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Intumescent mineral fire retardant systems in ethylene–vinyl acetate copolymer: Effect of silica particles on char cohesion

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Abstract

Silica particles of different physical properties (particle size, morphology and specific surface area) were introduced into an ethylene–vinyl acetate copolymer filled with an intumescent mineral fire retardant system containing magnesium hydroxide and organo-modified montmorillonites. The effect of silica particles on the cohesion and strength of the foamed combustion residue was studied by micro-indentation, concurrently with the characterization of material's fire behavior.

Silica particles seem to act as defects that generate cracks, decreasing the strength of the residue. This generation of cracks is connected to a lower cohesion of the residue, especially for silica particles of high specific surface area. In parallel, the presence of silica of high specific surface area, despite tending to decrease Time To Ignition, also improves self-extinguishing ability, thanks to a better thermal stability at higher temperatures, and reduces the maximum Heat Release Rate in cone calorimeter tests.

Keywords: Intumescence; Fire properties; EVA; Char

1. Introduction

Ethylene–vinyl acetate (EVA) copolymers are commonly used in the cable industry. The most effective halogen free fire retardant formulations for this kind of application are based on metal hydroxides, such as alumina trihydrate (ATH) or magnesium dihydroxide (MDH). Such mineral fillers act as fire retardants mainly through their endothermic dehydration, which implies very high filler contents in order to obtain satisfactory fire properties [1,2]. The interest in using EVA is that it can accept a high amount of such fillers and that the resulting flame retardant compounds still show processability [3,4]. The fact that high mineral loadings generally result in low mechanical performance of such compounds was the main reason for the development of formulations in which parts of the metal hydroxide fillers are substituted by high aspect ratio fillers such as organo-modified montmorillonites (oMMT) [5] or delaminated talcs [6]. Another reason is the intrinsic flame retardancy properties of such particles promoting charring of the polymer matrix.

Unexpectedly, such an approach led to the development of formulations in which a phenomenon of intumescence (swelling) occurs before ignition in cone calorimeter tests, leading to the formation of a foam-like structure, which then burns slowly due to the limitation of both heat transfer and diffusion of fuel and oxygen [6,7]. This intumescence (swelling) is the consequence of the trapping of the water vapour produced by metal hydroxides dehydration in the polymer matrix. This trapping was shown to be related to three phenomena caused by the presence of the lamellar particles (oMMT or high aspect ratio talcs [6]): heterogeneous bubble nucleation, increased viscosity and charring promotion [6].

Such formulations can be called "intumescent mineral fire retardant systems", as opposed to the conventional "intumescent systems" containing typically three active ingredients: an acid source, a carbonisation agent and a blowing agent [8].

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Table 1
Physical properties of the different silica used: median particle size (d_{50}) and specific surface area (SSA)

Silica	d_{50} (μm)	SSA (m^2/g)
Tixosil 38X (T38X)	250	147
Tixosil 73 (T73)	8	80
Tixosil 365 (T365)	3	139

Table 2
Composition (in weight fraction) of the different formulations studied

Formulation	EVA	MH	oMMT	T38X	T73	T365
EVA/MH	40	60	–	–	–	–
EVA/MH/oMMT	40	55	5	–	–	–
EVA/MH/oMMT/T38X	40	50	5	5	–	–
EVA/MH/oMMT/T73	40	50	5	–	5	–
EVA/MH/oMMT/T365	40	50	5	–	–	5

Another effect of the partial substitution of metallic hydroxide fillers by lamellar particles is the structuring of the foamed combustion residue, generally called char despite its mainly mineral nature. Such structuring influences the mechanical behavior of the combustion residue, nevertheless this effect is difficult to quantify.

The present work aims to investigate the effect of introducing silica particles of different physical properties on both fire retardancy and cohesion of the combustion residue, in the case of an intumescent mineral formulation based on MH and oMMT in EVA. Cohesion of the combustion residue is studied by a micro-indentation test developed in our laboratory.

2. Experimental

2.1. Materials

Ethylene–vinyl acetate (EVA) copolymer containing 28 wt% of vinyl acetate from DuPont (Elvax 260) was used. Magnesium hydroxide (Magnifin H10) and organo-modified montmorillonite (oMMT Nanofil 5: distearyl-dimethyl-ammonium ion exchanged bentonite) were supplied by Martinswerk (now Albemarle) and Sud Chemie (now Rockwood Holdings), respectively.

Three commercially precipitated silica of different median particle size (d_{50} measured by laser diffraction) and specific surface area (SSA, obtained from BET gas sorption measurements using N_2 as the sorbate gas) were provided by Rhodia (Table 1). These particles also differ in terms of morphology as can be seen on the SEM micrograph presented in Fig. 1. Despite having a specific surface area similar to that of *Tixosil T365, Tixosil 38X* shows a porous aggregated structure (large porous particles), while *Tixosil T365* is a very fine powder. Such a difference in morphology is particularly important in terms of effective contact surface between silica and polymer matrix.

2.2. Processing

Blending of molten EVA copolymer with the different fillers was done in a Haake internal mixer at 170 °C and 60 rpm for 10 min. Four millimeters thick sheets were then compression moulded at 140 °C at a pressure of 100 bars for 5 min. These sheets were cut into the requisite size, depending on the experiment to be performed. The different formulations studied are listed in Table 2. In all cases, the total filler content was 60% w/w.

2.3. Fire testing and thermal analysis

Epiradiateur tests (AFNOR NF P 92-505) were carried out in order to determine the flammability and the self-extinguishing ability of the different formulations. In this test, a radiator (500 W) is placed above the sample ($70 \times 70 \times 4$ mm^3). When the sample starts burning, the Time To (first) Ignition (TTI) is recorded. After ignition, the radiator is removed and the time of extinction is recorded. As soon as extinction occurs, the radiator (500 W) is replaced above the sample. This procedure is repeated for 5 min. The total number of ignitions (N) and the mean inflammation period (IP) are then calculated. Results presented correspond to mean values obtained from four experiments for each formulation (Table 3).

Cone calorimeter tests (ISO 5660) were performed on $100 \times 100 \times 4$ mm^3 samples placed horizontally with a flux of 50 kW/m^2. Only Time To Ignition (TTI) and Heat Release Rate (HRR) curves will be discussed. Results correspond to

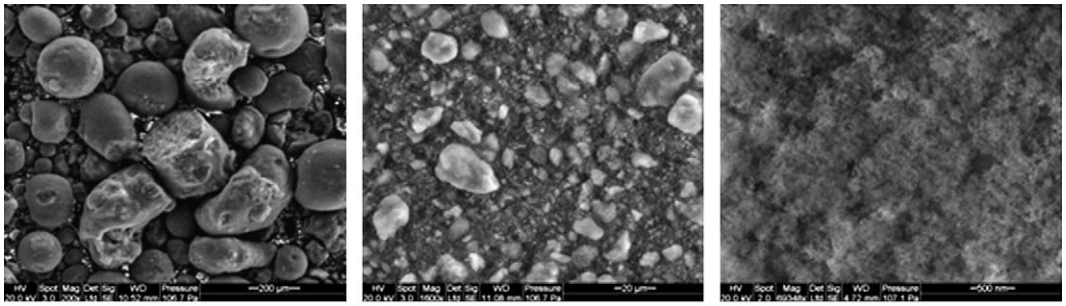

Fig. 1. Scanning Electron Microscopy micrographs of the different silica particles.