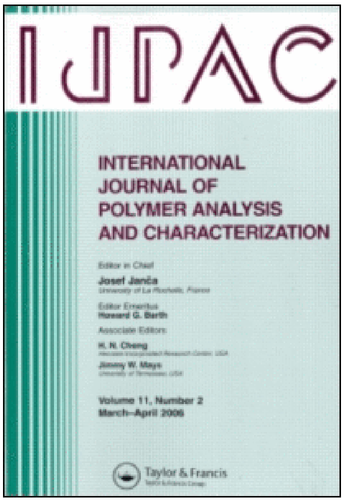

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# The Combined Action of Huntite and Hydromagnesite for Reducing Flammability of an Ethylene-Propylene Copolymer

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# The Combined Action of Huntite and Hydromagnesite for Reducing Flammability of an Ethylene-Propylene Copolymer

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The flammability of a filled ethylene-propylene copolymer is discussed. A mineral filler with 40% of hydromagnesite and 60% of huntite by weight is used as a flame retardant additive. Some burning characteristics and mechanical properties have been studied in relation to the amount of incorporation. Flammability was measured by the oxygen index method, the dripping test and the rate of spread of flame test. Thermal degradation was investigated by differential scanning calorimetry and thermogravimetry in combination with differential thermal analysis.

KEY WORDS Flame retardant, Huntite, Hydromagnesite, Flammability, Filler, Thermal degradation, Thermal analysis

## INTRODUCTION

The ability of hydrated inorganic fillers to flame retard polymers, principally the result of endothermic decomposition by release of water, is well known [1–8]. However, the flame retardant filler must have sufficient thermal stability during polymer processing such as extrusion and injection molding, must present a decomposition range compatible with the range of polymer thermal degradation and must confer acceptable mechanical properties for the composite material obtained.

Consequently, the choice of an inorganic retardant filler is dependent upon the nature of the polymer matrix to be retarded. Hence, the use, for example, of alumina trihydate (ATH) seems to be rather more suitable for thermoset resins than for thermoplastics with processing temperature above 250°C.

This paper reports on the use of Portakarb, which is a mineral filler with 40% of hydromagnesite $Mg_5[(OH)(CO_3)_2].4H_2O$ and 60% of huntite $CaMg_3(CO_3)_4$ by weight. An ethylene-propylene copolymer is filled with Portakarb and some burning characteristics and mechanical properties are reported in relation to the amount of incorporation.

## EXPERIMENTAL

### Materials

The compounds were prepared with a twin screw extruder BC21 (Clextral, Firminy, France) and injection moulding procedures (OTTO 95 Sandretto, Lorette, France) using the impact copolymer 3120 MN4 supplied by Appryl (Appryl, Lavera, France) and Portakarb obtained from Les Minerais de la Méditerranée (Les Minerais de la Méditerranée, Balaruc, France). Extrusion and injection moulding were carried out at temperatures around 200°C. The amount of incorporation was determined by calcination at 450°C, followed by the correction of the mass lost by the filler during this operation.

### Particle Size Measurement

To measure the particle size distribution of Portakarb, we have used a Coulter LS 130 (Coultronics France, Margency) unit in which sample particles are suspended in water. The LS 130 uses laser diffraction (light scattering) technology to determine particule size distribution by volume or surface area in the range between 0.1 μm and 900 μm.

### Thermal Analysis

Thermal properties were measured by the following methods: a differential thermal analysis instrument combined with a thermogravimetric apparatus TGDTA 92, (Setaram, Caluire, France). Standard alumina crucibles were used, and measurements were carried out in a dynamic air and nitrogen or argon atmosphere at a heating rate of 10°C/min up to 700°C with samples mass around 40 mg. Differential scanning calorimetry (DSC) (Setaram heat-flux DSC 111, Caluire, France) completed the evaluation of thermal degradation.

### Rate of Spread of Flame Test

The rate of spread of flame test (French specification NF P 92-504) serves as a complementary test to the epiradiateur test which determines the fire performance of samples. The rate of spread of flame test is used to determine the contribution to flame spread to enable a classification in categories M.1 (non-flammable) to M.4 (high flammability) to be made if a material melts rapidly without burning in the vicinity of the radiator in the epiradiateur test and if a material does not achieve classes M.1 to M.3 (moderately flammable). In the first case afterflame, nonpropagation of flame and falling off of burning or non-burning droplets is observed; in the second, flame spread rate is measured.[9] The apparatus is illustrated in Figure 1.

The rate of spread of flame, $v$, is computed from $v = 250/t$ where $t$ is the time in s required to reach the second reference mark.

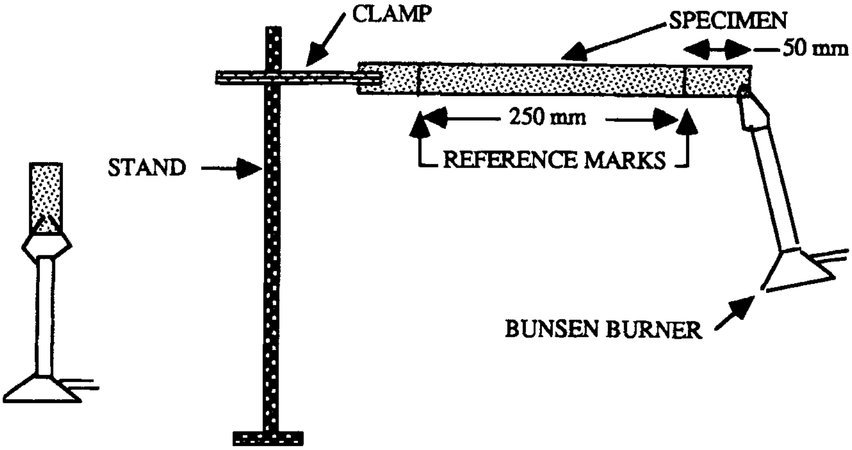

FIGURE 1 Determination of spread of flame rate. Left: Front view. Right: side view.

### Dripping Test

The dripping test (French specification NF P 92505) is a further complementary test to determine burning drops, a phenomenon which cannot be clearly assessed in the epiradiateur test. It is carried out if, during the relevant epiradiateur test, non-burning drops are observed or if the material withdraws very rapidly or without burning from the vicinity of the radiator. The material is classified in classes M.1 to M.4 depending on test performance [9]. A diagram of the test rig is presented in Figure 2.

If the geometry of the specimen is altered during the test, the distance of the radiator from the specimen must be readjusted to 30 mm. If the specimen ignites during the first 5 min, the radiator is removed 3 s after ignition; irradiation is continued as soon as the specimen extinguishes. During the second 5 min, irradiation is maintained throughout regardless of whether the specimen burns. Note is made of any dripping, whether the cotton wool ignites, the level of smoke development, appearance and amount of residues. Ignition of the specimen is noted if it is longer than 3 s.

The ignition source is a horizontal 500 W electric radiator and the radiation intensity on specimen, in a horizontal position (30 mm from radiator), is 3 W/cm$^2$. The test duration is 10 min and if the cotton wool ignites, the material is classified in class M.4.

### Limiting Oxygen Index (LOI)

Ferimore and Martin's limiting oxygen index (LOI) [10] is one of the several test methods for evaluating the burning behaviour of polymers. This test illustrates the relative flammability of materials and measures the minimum concentration of oxygen in an oxygen-nitrogen atmosphere that is necessary to initiate and support a flame for more than 3 minutes. The LOI-value is given in percent:

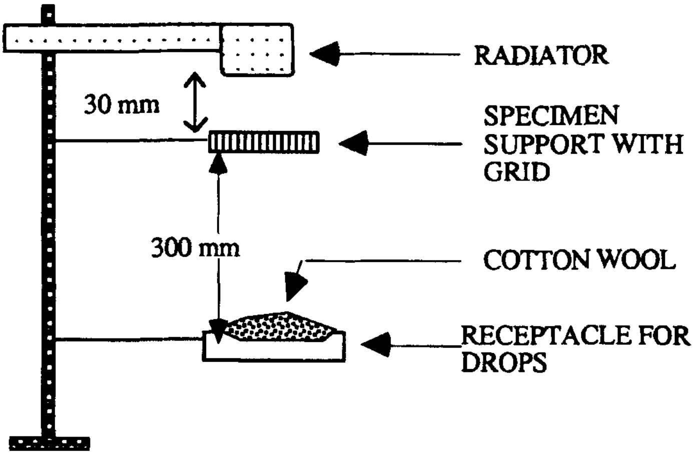

FIGURE 2 Test rig for burning drops.

$$\mathrm{LOI} = \frac{\text{volume of } O_2}{\text{volume of } O_2 + \text{volume of } N_2} \times 100$$

A LOI-value of 30 means that a material will burn in an atmosphere of 30% oxygen. The minimum oxygen concentration of the specimens were measured with a Stanton Redcroft instrument following the ISO 4589 specification (Fig. 3).

### Mechanical Properties

A universal test machine DY 26-100 kN (Adamel Lhomargy, Ivry sur Seine, France) was used for the evaluation of mechanical properties such as modulus according to the ISO 178 specification. A Zwick 5102 Pendulum Impact Testers (Zwick Gmbh & Co, Germany), with energy of 4 J, was used for determining the Charpy impact strength according to the ISO 179 specification. Specimens, 110 mm × 10 mm × 4 mm, were obtained by injection molding.

## RESULTS AND DISCUSSION

The chemical composition of Portakarb determined by X-ray fluorescence is reported in Table I. Figure 4 illustrates the particle size distribution of Portakarb. Differential thermal analysis (DTA) and thermogravimetry (TG) curves of Portakarb in nitrogen (Fig. 5) show two main endotherms, the first at about 330°C due to the dehydration of hydromagnesite and the second between 450°C and 600°C due to overlapping reactions of décomposition of huntite and hydromagnesite of the filler [11]. The mass lost between 100°C and 600°C

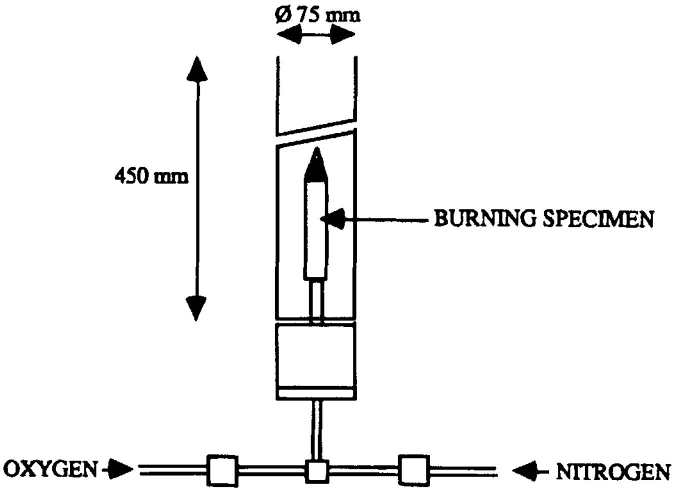

FIGURE 3 Oxygen index apparatus according to ISO 4589 specification.

TABLE I

Chemical Composition of Portakarb (%).

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $MgO$ | $CaO$ | $Na_2O$ | $K_2O$ | $TiO_2$ | Mass lost at 1050°C |
|---|---|---|---|---|---|---|---|---|
| 0.5 | 0.1 | 0.05 | 38 | 7 | 0.05 | 0.05 | 0.04 | 54.21 |

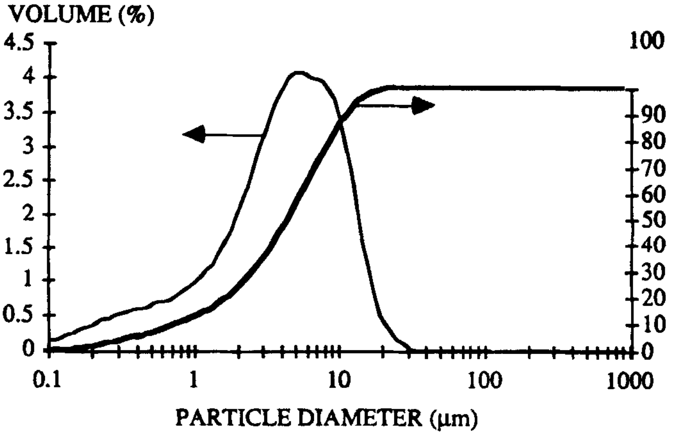

FIGURE 4 Particle size distribution of Portakarb from Coulter LS 130.

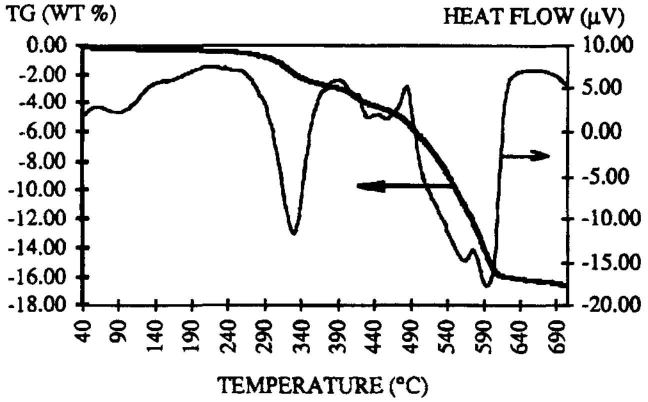

FIGURE 5 DTA and TG analysis of Portakarb in nitrogen.

equals 44%. The unfilled polymer exhibits in the same range, after the melting of crystallites at about 165°C, a single endothermic degradation (Fig. 6).

With the filled polymer's DSC and (in nitrogen) DTA curves (Fig. 7-A and Fig. 7-B), a new endotherm (peak around 300°C from DTA curves) appears due to the decomposition of the filler: the Portakarb decomposes before the degradation of the polymer matrix. Hence, the DTA thermograms of composites in air (Fig. 8) present no exothermic reactions between 320°C and 425°C as we see for the unfilled polymer.

Portakarb gives good flame retardant performance (Table II). This effective flame retardance is ascribable to the combined actions of dehydration of hydromagnesite between 250°C and 460°C, followed by the decomposition of a part of huntite at about 500°C (Fig. 5). These phenomena, as compared to those obtained with alumina trihydrate [5–6], have the following consequences:

- the endothermic decomposition of Portakarb (Fig. 7-B) cools the substrate and reduces thermal feedback to the solid phase. The temperatures observed from the burning face (Fig. 9) of filled and unfilled polymer decrease when the amount of portakarb increases.
- the release of water, mainly from hydromagnesite and a part of carbon oxide from huntite, dilutes the gaseous phases so that the lower ignition limit of the gas mixture is not exceeded: the exothermic reactions between 320°C and 425°C appears over 425°C.

The results of increasing amounts of incorporation and DTA diagrams (Fig. 10) of char combustion composites show the importance of dilution: the higher the amount of Portakarb, the higher the residues. DTA diagrams (Fig. 10) of these residues give more important decomposition when the amount of Portakarb increases; in fact the thermal feedback is lower (no more combustible) and complete decomposition of the filler does not occur. The efficiency of Portakarb due to this endothermic decomposition, in relation

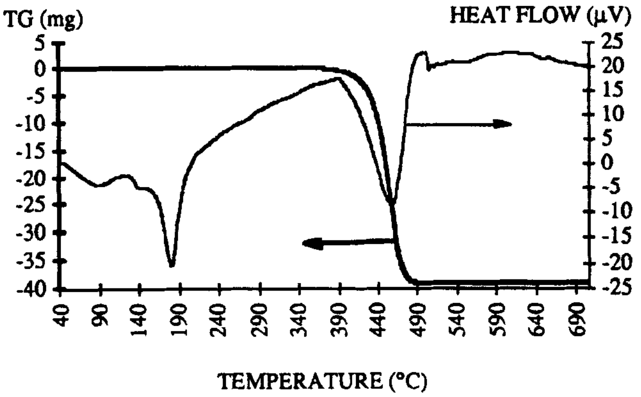

FIGURE 6 DTA and TG analysis of 3120 MN4 in nitrogen.

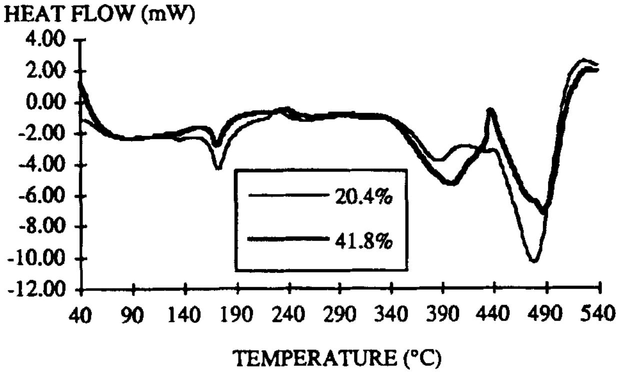

FIGURE 7-A DSC analysis of 20.4% and 41.8% w/w of filled polymer in nitrogen.

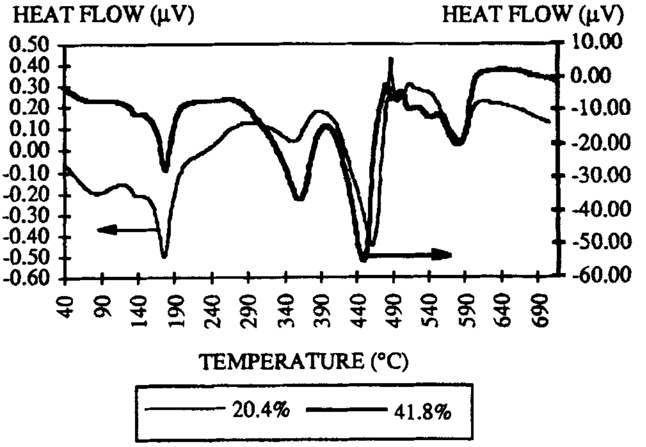

FIGURE 7-B DTA analysis of 20.4% and 41.8% w/w of filled polymer in nitrogen.

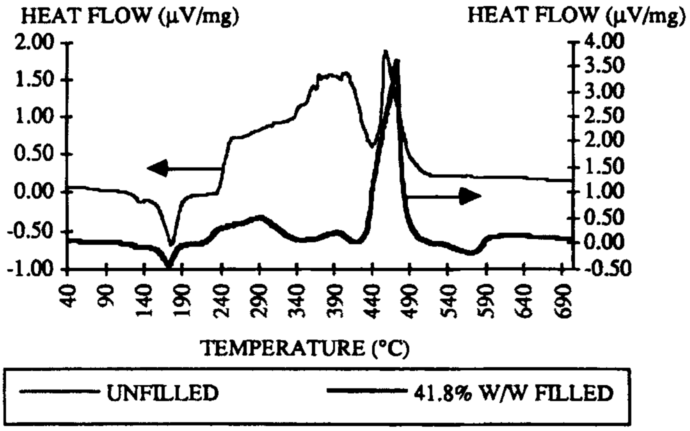

FIGURE 8 DTA analysis in air of unfilled and filled (41.8%) 3120 MN4.

TABLE II

Burning Characteristics of the Composites.

| Loading of Portakarb (wt %) | Rate of Spread (mm/s) | Dripping Test | Oxygen Index (%) |
|---|---|---|---|
| 0 | 0.64 | inflammation | 18.3 |
| 20.4 | 0.65 | inflammation | 20.3 |
| 25 | 0.46 | no inflammation | 21.1 |
| 34.8 | 0.5 | no inflammation | 21.2 |
| 41.8 | 0.28 | no inflammation | 24.5 |
| 48.5 | 0.12 | no inflammation | 24 |

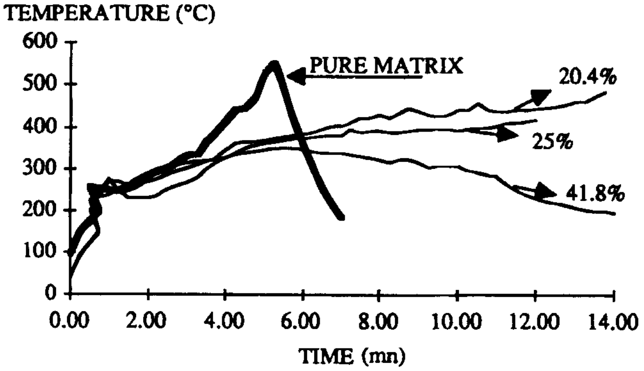

FIGURE 9 Temperatures of burning surfaces of pure matrix and composites.

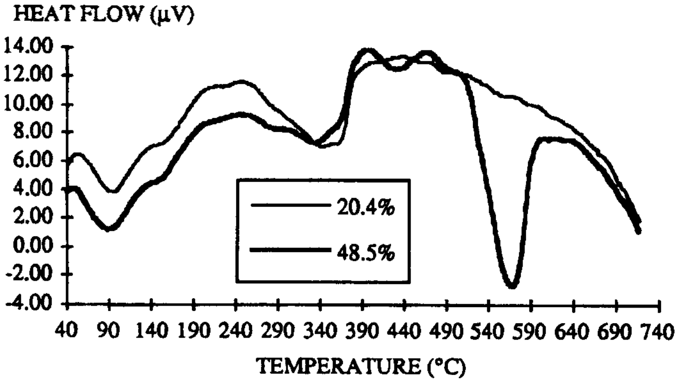

FIGURE 10 DTA analysis (in argon) of char residues 20.4% and 48.5% loading by weight.

to the amount of incorporation decreases with high filler levels. The effect of dilution (no more combustible) becomes more effective for high filler levels than the endothermic decomposition of the filler.

As compared to values obtained with alumina trihydrate [5–6], the oxygen indexes of our composites give comparable values. The oxygen index provides an evaluation of the intrinsic flammability of a polymeric material [12]. The value is 5.7 points higher for a loading of 48.5 w/w of Portakarb.

The rate of spread decreases while the amount of Portakarb increases (Table II) and in the dripping test, cotton wool does not ignite above 25% (Table II) by weight of Portakarb.

The flexural modulus of composites increases proportionally with loading while the Charpy impact strength decreases (Table III). Compared to values obtained with mica in the same matrix (3777 MPa and 6.9 kJ/m$^2$ respectively for flexural modulus and Charpy impact) [13], the mechanical properties are good; therefore the compatibility of Portakarb and the copolymer is acceptable.

## CONCLUSIONS

Portakarb gives good flame retardant performance by two physical actions: endothermic processes in the solid phase and dilution in gaseous phase. Portakarb is an effective flame retardant filler with good thermal stability, and its composites give acceptable mechanical properties.

TABLE III

Mechanical Characteristics of the Composites.

| Loading of Portakarb (wt %) | Flexural Modulus (MPa) | Charpy Impact (*KJ/m²*) |
|---|---|---|
| 0 | 1282 | - |
| 20.4 | 1809 | 43.6 |
| 25 | 2500 | 41.61 |
| 34.8 | 2605 | 38.67 |
| 41.8 | 3779 | 16.84 |
| 48.5 | 4309 | 9.21 |
| 40% MICA[13] ($d_{50} = 48\mu m$) | 3777 | 6.9 |

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