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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 ($CaSO_2 2H_2O$) 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

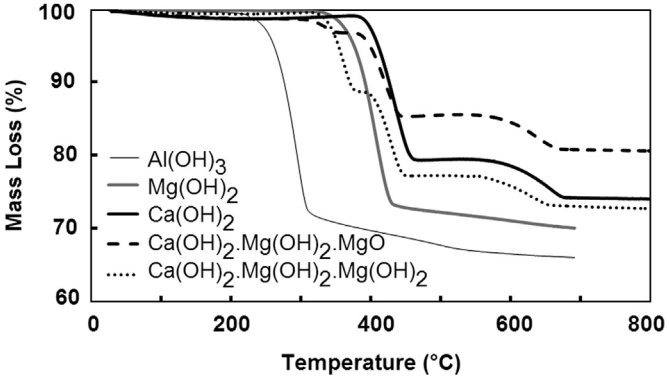

Fig. 1. TG analysis of aluminium hydroxide, magnesium hydroxide, calcium hydroxide, hydrated and partially hydrated dolimes (under air at 20 °C/min).

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.