

Flammability Characterization and Effects of Magnesium Oxide in Halogen-free Flame-retardant EVA Blends^{*}

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Abstract The effects of magnesium oxide (MgO) on the flame retardant performance of intumescent systems based on ammonium polyphosphate (APP) and pentaerythritol (PER) in ethylene vinyl acetate copolymer (EVA) were studied. The results showed that MgO affects both the quality and quantity of residual char. There is an optimal value for the loading amount of MgO. More or less MgO loading may cause the formation of defective char layers and worsen the flame retardancy of EVA. According to the results of limiting oxygen index (LOI), vertical flammability test (UL94 rating) and cone calorimetry (CONE), the best flame retardancy with a strong and well intumescent char is obtained from the sample with 1 wt% of MgO, which has the highest LOI value of 27.9, UL94 rating of V-0 and the lowest peak heat release rate of 242 kW·m⁻².

Keywords: Flammability; Magnesium oxide; Flame retardancy; Ethylene vinyl acetate copolymer; Intumescence.

INTRODUCTION

Ethylene vinyl acetate copolymer (EVA) is one of the important polyolefins with broad applications, such as hot melt adhesives, packaging, wire and cable insulation and carpeting^[1, 2]. However, its inherent flammability cannot meet industrial requirements in many cases. Inclusion of flame retardants is an effective route to endow EVA with flame retardancy, which can inhibit the ignition and cut down the heat release rate during combustion^[3].

For the environmental concerns, halogen-free flame retardants have aroused great attention in recent years, because halogen-containing flame-retardant materials produce a lot of smoke and toxic gases on burning^[4, 5]. Alumina trihydrate (ATH) and magnesium hydroxide (MDH) are used as common halogen-free flame retardants (FRs) for EVA^[6–8]. However, the typical loadings of ATH and MDH are more than 60 wt% which cause sharp decrease in both the mechanical properties and the crosslinking capability of EVA^[9, 10]. Intumescent flame retardants (IFRs), usually phosphorus-nitrogen containing compounds, are considered as other promising candidates for replacing halogen-containing agents since there are as yet no known environmental problems associated with their use^[11]. During combustion, IFRs form an intumescent char layer which acts as a physical barrier, reducing the heat flux from the flame to the polymer matrix and the transfer of fuel to the flame^[12]. Although the flame retardant efficiency of IFRs is higher than ATH and MDH, it is still lower than the

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halogenated flame retardants. 30 wt% or more of the IFR loading is needed to get a satisfactory flame retardant performance. Therefore, great attention has been focused on how to explore more efficient IFR systems.

It was reported that metal compounds could promote the dehydrogenation of the polymer and carbonization of the IFR system, and thus effectively improve the mechanical strengths and heat stabilities of char residues^[13–16]. Lewin and Endo found that divalent and transition metal compounds such as manganese acetate, zinc sulfate, aluminum acetate, *etc.*, improved the flame retardant performance of ammonium polyphosphate (APP)/pentaerythritol (PER) based intumescent system in polypropylene (PP)^[17]. Wu found that zinc and nickel salts and oxides can also enhance the flame retardancy of PP/APP/dipentaerythritol (DPER) system^[18]. Laachachi discovered that the combination of aluminum oxide (Al_2O_3) and a phosphorus compound AP752 leads to a synergistic flame retardant effect in polymethylmethacrylate (PMMA)^[19].

However, most of the cases reported in the flame retardant systems catalyzed by metal compounds were focused on PP, polyethylene (PE) or PMMA. The flame retardant EVA, which has a quite different degradation process, was randomly studied in such system. Besides, it is also noticed that the magnesium oxide (MgO), which is the dehydration product of MDH, was rarely reported in the IFR system. Similar to Al_2O_3 , MgO is a low-cost, atoxic and very common compound, which may have the potential to improve the efficiency of IFR.

In this work, MgO was incorporated in the intumescent system based on APP and PER, aiming to get a flame retardant EVA formulation with a low FR loading. The flame retardant mechanism of EVA/IFR/MgO system was also studied.

EXPERIMENTAL

Materials

EVA (KA-40, vinyl acetate content 25 wt%, melt flow index 20 g/10 min) was provided by Polyolefin Company (Singapore) Pte Ltd. Dialkyl peroxide (LUPEROX 101) was provided by French Arkema Corporation. APP (JLS-APP101R) was provided by Hangzhou JLS Flame Retardants Chemical Co. Ltd. PER (Size: 800 mesh) was provided by Qingdao New Materials Sci-Tech Industrial Park Development Co., Ltd. MgO (Purity: > 93%) was provided by Hebei Meishen Chemical Technology Group Limited.

Preparation of Fire Retardant EVA Blends

The EVA resin was blended with MgO and IFR in a twin-screw extruder with the temperature profile of 60 °C, 100 °C, 135 °C, 145 °C, 135 °C and 85 °C, and finally cut into pellets. The formulations are presented in Table 1. IFR shown in Table 1 represents the mixture of APP and PER with a mass ratio of 3:1, which usually gives the optimum flame retardant performance^[20]. The total amount of IFR was maintained at 25 wt% while the content of MgO was varied from 0.5 wt% to 3 wt%. After granulation, the prepared EVA/IFR/MgO pellets were transferred into a mold and heated at 140 °C in vacuum of –99 kPa for 5 min. When the pressure was increased to –50 kPa, the same pressure was kept for 30 s. Then the pressure was increased to –30 kPa and kept for another 30 s. At last, the samples were pressed at 1 MPa for 12 min, followed by cooling at room temperature.

Table 1. The formulation of flame retardant EVA with IFR and MgO

Sample ID	EVA ^a (wt%)	IFR (wt%)	MgO (wt%)
EVA	100		
EVA/IFR	75	25	
EVA/IFR/0.5MgO	74.5	25	0.5
EVA/IFR/1MgO	74	25	1
EVA/IFR/2MgO	73	25	2
EVA/IFR/3MgO	72	25	3

^a EVA represents the mixture of pure EVA mixed with LUPEROX 101 (0.7 wt%).

Characterization

Thermogravimetric analysis (TGA) was performed on a TG Q50 thermal analyzer in N_2 and air with a heating rate of 20 $\text{K}\cdot\text{min}^{-1}$ from room temperature to 600 °C. LOI values were determined using an HC-2 Oxygen Index

Instrument (Jiangning Analytical Instrument Co. Ltd., China). The dimension of the LOI sample sheets are $120\text{ mm} \times 6\text{ mm} \times 3\text{ mm}$ according to ASTM D2863. The vertical burning tests were conducted in a CZF-III Horizontal and Vertical Burning Tester (Jiangning Analysis Instrument Company, China) according to ASTM D3801, with the dimension of the specimens of $130\text{ mm} \times 13\text{ mm} \times 3\text{ mm}$. The cone parameters were measured according to ISO 5660 using a Cone Calorimeter (Govmark) at a heat flux of $50\text{ kW}\cdot\text{m}^{-2}$. The dimensions of all samples for cone test are $100\text{ mm} \times 100\text{ mm} \times 3\text{ mm}$.

RESULTS AND DISCUSSION

LOI and UL94 Rating

LOI and UL94 tests are widely used to determine the flammability of flame retardant materials^[21]. The LOI values and UL94 test results of the EVA blends are shown in Table 2. EVA is a highly inflammable polymeric material with a LOI value of only 20.7 and no rating in the UL94 test. After adding 25 wt% IFR into EVA, the LOI value of the EVA/IFR system increased to 24.9. However, the sample still failed in the UL94 test, indicating that 25 wt% IFR is not enough to form a protective char to prevent flammable dripping and the spread of the flame. It is interesting to find that loading MgO can significantly improve the flame retardancy of EVA/IFR blends. Seen from Table 2, loading 0.5 wt% of MgO led to an increase of 2.6 for the LOI value and a V-2 rating for the UL 94 test. When the content of MgO was increased to 1 wt%, the LOI value increased to 27.9 and the blend passed the UL 94 test with a V-0 rating blend.

Table 2. LOI and UL94 rating of the flame retardant EVA with IFR and MgO

Sample	t_1 (s)	t_2 (s)	UL94	LOI (%)
EVA	—	—	No rating	20.7
EVA/IFR	1.0	—	No rating	24.9
EVA/IFR/0.5MgO	0.8	19.4	V-2	27.5
EVA/IFR/1MgO	0.9	2.5	V-0	27.9
EVA/IFR/2MgO	0.9	27.9	V-1	26.3
EVA/IFR/3MgO	2.5	—	No rating	25.7

When heated in the combustion, APP undergoes the decompositions such as deamination and dehydration reactions with the release of NH_3 and H_2O . Then PER is phosphorylated by polyphosphoric acid or phosphoric acid, which is the decomposition product of APP. With further thermal pyrolysis of the phosphate ester, a crosslink structure of the subsequent residue can be formed and leads to a protective char layer. If the content of APP and PER mixture is not enough, the quality of the protective char may be deficient and easily broken. That will result in a lower LOI value and UL94 rating, as manifested by the data shown in Table 2. It had been reported that some metal ions, such as magnesium, can serve as catalysts in crosslinking and dehydration reactions^[17], which is very important to the char-formation process of the IFR system. In EVA/IFR/MgO blends, MgO favors the formation of a compact char layer which can efficiently block the melt dripping and the growth of flame and thus endow a better flame retardancy of EVA/IFR. However, it was also found that when the loading amounts of MgO were increased to 2 wt% or more, the LOI values of EVA blends decreased and the UL94 ratings degraded from V-0 to V-1 or even no rating. Although MgO enhanced the crosslink to make a more strong char, it also affected the intumescence of the char layer. It is known that the flame retardant mechanism of IFR is to form an intumescent char layer to protect the underlying matrix. Too much crosslink may weaken the intumescence ability of the char layer. Therefore, when the loading amounts of MgO exceed a suitable value, the char layer with insufficient intumescence will be formed, resulting in a worse flame retardancy.

Cone Calorimetry

Cone calorimetry is used for investigating the burning behavior of polymeric materials, which can provide various parameters such as time to ignition (t_{ign}), peak heat release rate (PHRR), total heat release (THR) and

average specific extinction area (ASEA)^[22, 23]. Figure 1 and Table 3 show the cone calorimetric data for the flame retardant EVA with IFR and different contents of MgO, respectively. It can be found that pure EVA burns very fast after ignition with a PHRR value of $593 \text{ kW}\cdot\text{m}^{-2}$ and a negligible char residue of 3.73 wt%. After the addition of IFR, reductions in PHRR and THR values by 11.0% and 23.5% are observed, indicating that IFR contributes to the decrease of the flammability of EVA. However, t_{ign} of EVA/IFR reduced from 76 s (for EVA) to 50 s, which is quite close to those in previous reports^[24, 25]. The addition of IFR to EVA is expected to increase the viscosity of the neat polymer, reducing heat exchange between the sample surface and the bulk of the sample^[24]. This will result in a rapid increase in the temperature of the sample surface which is exposed to the radiant source. Hence the time required for the sample to reach the pyrolysis temperature is reduced^[24].

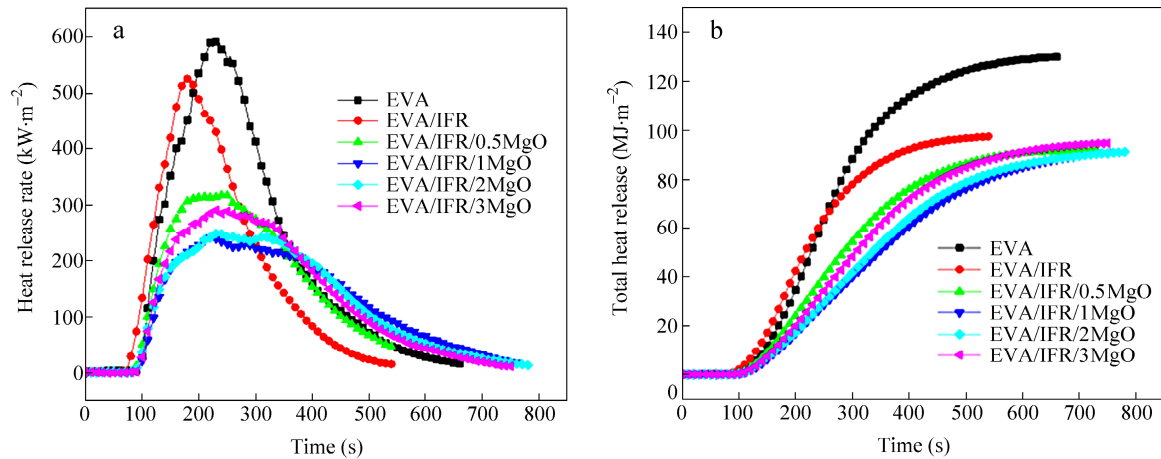


Fig. 1 (a) Heat release rate curves and (b) total heat release curves of the flame retardant EVA with IFR and MgO

Table 3. Combustion parameters obtained from burning in the cone calorimetric test

Samples	t_{ign} (s)	PHRR ($\text{kW}\cdot\text{m}^{-2}$)	THR ($\text{MJ}\cdot\text{m}^{-2}$)	ASEA ($\text{m}^2\cdot\text{kg}^{-1}$)	CO yield ($\text{kg}\cdot\text{kg}^{-1}$)	Residue (wt%)
EVA	76	593	130.2	607	0.0583	3.73
EVA/IFR	50	528	99.6	837	0.1921	10.79
EVA/IFR/0.5MgO	68	324	91.9	830	0.1292	13.05
EVA/IFR/1MgO	76	242	91.8	792	0.0920	17.92
EVA/IFR/2MgO	71	249	91.2	765	0.0788	20.39
EVA/IFR/3MgO	75	296	94.8	723	0.0733	17.68

Comparing the HRR and THR curves of the EVA/IFR blend, the loading of MgO makes a further decrease of HRR and the delay of ignition, suggesting that MgO has positive effect for the flame retardancy of EVA/IFR blend. The PHRR value of EVA/IFR/0.5MgO is $324 \text{ kW}\cdot\text{m}^{-2}$, which is 38.6% lower than that of EVA/IFR. When the content of MgO was increased to 1 wt%, the PHRR value decreased further to $242 \text{ kW}\cdot\text{m}^{-2}$. Similar trend could also be found in the THR data shown in Fig. 1 and Table 3. The THR values were decreased from $99.6 \text{ MJ}\cdot\text{m}^{-2}$ (for EVA/IFR) to $91.8 \text{ MJ}\cdot\text{m}^{-2}$ (for EVA/IFR/1MgO). However, when more MgO ($>1 \text{ wt}\%$) was added into the EVA/IFR blend, the PHRR and THR values began to increase again. Although the THR value of EVA/IFR/2MgO decreased to the lowest value, its PHRR value increased to $249 \text{ kW}\cdot\text{m}^{-2}$. When the amount of MgO was 3 wt%, the PHRR and THR values increased to $296 \text{ kW}\cdot\text{m}^{-2}$ and $94.8 \text{ MJ}\cdot\text{m}^{-2}$, respectively. Such results are in good agreement with the results of LOI and UL94 rating. It indicates that MgO does have an obvious improving effect on the flame retardancy of EVA/IFR only in an appropriate loading range. This could also be related to the carbonization process catalysed by MgO, which may significantly affect the quality and the intumescence ability of the char layer as discussed above.

Lack of enough MgO resulted in the formation of a weak char layer with less crosslink density, which is easy to rupture with the increase of temperature and gas pressure beneath it. Seen from Fig. 2, the char layer of

the EVA/IFR blend is not intact and its average height is only 8 mm, which cannot protect the polymer matrix obviously. After the incorporation of appropriate amounts of MgO into the EVA/IFR blend, *e.g.* EVA/IFR/1MgO, the char layer formed was strong enough and a height of 28 mm of the char demonstrated its



Fig. 2 Optical images of residues after the cone calorimetric test for the flame retardant EVA with IFR and MgO

good intumescence. When the loading amount of MgO was too much, the intense crosslink network hindered the intumescence of the char layer. The reduced height (25 mm) of the char layer of EVA/IFR/3MgO proved the descriptions mentioned above. Moreover, the char layer may be formed with less flexibility due to the intense crosslink, which may favor the formation of defects on the char surface and result in the release of the flammable volatiles. It can be manifested by the higher PHRR peak of EVA/IFR/3MgO in Fig. 1.

It is also noticeable in Table 3 that the values of ASEA were significantly decreased with increasing MgO contents. The yields of CO also followed the same trend, which were decreased by 33%–62% compared with that of the EVA/IFR blend. It is indicated that MgO suppresses the production of smoke, especially for the fatal CO. Such results are consistent with our previous study^[26, 27].

Thermal Analysis

After ignition, all the oxygen at the polymer-flame interface is consumed. This means that the thermal decomposition in an inert atmosphere is the appropriate condition for determining the fuel production rate of a flaming material^[28, 29]. Such process is always simulated by TGA in N₂. The thermal decomposition of the EVA blends in N₂ is shown in Fig. 3. The detailed data are summarized in Table 4. The T_{onset} (decomposition temperature at 5 wt% weight loss) of pure EVA resin is 332 °C and negligible residue was left at 600 °C. From the DTG curve for EVA resin, a two-step degradation is found: the evolution of acetic acid between 270 and 380 °C and hydrocarbonaceous chain degradation between 380 and 500 °C. The T_{onset} s of EVA/IFR decreased by 14 K due to the earlier degradation of IFR. And the T_{max} s (maximum decomposition temperature) were also decreased a little. It is due to the fact that phosphorus or polyphosphorous formed by the degradation of the phosphonate groups slightly accelerates the decarboxylic reaction and hydrocarbonaceous chain degradation, which leads to the increased residue formation by 6.8 wt%. After the incorporation of MgO in EVA/IFR, the char residue yields were increased obviously. At the same time, the T_{max} s did not show much difference indicating that the catalysis of MgO mainly occurred within IFRs. This result is in agreement with the reports of Chen^[30] and Song^[31] who observed that metal ions could enhance the charring behavior of the polymer with an intumescent fire retardant. And they attributed this behavior to the reaction between the metal ions and the polyphosphoric acid through salt bridges.

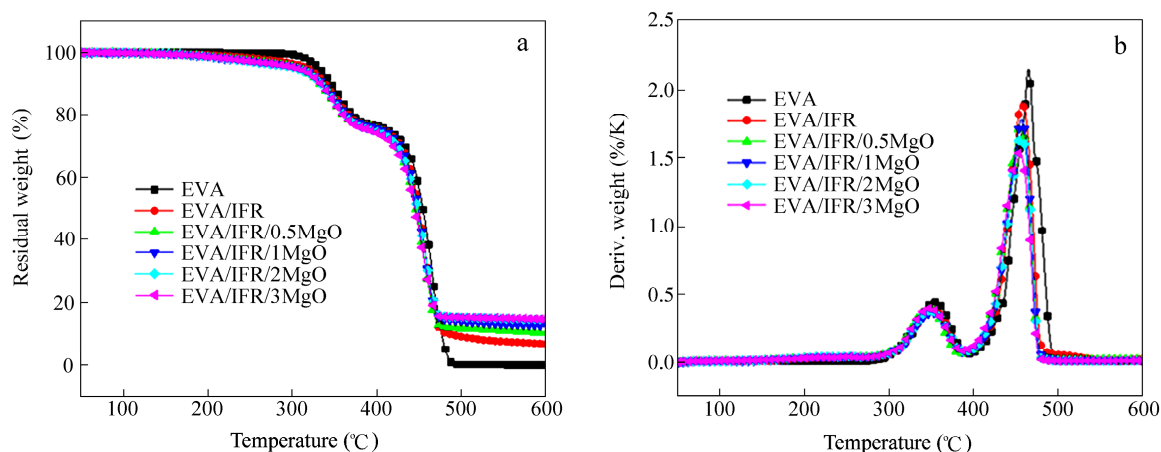


Fig. 3 TG (a) and DTG (b) curves of EVA, EVA/IFR and EVA/IFR/MgO in N₂

In order to investigate the effect of MgO on the thermal degradation of EVA blends in the atmosphere containing O₂, the TG analysis was also carried out in air. The thermal behavior and detailed data are shown in Fig. 4 and Table 5. All the samples showed two-stage degradation, which are similar to that in N₂. For pure EVA, the acetic acids split in β -elimination forming double bonds or crosslinks in the first step; the second step involves thermal decomposition of the resulting unsaturated or crosslinked backbone by thermal dissociation and

oxidation^[32], which leads to 0 wt% residues at the end of the degradation. With the loading of 25 wt% IFR, T_{onset} of EVA/IFR blend was lowered by 11 K because of the earlier degradation of IFR. While, the T_{max} s of two-stage degradation of flame retardant EVA increased by 7 K and 21 K, respectively, which indicates that IFR enhanced the thermal stability of EVA. After the addition of MgO with different contents, the T_{onset} and T_{max} s decreased obviously, and the $T_{\text{max}2}$ of some of samples were even lower than that of EVA. However, the residue weights are 0.21%–3.7% higher than that of EVA/IFR blend, which are mostly higher than the theoretical values. It is also noticed that the residue weights at 600 °C of EVA/IFR/1MgO and EVA/IFR/2MgO are higher than those of other samples, which is consistent with the results of cone test and may be ascribed to the similar reason mentioned above.

Table 4. TGA data of flame retardant EVA with IFR and MgO in N₂

Sample	T_{onset}^a (°C)	T_{max}^b (°C)		Residue at 600 °C (%)
		$T_{\text{max}1}$	$T_{\text{max}2}$	
EVA	332	354	465	0
EVA/IFR	318	353	458	6.8
EVA/IFR/0.5MgO	308	349	456	10.4
EVA/IFR/1MgO	307	351	457	12.7
EVA/IFR/2MgO	303	350	457	14.5
EVA/IFR/3MgO	307	347	454	14.6

^a Decomposition temperature at 5 wt% weight loss; ^b Maximum decomposition temperature

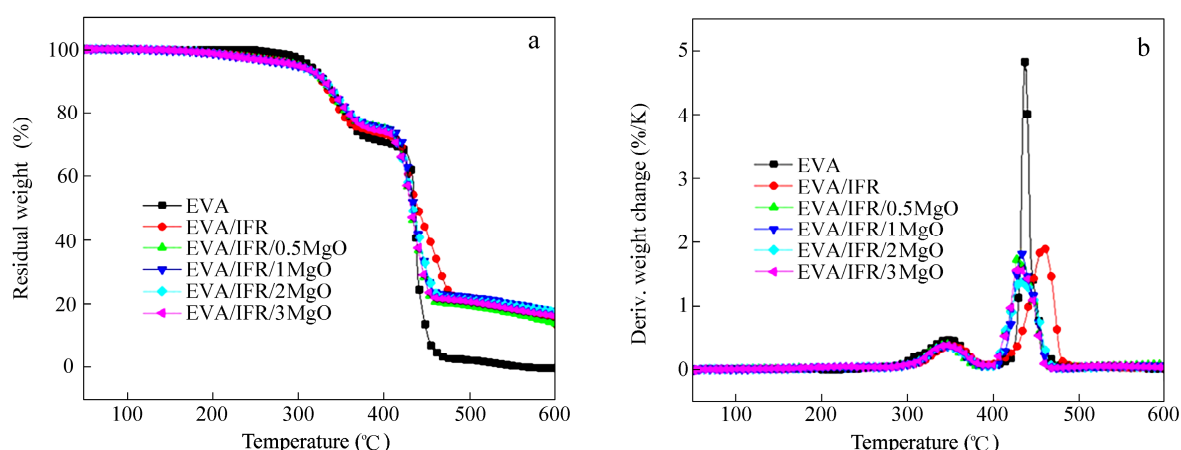


Fig. 4 TG (a) and DTG (b) curves of EVA, EVA/IFR and EVA/IFR/MgO in air

Table 5. TGA data of flame retardant EVA with IFR and MgO in air

Sample	T_{onset}^a (°C)	T_{max}^b (°C)		Residue at 600 °C (%)
		$T_{\text{max}1}$	$T_{\text{max}2}$	
EVA	313	347	437	0
EVA/IFR	302	354	458	13.68
EVA/IFR/0.5MgO	302	346	429	13.89
EVA/IFR/1MgO	296	343	434	17.46
EVA/IFR/2MgO	298	345	431	17.59
EVA/IFR/3MgO	298	346	429	16.25

^a Decomposition temperature at 5 wt% weight loss; ^b Maximum decomposition temperature

CONCLUSIONS

The effects of magnesium oxide on APP/PER based intumescent EVA systems were studied through LOI, UL-94 rating and cone calorimetric tests. The results showed that the loading of MgO affected the quality of

protective char layer significantly, which is ascribed to the catalysis of MgO on the decomposition and crosslink of APP/PER which may influence the strength and intumescence ability of char layer.

There was an optimum loading content of MgO. More MgO caused the bad intumescence of char layer and less MgO led to the weak char layer which was easy to be broken. Both of them may worsen the flame retardant performance of the material. EVA/IFR/1MgO has the highest LOI value of 27.9, the UL94 V-0 rating and the lowest PHRR value of $242 \text{ kW} \cdot \text{m}^{-2}$, which formed a well-intumescent and strong char layer. The TGA results showed that adding MgO into EVA/IFR increased the char residue yields obviously, while it did not affect the T_{max} very much. It is indicated that the catalysis of MgO on the crosslink network in the EVA/IFR system mainly occurred between IFRs, which does not affect the degradation of EVA significantly.

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