

## Fire retardancy of ethylene vinyl acetate/ultrafine kaolinite composites



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### ABSTRACT

The flame retardant effect of ultrafine kaolinite in Ethylene Vinyl Acetate copolymer (EVA) was studied and compared to that conferred by aluminum trihydrate (ATH). The thermal degradation and flammability of EVA composites were evaluated up to 60 wt% filler loading. Thermogravimetric (TG) and cone calorimeter analyses showed a higher decomposition temperature range and an improved FR performance for EVA/kaolinite composites in comparison to EVA/ATH composites. For a loading of 35 wt%, the peak of heat release rate (pHRR) of EVA/kaolinite was reduced by 55% compared to EVA/ATH. Moreover, we observed that kaolinite leads to a significant intumescent behavior during cone calorimeter tests. Finally, the rheology in the molten state of the different samples was studied and viscosity seems to play an important role on the fire retardancy of EVA/kaolinite composites.

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## 1. Introduction

Fire behavior of Ethyl Vinyl Acetate (EVA) copolymer has been extensively studied [1–9]. Many systems were proposed in the literature: halogenated compounds, phosphorated compounds and mineral fillers (micro and nanoparticles) [1,2,9–12]. Among those fillers, ATH is the most used flame retardant for EVA, particularly in the wire and cable industry. The dilution of fuel gases by water released by ATH above 200 °C and the associated endothermic effect are the most important mechanisms that improve the flame retardancy of the composites. Nevertheless, the high level of incorporation (at least 60 wt%) leads to a reduced flexibility, elongation at break and causes problems of processability. Mainly in combination with hydrated minerals, the use of clays as constituents of the flame retardant systems has been increasingly investigated. Recently many studies have involved the use of organically modified montmorillonite (oMMT), talc, halloysite or sepiolite as flame retardants or constituents of flame-retardant systems [5,7,11,13–18].

Other mineral fillers have been proposed to substitute ATH. The comprehensive study of Hull et al. [19] details the heat absorption of various hydrated fillers like calcium hydroxide, hydromagnesite,

huntite and some others. In all cases, the main contribution to the heat absorption is the endothermic effect. Therefore, using hydrated fillers should be more efficient than inert fillers. But mineral fillers could act through other effects than heat absorption.

Other minerals, like kaolinite have received less attention. Kaolinite is an aluminosilicate with theoretical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and basal interlayer space of 7.1 Å. Kaolinite is a 1:1 or TO type clay mineral, since it is formed by combining sheets of  $\text{SiO}_4^{4-}$  tetrahedra (T) and  $\text{Al}(\text{OH})_6^{3-}$  octahedra (O), in 1:1 proportion. The lamella remain attached to each other because they share common oxygen atoms, giving rise to the structure of the clay mineral [20,21]. It is widely used as paper filler and coating pigment. At the best of our knowledge, kaolinite is not widely used in polymer industry and few studies dealt with its use in polymers for mechanical or fire reaction purposes [22–25]. Therefore, in this study, the flame retardant effect of an ultrafine kaolinite in EVA was studied and compared with the most used filler in wire and cable industry: ATH.

Table 1 compares the temperature of decomposition, the water release and the associated endothermic decomposition energies for Kaolinite and ATH.

## 2. Materials and methods

Kaolinite (Paralux) used in this study from Brazilian deposits was supplied by Imerys. After mineralurgical treatments, a high

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**Table 1**  
Decomposition temperature and water release of kaolinite and ATH.

	Temperature of decomposition (°C)	Water release (%)	Energy of decomposition (J/g)
ATH Apyral 22	200–300	30	1054
Kaolinite	550–600	14	650 [26]

specific surface area was achieved:  $14.2 \pm 0.3 \text{ m}^2\text{g}^{-1}$  (Brunauer–Emmett–Teller (B.E.T) method, using  $\text{N}_2$  as adsorbed gas at 77 K on a Beckman Coulter SA3100 instrument). The average particle size ( $d_{50}$ ) of kaolinite obtained by laser particle-size analysis (Coulter LS230) was estimated around 0.8  $\mu\text{m}$ . Alumina hydroxide was supplied by Nabaltec Apyral 22, with a mean diameter of 12  $\mu\text{m}$  and a specific surface area of  $2 \text{ m}^2\text{g}^{-1}$ . This is a precipitated aluminum trihydrate which is commonly used for EVA in cable industry, mainly for the bending part of the cable. The EVA was Alcludia PA440 from Repsol and contained 28 weight-% of vinyl acetate.

### 2.1. Preparation of EVA composites

Compositions were extruded using a co-rotating twin-screw extruder (Clextral BC21 twin-screw extruder (Firminy, France), standard profile, length = 1200 mm, speed = 250 rpm, screw diameter = 20 mm,  $T = 120 \text{ }^\circ\text{C}$ – $160 \text{ }^\circ\text{C}$ ). The obtained pellets were injection molded (Krauss Maffei KM 50 t,  $T = 140$ – $160 \text{ }^\circ\text{C}$ , mold temperature =  $30 \text{ }^\circ\text{C}$ ) to obtain square specimens ( $100 \times 100 \times 4 \text{ mm}^3$ ).

### 2.2. Characterization

Thermogravimetric analysis (TGA) was carried out on 10–12 mg samples at  $10 \text{ }^\circ\text{C}\cdot\text{mn}^{-1}$  from 50 to  $800 \text{ }^\circ\text{C}$  under nitrogen or air flow using a Perkin–Elmer Pyris-1 TGA. A Scanning Transmission Electron Microscopy (FEI Quanta 200 SEM) was used to study the morphology of the samples. All images were obtained under high vacuum at a voltage of 15.0 kV. The cone calorimeter experiments were carried out using a Fire Testing Technology apparatus with an irradiance of  $50 \text{ kW}\cdot\text{m}^{-2}$ , according to ISO 5660 standard. PCFC analysis was carried out according to the method A (anaerobic pyrolysis) of the ASTM D7309 using a FTT apparatus with a heating

rate of  $1 \text{ }^\circ\text{C}\cdot\text{s}^{-1}$ , the maximum pyrolysis temperature was  $750 \text{ }^\circ\text{C}$  and the combustion temperature was  $900 \text{ }^\circ\text{C}$  (corresponding to complete combustion). The flow in combustor was a mixture of  $\text{O}_2/\text{N}_2$  20/80 at  $100 \text{ cm}^3\cdot\text{min}^{-1}$  and the sample weight was  $2 \pm 0.5 \text{ mg}$ . Viscosity measurements were carried out in dynamic mode at  $160 \text{ }^\circ\text{C}$  using 0.5% strain and a frequency ranging from  $10^{-1} \text{ s}^{-1}$  to  $10^2 \text{ s}^{-1}$  (ARES, Rheometric Scientific). All samples were characterized in triplicate and mean values are showed.

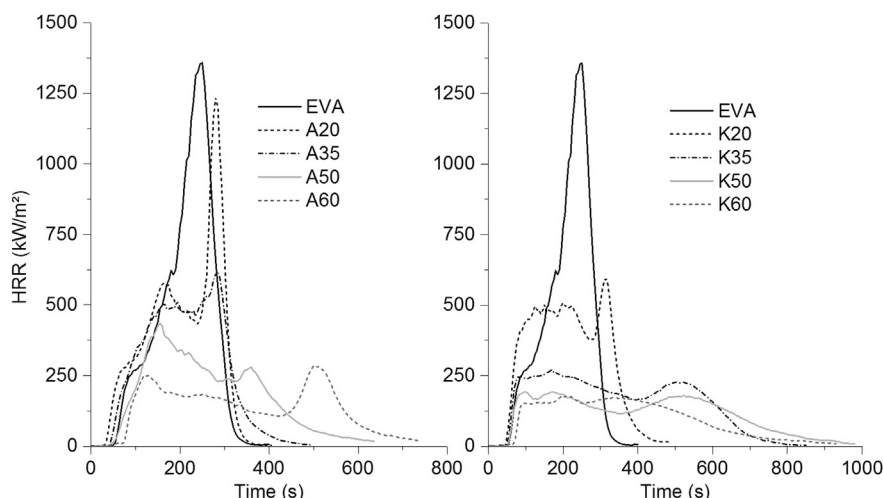
## 3. Results and discussion

### 3.1. Cone calorimeter results

The Heat release Rate (HRR) and Mass Loss rate (MLR) curves for the composites are shown in Figs. 1 and 2 and complete results are shown in Table 2. As expected, pHRR is clearly reduced when the fillers are added to the polymer. These results show that the weight percentage of ATH must be at least 60 wt% in order to reach a significant improvement in fire retardancy in terms of pHRR ( $<300 \text{ kW}\cdot\text{m}^{-2}$ ). Despite a lower amount in water (around 15 wt%) and higher temperatures for water release, EVA/kaolinite show a better flame retardancy than EVA/ATH. Even for 20 wt% of kaolinite, the samples show a significant decrease in pHRR. A loading of 35 wt% is enough to achieve a pHRR lower than  $300 \text{ kW}\cdot\text{m}^{-2}$ .

Mass loss rate curves (Fig. 2) show the same tendencies since no flame inhibition effect is expected for both fillers. MLR and HRR are related through the Effective Heat of Combustion (EHC). The combustion efficiency (defined as the ratio between the effective heat of combustion in cone calorimeter and the heat of complete combustion measured in PCFC) is similar for all composites ( $\chi = 1 \pm 0.1$ ). It means that the combustion is close to be complete (gases from pyrolysis are fully oxidized in the flame). Therefore, the only differences in EHC between EVA/kaolinite and EVA/ATH composites are due to the release of non-combustible gases. EHC values for EVA/ATH decrease as a function of filler loading, which confirms the influence of water release (fuel dilution). Since water release from kaolinite occurs during the test (as shown below), EHC does not change significantly (except for K60) because kaolinite releases only 14 wt% of water in the range 550– $600 \text{ }^\circ\text{C}$ . This temperature range and the limited amount of water released could not explain the very good performances of EVA/kaolinite composites.

The Total Heat release (THR) is similar for both fillers containing composites and decreases in proportion to the filler content. The



**Fig. 1.** Cone calorimeter tests for ATH and kaolinite EVA composites. Heat flux:  $50 \text{ kW}\cdot\text{m}^{-2}$ .

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