



Thermal stability and fire behaviour of flame retardant high density rigid foams based on hydromagnesite-filled polypropylene composites



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ABSTRACT

The present work deals with the development of new rigid polypropylene composite foams filled with high amounts of flame-retardant systems based on synthetic hydromagnesite, a basic magnesium carbonate obtained from an industrial by-product. A partially-interconnected cellular structure with a cell size around 100 μm was obtained for the hydromagnesite-filled PP foams. A 40% reduction of this cell size was observed when a small amount of a combination of montmorillonite and graphene layered nanoparticles was added to the hydromagnesite. The combination of hydromagnesite with an intumescent additive (ammonium polyphosphate) and layered nanoparticles led to improved thermal stability. In particular, the intumescent additive delayed the beginning of the thermal decomposition temperature and the layered nanoparticles split the second step of thermal decomposition in a third peak observed at higher temperatures. Improved flame retardancy, measured by means of cone calorimetry, was observed in the samples containing the intumescent additive. A novel normalized parameter, called foam efficiency ratio (FER), which takes into account the expansion ratio of the foam and the relation of its fire properties with that of the base solid, was also analyzed.

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1. Introduction

Polymeric foams are widely used in multiple fields due to their combination of lightness and properties such as reduced thermal conductivity or high energy absorption [1]. In the case of high density rigid polypropylene foams, their stiffness and strength make them suitable for bearing high loads without any significant dimensional changes, ideal for structural applications. Moreover, balanced mechanical properties, together with satisfactory thermal stability and a broad working temperature range, make these foams interesting for the construction and automotive sectors, among others [2,3]. However, polymer foams are highly flammable materials. Due to this fact, currently there is a great deal of interest in improving their fire performance, especially in industries that must comply with strict normative such as construction and building. The addition of flame retardants (FR) is thus essential in the development and application of new polymer-based fireproofing materials. Halogenated additives, although very effective in improving the flame retardancy of polymers, have been replaced

by others more environmentally friendly such as inorganic fillers. These fillers are commonly used as flame retardants in order to overcome the inherently low flame resistance of polymer foams [4]. Particularly, in PP foams they also enhance PP's melt strength during foaming as well as promote cell nucleation [5]. Aluminium and magnesium hydroxides are two of the most used inorganic flame retardants. These metal hydroxides undergo endothermic decomposition at a given temperature releasing water, which cools down the condensed phase and helps to dilute the gases in the gas phase [6]. Several studies have proved that a high amount of metal hydroxide is required in order to reach an adequate level of flame retardancy [7]. For instance, Antunes et al. reported a remarkable improvement in the flame retardancy of PP-based foams with the addition of very high concentrations of magnesium hydroxide (50 and 70 wt%) [8,9]. Intumescent systems are another kind of FR that are usually highly effective, acting during burning generating a carbon-rich foamed structure that hinders the access of oxygen to the polymer and prevents it from burning, also limiting the heat and gas transfer between the flame and condensed phase [10,11]. In order to further improve the fire performance of polymer foams, the combination of these conventional FR with low amounts of nanoparticles has emerged in the last years [12,13].

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Their synergistic effect has been quite studied; in fact, layered nanoparticles such as silicate-layered nanoclays have been proven to promote the formation of a more consistent protective layer at the material's surface during combustion [14], limiting polymer burning and ultimately resulting in reductions in the peak of heat release rate (PHRR) [15,16].

In this work we present the use in PP foams of a basic magnesium carbonate obtained from an industrial by-product [17] as an alternative to commercial endothermic flame retardants. This basic magnesium carbonate has also been combined with an intumescent system as well as with small amounts of functional nanoparticles, particularly a combination of a silicate-layered nanoclay and graphene nanoplatelets, in order to study possible synergy effects between systems as flame retardancy enhancers. Furthermore, a novel normalized parameter that evaluates the efficiency of foaming in the fire performance respect to the solid base material, so-called foam efficiency ratio (FER), is introduced in the present work.

2. Experimental

2.1. Materials

A polypropylene (PP) specifically formulated for foam applications was kindly supplied by Sekisui (Osaka, Japan). It contained 3.5 parts per hundred of resin (phr) of a chemical blowing agent (azodicarbonamide) and 2 phr of talc, used as nucleating agent.

Four different flame retardant systems, combining a basic hydrated magnesium carbonate (hydromagnesite), an intumescent additive based on ammonium polyphosphate, an organomodified-montmorillonite and graphene nanoplatelets, were incorporated into the PP. The synthetic hydromagnesite (H) was obtained in a pilot plant of *Magnesitas Navarras S.A.* (Navarra, Spain) according to the procedure presented in [17] and subsequently milled to an average particle size of approximately 20 μm . The employed montmorillonite (MMT) was a commercial grade (Nanofil SE 3000) of *Süd-Chemie* (Munich, Germany), modified with quaternary dimethyl-distearyl ammonium cations, having a specific surface area of 700 m^2/g . The graphene nanoplatelets (GnP) were supplied by *XG Sciences, Inc.* (Michigan, USA), with an average thickness of 6–8 nm and particle diameter of 15 μm , having a surface area of 120–150 m^2/g . These two nanoparticles were always used together in a 1:1 proportion and their incorporation was referred as N. The intumescent (I) formulation, with the commercial name of Budit 3167 and specially formulated for PP, was kindly supplied by *Budenheim Ibérica* (Barbastro, Spain). Additionally, 2 phr of stearic acid (95% of purity) from *Sigma-Aldrich Spain* (Madrid, Spain) was added to all formulations as processing additive.

2.2. Preparation of the composites and foams

2.2.1. Compounding and moulding

The several PP composites were prepared by melt-compounding the different components using a *Brabender Plasti-Corder* internal mixer, at a temperature of 170 $^{\circ}\text{C}$ and screw speed of

30–60 rpm during a mixing time of 6 min. Table 1 compiles the composition of the several prepared composites and their respective codes. As can be seen, we opted to choose what we considered the minimum composition of layered nanoparticles (a total of 2 wt%, equilibrated in a 1:1 proportion of MMT and GnP) that have already been shown in the literature to have significant effects in improving the fire retardancy of similar non-foamed systems.

In order to prepare solid foaming precursors, the molten composites taken from the internal mixer were placed into a circular-shaped mould ($\varnothing = 74$ mm and thickness = 3.5 mm) and subsequently compression-moulded by applying a heating temperature of 180 $^{\circ}\text{C}$ and a maximum pressure of 40 bar using a hot-plate press model PL-15 (*IQAP-LAP*, Spain). A final cooling stage was performed by applying the maximum pressure during 5 min by placing the mould with the sample in the cooling station of the hot-plate press.

2.2.2. Foaming

The compression-moulded discs were allowed to freely foam by the thermal decomposition of the blowing agent at a typical temperature of 200 $^{\circ}\text{C}$ during a minimum of 10 to a maximum of 25 min by placing the samples inside a closed chamber between the hot plates of the press. The produced foamed composites showed a final expansion ratio (ER), defined as the ratio between the density of the solid base composite and the density of the foam, between 1.2 and 1.4. Specimens were directly cut from the foamed materials and the solid skins generated during foaming removed prior to their cellular and fire behaviour characterizations.

2.3. Characterization of the composites and foams

2.3.1. Cellular structure

The density of both solid and foamed composites was measured according to ISO 845. The cellular structure of the foams was analyzed by means of scanning electron microscopy (SEM) using a *JEOL JSM-5610* microscope. Samples were prepared by cryogenically fracturing using liquid nitrogen and sputter depositing at their surfaces a thin layer of gold. The average cell size (ϕ) and cell nucleation density (N_f) were determined using the intercept counting method [18]. Two cell sizes were determined according to the direction of foam growth: ϕ_{VD} , where VD is the vertical foaming growth direction and ϕ_{WD} (WD: width direction). The cell aspect ratio (AR) was determined as the ratio between both cell sizes, i.e., $\text{AR} = \phi_{\text{VD}}/\phi_{\text{WD}}$.

2.3.2. Thermal stability

The thermal stability of the composites was characterized using a TGA/SDTA851 thermogravimetric analyzer from *Mettler Toledo* by placing solid samples with an average weight of 10 mg and applying a constant heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 30 to 600 $^{\circ}\text{C}$ under a nitrogen atmosphere.

2.3.3. Fire behaviour

The heat release rate (HRR) during combustion was determined using a cone calorimeter (*INELTEC*, Spain) according to ISO 5660 standard procedure. Solid and foamed circular specimens with a diameter and thickness of 72 mm and 6 mm respectively, were exposed horizontally to an external constant heat flux of 50 kW/m^2 . Reaction to fire parameters such as time to ignition (TTI), peak of the heat release rate (PHRR), fire performance index (FPI) and total heat released (THR) were measured. Moreover, in order to compare the PHRR and THR values of the solid and foamed composites, a normalized parameter, named foam efficiency ratio (FER) was determined. This normalized parameter was defined as the expansion ratio (ER) multiplied by the quotient between the value of the

Table 1
Composition of the solid PP composites.

Material code	H (wt%)	I (wt%)	MMT (wt%)	GnP (wt%)
PP	–	–	–	–
PPH	60	–	–	–
PPH/N	60	–	1	1
PPH/I	60	10	–	–
PPH/N/I	60	10	1	1

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