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Magnesium hydroxide/zinc borate/talc compositions as flame-retardants in EVA copolymer

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Abstract: The fire-resistance of EVA filled with ternary systems (magnesium hydroxide/zinc borate/talc) has been investigated. The release of water from $\text{Mg}(\text{OH})_2$ seemed to be the predominant phenomenon which acts in relation to fire-resistance. The presence of talc as a minor component, mainly in binary compositions by partial substitution of $\text{Mg}(\text{OH})_2$, appeared to enhance the flame-retardant properties. It acts by forming a diffusion barrier which is able to limit the transfer of degradation products and oxygen. Synergism was also noticed between talc and zinc borate at constant $\text{Mg}(\text{OH})_2$ loading in ternary compositions.

Keywords: magnesium hydroxide; talc; zinc borate; EVA; flame-retardant

INTRODUCTION

Talc has been incorporated into EVA containing mineral flame-retardant formulations with the aim of finding synergies in the flammability properties.

In previous studies,¹⁻³ talc was combined with brominated fire-resistant (FR) antimony trioxide blends in a PP-PE copolymer at constant total loading (40% ww). It was noticed that 50% of the brominated blend could be replaced by different talcs without significant loss of flame-retardant properties and with an improvement in the stiffness and maximal tensile stress of the filled copolymer. The use of pure and fine talcs with a high aspect ratio and large specific surface area gave the best results, both for flame-retardant and mechanical properties.

It was concluded that the high values obtained for the latter properties might be connected with the intensity of talc/polymer adhesion. It was also supposed that talc, because of lamellar character, could build a layer acting as a mass diffusion barrier for volatile combustible compounds issuing from the degrading polymer.

In this study, we investigate synergisms or additive effects with hydrated minerals used as FR additions in another type of copolymer, EVA, which degrades in two distinct steps.⁴ The first one is related to the loss and degradation of the vinyl acetate monomers with acetic acid formation and the second one concerns the ignition of the resulting fragments of ethylene.

We selected magnesium hydroxide because of its good effectiveness as a FR in EVA.⁵ Moreover, it was recently shown^{6,7} that it could present a synergism

with zinc borate at low borate contents to improve FR properties. Consequently, we focussed on binary and ternary compositions of the three minerals in EVA with a particular interest in compositions rich in magnesium hydroxide. The total loading was kept constant at 60% (w/w).

EXPERIMENTAL

The EVA copolymer used was a thermoplastic-elastomeric grade ELVAX[®] 260 (DuPont de Nemours) used in the cable industry. This copolymer has an MFI = 6 g/10 min, a molar mass of $82\,000\text{ g mol}^{-1}$ and a vinyl acetate content of 28% (w/w). The $\text{Mg}(\text{OH})_2$ was MAGNIFIN[®] H10 (Martinswerk) characterized by a median diameter of 0.85 micron and a specific surface area of $10\text{ m}^2\text{ g}^{-1}$. The zinc borate was FIREBRAKE[®] ZB (US Borax) characterized by the molecular formula $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ and a median diameter of 7 microns. Physico-chemical data about the talc are confidential.

The specimens of filled polymers ($110 \times 10 \times 4\text{ mm}^3$ dumbbells, $70 \times 70 \times 4\text{ mm}^3$ sheets, $127 \times 12.7 \times 3.2\text{ mm}^3$ barrels) were prepared in three steps:

- (1) twin-screw extrusion of masterbatches at 60% (w/w) for each mineral,
- (2) mixing of masterbatches by twin-screw extrusion and second extrusion of one-filler compositions,
- (3) Injection moulding of specimens for all testings performed according to ISO specifications.

Fire tests (LOI, UL 94, AFNOR NF P 92-505

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Formulations	LOI	UL 94	IT (s)	IP (s)	Tensile stress (MPa)	Elongation at break (%)
60% Mg(OH) ₂	52	V-0	97	9.8	8.7	204
60% BZn	24	V-2	65	9.7	5.3	173
60% Talc	–	NC	–	–	11.8	77
57% Mg(OH) ₂ +3% BZn	49.8	V-0	79	11.2	9.6	182
45% Mg(OH) ₂ +15% BZn	49	V-1	81	9.3	10.4	167
30% Mg(OH) ₂ +30% BZn	35.2	NC	64	17.6	8.5	171
57% Mg(OH) ₂ +3% Talc	56.4	V-0	102	9.8	10.2	161
45% Mg(OH) ₂ +15% Talc	49.4	V-0	93	9.8	11	117
30% Mg(OH) ₂ +30% Talc	38.2	NC	96	13.8	11.9	90
30% Mg(OH) ₂ +15% BZn+15% Talc	43.6	V-1	72	9.3	9.8	138
15% Mg(OH) ₂ +30% BZn+15% Talc	34.2	NC	70	9.8	7.1	154
15% Mg(OH) ₂ +15% BZn+30% Talc	34.6	V-2	74	10.7	9.2	111
20% Mg(OH) ₂ +20% BZn+20% Talc	33.4	V-1	72	10.5	9.3	132

Table 1. Comparison of fire and mechanical properties for the various compositions in EVA (60% total loading)

‘Epiradiateur test’) were carried out using standardized specimens. In the ‘Epiradiateur test’, a radiator (500 W) is placed on top of a sheet of plastic. The first ignition time (IT) was noted. Afterwards, the radiator was removed and replaced as soon as extinction occurs. The application of this device was repeated stepwise until successive extinctions took 5 min, the number of steps (N) and the mean ignition period (IP) were noted. Not less than four specimens were tested, for each filled composition.

The results of the fire tests were correlated with those of thermal analysis (Setaram TGDTA92 - Lyon (France)) performed on 10 mg samples. Thermogravimetric and differential thermal analysis (5 °C min⁻¹ up to 700 °C) were coupled with on-line Fourier transform infra-red spectroscopy (BRUKER IFS 66, Karlsruhe Germany). Integration of the IR spectra was made using the Gram-Schmidt orthogonalization method,^{8,9} initially developed for chromatography, which provides the evaluation of the quantity of each (or all) gaseous effluent(s) evolving from the sample in

function of time (or temperature) through a heated transfer pipe.

Rheological measurements (shear at steady state flow) carried out at 180 °C (Ares Rheometrics Scientific, Piscataway, NJ, USA) and tensile stress measurements (Adamel, Lyon France) were also used to characterize and understand the behaviour of filled EVA copolymers.

RESULTS AND DISCUSSION

The results are compiled in Table 1 and detailed in ternary diagrams (Figs 1–6), each apex of the triangle corresponding to EVA associated with only one filler.

The fire tests indicated that the best results were obtained for compositions in which Mg(OH)₂ was predominant. These results show that the flame-retardancy is mainly due to the decomposition of the hydrated filler. Magnesium hydroxide starts to break down above 300 °C. Conversion to magnesium oxide takes place in an endothermic reaction, which cools

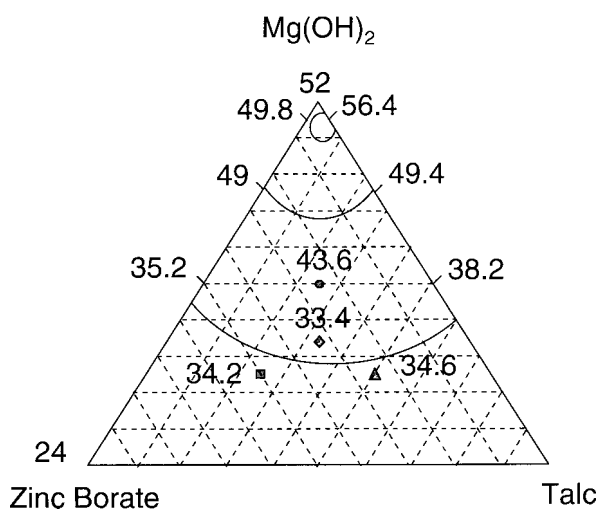


Figure 1. Limiting oxygen index (LOI) of the ternary filler compositions in EVA.

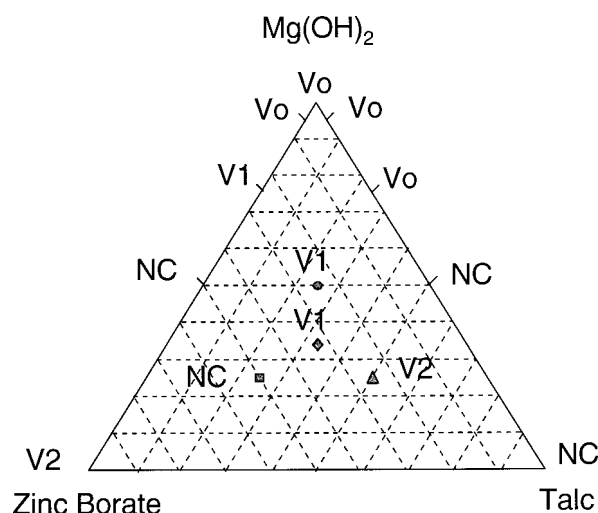


Figure 2. UL 94 tests of the ternary filler compositions in EVA.

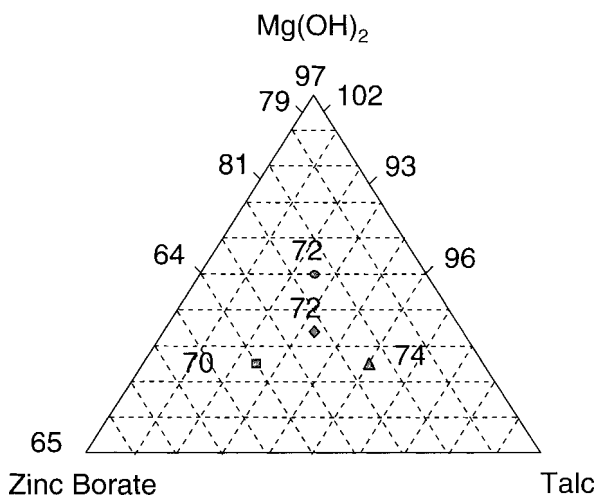


Figure 3. First ignition time of the ternary filler compositions in EVA.

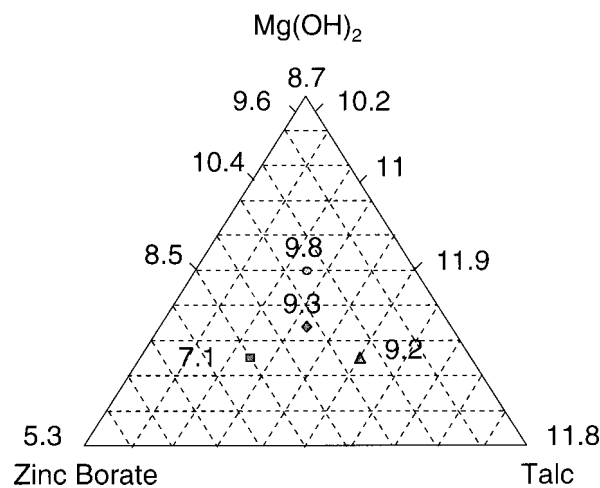


Figure 5. Maximal tensile strength of the ternary filler compositions in EVA.

the polymer, with release of water which dilutes the flammable pyrolysis gases.

In the region surrounding the $\text{Mg}(\text{OH})_2$ apex, we noted that the (limiting oxygen index) LOI of the EVA compounds can be increased to values greater than 50. In this region, the substitution of a minor part of $\text{Mg}(\text{OH})_2$ by talc appears advantageous. Experimental LOI of binary systems are greater than expected for a linear combination of the LOI of $\text{Mg}(\text{OH})_2$ and of talc separately. The presence of a maximum for the 57/3 composition is evidence of the synergism between $\text{Mg}(\text{OH})_2$ and talc (Fig 1) for high contents of the hydrated filler.

Conversely and contrary to other work^{6,7}, no synergism was noticed between $\text{Mg}(\text{OH})_2$ and zinc borate in binary compositions. Nevertheless, we noted a synergism between talc and zinc borate in ternary compositions when the loading of $\text{Mg}(\text{OH})_2$ is kept constant at 30%.

In the UL 94 test, the V-0 class is maintained at least up to a rate of substitution of 25% for talc in $\text{Mg}(\text{OH})_2$ -talc compositions (Fig 2). Beyond this

value, the talc seems to cause a ‘wick effect’ because mineral fillers tend to increase the thermal conductivity of the polymer. Moreover, this effect is stronger when the fillers are lamellar as in the case of talc.¹⁰ We found also the same kind of synergisms as those mentioned above for ternary systems in which the loading of $\text{Mg}(\text{OH})_2$ is kept constant.

As in the case of a PP-PE copolymer,¹ the presence of $\text{Mg}(\text{OH})_2$ strongly increases the time of first ignition in comparison with that of the unfilled copolymer (Fig 3). Since talc tends to stabilize this property, with a synergism for 3% talc in binary compositions, it can be assumed that this mineral plays a role in determining the rate of emission of combustible volatile gases causing ignition.

The median times of ignition are the shortest in the upper zone of corresponding diagram (Fig 4). It should be noted that all ternary compositions exhibit lower values than these observed for binary compositions with a loading of 30% in $\text{Mg}(\text{OH})_2$. Consequently, for this property also a synergism can be seen between talc and zinc borate.

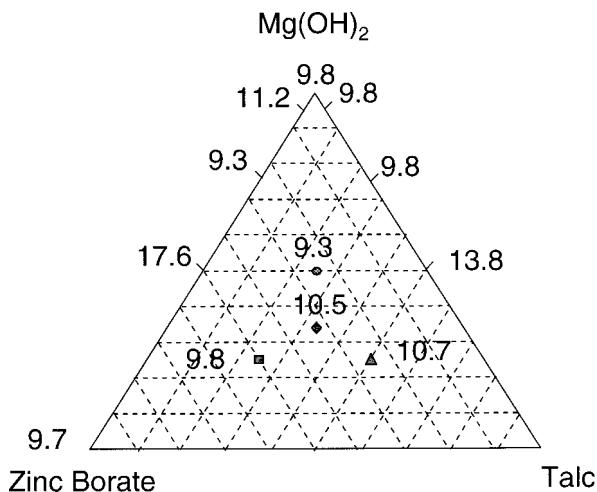


Figure 4. Mean ignition period of the ternary filler compositions in EVA.

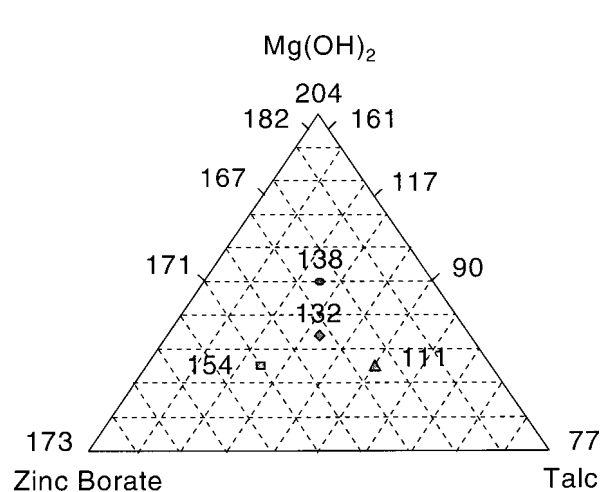


Figure 6. Elongation at break of the ternary filler compositions in EVA.

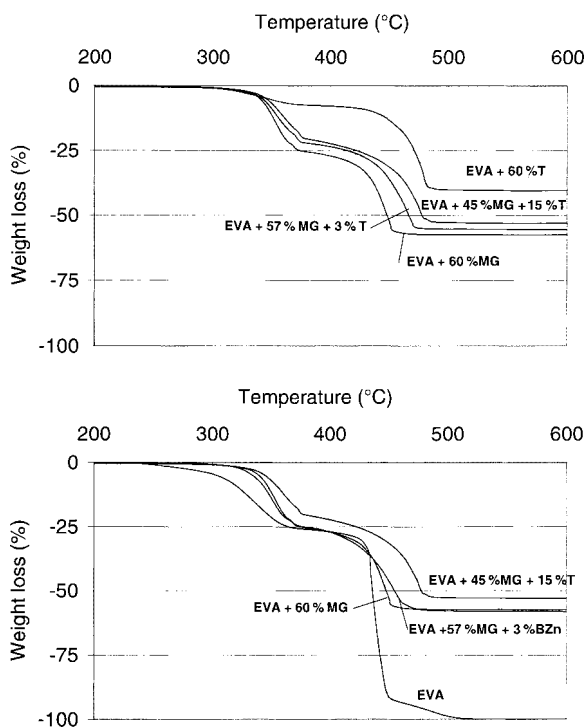


Figure 7. TGA curves of EVA and binary filler compositions in EVA.

Fire tests results show that synergisms exist for $Mg(OH)_2$ -talc binary compositions when $Mg(OH)_2$ is the main component and for $Mg(OH)_2$ -talc-zinc borate ternary compositions containing 30% $Mg(OH)_2$. The synergism $Mg(OH)_2$ -zinc borate mentioned by some authors^{6,7} was not observed. This could be ascribed to the differences existing

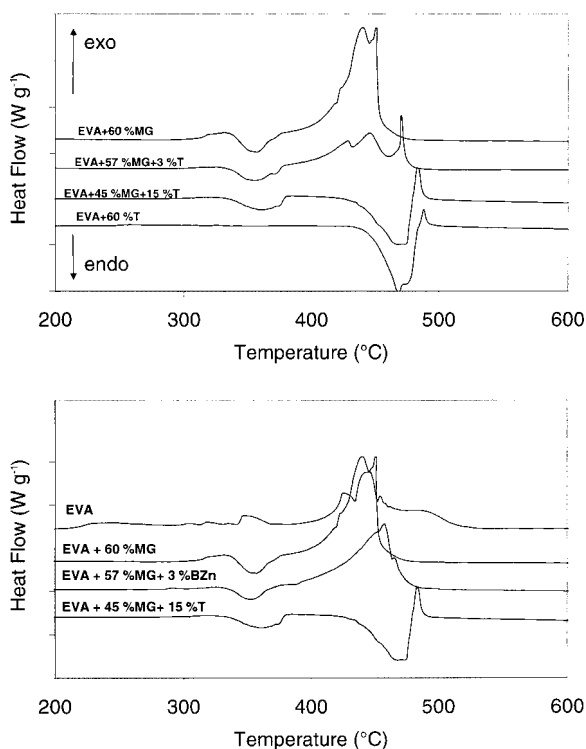


Figure 8. DTA curves of EVA and binary filler compositions in EVA.

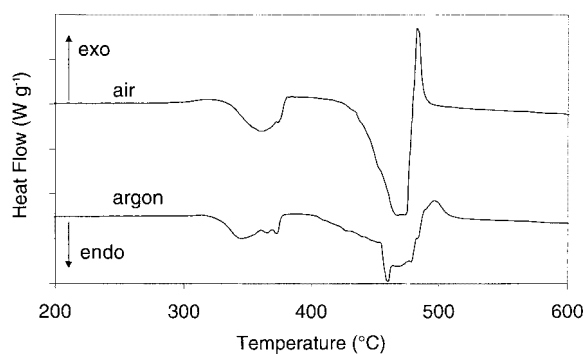


Figure 9. DTA curves of 45% magnesium hydroxide and 15% talc filled EVA.

between the materials used (viscosities of unfilled and filled EVA, vinyl acetate content of EVA, and origin, morphology, granulometry, surface treatment of $Mg(OH)_2$). In particular, as will be detailed further, the viscosity of the materials seems to play an important role on its behaviour when a heat source is applied.

The positive effect of talc was confirmed by the TGA-DTA/FTIR spectra. TGA curves (Fig 7) of EVA containing $Mg(OH)_2$ and a minor fraction of talc exhibit a shift towards high temperatures in comparison with EVA loaded with 60% $Mg(OH)_2$.

DTA and Gram Schmidt curves gave interesting information about the mechanism of action of talc. Figure 8 shows that the presence of talc inhibits the emission of acetic acid (lowering or disappearance of the corresponding exothermic peak). Moreover, an endothermic peak appears before the ignition of ethylenic chain fragments. It indicates that talc particles remaining at the surface of EVA after partial ignition create a mass transfer barrier for oxygen and combustibles. In this case, the endothermic breaking of EVA chains occurs without simultaneous ignition, as in non-oxidant conditions.

This assumption is confirmed in Fig 9 which shows that the DTA curves of 45% $Mg(OH)_2$, 15% The DTA curves of talc in air and argon are very similar. DTA and Gram Schmidt curves (Fig 10) also indicate that the temperature corresponding to the maximal

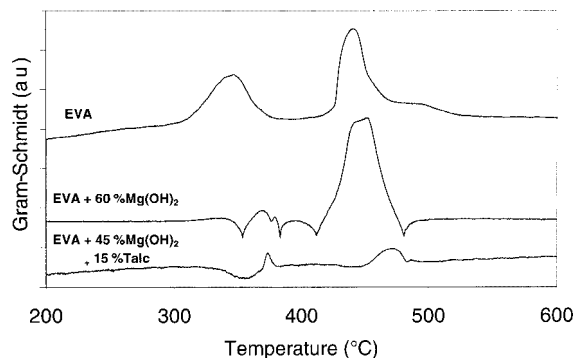


Figure 10. Gram-Schmidt curves of EVA, 60% magnesium hydroxide and 57% magnesium hydroxide/3% talc filled EVA.

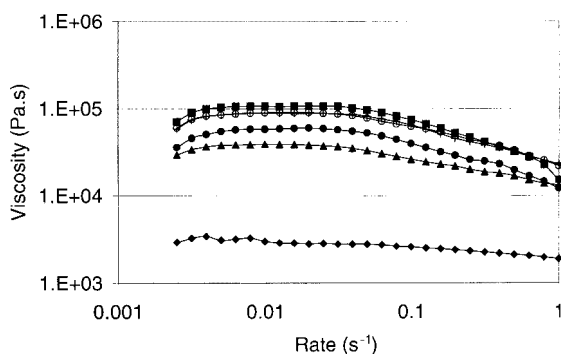


Figure 11. Viscosity of EVA and binary filler compositions in EVA (◆ pure EVA, ▲ 45% Mg(OH)₂ + 15% Zinc Borate, ● 60% Mg(OH)₂, ○ 57% Mg(OH)₂ + 3% Talc, + 45% Mg(OH)₂ + 15% Talc, ■ 30% Mg(OH)₂ + 30% Talc).

ignition is shifted towards higher temperatures in presence of talc.

Nevertheless, this synergistic effect due to the talc may be dependent on the rheological behaviour of the filled polymer when a heat source is applied.

Rheological measurements at 180 °C show that talc, in comparison with Mg(OH)₂ and particularly zinc borate, confers a higher viscosity in the Newtonian plateau region (Fig 11). A high level of viscosity (*ceteris paribus*) can be favourable for UL 94 and NFP 92–505 tests because the presence of talc seems to prevent the creep of specimens and thereby stabilize the formation of a carbonized surface layer. Moreover, the high values of viscosity due to talc indicate a good talc/EVA adhesion.

This is confirmed by the highest values of maximal tensile stress (Fig 5) when talc is present. However, the incorporation of talc leads consequently to a decrease of elongation at break (Fig 6).

CONCLUSION

The role of talc in binary Mg(OH)₂-talc and ternary

Mg(OH)₂-talc-zinc borate filler compositions incorporated at 60% (w/w) in EVA has been investigated. The advantage of talc is related to the existence of synergisms, particularly in binary systems, with Mg(OH)₂ and at low percentages of talc. Beyond a rate of substitution of 25% for talc in Mg(OH)₂-talc compositions, the increase of conductivity caused by the lamellar particles of talc and the lack of water issued from Mg(OH)₂ limits the fire-resistance of the material.

The positive role of talc is mainly ascribed to the constitution of a mineral barrier, which appears when the material decomposes.

In addition, since the first step in the degradation of EVA is delayed in presence of talc, we can also assume that talc not only acts by forming a mass transfer barrier (for volatile gases and oxygen) at the polymer surface but also by reducing the mobility of polymer chains even after they break during degradation.

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