



## Synergistic flame retardant effect of metal hydroxide and nanoclay in EVA composites

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### ABSTRACT

This study focused on the flame retardancy of ethylene-vinyl acetate copolymer (EVA) in combination with metal hydroxide and nanoclay. Fire tests, such as limiting oxygen index (LOI), flammability (UL-94), cone calorimeter, and smoke density chamber were employed to evaluate the effect of composition variation for the metal hydroxide and the nanoclay in EVA composites. The experimental results showed that when the nanoclay of 1 or 2 weight per cent was substituted for the aluminum hydroxide or magnesium hydroxide in EVA blends, the LOI value was significantly improved while the V-0 rating was maintained. The data obtained from the cone calorimeter test indicated that the peak heat release rate (pk-HRR) is reduced by about 28%–47%. The smoke density data (maximal smoke density,  $D_m$ ) showed a reduction by about 16%–25%. The thermogravimetric analysis (TGA) data also showed that the nanoclay increased the thermal stability and char residue of the EVA samples. Hence, it is suggested that the metal oxide layer on the burning surface is reinforced by the formation of silicate layer, which is both structured and compacted and acts as the insulation, and the newly formed layer responds to the synergistic effect of flame retardancy as well as smoke suppression observed in the EVA blends.

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## 1. Introduction

The ethylene-vinyl acetate copolymer (EVA) is widely used in construction, transport, and electronic engineering due to the excellent mechanical property [1]. But the EVA is flammable, thus, the flame retardant agent must be added to reduce the flammability of the EVA. In recent years, the application of non-halogenated fire retardants is widespread due to minimization of the health and environmental risks.

Metal hydroxide, used as a halogen-free flame retardant material, produces an endothermic reaction during the combustion, which reduces polymer surface temperature and frees water molecules to dilute the concentrated combustible gas. Further, the metal oxide builds a protective layer on the surface, which cuts off sources of heat at the point of the combustion and also inhibits the release of flammable gas, thus reducing the flame and smoke effects [2,3]. There is already an abundance of literature reporting on the flame retardancy and smoke suppression of EVA with metal hydroxide, such as magnesium hydroxide or aluminum hydroxide [4,5]. To be an effective flame retardant, the metal hydroxide

requires at least 50 wt% of the EVA. However, the physical and mechanical properties of the polymer will be affected by adding too much flame retardant. Thus finding the appropriate metal hydroxide to be added into the polymer will not only reduce the amount of the flame retardant but also maintain the physical and mechanical properties of the polymer [6–12].

In recent reports, the nanoclay added into the polymer, may improve the material's thermal stability, flame retardancy, and mechanical property, and lower the material's smoke density [13–25]. This study attempts to demonstrate the synergistic flame retardant effect of the metal hydroxide in combination with the nanoclay for EVA blends. Also under investigation is the minimal quantity of the nanoclay required for inhibiting the flame and the smoke in EVA composites.

## 2. Experimental

### 2.1. Materials

The ethylene-vinyl acetate copolymer was supplied by USI Corporation containing 25% vinyl acetate with a melting point of 77 °C and a melt flow index of 2.0 g/10min. The nanoclay, Cloisite 30B, which was a natural montmorillonite (MMT) modified by

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methyl tallow bis-2 - hydroxyethyl ammonium cation, supplied by Southern Clay Products, Inc, USA. The magnesium hydroxide (Magnifin H10, MH) was obtained from Albemarle Corporation, with a median particle size of 0.80–1.10  $\mu\text{m}$  and a specific surface area (BET) of 9.0–11.0  $\text{m}^2/\text{g}$ . The aluminum hydroxide (H-42M, ATH) was supplied by Showa Denko Corporation, with a median particle size of 1.0  $\mu\text{m}$  and a specific surface area (BET) of 5.0  $\text{m}^2/\text{g}$ .

## 2.2. Sample preparation

The samples were prepared via a two-step process. In the first step, EVA and nanoclay were mixed at a temperature of 120  $^{\circ}\text{C}$  in a Barbender PLE-331 mixer, with a rotation speed of 40 rpm for 20 min. In the second step, The EVA/nanoclay composites with a desired amount of metal hydroxide (MH, ATH) were mixed on a 6'' two-roll mill (Yowchuan, Taiwan), with a rotation speed of 32 rpm for 10 min. After mixing, the samples were hot-pressed under 100 MPa to sheets of a suitable thickness for 5 min at 150  $^{\circ}\text{C}$ . The samples and compositions prepared are listed in Table 1.

## 2.3. Characterization

### 2.3.1. Thermal analysis

EVA, EVA/metal hydroxide and EVA/metal hydroxide/nanoclay composites were evaluated by thermogravimetric analysis for the thermal stability (TA Instruments, TGA Q50). Each sample (10–15 mg) was examined under an air flow and at heating rate of 20  $^{\circ}\text{C}/\text{min}$  from room temperature to 700  $^{\circ}\text{C}$ .

### 2.3.2. Flame testing

**2.3.2.1. Limiting oxygen index (LOI) and UL-94 testing.** Limiting oxygen index values were measured using an ON-1 type instrument (Suga Test Instrument Co. Ltd) on the specimens of 100  $\times$  6.5  $\times$  3 mm size according to the standard limiting oxygen index test, ASTM D2863-77.

The UL-94 vertical burning tests were carried out using a CLE-01 type instrument (Yuan-Chiao Co. Ltd) on the sheets of 120  $\times$  13  $\times$  3 mm size according to the standard UL-94 test, ASTM D635-7.

**2.3.2.2. Cone calorimeter test.** Cone calorimeter experiments were performed at an incident heat flux of 50  $\text{kW}/\text{m}^2$  using the Atlas Cone 2. The heat release rate (HRR) was measured for EVA and EVA composites. The data including peak heat release rate (pk-HRR), the time for ignition of the specimen, the total heat release, and the time for sustained ignition were obtained. Results for pk-HRR are reported in this paper for the specimens of 100  $\times$  100  $\times$  6 mm size according to the ASTM E1354 standard. Extinction coefficient (Ext Coef) is another important parameter obtained from the cone

calorimeter test. It represents the concentration of the smoke released from the material during combustion.

**2.3.2.3. Smoke density chamber test.** Smoke density chamber test was carried out using the FTT NBC SDC type in a constant-condition fume cupboard. The material was introduced on a suitable sample dish and heated from beneath with a small electric furnace (smoldering condition) or with the same furnace together with a small ignition flame (flaming condition).

The small furnace was set so that the sample received 2.5  $\text{W}/\text{cm}^2$  thermal energy. The light transmission through the smoke, resulting from the burning or the combustion of the sample, was detected by a photocell. Specimen dimensions were 75  $\times$  75  $\times$  1.5 mm according to the ASTM E662 standard. The smoke density of EVA composite was measured during the combustion. The maximal smoke density ( $D_m$ ) was obtained for each sample. The amount of light transmission can be used to calculate the specific optical density ( $D_s$ ). The  $D_s(t)$  was calculated by Eq. (1).

$$D_s(t) = 132 \times \log \frac{100\%}{T(t)} \quad (1)$$

Where  $D_s(t)$  is the specific optical density at time  $t$ ,  $T(t)$  is the light transmission (%) at time  $t$  and 132 is the factor resulting from the volume of the light beam and the exposed specimen surface area. The VOF4 is another assessment of the effective suppression of smoke when the material is burned. The VOF4 is integral of the  $D_s(t)$  curve calculated from  $t = 0$  min to  $t = 4$  min using the trapezoid rule with the time interval  $\Delta t = 1$  min. The VOF4 was calculated by Eq. (2).

$$VOF4 = \sum_{n=0}^{n=3} \frac{\Delta t [D_s(n) + D_s(n+1)]}{2} \quad (2)$$

### 2.3.3. Mechanical properties test

The mechanical properties were measured using Monsanto tensile tester (Tensometer 10) according to the ASTM D638 standard with a crosshead speed of 20  $\text{mm}/\text{min}$  at  $25 \pm 2$   $^{\circ}\text{C}$ . In the above-mentioned measurements, five samples at least were analyzed in order to get the reproducible average values.

## 3. Results and discussion

### 3.1. Thermal analysis

The TGA thermograms of EVA, EVA/ATH, and EVA/MH are shown in Fig. 1. These curves exhibit two decomposition temperature ranges. In the curve for the composite containing ATH, the weight loss in the first step decomposition temperature range, 250–320  $^{\circ}\text{C}$ , is higher than that of EVA. This temperature range is the onset of ATH dehydration. The curve for EVA/MH shows a higher first step decomposition temperature range, 320–380  $^{\circ}\text{C}$ , and the weight loss for EVA/MH is lower than that for EVA/ATH. In this temperature range, the dehydration reaction occurs with the formation of a magnesium oxide layer. With this higher dehydration temperature range, EVA/MH composite shows better thermal stability than that of EVA/ATH composite. The curves for EVA and EVA/MH indicate an abruptly change in the second step decomposition temperature range, 380–500  $^{\circ}\text{C}$ . In the temperature range, 380–450  $^{\circ}\text{C}$ , the weight loss for EVA/MH is mild, and EVA almost loses 70% of its weight. The EVA/MH composite speeds up the weight loss process when the temperature increases beyond 450  $^{\circ}\text{C}$ . Above 500  $^{\circ}\text{C}$ , the EVA in composite is decomposed and the metal hydroxide almost converts to metal oxide [4,23]. Char yields of EVA/MH and EVA/ATH are almost the same.

**Table 1**  
Sample codes and compositions.

Sample	Composition			
	EVA	(wt%)		
		MH	ATH	Nanoclay
EVA	100	0	0	0
EVA/MH	50	50	0	0
EVA/ATH	50	0	50	0
EVA/MH/C1	50	49	0	1
EVA/MH/C2	50	48	0	2
EVA/MH/C4	50	46	0	4
EVA/MH/C6	50	44	0	6
EVA/ATH/C1	50	0	49	1
EVA/ATH/C2	50	0	48	2
EVA/ATH/C4	50	0	46	4
EVA/ATH/C6	50	0	44	6

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