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Synthetic hydromagnesite as flame retardant. Evaluation of the flame behaviour in a polyethylene matrix

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Abstract

Synthetic hydromagnesite obtained from an industrial by-product was evaluated as a non-halogenated flame retardant. It was used in combination with aluminium hydroxide (ATH) and compared with commercial flame retardants like magnesium hydroxide (MH) and natural hydromagnesite–huntite (U) in a polyolefin system of low-density polyethylene/poly(ethylene-*co*-vinyl acetate) (LDPE/EVA).

The thermal stability and flame behaviour of the halogen free flame retarded composites were studied by thermogravimetric and differential thermal analysis (TG-DTA), limiting oxygen index (LOI), epiradiateur and cone calorimeter. It has been shown that synthetic hydromagnesite could be an alternative solution to the use of MH in non-halogenated flame retardant systems in EVA.

Keywords: Flame retardancy; Hydrated fillers; Hydromagnesite; LDPE/EVA blends

1. Introduction

Low-density polyethylene/poly(ethylene-*co*-vinyl acetate) (LDPE/EVA) blends are widely used in the wire and cable industry as insulating materials due to their good mechanical and physical properties [1]. However, the flammability of these materials represents a drawback that restricts their applications. Flame retardancy of polyolefins is usually enhanced by physical incorporation of additives [2]. The tendency to eliminate halogen-based substances to reduce smoke toxicity during combustion has promoted research on halogen free formulations [3,4]. The use of metal hydroxides, i.e. aluminium hydroxide (ATH) or magnesium hydroxide (MH) has been extensively described [5,6]. These compounds act both in the condensed and the gas phase following endothermic decomposition with water release, which reduces the temperature of the material and surrounding gas phase and dilutes the fuel supply [7].

Basic magnesium carbonates have also been reported as suitable inorganic flame retardants for thermoplastics [8,9]. These fillers decompose through an endothermic reaction in the range of combustion temperatures of the polymer evolving water and carbon dioxide.

In a previous work [10] we studied the optimisation of the physical characteristics (particle size, surface treatment etc.) of a synthetic hydromagnesite in order to be employed as flame retardant filler in polyolefins. It was a basic magnesium carbonate with formula $5MgO \cdot 4CO_2 \cdot 5H_2O$ that undergoes an endothermic decomposition evolving water vapour and carbon dioxide, with a total associated heat of 800 J/g and a final weight loss of 54% in the temperature range of 200–550 °C. It was obtained from an industrial by-product rich in magnesium oxide [11]. In that work, the flame retardant behaviour of pure synthetic hydromagnesite (HM) in EVA was studied and compared with that of natural hydomagnesite–huntite commercial mixture, as

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well as with that of commercial synthetic magnesium hydroxide. The results showed HM to have accurate thermal decomposition behaviour, as well as similar limiting oxygen index (LOI) values in EVA than the commercial fillers. It was concluded that HM is a promising flame retardant filler for polyolefins.

In the present work the flame retardant properties of synthetic hydromagnesite have been evaluated in a LDPE/EVA matrix. Due to that different flame retardant fillers are usually mixed to obtain synergistic flame retardant effects in polymers, and different formulations have been studied here, in which ATH was combined with synthetic hydromagnesite or, for comparison purposes, with commercial grades of magnesium hydroxide or with mineral hydromagnesite–huntite.

2. Experimental

2.1. Materials

Low-density polyethylene, Lupolen 3020H, was supplied by Basell. Poly(ethylene-*co*-vinyl acetate) (EVA) was the cable grade Escorene Ultra UL00728 with 27.5% of vinyl acetate. ATH Martinal OL-104 and Magnifin (MH) H5 KV were both supplied by Martinswerk. Natural hydromagnesite–huntite Ultracarb (U) C5-10 was produced by Minelco Specialities Ltd and synthetic hydromagnesite (HM) was obtained in the pilot plant of Magnesitas Navarras S.A. [12]. Both U and HM had a 1% stearic based coating [10].

2.2. Polymer compounding

The polymer matrix used was a blend of LDPE and EVA in a ratio of 3:1 commonly employed in the wire and cable industry. The filled composites were processed using a Collin 25 mm twin screw extruder and subsequently pelletised and compression moulded at 160 °C to obtain 1 and 4 mm thick sheets. The samples and compositions prepared are listed in Table 1, the filler loading expressed as phr (parts per hundred of resin).

2.3. Characterization

2.3.1. Thermal analysis

A TGDTA92 Setaram device was employed to perform thermogravimetric (TGA) and differential thermal analysis (DTA) in air flow and at a heating rate of 10 °C/min from 30 to 800 °C.

Table 1
Sample codes and compositions

Sample	Composition (phr)					
	LDPE	EVA	ATH	HM	MH	U
LDPE/EVA	75	25	0	0	0	0
ATH/HM	75	25	75	75	0	0
ATH/MH	75	25	75	0	75	0
ATH/U	75	25	75	0	0	75

2.3.2. Flame testing

2.3.2.1. Limiting oxygen index (LOI). LOI corresponds to the minimum percentage of oxygen needed for the combustion of specimens measuring 80 × 10 × 1 mm in an oxygen–nitrogen atmosphere in accordance with ISO 4589 standard.

2.3.2.2. Cone calorimeter. The cone calorimeter is a small-scale test that provides results in good agreement with large-scale fire tests. Several combustion parameters were determined.

- Heat release rate (HRR) as function of time.
- Peak of heat rate release (PHRR), which is considered as the parameter that best expresses the maximum intensity of a fire indicating the rate and extent of fire spread.
- Time to ignition (TTI) and the fire performance index (FPI) defined as the ratio of TTI and PHRR that is a parameter related with the time available to escape in a real fire situation [13].

Parameters related with the smoke evolution were also obtained, such as total smoke released (TSR) calculated by integrating the rate of smoke released (RSR) curve, average of CO emission (Av. CO emission), CO/CO_2 weight ratio and smoke density, measured by the decrease in transmitted light intensity of a helium neon laser beam photometer, and expressed in terms of average smoke extinction area (AvSEA) [14].

The cone calorimeter tests were carried out following the procedures indicated in the ISO 5660 standard with a FTT cone calorimeter. Square specimens (100 × 100 × 4 mm) were irradiated with a heat flux of 50 kW/m^2.

2.3.2.3. Epiradiateur. An epiradiateur device (AFNOR NF P 92-505) was employed to measure the extinguishability of combustion.

Sheet samples with 70 × 70 × 4 mm dimensions were placed on a metallic grid below a heat source of 500 W, which was removed and replaced after each ignition and extinguishing. Four samples for each composition were tested and the parameters determined were the number of ignitions and the average value of combustion extent during the first 5 min of combustion.

3. Results and discussion

3.1. Thermal stability

The thermal decomposition of the fillers was studied by TGA and DTA. Fig. 1 shows the TGA curves and the derivative thermograms (DTG). From the DTA plots (Fig. 2) the endothermic processes occurring during the thermal decomposition were analysed. The thermal decomposition of metal hydroxides begins around 190 °C for ATH and 340 °C for MH and takes place in the temperature range of 190–350 °C and 340–450 °C, respectively. Both basic magnesium carbonates,