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Synergistic effects of zinc oxide with layered double hydroxides in EVA/LDH composites

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Abstract The synergistic effects of zinc oxide (ZnO) with layered double hydroxides (LDH) in ethylene vinyl acetate copolymer/LDH (EVA/LDH) composites have been studied using thermal analysis (TG), limiting oxygen index (LOI), UL-94 tests, and cone calorimeter test (CCT). The results from the UL-94 tests show that the ZnO can also act as flame retardant synergistic agents in the EVA/LDH composites. The CCT data indicated that the addition of ZnO in EVA/LDH system can greatly reduce the heat release rate. The TG data show that the ZnO can increase the thermal degradation temperature and the charred residues after burning.

Keywords Synergistic effect · Layered double hydroxide · Halogen-free flame retardant

Introduction

In recent years, a great deal of attention has been paid to the application of halogen-free flame retardant polyolefin insulated wire and cable because halogen-containing polyolefin materials give rise to toxic gas and smoke that can choke people exposed to the toxic and acidic fumes and can damage costly equipment. Layered double hydroxides (LDH) as an environmentally friendly halogen-free flame retardant additive have been extensively used in polyolefin materials. But many studies show that more than 60% LDH loading in the polyolefin blends is required to obtain an adequate level of flame retardant properties. Such high loadings lead to great losses in the mechanical properties of the flame retardant polyolefin materials, because of the poor compatibility between inorganic additives and polymer resin [1]. To minimize this effect, surface treatment of LDH by coupling agents has been widely used to improve their compatibility [2]. However, this kind of improvement of mechanical properties is not only very limited, but also this surface modification brings the deterioration of flame retardant properties, because most of organic coupling agents are flammable [3]. On the other hand, many studies show that the synergistic effects of some halogen-free flame retardant agents, such as ammonium polyphosphate (APP) [4–6], hyperfine magnesium hydroxide [2, 7], and red phosphorus [8] with LDH, can enhance flame retardancy and reduce the high loading level of LDH and thus improve the mechanical properties of the flame retardant materials.

In the present work, the effects of ZnO and LDH on the flame retardant and thermal properties of the EVA/LDH/ZnO composites have been studied using limiting oxygen index (LOI), UL-94 tests, cone calorimeter test (CCT) and thermal analysis (TG).

Experimental

Materials

EVA14 (containing 14 wt% vinyl acetate) was bought from Sumitomo Chemical Co., Ltd. (Japan). LDH treated with stearic acid with a median particle size of ≈50 nm (90% of particles less than 100 nm) was kindly supplied by Beijing University of Chemical Technology. For LDH, its typical formula is $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, and the layer space of LDH is 0.79 nm (d003). ZnO, supplied from the First Reagent Co. of Shanghai, was used as received.

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Sample preparation

All the samples were prepared by using a Haake Rheomix Banbury mixer with the same procedures. EVA was added into the mixer with rotational speed of 20 rpm at 160 °C. LDH filler and ZnO 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 molded at 160 °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 $100 \times 6.5 \times 3\ \mathrm{mm}^3$.

UL 94 testing

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 specimens used were of dimensions $130 \times 13 \times 3\ \mathrm{mm}^3$.

Cone calorimeter

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions $100 \times 100 \times 3\ \mathrm{mm}^3$ was wrapped in aluminium foil and exposed horizontally to an external heat flux of 35 kW/m^2.

Thermogravimetric analysis

Thermogravimetric analysis was carried out in air on a STA 409C TG apparatus (Netzsch Company, German) with crucible sample holders, at a heating rate of 10 °C/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 and to screen flame retardant formulations. Table 1 lists the related LOI and UL-94 data obtained from different loading of ZnO. It can be seen from Table 1 that the LOI value of EVA1 containing 120 phr LDH increases rapidly to 39.0 from 17.0 of original EVA without any additive. The LOI values of samples (EVA1 to EVA3) gradually decrease to 38.0 with increase in the loading of ZnO in the formulation. The decrease of LOI may be the fact that the loading of LDH is decreased. The results obtained from the UL-94 tests show that 2 phr ZnO can make the EVA/LDH/ZnO pass the UL 94 test. These results indicate that the addition of a suitable amount of ZnO can increase the flame retardance of EVA/LDH blends.

Table 1 The formulations of the EVA/LDH/ZnO composites

Sample code	EVA/phr	LDH/phr	ZnO/phr	LOI	UL 94
EVA0	100.0	–	–	17.0	No rating
EVA1	100.0	120.0	–	39.0	V-1
EVA2	100.0	118.0	2.0	38.5	V-0
EVA3	100.0	115.0	5.0	38.0	V-0

ZnO is usually considered to be inert for UL 94 test in fire-retarded systems. However, the above data indicate that the fire-resistance performances of EVA/LDH blends are enhanced by partly substituting LDH with ZnO. The mechanism of the enhancement in UL 94 rating is mainly due to the physical process in the condensed phase, as reported in the literature [9–11]. The addition of ZnO also increases the polymer melting viscosity, which favors the UL-94 test [12].

Cone calorimeter study

Heat release rate

The cone calorimeter based on the oxygen consumption principle has widely been used to evaluate the flammability characteristics of materials. Although a cone calorimeter test is in a small-scale, the obtained results have been found to correlate well with those obtained from a large-scale fire test and can be used to predict the combustion behaviour of materials in a real fire [13]. The heat release rate (HRR) measured by cone calorimeter is a very important parameter as it expresses the intensity of a fire, which in turn determines other parameters, such as MLR, SEA and fire growth rate. A highly flame retardant system normally shows a low av-HRR value. The pk-HRR value is used to express the intensity of a fire. The changes of HRR as a function of burning time for different samples are shown in Fig. 1.

It can be found from Fig. 1 that pure EVA (EVA0) burns very fast after ignition. A very sharp HRR curve appears at the range of 80–250 s, whereas EVA1 with 120 phr LDH shows a dramatic decline of the HRR curve and its combustion is prolonged to 390 s from the 250 s of

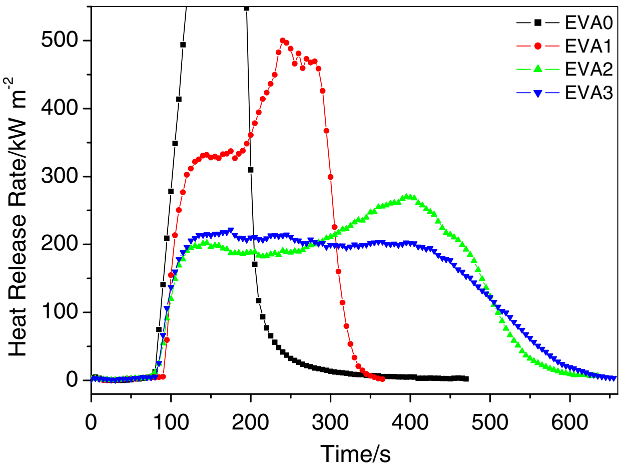

Fig. 1 Heat release rates versus burning time for different blends

the control EVA0. The HRR of EVA1 shows three separate small 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 Fu [14, 15]. The HRR values of other samples (EVA1 to EVA3) decrease with increasing loading of ZnO, and their multiple peak features is not as obvious as for EVA1. Their burning was also prolonged to 550–590 s. EVA3 with 5 phr ZnO shows the lowest HRR value among the above samples.

ZnO is usually considered to be an inert additive in cone calorimeter test in fire-retarded systems. The mechanism of the reduction in HRR is mainly due to the physical processes instead of chemical process in the condensed phase, as reported in the literature [10]. ZnO has a large surface area and low density, tending to migrate near the regressing sample surface without sinking through the polymer melt layer during the gasification/burning process [16, 17]. The accumulated ZnO consequently formed a charred layer by collaborating with LDH, which acts as a heat insulation barrier. This charred layer prevented heat transfer and transportation of degraded products between melting polymer and surface, thus reduced the HRR and related parameters.

Mass loss rate

The primary parameter responsible for the decreased HRR of the composites is the mass loss rate (MLR) during combustion, which was significantly reduced compared to those values observed for pure EVA (Fig. 2). These MLR data essentially mirror the HRR data. These similarities indicate that the mechanism of the observed reduction in HRR and also in MLR depends mainly on the condensed phase process instead of the gas phase process.

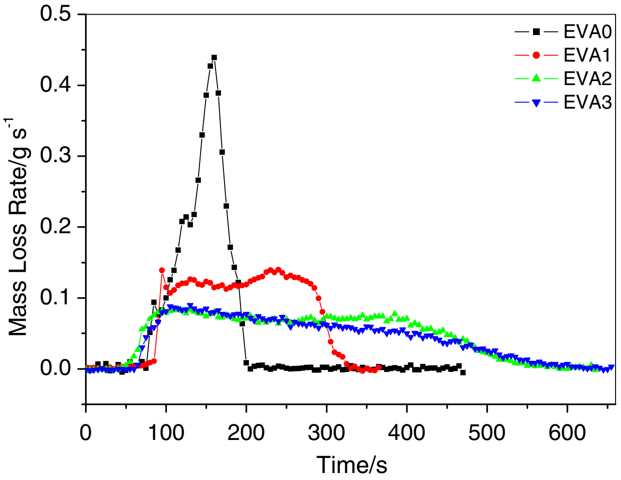

Fig. 2 Mass loss rates versus burning time for different blends

Mass

Figure 3 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 the compact char residue of EVA2 and EVA3 formed on the surface of the sample.

Total heat release

Figure 4 presents the total heat release (THR) for all the samples. The slope of THR curve can be assumed as representative of fire spread [18]. From Fig. 4, it can be seen that the THR is decreased by the flame retardants. It is very clear that the flame spread of samples (EVA1–EVA3) has

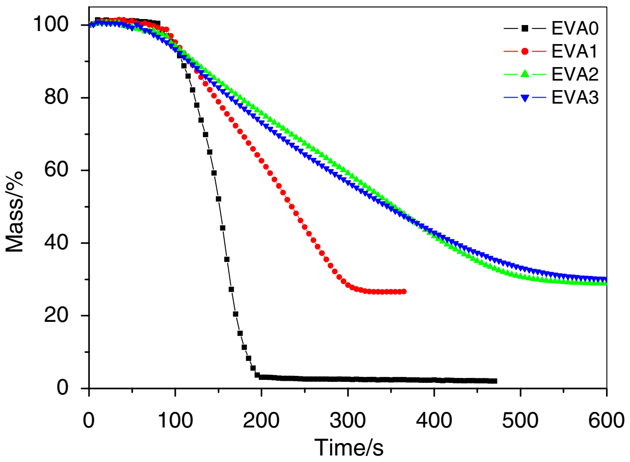

Fig. 3 Mass versus burning time for different blends

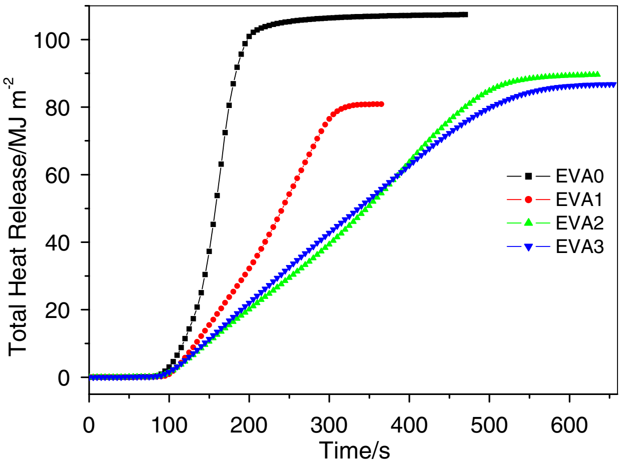

Fig. 4 Total heat releases versus burning time for different blends

decreased, and the flame spread of samples EVA2 and EVA3 is comparatively the lowest. It is also suggested there is a synergistic effect of flame retardance between LDH and ZnO.

CO and CO_2 production rates

Figures 5 and 6 show the CO and CO_2 produced from EVA and flame retardant EVA under a heat flux of 35 kW/m^2. The incomplete combustion of flame retardant composite systems can be seen in the CO production rate. Compared to pristine EVA, the CO production rate of flame retardant systems is highly decreased throughout the whole range of fire in the experiments. Furthermore, with the addition of ZnO, the CO production rate decreases.

It has been reported the hydroxides retardants generate incombustible gases to extinguish fire by increasing CO production [19]. It is very interesting that the carbon monoxide production rate is greatly decreased with the addition of ZnO. The above phenomena can be illustrated in the following. ZnO can catalyze EVA carbonization (Fig. 3). That is, there is more compact char residue formed on the surface of the sample with ZnO. The compact char residue can restrain combustible gases, so the released flammable gases can be complete combustion, which leads to the little carbon monoxide production rate. Another reason may be that the carbon monoxide can be oxidized to carbon dioxide under the catalyzing of ZnO which can migrate onto the surface of the sample [16, 17].

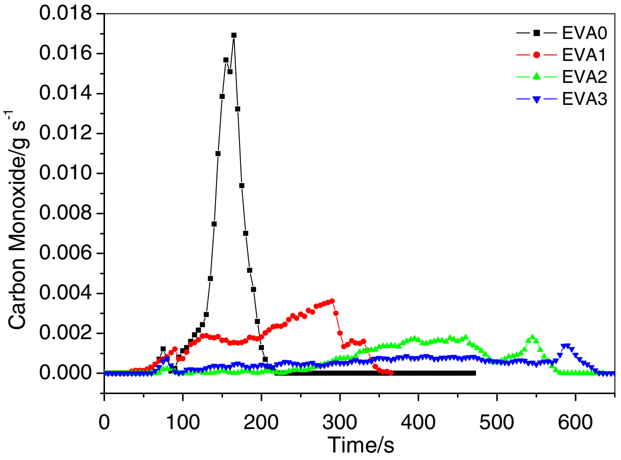

Fig. 5 Carbon monoxides versus burning time for different blends

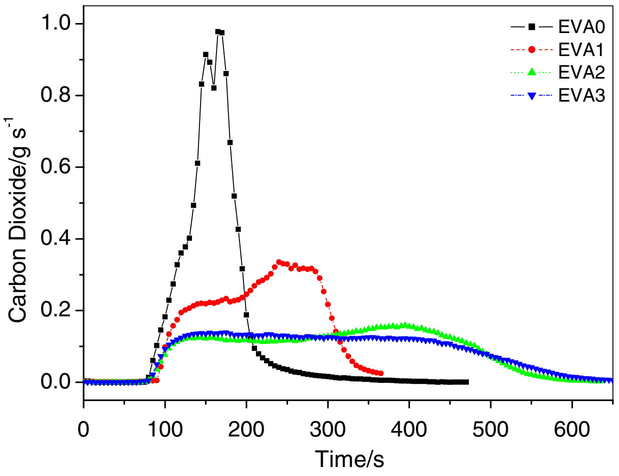

Fig. 6 Carbon dioxides versus burning time for different blends

The CO_2 production rates of the flame retardant systems significantly decrease because the compact char residue prevent combustible gases from being diffused into air, resulting in a complete combustion of the released flammable gases. The CO_2 production rates data essentially mirror the HRR data.

Thermogravimetric analysis

Thermogravimetric (TG) analysis is always used to study the thermal properties ot flame retardant materials [20–24]. TG curves for EVA and its composites are shown in Fig. 7. EVA undergoes two degradation steps as shown in Fig. 7. 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 [25, 26].

From Fig. 7, it can be found that EVA1 shows lower decomposition rate in the second step but higher in the first step than EVA0. The incorporation of LDH 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 LDH. Polymer/clay nanocomposites have been studied widely [27, 28] and

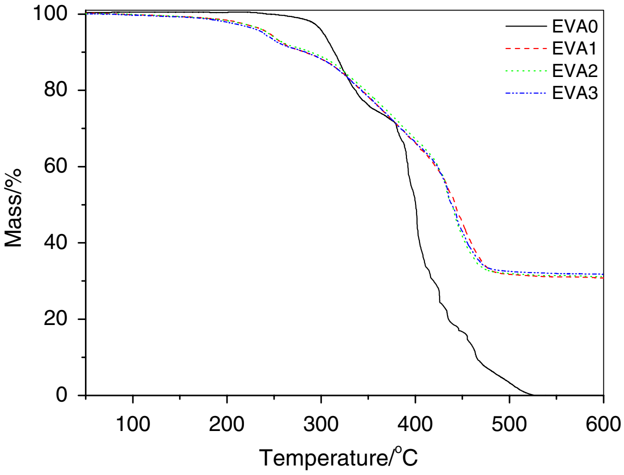

Fig. 7 TG curves versus temperature for different blends

Costache reported similar catalyzing function of –OH groups on the edges of montmorillonite layers.

To our surprise, ternary composites, which contain both ZnO and LDH, show high thermal stability at high temperatures. This should be the main reason that the ternary composites has better flame retardancy than EVA/LDH has at the same LDH loading. This result correlated well with the results of cone calorimeter test.

Conclusion

ZnO has a good flame retardant synergistic effect with LDH in the EVA/LDH/ZnO blends. Suitable amounts of ZnO can enhance UL-94 rating. The cone calorimeter test data reveal that the values of HRR, MLR, Mass, THR, CO and CO_2 of EVA/LDH/ZnO blends apparently decrease with increasing amount of ZnO. The TG show that the weight loss rates decrease with increase in the amount of ZnO. The synergistic flame retardant mechanism of ZnO with LDH in the EVA blends is due to its physical effect in the condensed phase.

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