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Ethylene-vinyl acetate copolymer/aluminium trihydroxide composites: A new method to predict the barrier effect during cone calorimeter tests

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ABSTRACT

This study presents the use of oedometric compression test in order to evaluate the breakdown of a protective layer acting as a diffusion barrier ("barrier effect") occurring during cone calorimeter tests for ethylene-vinyl acetate copolymer/aluminium trihydroxide (EVA/ATH) composites. The formation of an alumina layer at the sample surface during burning insulates thermally the underlying material and reduces the heat release rate. The efficiency of this barrier depends on the cohesion of the layer formed. This cohesion depends on the ability of the particles (ATH and synergistic mineral fillers) to self-arrange. During the test, the breakdown of this barrier can lead to an increase in HRR.

The oedometric compression test allows assessing the ability of fillers to form a cohesive layer. Results obtained from compression modulus of filler powders are directly related to some aspects of the heat release rate curve of composites measured in cone calorimeter tests. Indeed, the appearance and the intensity of the second pHRR (related to the breakdown of the barrier layer) in cone calorimeter test are related to the slope of oedometric compression curve.

1. Introduction

Due to their properties and processing characteristics, ethylene-vinyl acetate (EVA) copolymers are commonly used in the wire and cable industry. However, these polymers are easily flammable, so flame retardant (FR) systems have to be introduced during the process [1]. In EVA copolymers, hydrated mineral fillers, such as alumina trihydroxide (ATH) and magnesium dihydroxide (MH) are widely used in fire retardancy systems at very high loadings (up to 65 wt%).

The interest of hydrated mineral fillers (hydroxides and hydroxycarbonates) is mainly based on the following fire retardant mechanisms, described below [2]:

Dilution of the solid combustible fraction; endothermic decomposition of the filler; dilution of fuels in gaseous phase; formation of a protective barrier.

The efficiency of hydrated mineral fillers on fire retardancy depends on the amount of released molecules, on the related enthalpy of reaction and on the temperature range of filler decomposition. For example, ATH decomposes into boehmite at 180–200 °C, releasing two molecules of water. Then, the boehmite formed decomposed at higher temperature (500–550 °C), leading to alumina with the release of a third molecule of water. The whole decomposition absorbs 1.3 kJ/g, as an endothermic reaction [3].

The barrier effect is then provided by the alumina and depends on the organisation of the particles at the surface of the polymer [4]. It seems that a compact layer of inert fillers leads to a more efficient insulation from the heat and also restricts the diffusion of fuels into the flame. A model proposed by Staggs also confirms this observation [5]. The efficiency of this barrier can be improved by the presence of synergistic additives, which helps the formation of a cohesive structure [6–9]. Moreover, geometric characteristics such as particle size, aspect ratio and size distribution of alumina particles could play an essential role on the organisation of the protective layer [10].

The effect of the particle size of hydrated fillers was studied, regarding the relative efficiency in fire retardancy tests [11]. In a

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previous study, carried out at our laboratory, it was shown that a better flame resistance can be reached by using a combination of different particles sizes [12]. This result was due to a more compact organisation of particles.

Represented as spheres, a packing of monodisperse particles presents voids between them, in which smaller particles can intercalate [10].

Benezet et al. showed that the shape of particles is a major parameter regarding the compactness and the compressibility of a powder sample [13]. A bimodal distribution theoretically leads to a more compact packing at the surface of the burning polymer. This packing can be estimated by a compression test, forcing the particles to reach the optimal organization [14,15].

Concerning the barrier effect due to a packing of inorganic fillers, Hshieh et al. worked on deposited silica-ash layer in silicones [16]. In this work, silica-ash samples of different thicknesses were placed on a sensor, under the cone calorimeter. The authors showed that the presence of a barrier effect due to the organisation of particles improves the fire resistance of materials.

In the present study, an adapted oedometric method was used [17]. The oedometric compression is a method generally used for the analysis of soils in civil engineering [17,18]. In the present case, a uniaxial compression at constant speed was used to measure the vertical tension during the test and the maximum resistance of the sample toward the force applied. This resistance is closely related to the deformation of the sample along the axe of compression.

We assumed that the resistance during an oedometric compression for a heterogeneous mixture of particles can be related to its optimum packing, and so its ability to form a cohesive layer during a fire test. Cone calorimetry was widely used to investigate the mechanisms of action of fire retardants. Both physical and chemical effects are taken into account using this device. The barrier effect can be visualized, on cone calorimeter curves, by a gradual decrease of the heat release rate after a first peak. A longer decrease corresponds to a more efficient barrier effect [19]. The protective role of the barrier effect is disrupted when the cracking of the layer occurs. This is represented on cone calorimeter curves by an increase of the heat release rate, i.e. a second peak.

2. Experimental

2.1. Materials

The EVA copolymer used was a thermoplastic-elastomeric grade Alcudia® PA-440 (Repsol), with a melt flow index of 7 g/10min (190 °C, 2.16 kg) and a vinyl acetate content of 28 wt%. Aluminium trihydroxides (ATH) were supplied by Alteo (SH15, SH20, SH100 and SH30N) and Albemarle (OL-104 LEO), with various particle size distribution, aspect ratio and specific surface area. SH20, SH100 and OL-104 LEO are precipitated ATH, with a pseudo-spherical shape. SH15 and SH30N are grinded ATH, with a platelet shape. Median diameters (D_{50}) were determined by laser diffraction.

Some silica-based synergistic agents were selected: two non-commercial grades of crushed diatomite (raw and calcined) and a spherically-shaped amorphous silicon dioxide supplied by Elkem (Sidistar® T-120). Some major characteristics are presented in Table 1. The calcination of diatomite was made during 1 h at 1000 °C under air [20]. Calcination of diatomite led to an internal sintering [21], entailing a decrease of the porosity and internal surface, and hence of the global surface area. This was confirmed by S_{BET} measurements presented in Table 1.

Powder true density was measured using a helium pycnometer AccuPyc 1330 (Micromeritics). Specific surface area (S_{BET}) was measured by N_2 adsorption at 77 K (BET method), using an SA 3100 analyser (Beckman–Coulter). Particle size (D_{50}) was measured in water with a laser diffraction particle size analyser LS 13320 (Beckman–Coulter), using an ultrasonic device to break particles agglomerates. Main characteristics of the fillers are given in Table 1.

2.2. Processing

Processing was carried out by incorporating the fillers into EVA using a twin-screw extruder (Clextral BC21, 900 mm) at 160 °C and then pressed using an injection moulding machine (Krauss-Maffei 50T-KM50/180CX). Sheets of 100 × 100 × 4 mm^3 were prepared at 140 °C under a pressure of 100 bars. Table 2 summarizes all the formulations prepared. The total filler content was 60 wt% for each formulation. Only sample 14 contains 45% of fillers due to the volume restriction of the twin-screw extruder.

2.3. Characterizations

Flammability was studied using a cone calorimeter (Fire Testing Technology - FTT) according to the ISO 5660 standard (sample dimensions 100 × 100 × 4 mm^3). External heat flux was set to 50 kW/m^2. The variations of Heat Release Rate (HRR), peaks of Heat Release Rate (pHRR), time to pHRR (tpHRR) and Total Heat Release (THR) were measured. In this study, the second part of the curve (specifically the second peak of HRR related to the breakdown of the barrier layer, pHRR2) was scrutinized (see Fig. 1).

The theoretical mass loss of samples was measured by thermogravimetric analysis (TGA), using a Pyris 1 TGA (Perkin Elmer). The analyses were made under air, from 20 to 900 °C at 10 °C/min.

An adapted two-piston oedometric compression cell was designed (Fig. 2). A mass of 10 g of product was introduced in the cell for each test. The two-piston system was chosen for easier sample release and cleaning. A classic oedometric test uses a non-deformable compression cell, in which the sample is introduced. In the present case, the smaller piston acts as the bottom of the compression cell, and will not move during the test. The force is applied by means of the bigger piston. The compression was carried out using a Z010 Material Testing Equipment (Zwick) with a 10 kN sensor, at a speed of 10 mm/min. The procedure was validated by reproducibility tests.

A schematic representation of the uniaxial oedometric compression test is shown in Fig. 3.

Table 1
Characteristics of fillers.

Filler	Denomination	Powder true density (g/cm^3)	S_{BET} (m^2/g)	D_{50} Laser (μm)	Mineral composition
SH15	A1	2.48	20.58	1.7	$Al(OH)_3$
SH20	A2	2.45	3.93	2.1	$Al(OH)_3$
SH100	A3	2.44	2.94	10.3	$Al(OH)_3$
SH30N	A4	2.51	10.61	2.8	$Al(OH)_3$
OL-104 LEO	A5	2.52	4.76	1.9	$Al(OH)_3$
Sidistar®T-120	S1	2.24	19.22	0.2	SiO_2
Crushed diatomite (raw)	S2	2.17	23.43	2–5	SiO_2
Crushed diatomite (calcinated)	S3	2.37	13.71	2–5	SiO_2