ABSTRACT

The flammability characterization and synergistic flame retardant mechanism of lanthanum oxide (La$_2$O$_3$) in the ethylene-vinyl acetate/aluminium hydroxide (EVA/ATH) composites were studied by limiting oxygen index (LOI), UL 94 test, cone calorimeter test (CCT), and thermogravimetric analysis (TGA). The results showed that the addition of a given amount of La$_2$O$_3$ apparently increased the LOI value, which for the sample with 1.5 wt% La$_2$O$_3$ reached 37.5. However, the addition of La$_2$O$_3$ cannot enhance the ratings of UL 94 test. The data obtained from the CCT indicated that the addition of La$_2$O$_3$ greatly prolonged the time to ignition, increased the fire performance index (FPI), and predictably reduced the fire growth index (FGI). It has been found that there is a synergistic flame retardant effect between La$_2$O$_3$ and ATH in EVA/ATH/La$_2$O$_3$ composites. The synergistic mechanism between La$_2$O$_3$ and ATH is due to its physical process in the condensed phase, as revealed by CCT data showing that the addition of La$_2$O$_3$ can make the formation of a more thermally stable barrier, and the residual char of the system with La$_2$O$_3$ is higher than that of the system without La$_2$O$_3$. A compact barrier produced by La$_2$O$_3$ collaborating with ATH consequently leads to the decrease of heat release rate, mass, and total release rate as detected by CCT. TGA results showed that La$_2$O$_3$ can enhance the thermal stability of the flame retardant composites at high temperature.

INTRODUCTION

Ethylene-vinyl acetate (EVA) copolymers with different acetate contents are extensively used in many fields, especially in the cable industry as excellent insulating materials with good physical and mechanical properties [1].

However, EVA copolymers are particularly flammable and emit a large amount of smoke while burning, which restricts their practical applications. Therefore, it is very important to improve the flame retardancy in the applications of EVA materials.

In recent years, developing halogen-free flame retardant polymeric materials has become a potential trend. Many investigations have demonstrated that aluminium hydroxide known as aluminium trihydrate (ATH) is a non-toxic and smoke suppressing halogen-free flame retardant additive in flame retarded polymeric materials. However, ATH has an essential disadvantage that more than 60 wt% ATH loading is
required to meet flame retardant properties, which could be detrimental to the mechanical properties of flame retardant materials. Many investigations have been done on ATH incorporated with other halogen-free flame retardant synergistic agent [2-10] to enhance flame resistance and decrease its high loading level of ATH. Ramazani et al. reported the synergistic effect of zinc borate with ATH in flame retardancy and physical-mechanical properties of propylene composites [3]. Schartel et al. studied the flame retardant effect of phosphonium-modified layered silicate with ATH in epoxy resins nano-composites [6].

Very recently, it has been reported that La$_2$O$_3$ can be used as synergism in intumescent flame retardant systems [11,12]. Li et al. have reported the synergistic effect of lanthanum oxide on a novel intumescent flame retardant polypropylene system [11]. Wu et al. have reported the synergistic effect of lanthanum oxide on intumescent flame-retardant polypropylene-based formulations [12]. However, no work has been done on the synergistic flame retardant effect of La$_2$O$_3$ in EVA/ATH composites.

In the present work, the role of La$_2$O$_3$ in the EVA/ATH composites was studied. The aim of this paper is to decrease the loading of ATH and investigate the effect of La$_2$O$_3$ on the flame retardancy, thermal stability, and morphological structure of char residue of the composites. The effect of La$_2$O$_3$ on the flame retardancy and the thermal stability of the composites were studied by limiting oxygen index (LOI), UL 94 test, cone calorimeter test, and thermogravimetry analysis (TGA), respectively. Photograph was used to analyze the morphological structure of the chars formed from the EVA composites.

### EXPERIMENTAL

#### Materials

EVA-14 (containing 28 wt% vinyl acetate) was bought from Sumitomo Chemical Co., Ltd. (Japan). ATH was supplied by Hefei Keyan Institute of Chemical Engineering. Lanthanum oxide (La$_2$O$_3$) with an average particle size of 3 μm was obtained from Rare Earth Hi-Tech (China). The formulations are given in Table 1.

#### Preparation of Samples

All the samples were prepared by using a mixer with the same procedures. EVA was added into the mixer with rotational speed of 20 rpm at 120°C. ATH filler and La$_2$O$_3$ were added after EVA polymer was melted and the mixing was carried out at 50 rpm for 10 min. The obtained composites were finally compression moulded at 120°C for 10 min under 10 MPa into sheets of suitable thickness. Samples for testing were cut from the compressed sheets according to the standards mentioned in the following part.

#### Measurements

**Limiting Oxygen Index**

Limiting oxygen index (LOI) was measured according to ASTM D 2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 100 mm×6.5 mm×3 mm.

**UL 94 Test**

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The

<table>
<thead>
<tr>
<th>Sample code</th>
<th>EVA (wt%)</th>
<th>ATH (wt%)</th>
<th>La$_2$O$_3$ (wt%)</th>
<th>LOI</th>
<th>UL 94 test</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA-0</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
<td>17.0</td>
<td>No rating, dripping</td>
</tr>
<tr>
<td>EVA-1</td>
<td>45.0</td>
<td>55.0</td>
<td>-</td>
<td>35.2</td>
<td>No rating, dripping</td>
</tr>
<tr>
<td>EVA-2</td>
<td>45.0</td>
<td>54.0</td>
<td>1.0</td>
<td>36.8</td>
<td>No rating, dripping</td>
</tr>
<tr>
<td>EVA-3</td>
<td>45.0</td>
<td>53.5</td>
<td>1.5</td>
<td>37.5</td>
<td>No rating, dripping</td>
</tr>
<tr>
<td>EVA-4</td>
<td>45.0</td>
<td>53.0</td>
<td>2.0</td>
<td>37.4</td>
<td>No rating, dripping</td>
</tr>
<tr>
<td>EVA-5</td>
<td>45.0</td>
<td>52.5</td>
<td>2.5</td>
<td>37.0</td>
<td>No rating, dripping</td>
</tr>
</tbody>
</table>

Table 1. The results of LOI and UL 94 test of EVA/ATH/La$_2$O$_3$ compositions.
specimens used were of dimensions 130 mm×13 mm×3 mm.

**Cone Calorimeter Test**
The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimension 100 mm×100 mm×4 mm was wrapped in aluminium foil and exposed horizontally to an external heat flux of 50 kW/m².

**Thermogravimetric Analysis**
Thermogravimetric analysis was carried out in nitrogen on a STA 409C TGA apparatus (Netzsch Company, German) with crucible sample holders, at a heating rate of 10ºC/min.

**RESULTS AND DISCUSSION**

**LOI and UL 94 Rating**
The LOI and UL 94 tests are widely used to evaluate flame retardant properties of materials. Table 1 presents the LOI values and UL 94 tests results of the flame retarded EVA composites. It can be observed from Table 1 that the LOI value of sample EVA-1 containing 55 wt% ATH increases rapidly to 35.2 from 17.0 of original EVA sample EVA-0 without any additive. The LOI values of samples (EVA-1~EVA-3) gradually increase to 37.5 with the increasing of La₂O₃. However, the LOI value of sample EVA-5 decreases to 37.0 when the loading of La₂O₃ reaches 2.5 wt%. These results indicate that the addition of a suitable amount of La₂O₃ can increase the flame retardancy of EVA/ATH composites. The addition of La₂O₃ also increases the polymer melting viscosity, which favours the LOI test [13]. However, the results obtained from the UL 94 tests show that all samples have no ratings.

**Cone Calorimeter Study**

**Heat Release Rate**
While the LOI and UL 94 tests are widely used to evaluate the flame retardancy of materials, especially for screening flame retarded formulations of polymers, the cone calorimeter provides a wealth of information on the combustion behaviour [14]. Some cone calorimeter results have been found to correlate well with those obtained from large-scale fire tests and can be used to predict the behaviour of materials in real fires [15]. For example, the peak heat release rate (PHRR) is an important parameter, which can be used to evaluate the intensity of fires [16].

Fire performance of flame retardant EVA composites was tested using cone calorimeter. From Figure 1, it can be found that pure EVA (EVA-0) burns very fast after ignition. A very sharp heat release rate (HRR) curve appears at the range of 30~220 s, whereas sample EVA-1 with 55.0 wt% ATH shows a dramatic decline of the HRR curve and its combustion time is prolonged to 750 s from 220 s of the control sample EVA-0.

The HRR of samples (EVA-1~EVA-5) shows two separate peaks during burning, which indicates the gradual burning of the specimen through the thickness after the initial charred layers were formed. This combustion feature of multiple HRR peaks has also been reported by Grexa and Bras et al. [17,18]. EVA-2 with 1 wt% La₂O₃ shows its combustion time is prolonged to 800 s from 750 s of the control EVA-1. With the addition of La₂O₃, the burning time is prolonged. The first PHRR of the flame retardant samples almost does not change with the addition of La₂O₃. However, the second PHRR decreases with the addition of La₂O₃, which indicates that La₂O₃ contributes to decrease the flammability of materials. For example, comparing the HRR curve of EVA-2

![Figure 1. Heat release rate (HRR) curves of EVA/ATH/La₂O₃ composites.](image-url)
with that of EVA-1, incorporation of 1 wt% La$_2$O$_3$ into EVA/ATH composites makes a decrease of the second PHRR. To our surprise, a further reduction of the second PHRR (curve EVA-3~EVA-5) was obtained with La$_2$O$_3$ content increasing. The above results indicate the incorporation of La$_2$O$_3$ into the ATH flame retardant system can help to improve the flame retardancy of EVA. La$_2$O$_3$ does not act as a component which accelerates the burning of EVA, but as a synergism of ATH to reduce the heat release rate of EVA. It is important to find out the reason that the La$_2$O$_3$ could improve the flame retardancy of EVA/ATH composites.

La$_2$O$_3$ is usually considered to be an inert additive in flame retardant systems. However, the above data indicate that the flame retardant performances of EVA/ATH composites are enhanced by partly substituting ATH with La$_2$O$_3$. The mechanism of the reduction in heat release rate is mainly due to the physical and chemical processes in the condensed phase, as reported in the literature [11,12]. La$_2$O$_3$ tends to accumulate near the regressing sample surface without sinking through the polymer melt layer during the gasification/burning process [19,20]. The accumulated La$_2$O$_3$ consequently forms a charred layer by collaborating with ATH, which acts as a heat insulation barrier. This charred layer prevents heat transfer and transportation of degraded products between melting polymer and surface, thus reduces the HRR and related parameters.

Char Residue
Figure 2 shows the weight of the char residues. During combustion, a compact char may occur on the surface of the burning creating a physical protective barrier on the surface of material. The physical process of the char would act as a protective barrier in addition to the compact shield and can thus limit the oxygen diffusion to the substrate or give a less disturbing low volatilization rate. In this study, it was found that there is some compact char residue formed on the surface of the samples (EVA-1~EVA-5). The effect of the heat insulation barrier becomes excellent with the addition of La$_2$O$_3$.

Total Heat Release
Figure 3 presents the total heat release (THR) for all the samples. The slope of THR curve can be assumed as representative of fire spread [21]. In Figure 3, it is observed that the THR is decreased by the addition of La$_2$O$_3$. It is very clear that the flame spread of samples (EVA-0~EVA-5) has decreased, and the flame spread of sample EVA-3 is comparatively the lowest. These phenomena can also be explained by the fact that the migration of La$_2$O$_3$ onto the surface of the sample, which can barrier from the flame zone to the underlying materials, and restrain the flammable gases to flame zone. Another important reason may be that La$_2$O$_3$ can capture free radicals from the decomposition of EVA. It is also suggested...
Figure 4. Fire performance index (FPI) for different composites in cone calorimeter test.

that there is a synergistic effect of flame retardancy between ATH and La$_2$O$_3$.

Fire Performance Index and Fire Growth Index
The fire performance index (FPI) and fire growth index (FGI) are parameters calculated from the directly measured data of cone calorimeter experiments, and can be used to give an overall assessment of the fire safety of a material in the cone calorimeter test [22,23]. FPI (m$^2$/s/kW) and FGI (kW/m$^2$/s) are respectively defined as the ratio of the TTI to the peak HRR and the ratio of the peak HRR to the TTP. The higher the value of the FPI or the lower the value of the FGI, the higher would be the product’s safety rank. From Figures 4 and 5, it is found that the FPI increases and the FGI decreases with the addition of La$_2$O$_3$. Sample EV A-3 has the highest FPI and lowest FGI, which indicates 1.5 wt% loading of La$_2$O$_3$ has the best flame retardancy on EVA/ATH composites.

Figure 5. Fire growth index (FGI) for different composites in cone calorimeter test.

Thermogravimetric Analysis Study
TG curves for EVA and its composites are shown in Figure 6. EVA undergoes two degradation steps as shown in Figure 6. The first decomposition step is due to the loss of acetic acid and the second involves random chain scission of the remaining material, forming unsaturated vapour species, such as butene and ethylene [24,25].

From Figure 6, it can be found that EVA-1 shows lower decomposition rate in the second step but higher in the first step than EVA-0. The incorporation of ATH lowers the decomposition rate of the second step but accelerates the loss of acetic acid. It is obvious that the -OH groups on the fillers can assist β-hydrogen leaving. That is to say that the loss of acetic acid can be catalyzed by ATH. To our surprise, ternary composites, which contain both La$_2$O$_3$ and ATH, show very similar degradation behaviour with EVA-1. Polymer/clay nanocomposites have been studied widely and Costa et al. [26] reported similar catalyzing function of -OH groups on the edges of montmorillonite layers [26,27]. It is obvious that the

Figure 6. TG curves of EVA and flame retardant EVA.
inclusion of La$_2$O$_3$ in ternary composites does not result in high char residue. These results reflect the char residue results in the CCT test. It should be figured out that the thermal stability of EVA-3 is higher than other samples at the temperature between 250°C and 325°C, which can explain that EVA-3 sample shows the best flame retardancy.

**Digital Photos of Residues**

Figure 7 is a collection of digital photos of residues of EVA/ATH/La$_2$O$_3$ series. It can be observed that the char residue on the surface of sample EVA-1 without...
La$_2$O$_3$ is very loose; however, a coherent and dense char residue can be formed on the surface of the sample with La$_2$O$_3$. Furthermore, for EVA/ATH/La$_2$O$_3$ series, there is more and more coherent char formed on the surface of the sample with the addition of La$_2$O$_3$, as shown in Figure 7. From the char structure, we can explain the combustion phenomenon of the flame retardant EVA composites. The formation of the efficient char can prevent the heat mass transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning and retard the pyrolysis of polymers. It can be illustrated that the mass increases with the addition of La$_2$O$_3$ from 300 s to 800 s (Figure 2). As a result, HRR values are reduced, as shown in Figure 1.

CONCLUSION

It has been found that La$_2$O$_3$ has synergistic flame retardant effect with ATH in EVA/ATH/La$_2$O$_3$ composites. A suitable amount of La$_2$O$_3$ can increase the LOI value. The optimum amount of La$_2$O$_3$ is 1.5 wt%. The synergistic mechanism of La$_2$O$_3$ with ATH is mainly due to its physical effect in the condensed phase, as revealed by CCT data showing that addition of La$_2$O$_3$ can lead to the formation of a more thermally stable barrier, and the residual char of the system with La$_2$O$_3$ is higher than that of the system without La$_2$O$_3$. A more compact barrier produced by La$_2$O$_3$ collaborating with ATH consequently leads to the decrease of HRR, mass, and THR as detected by CCT.

ACKNOWLEDGEMENT

The Foundation of State Key Laboratory of Fire Science (No HZ2008-KF01) is gratefully acknowledged.

REFERENCES

11. Li YT, Li B, Dai JF, Jia H, Gao SL, Synergistic effects of lanthanum oxide on a novel intumes-


