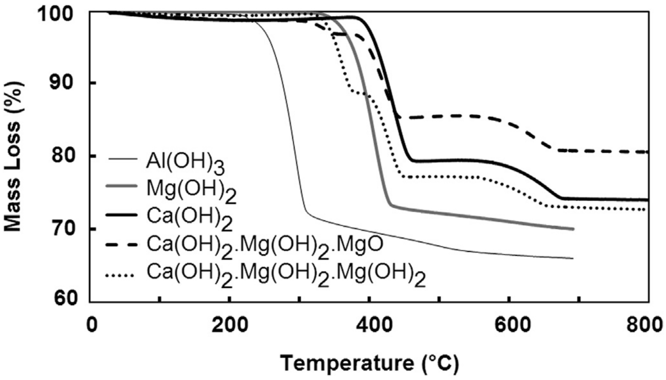

Fig. 1. TG analysis of aluminium hydroxide, magnesium hydroxide, calcium hydroxide, hydrated and partially hydrated dolimes (under air at 20 °C/min).

Table 1
Physical properties of the fillers used in this study.

Fillers	Chemical Formula	Chemical composition[a]	D50 (μm)[b]	SSA (m^2/g)[c]
Aluminium hydroxide	$Al(OH)_3$	$Al(OH)_3$ (98.8%)	2.2	14.1
Magnesium hydroxide	$Mg(OH)_2$	$Mg(OH)_2$ (100%)	1.1	9.5
Hydrated lime (HS)	$Ca(OH)_2$	$Ca(OH)_2$ (94.6%) $CaCO_3$ (4.7%) Impurities[d] (0.99%)	6.8	41.3
Hydrated lime (MS)	$Ca(OH)_2$	$Ca(OH)_2$ (92.8%) $CaCO_3$ (5.9%) Impurities[d] (1.26%)	3.2	14.8
Hydrated lime (LS)	$Ca(OH)_2$	$Ca(OH)_2$ (96.4%) $CaCO_3$ (1.5%) Impurities[d] (1.68%)	3.5	7.5
Partially hydrated Dolime[f]	$Ca(OH)_2 \cdot yMg(OH)_2 \cdot (1\text{-}y)MgO$	$Ca(OH)_2$ (55.3%) $CaCO_3$ (4.8%) CaO (1.8%) MgO (24.6%) $Mg(OH)_2$ (11.1%) Impurities[e] (2.45%)	2.7	11.3
Completely hydrated Dolime	$Ca(OH)_2 \cdot Mg(OH)_2$	$Ca(OH)_2$ (55.1%) $CaCO_3$ (3.4%) $Mg(OH)_2$ (40.0%) Impurities[e] (0.47%)	2	17.7

[a] Given by the supplier, the remaining content to reach 100% in some fillers is supposed to be water.
[b] By laser granulometry after 1 min of sonication (Sonics VC750 – 750W).
[c] From BETmeasurements.
[d] $MgO + SiO_2 + Al_2O_3 + Fe_2O_3 + MnO + P_2O_5 + K_2O + SO_3$.
[e] $SiO_2 + Al_2O_3 + Fe_2O_3 + MnO + P_2O_5 + K_2O + SO_3$.
[f] For simplicity, partially hydrated dolime will be denoted $Ca(OH)_2$. $Mg(OH)_2$. MgO instead of $Ca(OH)_2$. y $Mg(OH)_2$. (1-y) MgO.

amount of water released during the first decomposition step was reduced to ca. 3 wt%. It is worth pointing out some slight differences between the chemical composition as determined by TGA analysis (recorded under air at 20 °C/min) (Fig. 1) and the data provided by the supplier. These differences seem to be attributed to the aging and some slight carbonation of $Ca(OH)_2$ and/or to a difference between the analysis conditions.

2.2. *Processing*

Blending of fillers (50 wt%) within molten polymer (MDPE, PP and PS) was carried out in a Brabender internal mixer at 180 °C for 10 min (2 min mixing at 30 rpm followed by 8 min at 60 rpm) while melt compounding of the EVA and fillers (60 wt%) were performed by co-rotating twin screw extruder (Leistritz) (screw diameter: 18 mm; L/D = 50). The extrusion zone temperature ranged from 180 to 240 °C at 50 rpm except when ATH is used (extrusion temperature from 160 to 180 °C).

For the mass loss calorimeter test, plates ($100 \times 100 \times 4$ mm^3) were compression molded at 180 °C using an Agila PE20 hydraulic press. More precisely, the material was first pressed at low pressure for 200 s (three degassing cycles), followed by a high-pressure cycle at 150 bars for 180 s. The samples were then cooled down under pressure (80 bars).

2.3. *Thermal analysis and fire testing*

Thermogravimetric analyses (TGA) were carried out on a TGA Q50 device from TA Instruments. The filler and MDPE-$Ca(OH)_2$ composites (10 mg) were submitted to a temperature ramp from 25 to 800 °C at a heating rate of 20 °C/min. All the TGA experiments were performed under a flow of 60 ml/min of air using.

The fire behaviour was tested by a FTT (fire testing technology) mass loss cone calorimeter on samples according to the ISO 13927 standard. A $100 \times 100 \times 4$ mm^3 sheet was exposed to a radiant cone (50 kW/m^2) using a forced ignition. Results correspond to mean values obtained from 3 experiments for each formulation, for which a typical variation of 10% was observed. Only Time To Ignition (TTI) and Heat Release Rate (HRR) curves will be discussed.

2.4. *Structural characterization and residue cohesion*

X-ray diffraction analysis (XRD) data were collected using a Bruker D8 Advance diffractometer with Cu Ka radiation (1.541 Å). The scattering angle (2θ) domain studied ranged from 25 to 55°, with a rotation step scanning of 0.020° and a step time of 1.2 s.

The cohesion of the mass loss cone calorimeter combustion residue was evaluated by using Digital Force Gauge (DFG S50) Chatillon® from AMETEK (8600 Somerset Drive, Largo, FL 3377, USA). The sample (with a square of at least 10 mm side) was placed in contact between a rectangular metal fixed plate (100×200 mm) and a second smaller metal plate (circular with a diameter of 12 mm). The second plate being connected to a gauge of force, the force applied to the sample by the mobile plate at the instant of the failure of the sample can be determined. The measurement is performed on 3 samples for each combustion residue. The value obtained, expressed in Newton (N), can be normalized by the surface of the circular mobile plate in order to determine the mechanical resistance in compression of the residue in Pascal. This method is applicable only for the residues of combustion in which it is possible to take 3 samples whose sections are comparable with a square of at least 10 mm side, i.e. section is at least as large as the surface of the mobile plate used for this measurement.

3. Results and discussion

3.1. *Fire properties of $Ca(OH)_2$-based compositions*

The effect of the incorporation of the different fillers on the fire properties of MDPE have been investigated by the mass loss calorimeter test (Fig. 2).

The incorporation of MDH particles leads to a highest increase of time to ignition owing to it endothermic decomposition and to the catalytic formation of a carbonaceous layer before the ignition. In fact, in contrast with ATH that leads also to important endothermic effect, the catalytic action of MgO, which leads to the formation of black protective film at the surface of the sample in the pre-ignition period, contributes to the increase in time to ignition [13]. Furthermore, in the case of MDPE containing $Ca(OH)_2$, an improvement of the resistance to ignition was also observed even if the decomposition temperature of this hydrate started at higher temperatures. This could be explained by an increase of the thermal conductivity of the composite thanks to the presence of higher amounts of inorganic fillers (because of a delayed decomposition), which led to a faster energy dissipation through the materials reducing then the rate of the increase in temperature at the surface of the sample.

Regardless of filler composition, a substantial decrease in pHRR values by at least 74% was observed with respect to pristine MDPE. The pHRR reduction is slightly higher when ATH or MDH fillers were used. However, in the case of ATH and MDH based composites, a second HRR peak appears at around 600 s and corresponds to the collapse of the combustion residue that decayed to form a pile of debris at the end of the test (Fig. 3). In contrast, the combustion of MDPE composites containing $Ca(OH)_2$ fillers led to the formation of intumescent mineral residues (Fig. 4) which favored a gradual spreading of the release of heat during the combustion as can be seen on Fig. 2. The formation of this kind of residue is very important because it keeps the flame retardant action of the system effective even after the total decomposition of the hydroxide. It is worth noting that the cohesion of the mineral residue seems to be higher when $Ca(OH)_2$ HS is used.

The evaluation of the cohesion of the mass loss residue, by using Digital Force Gauge, confirmed that the higher the surface area of calcium hydroxide, the higher the cohesion of the residue (Table 2). In fact, the stress at break of the residue increased with the increase of the surface area of the hydroxide, from 8 to 71 and 110 kPa for $Ca(OH)_2$LS, $Ca(OH)_2$MS and $Ca(OH)_2$HS respectively. In a previous

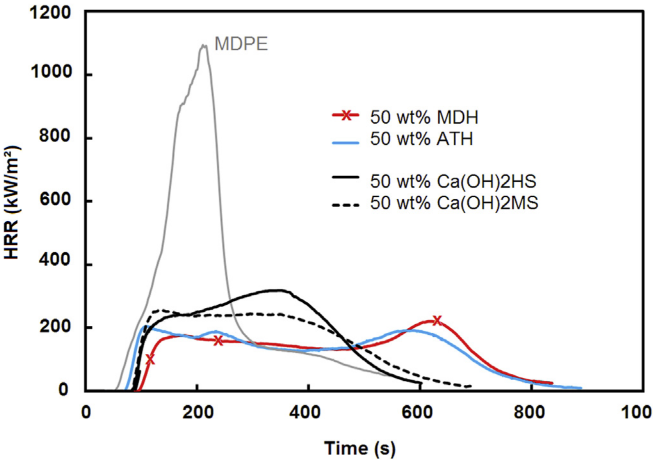

Fig. 2. Heat release rate curves of pristine MDPE, MDPE filled with 50 wt% of ATH, MDH or calcium hydroxide (50 kW/m^2).

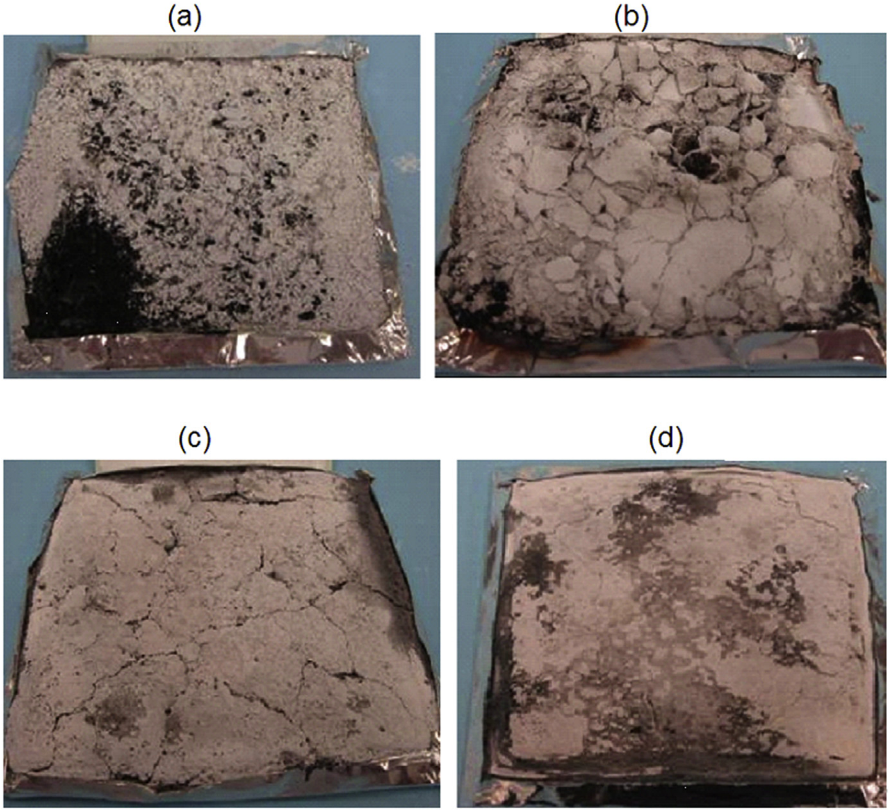

Fig. 3. Pictures of the combustion residues obtained after mass loss calorimeter of: (a): MDPE/50 wt% MDH; (b) MDPE/50 wt% ATH; (c): MDPE/50 wt% $Ca(OH)_2$MS; (d): MDPE/50 wt % $Ca(OH)_2$HS.

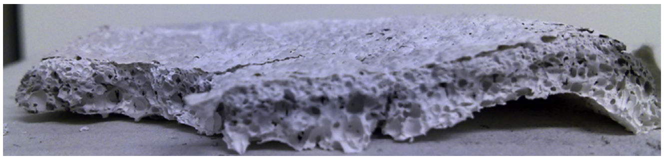

Fig. 4. Pictures of the combustion residues obtained after mass loss calorimeter of MDPE/50 wt% $Ca(OH)_2$HS.

Table 2
Effect of SSA of $Ca(OH)_2$ on the stress at break of the mineral residues obtained during mass loss cone calorimeter test of MDPE filled with 50 wt% of $Ca(OH)_2$.

Composition	Stress at break (kPa)
MDPE - 50% $Ca(OH)_2$LS	8 ± 5
MDPE - 50% $Ca(OH)_2$MS	71 ± 37
MDPE - 50% $Ca(OH)_2$HS	110 ± 35

paper [29], we described the mechanism responsible of generation of the intumescent mineral residue in the presence of calcium hydroxide. The X-ray diffraction analysis of the mineral composition, along the thermo-oxidative decomposition of samples in a furnace revealed the unexpected presence of characteristic peaks of calcium carbonate ($CaCO_3$) in the first degradation step at 450 °C. The 450 °C calcination of $Ca(OH)_2$ in the presence of the combustible polymer, led to a competition between dehydration (CaO formation) and recarbonation ($CaCO_3$ formation). It is worth noting that CaO can also recarbonate, but this reaction is known to be quite slower and occurs at higher temperature (around 600 °C). These results suggest that a large part of $Ca(OH)_2$ reacts with CO_2 coming from the thermo-oxidative degradation of the polymer to form this calcite. The formation of calcium carbonate during thermal decomposition of polymers filled with calcium hydroxide was already reported as large part of the formed residue [30,26]. However, this calcium carbonate was expected to result from the carbonation of calcium oxide, formed after the dehydration of calcium hydroxide at higher temperature and not from the reaction between calcium hydroxide and CO_2 at relatively low temperature (below 450 °C). The thermogravimetric analysis of several MDPE-Ca-based hydrated fillers showed that the experimental weight residue, formed at 600 °C, was higher than that calculated from TGA curves of the pristine fillers and assuming that MDPE was totally degraded at 600 °C. This result confirms that a part of the polymer remained in the combustion residue as char or more likely in the form of CO_2 of the so-generated calcite.

The chemical reaction between calcium hydroxide and the CO_2 produced during the combustion represents the key-parameter that seems to be responsible for the fire behaviour of Ca-based composites. As a result, increasing the SSA of the hydroxide led to an improvement of the cohesion of the residue and to some increase in pHRR due to the exothermicity of the carbonation reaction. A calcium hydroxide with medium SSA seems to be a good compromise between pHRR and the mechanical resistance of the residue.

Calcium hydroxide is also effective as flame retardant agent in EVA copolymer. In comparison with pristine EVA, the incorporation of 60 wt% of $Ca(OH)_2$ leads to a large decrease in pHRR values. The pHRR value was reduced by about 75% in the presence of 60 wt% $Ca(OH)_2$ whereas it decreased by only 57 wt% when the same quantity of MDH was used (Fig. 5). The highest reduction of pHRR observed is due to the formation of a cohesive residue in contrast to

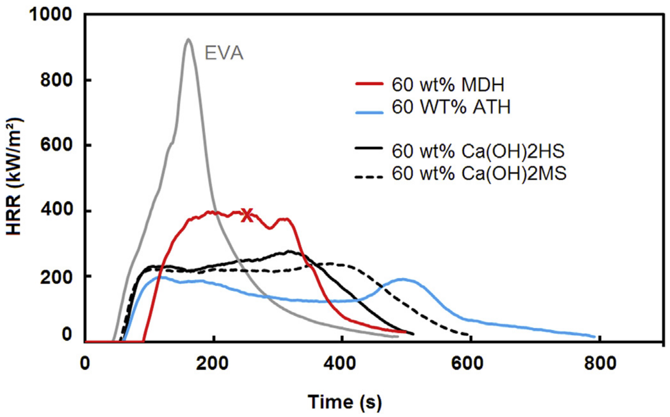

Fig. 5. Heat release rate curves of pristine EVA, EVA filled with 60 wt% of ATH, MDH or calcium hydroxide (50 kW/m^2).

MDH that leads to the formation of pile of debris at the end of mass loss test (Fig. 6).

It is interesting to note that the char characteristics of ATH and MDH containing samples are significantly different (see Fig. 6). The mass loss residue of EVA/ATH composition is more homogenous than that formed when MDH is used. The uniform char of the ATH-based composite may have contributed to a lower pHRR of the sample. This kind of observation has been already reported by Lin et al. [30]. $Ca(OH)_2$HS allows also strong decrease of pHRR in the case of both polypropylene (PP) and polystyrene (PS) (Fig. 7) thanks to the generation of a cohesive mineral residue.

3.2. Fire retardant behaviour of $Ca(OH)_2$ in mixture with ATH and MDH

As described in section 2.1, the endothermic dehydration of calcium hydroxide occurs at high temperature, from 370 °C to 470 °C. Therefore, its use in combination with other metallic hydroxides permits to broaden the temperature range of the FR system action. In addition to that, the combustion of calcium hydroxide-based composite leads to the formation of a cohesive residue thanks to the formation of calcium carbonate at the earliest stages of the combustion. For all these reasons, calcium hydroxide is a promising metallic hydroxide which seems advantageously used in combination with ATH or MDH particles.

Indeed, the partial substitution of 10 or 20 wt% of ATH particles by $Ca(OH)_2$HS leads to a significant reinforcement of the char cohesion as can be seen on Fig. 9 and confirmed by the mechanical testing of the residue. In fact, the stress at break of MLC residue of MDPE filled with ATH/$Ca(OH)_2$HS combinations increases from 4 kPa with 10% $Ca(OH)_2$HS to around 10 kPa when 20% of $Ca(OH)_2$HS is used. It is worth noting that the mechanical resistance of ATH based composite residue was not possible to determine since the residue was formed by a pile of debris. Even if the amount of ATH in the blend decreases, HRR curves of MDPE filled with ATH/$Ca(OH)_2$HS combinations are similar to that obtained with 50 wt% ATH (Fig. 8). The improvement of the char cohesion contributes positively to a lower pHRR. The same behaviour is also observed in the case of partial substitution of MDH by $Ca(OH)_2$HS, i.e. conservation of low HRR level (Fig. 8) with the disappearance of the second HRR peak due to the increase of the cohesion of the residue (Fig. 9). These results showed that the use of calcium hydroxide in combination with MDH or ATH provides a synergistic effect allowing the generation of more cohesive residue and similar HRR

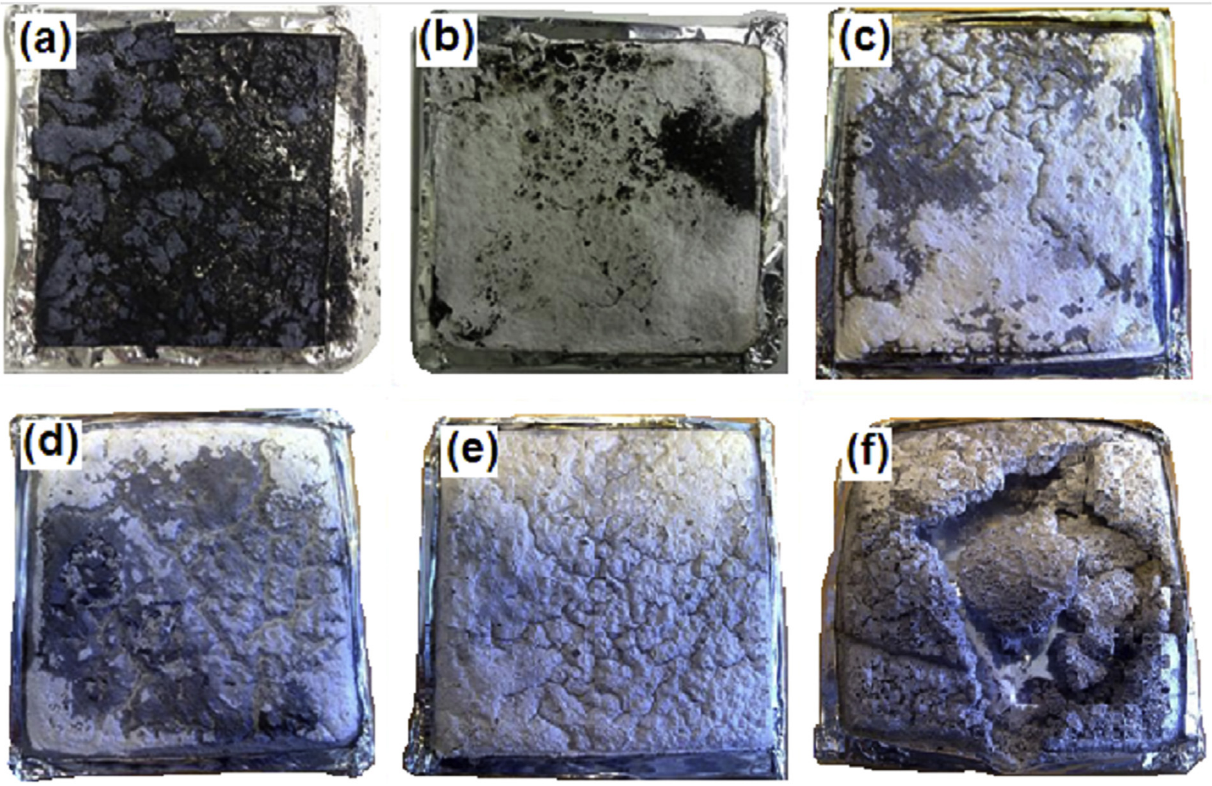

Fig. 6. Pictures of the mass loss combustion residues of EVA filled with 60 wt% of MDH (a), ATH (b), $Ca(OH)_2$MS (c), $Ca(OH)_2$HS (d), partially hydrated dolime (e) and hydrated dolime (f).

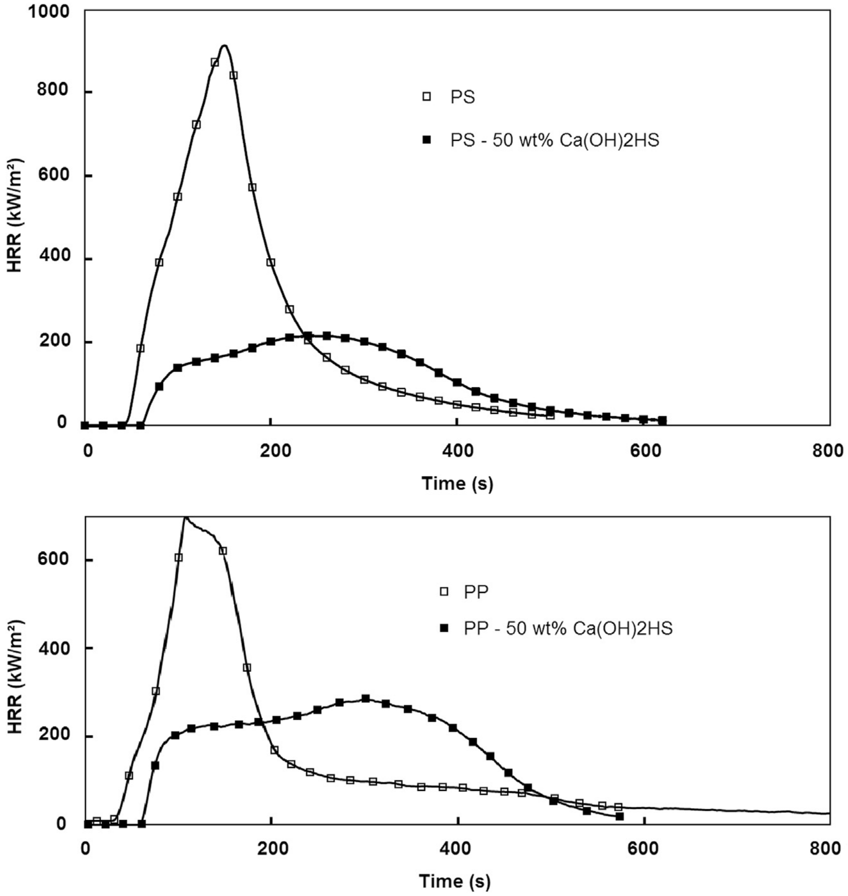

Fig. 7. HRR curves of pristine PS, pristine PP and the corresponding composites containing 50 wt% of calcium hydroxide.

curves with respect to composites containing ATH or MDH separately.

3.3. *Fire properties of partially or completely hydrated dolimes composites*

Partially or completely hydrated dolimitic limes are interesting natural fillers that could be advantageously used as flame retardant additives for polyolefins. In fact, these natural fillers contain both magnesium and calcium hydroxides in their chemical structure and thus allow a broad endothermic decomposition range (Fig. 1) in addition to the possible generation of cohesive residue thanks to the presence of calcium hydroxide.

HRR curves of MDPE and EVA filled with partially and completely hydrated dolimes are presented in Fig. 10 and summarized in Table 3. In the case of MDPE composites, the amount of $Mg(OH)_2$ in the filler did not appear to affect significantly the resistance to ignition since the composites filled with the two hydrated dolimes displayed very similar ignition times (74 s). In contrast, in the case of filled EVA compositions, the hydration level of dolimes affects significantly the resistance to ignition. In fact, TTI increases with increasing the amount of $Mg(OH)_2$ in the fillers, from 54 s to 82 s when partially hydrated and completely hydrated dolimes are used, respectively. The effect of $Mg(OH)_2$ on TTI seems to be ascribed to the higher amount of water release for hydrated dolimes. The effect of hydration level of dolimes on TTI that is observed only in the case of EVA composites could be explained by two mechanisms, (i) the action of acetic acid that accelerates MDH dehydration via an acid-base interaction [33] and to (i) the charring effect induced by MDH that seems to be more significant in EVA than in MDPE since polyethylene is not a charring polymer. However, it should also be noted that the loading level of fillers is higher in EVA (60 wt%) with respect to MDPE (50 wt%). As a result, the difference between the endothermic contributions of completely and partially hydrated dolimes is lower in MDPE than in EVA. The incorporation of these fillers leads to a reduction of total heat release in both MDPE and EVA based compositions. This reduction is due to the fact that 60 wt% of combustible polymer is replaced by hydrated fillers that release water by endothermic decomposition. Time of pHRR is higher in the case of MDPE filled with 50 wt% of MDH because of the presence of a second HRR peak attributed to the degradation of the residue. This peak is not observed in the case of MDPE/Ca-based compositions, since the combustion of these compositions leads to cohesive residue. Total Heat Released (Total HR) is slightly decreased in both MDPE and EVA compositions. This reduction is similar for all compositions except for MDPE containing 50 wt% of partially hydrated dolime which shows a little higher value (122) in comparison with 100 MJ/m^2 for the other composites.

In comparison with pristine polymers, a large decrease in pHRR values for all the compositions was observed. The pHRR reduction is not affected by the hydrated level of dolimes. In the case of MDPE, the incorporation of partially or completely hydrated dolimes leads to pHRR value lower to that obtained with calcium hydroxides but similar to that obtained with 50 wt% of MDH. In contrast, the incorporation of hydrated dolimes in EVA leads to a higher pHRR reduction than MDH. In fact, the pHRR value was reduced by about 75% in the presence of 60 wt% hydrated dolimes whereas it decreased by only 57 wt% when the same quantity of MDH was used. In both MDPE and EVA, the incorporation of partially or completely hydrated dolimes leads to the formation of an intumescent mineral residue (Figs. 6 and 11). As in the case of MDPE filled with calcium hydroxide, the evolution of the mineral structure of samples calcinated in the furnace showed the presence of chalk at 450 °C [27]. This result indicates that the generation of a cohesive mineral residue is also possible in the case of partially hydrated and completely hydrated dolimes thanks to the formation of calcium carbonate. In contrast with MDH and ATH, Ca-based hydrated minerals released water during a wider temperature range that affected also the structuration of the residue, by suppressing the formation of large cavities that can decrease the cohesion of the residues. In fact, the water liberation kinetic is an important parameter affecting the cohesion and structuration of an intumescent mineral residue [21].

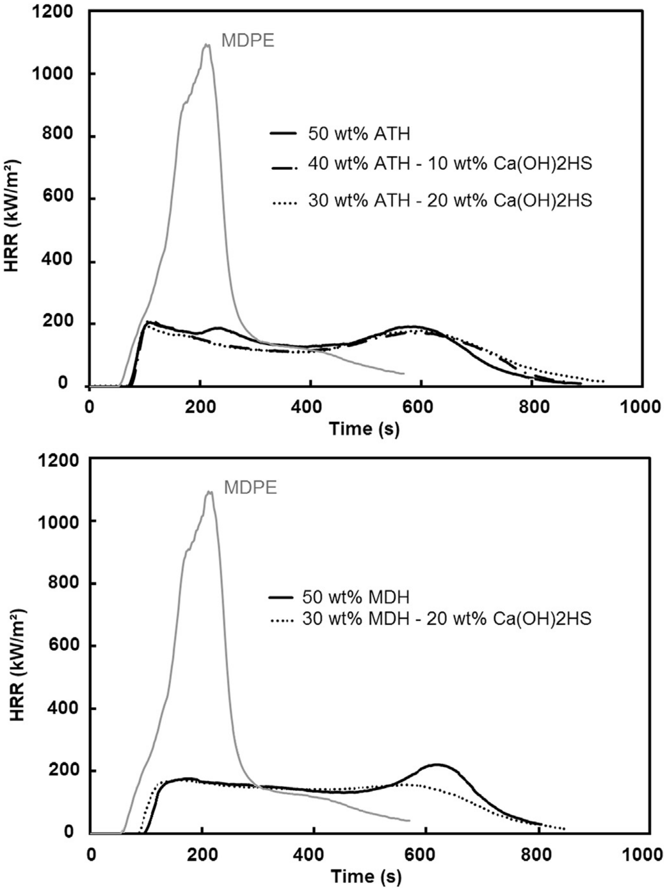

Fig. 8. Heat release rate of MDPE filled with ATH or MDH partially substituted by $Ca(OH)_2$HS.

These results suggest that completely hydrated dolime is an adapted flame retardant additive for EVA since its incorporation leads to a strong reduction of pHRR values, significant increase of time to ignition and to the generation of intumescent mineral residue. However, the visual inspection of the combustion residue of EVA/completely hydrated dolime showed the formation of cracks suggesting some weaker cohesion (Fig. 11). In contrast, the intumescent residues formed during the combustion of EVA containing 60 wt% of calcium hydroxide or partially hydrated dolime proved more cohesive. This is probably a consequence of the production of acetic acid during EVA degradation (deacylation), that can then react with $Mg(OH)_2$, via an acid-base interaction leading to an acceleration of MDH dehydration [33] and solubilization of a part of MDH particles that would then act as defects in the structure of the residue. This endothermic release, as well as the secondary effects like the formation of a cohesive residue, makes partially hydrated dolime a potential fire retardant and resistant additive.

4. Conclusions

In the present study, the effect of incorporation of Ca-based hydrated minerals, such as calcium hydroxide, partially and completely hydrated dolimes on the flame properties of polyolefinic matrices was reported. Mass loss calorimeter experiments showed that both MDPE and EVA composites exhibited a strong decrease of pHRR and led to the generation of intumescent mineral residues during combustion.

The use of these fillers into polyolefinic matrices allows strong reduction of pHRR level, similar and even lower than that the values obtained with traditional ATH and MDH fillers. In addition, the incorporation of Ca-based fillers within MDPE led to the formation of a cohesive intumescent mineral residue thanks to the carbonation reaction of calcium hydroxide that occurs at lower temperature (450 °C) in the presence of combustible polymer. Furthermore, the cohesion of the residue was improved when $Ca(OH)_2$ with higher surface area was used.

In the case of the EVA composites, the incorporation of Ca-based hydrated minerals induced the formation of a cohesive residue only when calcium hydroxide or partially-hydrated dolime were used. In fact, EVA/completely hydrated dolime composites led to the formation of an easily cracked intumescent residue during the combustion. Such a decrease in the cohesion of the residues was also observed in the case of fillers that contain higher amount of $Mg(OH)_2$. This suggests that the presence of $Mg(OH)_2$ was

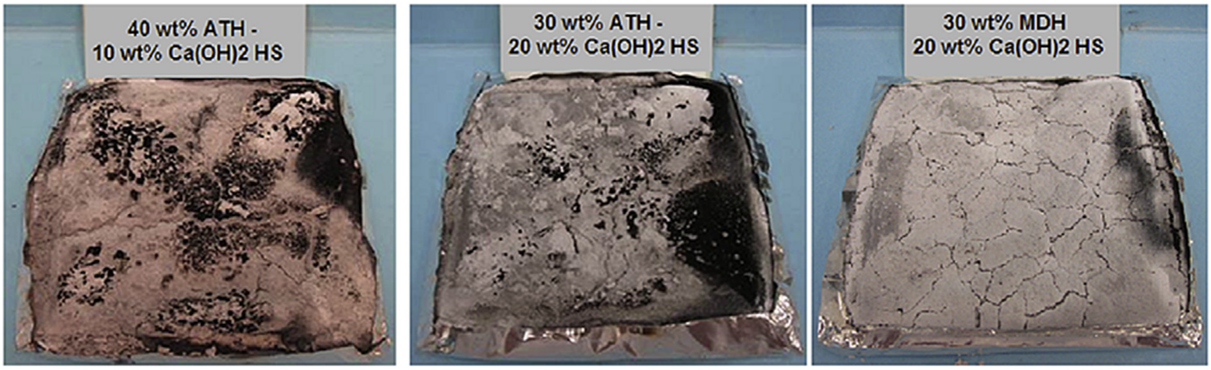

Fig. 9. Pictures of the mass loss combustion residues of MDPE filled with ATH or MDH partially substituted by $Ca(OH)_2$HS.

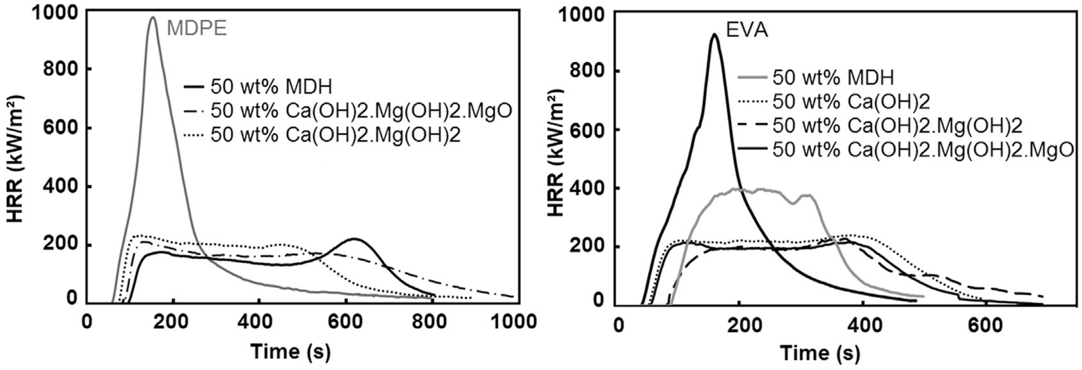

Fig. 10. HRR curves of MDPE and EVA filled with several Ca-based hydrated minerals (50 Kw/m^2).

Table 3
Time to ignition (TTI), peak of heat release (pHRR), time of peak of heat release (TpHRR) and Total heat released (Total HR) values of MDPE and EVA composites.

	TTI (s)	pHRR (kW/m^2)	TpHRR (s)	Total HR (MJ/m^2)
MDPE	54	1090	212	150
MDPE - 50% $Mg(OH)_2$	90	220 (~−80%)	620	97
MDPE - 50% $Al(OH)_3$	74	210 (~−80%)	112	100
MDPE - 50% $Ca(OH)_2$	77	252 (~−77%)	130	100
MDPE - 50% $Ca(OH)_2 \cdot Mg(OH)_2 \cdot MgO$	78	211 (~−80%)	120	122
MDPE - 50% $Ca(OH)_2 \cdot Mg(OH)_2$	74	231 (~−79%)	120	110
EVA	38	923	160	103
EVA - 60% $Mg(OH)_2$	86	394 (~−57%)	200	90
EVA - 60% $Ca(OH)_2$	50	238 (~−74%)	380	92
EVA - 60% $Ca(OH)_2 \cdot Mg(OH)_2 \cdot MgO$	54	226 (~−75%)	385	80
EVA - 60% $Ca(OH)_2 \cdot Mg(OH)_2$	82	214 (~−77%)	372	74

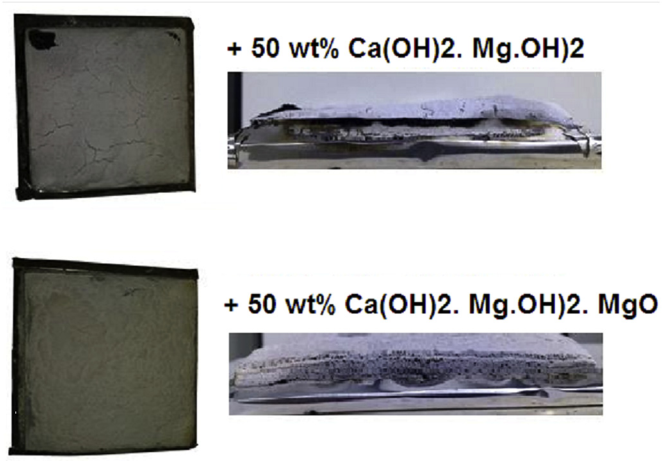

Fig. 11. Pictures of the mass loss combustion residues of MDPE filled with hydrated and partially hydrated dolimes.

responsible for the decrease of the mechanical resistance of the residue. Unlike MDPE, EVA is a polar polymer which produces acetic acid during its first degradation step (via deacylation reaction). The formed acid react with $Mg(OH)_2$, via an acid-base interaction that leads to an acceleration of MDH dehydration [31] and may solubilize a part of MDH particles therefore acting as defects in the structure of the residue.

To conclude, this study shows that calcium-based hydroxides constitute very promising halogen-free flame retardants and flame retardant additives for polyolefins, with a performance similar to MDH in the cone calorimeter test (flame-retardancy) and an additional functionality thanks to the formation of a cohesive $CaCO_3$ combustion residue (fire-resistant).

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