Effect of EVA on thermal stability, flammability, mechanical properties of HDPE/EVA/Mg(OH)$_2$ composites

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Abstract. In this work, ethylene vinyl acetate (EVA) is introduced to improve the properties of high-density polyethylene (HDPE)/magnesium hydroxide (MH) composites. The thermal stability, flame retardancy and mechanical properties of HDPE/EVA/MH composites are investigated and discussed. With increasing content of EVA, the limiting oxygen index (LOI) of the composites increases. The thermal stability analysis shows that the initial decomposition temperature begins at a low temperature; however, the residues of the composites at 600°C increase when HDPE is replaced by small amounts of EVA. The early degradation absorbs heat, dilute oxygen and residue. During this process, it protects the matrix inside. Compared with the HDPE/MH and EVA/MH composites, the ternary HDPE/EVA/MH composites exhibit better flame retardancy by increasing the LOI values, and reducing the heat release rate (HRR) and total heat release (THR). With increasing content of EVA, the mechanical properties can also be improved, which is attributed to the good affinity between EVA and MH particles.

1. Introduction
Polyethylene (PE) has numerous advantages such as balanced mechanical properties, chemical resistance, low cost and good process ability [1-2]. These properties have led to its wide use in many fields. PE is flammable and its limiting oxygen value is very low. Its flammability limits its applications to a certain extent. In the past decades, the flame retardant investigation of PE has attracted much attention.

In order to improve the flame retardancy of PE, an efficient method is to blend flame retardants with PE. Among the flame retardants, magnesium hydroxide (MH) has been the focus of many researchers due to its halogen-free, non-toxic and inhibiting smoke feature [3-4]. MH produces an endothermic reaction during combustion, which decreases the surface temperature of the polymer. In addition, free water can dilute the combustible gas, and the produced metal oxide (MgO) cuts off sources of heat between the matrix and the surface [5-6]. But the flame retardant efficient of MH is very low; more than 60% MH is required to reach combustion resistance [7]. Large amount of MH will lead to a sharp decrease in mechanical properties which results from poor compatibility.
In order to overcome the poor compatibility, elastomers, such as ethylene-propylene-diene monomer (EPDM), ethylene-octylene copolymer (POE), ethylene vinyl acetate (EVA), thermoplastic polyurethanes (TPU) etc., will be blended with the polymer [8-11]. Among the elastomers, EVA is suitable to blend with PE. This is because EVA can be well miscible with PE because of the presence of similar ethylene chain. In addition, it can also improve flexibility, toughness, environmental stress-cracking resistance due to the inner structure of EVA macromolecules [12]. At the same time, functionalized inorganic particles in the form of polymer/inorganic filler composites have exhibited remarkable performance [13-15]. Su, J. H.; et al. [16] have prepared graphene by the thermal reduction and the graphene is treated by stearic acid to improve its lipophilicity and dispersion in low density polyethylene. Actually, the inorganic fillers modified by the coating and surface treatment with various methods have become the research focus for inorganic particles/polymer composites with improved properties [17-18].

In this work, EVA is introduced to improve the properties of HDPE/MH composites, and the effect of the addition of EVA on the thermal stability, flammability, mechanical properties of HDPE/EVA/MH composites have been studied and discussed by utilizing thermal gravimetric analysis (TGA), limiting oxygen index (LOI), cone calorimeter tests (CCT), and tensile testing instruments.

2. Experiments

2.1. Materials

High-density polyethylene (HDPE, 5000S, MFR=0.923g/10min) was acquired from Lanzhou Petrochemical Company, China Petroleum. EVA (7240M, VA=15wt%, MFR=1.5g/10min) was supplied by TAISOX, Taiwan. Magnesium hydroxide (Mg(OH)$_2$, MH) (average particle size=1.5μm) was obtained from Yantai FR Chemical Technology Co., Ltd. The PE-g-MAH and silane coupling agent are commercial products.

2.2. Preparation of samples

Dried HDPE, EVA and Mg(OH)$_2$ powders are premixed according to the formulation (Table 1), and then compounded in a twin-screw extruder (ModelHFB-150/3300, made in Nanjing Ruiya Polymer Processing Equipment Co., Ltd., China). The temperatures from hopper to die are 140, 150, 160, 170 and 180°C, respectively, and the screw speed is 150rpm. All the samples are hot-pressed at 180°C under 8MPa into sheets of suitable thickness for tests and characterization. The samples used for mechanical properties are injected to model using EM80-V made by Zhende Company.

| Samples | HDPE (phr) | EVA (phr) | MH (phr) |
|---------|------------|-----------|----------|
| E0      | 100        | 0         | 100      |
| E20     | 80         | 20        | 100      |
| E40     | 60         | 40        | 100      |
| E60     | 40         | 60        | 100      |
| E80     | 20         | 80        | 100      |
| E100    | 0          | 100       | 100      |

2.3. Measurements and characterization

Thermogravimetric analysis (TGA): the thermal properties of the composites are performed on a NETZSCH TG 209F1 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen flow with a flow rate of 60 mL/min and the scan ranged from 30 to 700 °C. And the weight of each sample was about 10 mg.
Limited oxygen index (LOI)-LOI is tested by using a JF-4 oxygen index instrument (Jiangning Analysis Instrument Company, China) on the specimen of dimensions 120×6.5×3mm³ according to the standard ASTM D2863-77.

Cone calorimeter test. The cone calorimeter (Stanton Redcroft, UK) tests are carried out on a sheet of (100×100×3 mm³) according to ISO 5660 standard procedures. Each sample is wrapped in aluminium foil and exposed horizontally to an external heat flux of 35kW/m².

Mechanical property tests. Tensile properties are measured by a tensile testing machine AGS-J (Shimadzu Company, Suzhou) according to ASTM D412-1998 at room temperature. The test is performed at a crosshead speed of 50mm/min.

Phase morphology. The cryo-fractured samples are prepared under N₂ liquid for an hour, and then micrographs are taken under common high depth of field microscope.

3. Results and discussion

3.1. Thermal stability

The TGA and derivative thermogravimetric (DTG) curves of the HDPE/MH, EVA/MH, HDPE/EVA/MH composites are shown in Figure 1. The temperatures at 5wt% weight loss, 50wt% weight loss and the maximum decomposition rate are recorded as \( T_{\text{onset}} \), \( T_{50\text{wt}\%} \) and \( T_{\text{peak}} \), respectively, and the detailed data are listed in Table 2. As shown in Figure 1, the HDPE/MH composites begin to decompose at 397.6°C while the EVA/MH composites begin to decompose at 335.2°C. The temperature of maximum mass loss also shifts to low temperature. These indicate that the thermal stability of EVA is lower than that of HDPE. The initial decomposition temperature of the ternary HDPE/EVA/MH composites is reduced by 37°C compared with HDPE/MH composites. This is attributed to the loss of acetic acid from EVA occurring at a low temperature [19].
Figure 1. Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) of HDPE/MH, HDPE/EVA/MH, and EVA/MH composites.

Table 2. Detailed data from TGA and DTG of HDPE/EVA/MH composites.

| Samples | $T_{\text{onset}}$ (°C) | $T_{50\%}$ (°C) | $T_{\text{peak}}$ (°C) | Residue at 600°C (wt%) |
|---------|------------------------|----------------|------------------|---------------------|
| E0      | 397.6                  | 471.8          | 467.4            | 33.2                |
| E20     | 360.5                  | 465.1          | 461.2            | 35.5                |
| E100    | 335.2                  | 461.2          | 458.2            | 33.4                |

However, HDPE/EVA/MH composites display two-step degradation. The first stage occurs at temperatures in the range of 300–400°C; the mass loss involves the deacylation of EVA phrase through radical and ionic β-elimination mechanism and degradation of MH[6, 20]. The second stage occurs at temperatures in the range of 400–550°C, which is attributed to the degradation of HDPE and the back bone of the EVA which forms in the first step and the formation of transvinylenes accompanied by main chain scission in the second step. Compared with the binary composites, the residue of the ternary composites at 600°C is increased by 2.3% and 2.1%. The above results indicate that the thermal stability of HDPE/MH composites decreases with the incorporation of EVA, but the
residue of HDPE/EVA/MH composites increases after combustion. The residue may be in favor of good flame retardancy.

3.2. Flammability
Flammability of HDPE/EVA/MH composites is evaluated by LOI and Cone calorimeter test (CCT). The effect of EVA on the LOI of HDPE/EVA/MH composites is shown in Figure 2. When the EVA content increases from 0 to 20phr, a slight decrease in LOI is observed. The reason for this is not yet clear. However, more EVA can enhance LOI values of HDPE/EVA/MH composites. It can be observed from Figure 2 that the LOI values increase from 30.3% to 35.3% when the content of EVA increases from 20 to 100phr. This indicates that the addition of EVA can improve the flame retardancy of HDPE/EVA/MH composites. The positive effect of EVA on the flame retardancy is mainly attributed to the strong interaction between EVA and MH. The interaction of EVA and MH is shown in Figure 3. As is shown in Figure 3, the MH particles preferentially disperse in EVA. In addition, the strong interfacial bonding between particle and matrix improves the flame retardancy of the composites.

![Figure 2. LOI values of HDPE/EVA/MH composites with various contents of EVA.](image1)

![Figure 3. Micrographs of HDPE/MH and HDPE/EVA/MH composites with MH content of 5% and the ratio of HDPE/EVA is 4:1.](image2)

Besides, the cone calorimeter test has been widely used to evaluate the flammability of materials because it can predict the combustion behavior of materials during interaction with flames. Figure 4 presents the heat release rate (HRR) versus time curves of HDPE/EVA/MH composites. HDPE/MH composites are ignited for 157s, and have a flat heat release peak. Compared with HDPE/MH composites, EVA/MH composites have a short ignition time of 140s and the sharp peak heat release rate (PHRR) value reaches 183.7kW/m², and then decreases dramatically.
However, when a small amount of HDPE is replaced by EVA, it is interesting to observe that HRR is suppressed. The HRR curve of HDPE/EVA/MH composites has two peaks. The ignition time is delayed by 183s and the PHRR value decreases to 104.99 kW/m$^2$. The flammability of the composites is restrained, and the possible reason may be that MH disperses in the EVA which needs more oxygen to burn, and the phenomenon is also proved by LOI curves (Figure 2). This indicates that combination of HDPE, EVA and MH shows a better fire resistance.

The total heat release (THR) curves for the above sample are shown in Figure 5. The trend in THR is the same as HRR. The reduction in heat release can be explained by the amount of chars formed on the surface of the polymer matrix, and the formed char limits the combustion products in making the transition to the gas phase. Figure 6 shows the photographs of HDPE/MH, HDPE/EVA/MH, and EVA/MH composites after combustion. The thick and compact residues can protect the inside matrix and reduce heat release.

### 3.3. Tensile behaviors

The stress-strain curves of HDPE/EVA/MH composites, with various EVA content, are shown in Figure 7. The Young's modulus and tensile strength of HDPE/EVA/MH composites with various contents of EVA are shown in Figure 8. The previous study has shown that the incorporation of 50wt% MH to HDPE leads to a significant decrease in elongation at break. In order to solve this problem, elastomer EVA is added to HDPE/MH composites. It is clear that the tensile behaviors are strongly dependent on the EVA content. Elongation at break is directly ameliorated due to the addition of EVA and increases monotonically with increasing EVA concentration. However, EVA has negative effects on the Young’s modulus and tensile strength. Compared with HDPE/MH composites, Young’s modulus and tensile strength of HDPE/EVA/MH composites cause a more visible drop with the addition of EVA, and decrease with increasing EVA content. Actually, there is a close relationship between the locations of filler [21]. In the HDPE/EVA/MH composites, MH is usually situated in EVA phase. Behradfar et al. [22] reported a preferential dispersion of clay in the elastomer EVA phase. Thus the most plausible factor for the change in tensile properties is ascribed to the location of filler in the elastomer phase. Figure 3 is also a proof for preferential location in EVA.
4. Conclusions
The HDPE/EVA/MH ternary composites were successfully prepared by using a twin-screw extruder. The thermal stability, flame retardancy and mechanical properties of HDPE/EVA/MH composites were studied and discussed. With increasing content of EVA, the LOI values of the composites increase. The thermal stability data show that the initial decomposition temperature of the composites begins at a low temperature while residue at 600°C increases when a small amount of HDPE is replaced by EVA. The early degradation absorbs heat; dilute oxygen and residue produced by early decomposition protects the matrix inside. Therefore, the HDPE/EVA/MH composites can show a better flame retardancy than the HDPE/MH composites as well as the EVA/MH composites. The tensile properties of the HDPE/EVA/MH ternary composites are strongly influenced by the incorporation of EVA elastomer. MH has a tendency for location in EVA. A good affinity between EVA and MH leads to good flame retardancy and mechanical properties of the composites.

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