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Competitiveness and synergy between three flame retardants in poly(ethylene-*co*-vinyl acetate)

Henri Vahabi [a, *], Amin Raveshtian [b], Mohammad Fasihi [b, **], Rodolphe Sonnier [c], Mohammad Reza Saeb [d], Loïc Dumazert [c], Baljinder K. Kandola [e]

[a] *Université de Lorraine, Laboratoire MOPS E.A. 4423, Metz F-57070, France*
[b] *School of Chemical Engineering, Iran University of Science and Technology, Tehran 16846-13114, Iran*
[c] *Centre des Matériaux des Mines d'Alès (C2MA) - 6, Avenue de Clavières 30319 Alès Cedex, France*
[d] *Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran*
[e] *Institute for Materials Research and Innovation, University of Bolton, Bolton BL3 5AB, United Kingdom*

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ABSTRACT

This work seeks to address the effect of simultaneous use of three flame retardants, having three different modes of action, (magnesium hydroxide, expanded and expandable graphite) on the thermal degradation and flame retardancy of poly(ethylene-co-vinyl acetate). Thermal conductivity of samples was measured in order to investigate the effect of the use of expanded and expandable graphite on the time-to-ignition and the peak of heat release rate in cone calorimeter test. Thermal shielding performances of chars were studied as well. It was found that there is an optimum ratio between expanded and expandable graphite in order to control thermal conductivity and therefore fire properties. Some correlations were also found between the char thickness and the first peak of heat release rate.

1. Introduction

Poly(ethylene-co-vinyl acetate) (EVA) copolymer has been widely used in a variety of areas such as cable and wire insulation, adhesive, solar energy, construction, and packaging industries [1,2]. However, EVA is known as a highly flammable polymer. The fire behavior of EVA has been extensively studied over recent years. In this regard, the effect of different "additive flame retardant" systems on the flame retardancy of EVA has been investigated [3–11]. Among flame retardants incorporated into EVA, metallic hydroxides, magnesium hydroxide (MDH) and alumina trihydrate (ATH) have been comprehensively studied in view of their exceptional efficiencies. The mechanism of action of MDH is similar to that of ATH consisting of an endothermic reaction, through release of water followed by formation of a protective mineral layer (MgO and Al_2O_3) on the surface of polymer during the course of combustion. Fire properties of EVA were significantly governed by the individual and/or simultaneous use of MDH and ATH.

The combination of MDH or ATH with different flame retardants has also been examined to attain synergistic effects on fire properties of EVA. This strategy allows decreasing the incorporation level of flame retardant in EVA, and thus improving mechanical properties. Almost all additives have been considered, most often to improve the cohesion of the mineral barrier formed by the accumulation of alumina or magnesium oxide on the top surface of the composite during combustion. The cohesion of the formed residue during combustion, which is of crucial importance in cable and wire insulation applications, as well as its thickness more or less determine the flame retardancy properties [12–14]. For example in cable industry, the NFC 32070 CR1 standard test imposes that cables sustain electrical power where jackets must protect the copper [15,16]. Generally, synergist is used at 1–5 wt.%, but in some cases higher contents (>10 wt.%) are used. Zinc, calcium or melamine borate [17–22], montmorillonite [9,23–30], talc [11,20], silica and silicon-based fillers [31–34], layered double hydroxide [35], and carbon nanotubes [23,36] have been considered in this context.

Expandable graphite (EG), also known as intumescent flake

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* Corresponding author.
** Corresponding author.
E-mail addresses: henri.vahabi@univ-lorraine.fr (H. Vahabi), mfasihi@iust.ac.ir (M. Fasihi).

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graphite, is a form of intercalated graphite used to promote intumescence and efficiency of barrier layer during burning in EVA [37–39]. Expanded graphite (EDG) generally assists in heat dissipation on the surface of the polymer, and therefore delays the increase in surface temperature [40,41]. It has been observed that Time-To-Ignition (TTI) increases when EDG is incorporated into a polymer [42]. However, the increase in TTI could be counterbalanced by the acceleration of the Heat Release Rate (HRR); and consequently an increased HRR peak, as reported by Patel et al. [43]. Such phenomena were explained by heat transfer from the surface to the bulk of sample. It was observed that TTI increases because of the increase in the thermal conductivity of polymer in the presence of heat conductor additive as EDG, followed by a fast heating of the bulk leading to a rise in pHRR [44,45]. Despite such a history behind the use of EDG as an efficient flame retardant, to the best of the knowledge of authors of this work, its synergistic potential in combination with MDH or ATH has not been examined yet.

The present work aims to (*i*) investigate the combination effect of three different flame retardants (MDH, EG and EDG) each one providing their own action towards fire properties improvement of EVA; (*ii*) the competiveness and/or synergy between EG and EDG and their simultaneous influence on two crucial parameters, TTI and intumescence, as well as thermal conductivity, Scheme 1. The efficiency of hybrid flame retardant systems developed in this work, which contains different amounts of MDH, EG, and EDG was assessed using a complete set of experiments performed on composite samples including microscopy, thermogravimetric analysis, thermal conductivity, and cone calorimetry analyses.

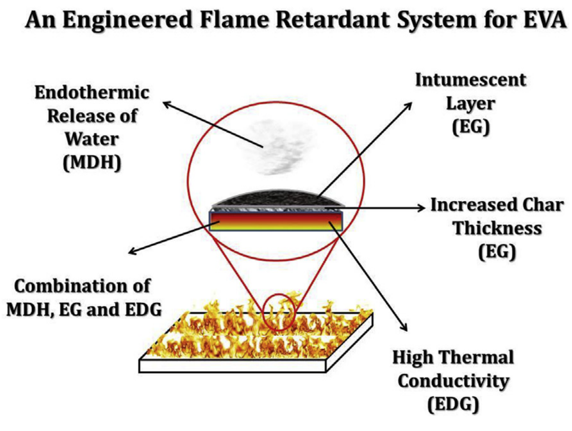
2. Experimental

2.1. Materials

Ethylene vinyl acetate copolymer, EVA 1316 (MFI = 0.8 g/10min; vinyl acetate content = 18 wt.%), was purchased from Hanwa Chemical, South Korea, and used as matrix. Three types of fillers were used as flame retardants: Magnesium dihydroxide (MDH) was purchased from Daejung Chemicals & Metals Co. Ltd, South Korea, while expandable graphite (EG) (expansion ratio = 200 cc.g^{-1}; particle size > 300 μm) and expanded graphite (EDG) (average particle size = 100 μm) were both obtained from Ito Kokuen Co., Japan.

2.2. Sample preparation

EVA and flame retardants were mixed in a batch melt mixer (Brabender W50 EHT) at 150 °C and a rotor speed of 80 rpm. First, EVA was fed into the mixing chamber and after melting, MDH, expanded and expandable graphite were added to the mixer, respectively. The total mixing time for all samples was fixed at 10 min. Neat EVA was prepared under the same condition, for comparison. The samples nomenclature and composition are given in Table 1. After the melt mixing completed, the samples were compression-molded at 180 °C under 10 MPa for 10 min in a square 100 mm × 100 mm × 4 mm mold.



Scheme 1. Contribution of MDH, EDG and EG to flame retardancy of EVA.

2.3. Instrumentation

Morphology of composites was observed by a scanning electron microscope (FEI Quanta 200 SEM). All micrographs were obtained under high vacuum at a voltage of 10 kV with a spot size of 4 and a working distance of 8–10 mm. Small bars of EVA composites were cryofractured in the liquid nitrogen into two pieces. Prior to microscopic measurements, the cryofractured surfaces were sputter coated with carbon to make them conductive.

Thermal decomposition was investigated using a Setaram Labsys Evo thermogravimetric analyzer. All measurements were performed under nitrogen with a heating rate of 10 °C.min^{-1}. The sample weight was 30 ± 2 mg. Cone calorimeter tests were performed on 100 × 100 × 4 mm^3 sheets using an incident heat flux of 50 kW m^{-2}, according to ISO 5660. Peak of Heat Release Rate (pHRR), Total Heat Release (THR), Total smoke production (TSP), and Time-To-Ignition (TTI) were recorded from this test. Three experiments were performed for each sample. Accuracy is estimated to be around 5%. The appearance of the residual chars after the cone calorimeter tests was observed by a digital camera to assess the intumescence and char integrity.

Thermal diffusivity α (m^2.s^{-1}) was measured using a Laser Flash apparatus (XFA600 from Linseis). The specimens were stamped from compression-molded 100 × 100 × 4 mm^3 sheets, thinned to a thickness of 2 mm and coated with graphite on both surfaces. Measurements were carried out at room temperature in vacuum.

Thermal diffusivity, α is closely related to thermal conductivity, known as the equation (1):

$$\alpha = \lambda/\rho c \qquad (1)$$

Thermal conductivity was calculated using typical values of density ρ and specific heat c. These values can be found in the literature for EVA and fillers. These values are shown in Table 2. Even if thermal conductivity changes during burning, the measurement of its initial value is useful to understand the changes in time-to-ignition.

Table 1
Name and composition of the samples prepared in this study.

Sample code	EVA (wt.%)	MDH (wt.%)	EDG (wt.%)	EG (wt.%)
E100	100	0	0	0
EM-50	50	50	0	0
EM-45	50	45	5	0
EM-40	50	40	10	0
EM-35	50	35	15	0
EM-30	50	30	20	0
EME-15	50	30	15	5
EME-10	50	30	10	10
EME-5	50	30	5	15
EME-0	50	30	0	20