Synthetic Hydromagnesite as Flame Retardant. A Study of the Stearic Coating Process

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Summary: A synthetic hydromagnesite obtained from an industrial by-product rich in magnesium oxide was employed and evaluated as a non-halogenated flame retardant for poly(ethylene-co-vinyl acetate).
The filler was characterized with different techniques (such as specific surface area, TGA, particle morphology and size measurements, WAXS). Significant differences were found between the synthetic hydromagnesite and the natural one.
Synthetic hydromagnesite was coated with stearic acid and the effectiveness of the coating process was studied by the dye adsorption method and sedimentation volume measurements. The amount of coating agent ranged from 1 to 4.5%. This factor was found to have a significant effect on the thermal decomposition behaviour of the filler.
A poly(ethylene-co-vinyl acetate) (27% of VA) was filled with the coated synthetic grades of hydromagnesite as well as with two commercial flame retardants and different physicochemical properties were evaluated, including their flame retardant effect.

Keywords: coatings; fillers; flame retardance; thermogravimetric analysis (TGA); thermoplastics

Introduction

Hydromagnesite, a basic magnesium carbonate, is referred to in literature[1] as a flame retardant filler for polymers in cable applications. The synthetic hydromagnesite used in this study is a basic magnesium carbonate, obtained by Magnesitas Navarras S.A from an industrial by-product rich in magnesium oxide[2], with a chemical composition corresponding with the formula $5MgO_4CO_25H_2O$. In the temperature range of 200-550°C it undergoes an endothermic decomposition with an associated heat of 800 J/g

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and a final weight loss of 54%. The steps of this decomposition reaction are shown below; as can be seen there is an initial release of water in the form of steam followed by a final step where carbon dioxide is evolved and magnesium oxide is formed [3].

$$4MgCO_3{\cdot}Mg(OH)_24H_2O \rightarrow 4MgCO_3{\cdot}Mg(OH)_2 + 4H_2O$$

$$4MgCO_3{\cdot}Mg(OH) \rightarrow 4MgCO_3{\cdot}MgO + H_2O$$

$$4MgCO_3{\cdot}MgO \rightarrow 5MgO + 4CO_2$$

This endothermic breakdown, as well as the secondary effects like dilution and cooling of the gas phase by water vapor and carbon dioxide released and formation of ceramic substrates, make hydromagnesite a potential flame retardant in the polymer field, acting with a mechanism similar to those of metal hydroxides like aluminium or magnesium hydroxide [4,5].

Experimental

The process of obtaining hydromagnesite involves the formation of a $Mg(HCO_3)_2$ solution by carbonation of a MgO-containing residue slurry and further precipitation of hydromagnesite by addition of pure magnesium oxide as the precipitating agent [6].

In order to achieve a good performance as flame retardant, a high loading of hydromagnesite in the plastic system is usually required. Surface modification with fatty acids is used to improve polymer processing and final properties of polymer compounds, as well as reducing the agglomeration tendency of the filler [7,8].

The dry blending coating process was developed in a double jacket high-speed homogenizer initially heated at 40-45ºC. The temperature was increased up to 60°C and afterwards the system was slowly cooled to room temperature. The stearic acid used was of pharmaceutical grade provided by Roig Farma. The amount of coating agent was ranged from 1 to 4.5% to evaluate the influence of this factor on the thermal decomposition behaviour of the hydromagnesite and the compounds prepared thereof.

The poly(ethylene-co-vinyl acetate), EVA, (Escorene Ultra UL00728, 27% of VA) and the different coated grades of hydromagnesite were mixed in a two roll mill at 75-80ºC. The obtained compounds were compression moulded to produce 1 mm thick sheets. In order to establish a comparison with commercial inorganic flame retardants, compression moulded sheets were prepared with Magnifin H5 KV, a magnesium hydroxide grade with an organic surface treatment, and Ultracarb C5-10, a natural obtained hydromagnesite and huntite coated with 1% of stearate.

Specific density, specific surface and particle size distribution and morphology were measured in order to characterize the synthetic coated and uncoated hydromagnesite. Specific density was measured with an helium picnometer and specific surface area by the single point BET method. Particle size distribution was determined by light scattering with a Beckman Coulter LS 13 320 apparatus. Particle morphology could be observed by scanning electron microscopy (SEM).

The effectiveness of coating was evaluated by the dye adsorption method using red acid Ponceau 3R, known to adsorb onto $Mg(OH)_2$[9]. An excess of dye was added to the sample and the unbound mass was determined by visible spectroscopy using a Shimadzu UV-2101 PC spectrometer working in the range of 190-800nm.

Sedimented volume measurements of the different hydromagnesite grades in hexane were also carried out to evaluate differences in the behaviour between treated samples. The experimental procedure is accurately described in literature [9].

Thermogravimetric analyses (10ºC/min, O_2 atm) were performed in a Setaram TG DTA92 thermobalance. Wide-angle x-ray scattering (WAXS) was employed to get information about the crystalline phases (magnesium oxide) formed during the hydromagnesite thermal decomposition.

Flame retardant filled EVA samples were characterized by values of powdered filler concentration, density, Vicat softening point, hardness, tensile properties and SEM micrographies of the surface fracture were obtained. Furthermore, values of oxygen index and dropping time after flame application were obtained to evaluate the flame retardant behaviour of these EVA compounds. The average dropping time (DT) was measured as the time that a specimen of dimensions 120 mm x 10 mm x 1 mm takes to drop after applying a normalized flame with bottom ignition for 10 seconds.

Results and Discussion

Hydromagnesite samples are coded as follows: uncoated hydromagnesite (UH); surface coated samples of hydromagnesite with different concentration of stearic acid ranged from 1 to 4.5 wt% (H1-H4.5).

The density mean value of UH was 2.43 g/cm^3. In surface-treated filler samples this value was found to be reduced to 2.27 g/cm^3 independently of the percentage of coating applied. The specific surface area was not modified by the coating, all the samples having a value near to 24 m^2/g.

The coating effectiveness parameter was defined as the mass of adsorbed red acid relative to the initial dye mass (χ). Stearic acid presented no dye adsorption, while hydromagnesite showed affinity to adsorb acid dyes like Ponceau 3R. The amount of adsorbed dye decreased significantly beyond 2% of stearic acid, which could be due to a variation of the free hydromagnesite specific surface. Values of sedimented volume decreased with coating agent added up to 3% of stearic acid, probably due to a polarity reduction, and then remained steady.

Table 1. Hydromagnesite grades values of density, sedimented volume and coating effectiveness parameter.

Samples	Density (g/cm^3)	V_{sed} (ml)	X
UH	2.43	53.0	0.34
H1	2.27	44.0	0.33
H2	2.27	27.0	0.32
H3	2.26	24.0	0.22
H4	2.28	23.5	0.25
H4.5	2.27	24.0	0.26

Thermogravimetric analyses (TGA) were performed to study the thermal behaviour of the samples. As mentioned before, thermal decomposition of uncoated hydromagnesite follows three steps within the temperature ranges of 210-250°C, 370-420°C and 480-530°C. The effect of increasing the amount of stearic acid has been related with changes in the thermal decomposition kinetics of the hydromagnesite, as is depicted in the TGA shown in Figure 1.

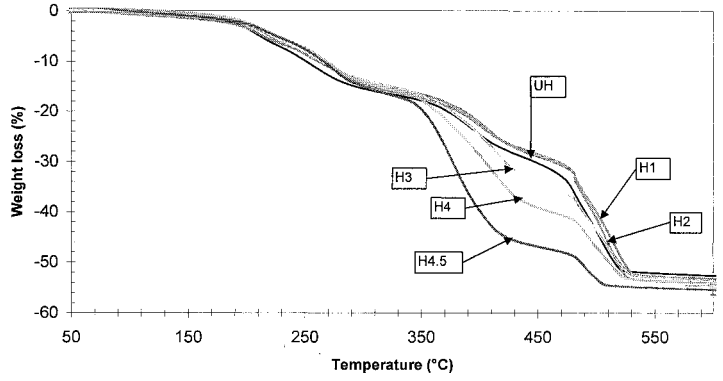


Figure 1. TGA plots of hydromagnesite grades.

Substantial differences were found in the temperature range from 320 to 480 ºC corresponding to decomposition steps that result in H_2O and CO_2 liberation, and oxide formation. A remarkable increase in the decomposition rate was observed at the beginning of that interval as the coating level was increased in the filler. The filler uncoated and coated with the lower levels of stearic acid (< 2 wt %) did not follow this trend, having similar behaviour to the unmodified filler.

To analyse the differences in the oxide formation, UH and H4.5 samples were heated at 400ºC for one hour, afterwards WAXS patterns were recorded (Figure 2). The MgO presence was observed in both samples, but the H4.5 sample clearly showed a more intense and defined MgO signal. The shape of the diffraction peaks suggest higher crystallinity in MgO formed from the H4.5 sample, which would be in good agreement with a higher oxide formation rate.

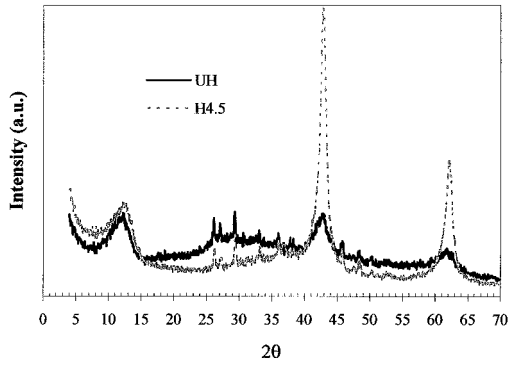


Figure 2. X-Ray patterns of samples after thermal treatment at 400ºC.

Aspects like particle size and morphology usually require to be controlled to guarantee optimal final properties of the polymer compounds.

Numerical particle size distribution showed no significant differences among uncoated hydromagnesite and coated samples, giving a mean particle size (d_{50}) of 0.1μm for UH and 0.09μm for the coated grades. However, the volumetric distribution exhibited higher particle size values (d_{50} = 13.3 μm for coated particles; d_{50} = 16 μm for UH). This discrepancy could probably be due to the presence of agglomerates. Also, the volumetric distribution was found to be broader than the numerical one, with the d_{90} values 57μm and 38μm for uncoated and coated filler respectively. This improvement

may be attributed to a decrease in the level of agglomerates because of the coating process. In Figure 3 a SEM micrograph of H1 sample is shown. The morphology of these particles forming fine platelets can be observed.

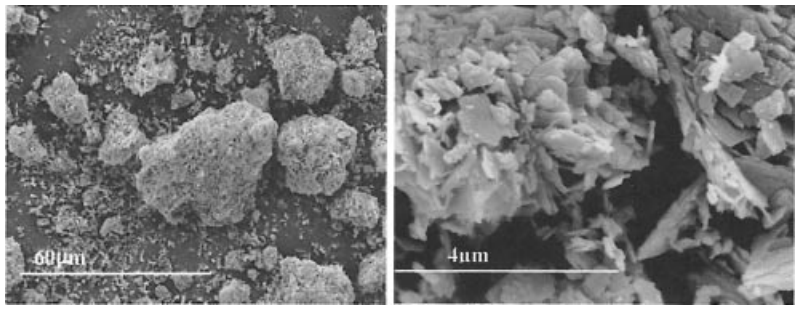


Figure 3. General aspect and magnification of H1particles by SEM.

A mixture of hydromagnesite with huntite, named Ultracarb®, was also studied for comparison. It presented a bimodal size distribution, Figure 4. The first curve reported values smaller than one micron and the second had a mean value near 3µm. As can be seen in Figure 4, morphological aspect of the Ultracarb® particles, forming thin platelets, was similar to the particle shape of synthetic hydromagnesite.

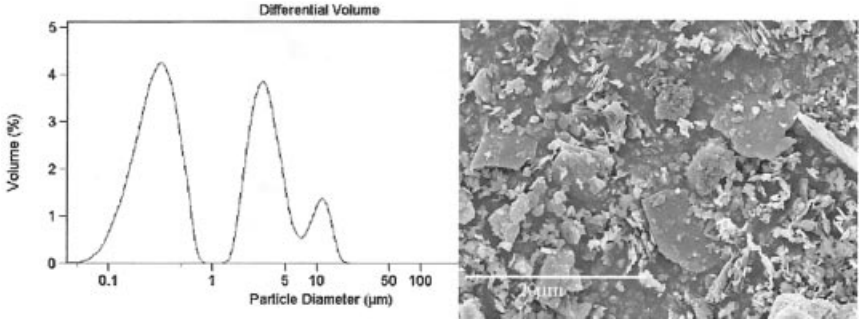


Figure 4. Ultracarb volumetric particle size distribution and SEM image.

The presence of aggregates could result in a poor homogeneity in the filled polymer, affecting its mechanical properties. In order to improve this aspect the optimal milling time for the hydromagnesite was studied. In Figure 5 volumetric particle size distributions of hydromagnesite samples milled for 0.5 and 5 minutes are compared.

The improvement obtained with a 5 minutes grinding step is also confirmed with the SEM picture presented in Figure 5. Higher milling times do not present significant reduction in the particle size.

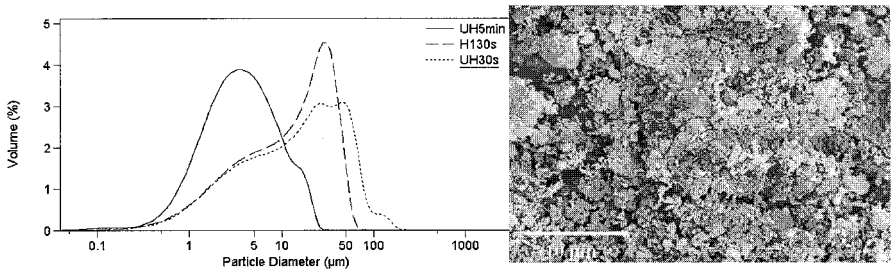


Figure 5. Variation of hydromagnesite particle size and volumetric distribution with milling time.

The nomenclature employed for the filled polymers was as follows: EVA filled with uncoated hydromagnesite (EUH); EVA filled with hydromagnesite treated with stearic acid from 1 to 4.5wt% (EH1-EH4.5); EVA filled with Ultracarb C5-10 (EU) and EVA filled with Magnifin H5 KV (EMn).

Table 2 summarizes some relevant characteristics of the compounds. As expected, the density value was in concordance with the filler concentration determined by ashing. The Vicat temperature was almost independent of the filler loading, although a slight decrease seemed to be observed due to the high surface coating levels.

The highest DT value was found for EH2 sample. Despite DT values show considerable error limits (between 5-15%), this good fire response was confirmed by the limiting oxygen index results. The oxygen index found for sample EH2 was 32.9. From this point a progressive decrease could be observed as coating level was increased.
There were many factors affecting the fire behaviour of these samples, the most important ones being the filler loading and the percentage of added coating agent. This last factor being responsible for the filler decomposition changes as mentioned before.

Table 2. Concentration, density, Vicat softening temperature (VST), dropping time (DT) values and oxygen index (OI) measured for hydromagnesite filled EVA compounds.

Sample	Filler (%)	ρ (g/cm^3)	VST (°C)	DT (s)	OI (%)
EUH	50	1.29	54.3	14	24.5
EH1	55	1.37	56.9	21	31.9
EH2	57	1.43	53.8	38	32.9
EH3	56	1.40	53.4	23	29.8
EH4	57	1.45	53.9	19	29.2
EH4.5	56	1.37	50.4	17	27.6

Standard tensile specimens were machined from the moulded plaques and tests were performed at room temperature and at a cross-head speed of 10 mm/min. Although tensile properties (Table 3) were highly dependent on the filler loading substantial differences related to the coating concentration were noticed. Secant elasticity modulus at 1% of strain ($E_{1\%}$) as well as hardness values increase with filler loading up to 2% of stearic acid with a progressive reduction of these values for samples EH3 and EH4.5 that could indicate a plasticizer effect of the stearic acid on EVA compounds. This apparent plasticizing effect could also justify the higher elongation at break of samples with an excess of coating agent. A high value of elongation at break (70%) resulted for EUH sample. The cause of that would be the low filler content (50%) in this compound. Tensile strength (σ) increased up to 2-3% of stearic acid and showed a reduction in samples with an excess of this coating agent. Higher adhesion between filler and matrix would explain the increase in tensile strength. A SEM study of the tensile fracture surfaces was carried out. In Figure 6 the interface adhesion induced by the stearic acid on the EVA-hydromagnesite compounds can be observed.

The comparative results obtained with the EVA compounds filled with the different inorganic flame retardants are summarized as follows. Synthetic hydromagnesite compounds had higher $E_{1\%}$ and σ, but less deformability than Ultracarb and Magnifin compounds (Table 4). Furthermore, as depicted in Figure 7, higher deformability of the polymer matrix was observed for EMn and EU samples. Differences observed in $E_{1\%}$ may be attributed to the differences among the fillers such as particle size distributions or coating treatment. The low value of $E_{1\%}$ in EMn could be related with the surface

coating of this filler with a silicone derivate. On the other hand, the good adhesion of coated hydromagnesite-EVA compounds observed by SEM would be responsible of the higher value of $E_{1\%}$. Dropping time and oxygen index values were strongly affected by the filler content.

Table 3. Mechanical properties of filled EVA.

Samples	$E_{1\%}$ (MPa)[a]	σ (MPa)[b]	ε (%)[c]	Hardness (Shore D)
EUH	107	6.1	70	40
EH1	180	7.6	27	44
EH2	222	8.7	46	47
EH3	181	8.4	54	46
EH4	162	7.6	52	44
EH4.5	165	7.7	80	42

[a] Secant elasticity modulus at 1% of strain. [b] Tensile strength. [c] Elongation at break.

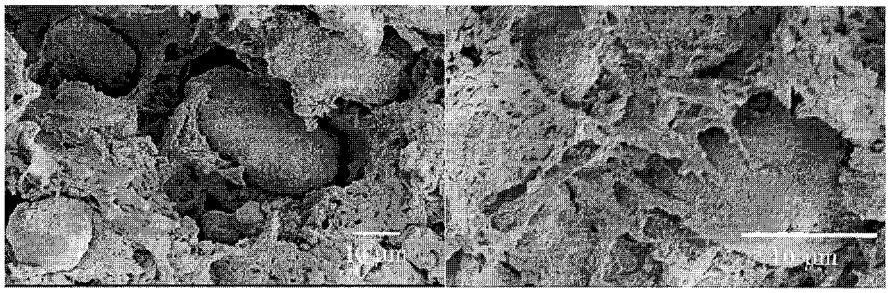
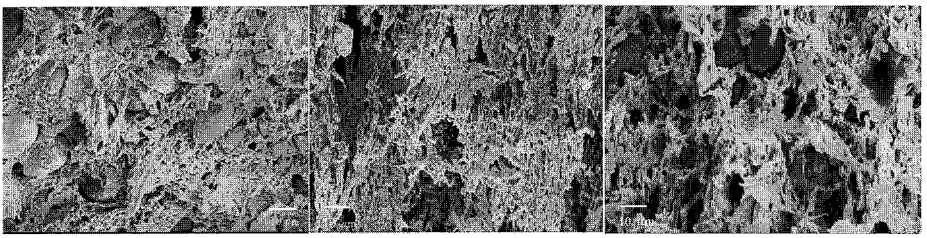


Figure 6. Fracture surfaces of EUH and EH1 showing different adhesion particle-matrix.

Table 4. Characterization of hydromagnesite, Ultracarb and Magnifin filled EVA compounds.

Samples	Filler (%)	ρ (g/cm^3)	VST (°C)	DT (s)	OI (%)	$E_{1\%}$ (Mpa)	σ (Mpa)	ε (%)
EH1	55	1.37	56.9	21	31.9	180	7.6	27
EU	63	1.51	57.4	45	34.7	122	6.5	149
EMn	60	1.46	57.4	19	39.2	75	6.7	204



(a) (b) (c)

Figure 7. Fracture surface SEM images of EH1 (a), EMn (b) and EU (c).

Despite this, it could be considered that the fire performances of the synthetic hydromagnesite compounds were comparable with the commercial flame retardants studied. Reduction of filler particle size and therefore a narrow distribution could improve mechanical properties of synthetic hydromagnesite filled EVA compounds.

Conclusions

Synthetic hydromagnesite has proven to be suitable filler for flame retardant polymer formulations, comparable to commercial grades based on natural hydromagnesite as well as to other inorganic flame retardant fillers.

An optimal content of stearic acid as coating agent was found within the range 1-2%. Higher percentages of stearic acid seemed to induce adverse effects during the thermal decomposition of hydromagnesite and on the flame retardant behaviour of filled EVA compounds.

The homogeneity of synthetic hydromagnesite particle size distribution was remarkably improved by the addition of a controlled milling step in the production process.

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