Thermal and flame retardant properties of novel intumescent flame retardant low-density polyethylene (LDPE) composites

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Abstract A char-forming agent (CFA) and silica-gel-microencapsulated ammonium polyphosphate (MCAPP) were selected to form novel intumescent flame retardant system (IFRs), and then the influence of this novel IFRs on the thermal and flame retardant properties of low-density polyethylene (LDPE) were studied. The results of cone calorimetry show that the flame retardant properties of LDPE with 30 wt% novel IFR (CFA/MCAPP = 1:3) improve remarkably. The heat release rate peak, total heat release (THR) decreases, respectively, from 1479.6 to 273.5 kW m^{-2} and from 108.0 to 80.5 MJ m^{-2}. The LDPE composite with CFA/MCAPP = 1:3 has the excellent water resistance, and it can still obtain a UL-94 V-0 rating after treated with water at 70 °C for 168 h.

Keywords Low-density polyethylene · Fire retardant · Cone calorimeter · Intumescent

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Introduction

Low-density polyethylene (LDPE) is a widely used polyolefin due to its excellent properties, such as easy processability, chemical corrosion resistance, electrical insulation properties, and so on. However, easily flammable property limits its applications, so it is necessary to prepare these plastic composites with good flame retardant properties. In order to achieve above aim, many methods for improving fire retardancy of LDPE are investigated, and one of the most promising methods is intumescent flame retardant (IFR) method [1–4].

Among many IFR LDPE methods, a widely used and high effective IFRs system is based on ammonium polyphosphate (APP) and pentaerythritol (PER) [3, 4]. Unfortunately, APP and PER have poor water resistance, so the flame retardant effect of those IFR system is not permanent, which limits the application of IFRs in LDPE composites. In order to overcome the above problem, some researchers synthesized new carbon sources which are resistant to water solution. Among those new char formers, triazines derivative—char-forming agent (CFA) containing hydroxyethylamino, triazine rings and ethylenediamine into groups has attracted more and more attention due to its excellent flame retardant properties and water resistance. Until now, CFA has been used in PP, EVA, and so on [5–8]. However, IFRs contain three main ingredients: an acid source, a carbon source, and a gas source, so in order to make the IFR LDPE with excellent water resistance, just using novel carbon source is not enough. Another solution to over poor water resistant problem of flame retardants is microencapsulation. Microencapsulation can protect encapsulated substances from some degrading reagents such as water. Mircroencapsulated APP has been synthesized with different materials such as polyurethane,

PVA–melamine–formaldehyde resin, urea–melamine–form-aldehyde resin, silica-gel, and so on, and has been used in flame retardant polymer such as PP, PU, and so on [9–14].

In this study, in order to prepare flame retardant LDPE composites with good flame retardant properties and excellent water resistance, we combined above two methods to prepare flame retardant LDPE composites. CFA and silica-gel-microencapsulated APP (MCAPP) were selected to form novel IFRs. The influence of IFRs on thermal and flame retardancy properties of LDPE have been investigated. Through this study, we hope to provide efficient IFRs with excellent water resistance ability for LDPE composites.

Experiment

Materials

LDPE (DFDA-7042, MI = 2.0 g/min) was supplied as pellets by Yangzi Petrochemical Co. (China). CFA was kindly provided by KeYan Co., and the structure of CFA is shown in Fig. 1. Silica-gel MCAPP is a kind of APP which is well microencapsulated by SiO_2 gel, and the phosphorus atom of MCAPP is 1.84% is also kindly provided by KeYan Co.

The preparation of samples

LDPE, MCAPP, and CFA were dried in a vacuum oven at 80 °C overnight before use. Then LDPE, MCAPP, and CFA were melt-mixed in a twin-roller mill (KX-160, Jiangsu, China) for 10 min; the temperature of the mill was maintained at 160 °C and the roller speed was 60 rpm. The samples are listed in Table 1. The prepared composites were hot-pressed into sheets with suitable thickness and size for UL-94, LOI and cone calorimeter tests.

Characterization

Thermogravimetric analyses (TG) were carried out using a Shimadzu TGA50H thermo-analyzer instrument from 25 to 700 °C at a linear heating rate of 10 °C min^{-1} under an air
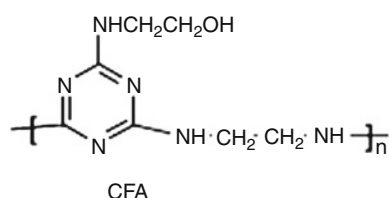

Fig. 1 The structure of CFA

Table 1 Formulations of the flame retardant LDPE composites

Sample	LDPE	MCAPP	CFA	UL-94
LDPE0	100			Burning
LDPE1	62	30		Burning
LDPE2	70		30	Burning
LDPE3	70	22.5	7.5	V-0
LDPE4	70	20	10	V-0
LDPE5	70	15	15	V-2
LDPE6	70	10	20	Burning

flow rate of 25 mL min^{-1}. Samples were measured in an alumina crucible with a mass of about 10 mg.

TG analysis–infrared spectrometry (TG–IR) was performed using the TG analyzer that was linked to the Nicolet 6700 FTIR spectrophotometer. About 5.0 mg of the sample was put in an alumina crucible and heated from 30 to 600 °C. The heating rate was 20 °C min^{-1} (nitrogen atmosphere, flow rate of 60 mL min^{-1}).

The combustion properties were evaluated using a cone calorimeter, and all samples ($100 \times 100 \times 3$ mm^3) were exposed to a Stanton Redcroft cone calorimeter under a heat flux of 30 kW m^{-2} according to ISO-5660 standard procedures.

The scanning electron microscopy (SEM) image of the residue after the cone calorimetry experiment was taken using a DXS-10 scanning electron microscope produced by Shanghai Electron Optical Technology Institute. The char was placed on the copperplate, and then coated with gold/palladium alloy ready for imaging.

LOI was measured according to ASTM D2863, and the apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens dimensions used for test were $100 \times 6.5 \times 3$ mm^3. The vertical burning test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China), and the specimens used for the test is $100 \times 13 \times 3$ mm^3.

Results and discussion

LOI and UL-94 analysis of flame retarded LDPE composites

Figure 2 and Table 1 show the LOI and UL-94 results of LDPE composites with 30 wt% flame retardant loadings. The LOI value of pure LDPE is 17.5. When CFA and MCAPP are added, the LOI value of LDPE composite is greatly increased and the LOI increases with an increasing content of MCAPP. The LOI value of LDPE/CFA/MCAPP (1:3) reaches to the maximum (29.0). The LOI value of
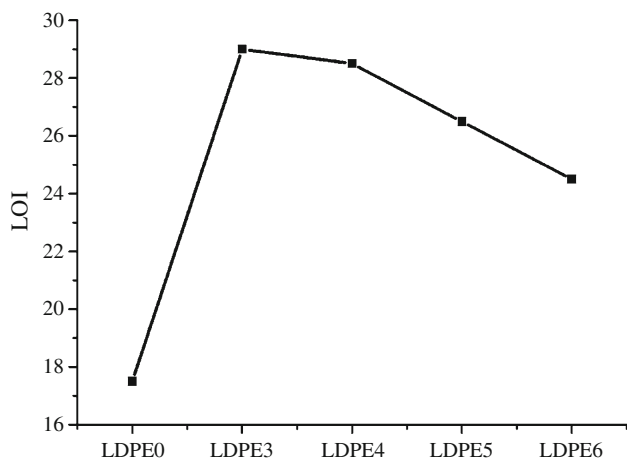
Fig. 2 The LOI value of LDPE and flame retardant LDPE composites

Fig. 3 The TG curves of pure LDPE and flame retardant LDPE composites

LDPE/CFA/MCAPP (2:1) shows the lowest value of 24.5. The experimental results of vertical burning rate show that with only addition of MCAPP or CFA alone, the samples burn seriously, and can not pass UL-94 rating. While the LDPE/CFA/MCAPP samples give a V-0 rating when the mass ratio of CFA to MCAPP is 1:3 or 1:2 with 30 wt% loadings. However, when the mass ratio of CFA to MCAPP is 2:1, the LDPE falls to pass UL-94 rating. The LOI and UL-94 results reveal that CFA and MCAPP have synergistic effect, and the suitable ratio of CFA and MCAPP plays an important role in improving the flame retardant property of LDPE composites.

In order to further investigate the water resistance of flame retardant LDPE composites, LDPE3 and LDPE4 are treated with water at 70 °C for 168 h, and then their flame retardant properties are evaluated. From UL-94 test, it can be found that the sample LDPE3 and sample LDPE4 with CFA/MCAPP = 1:3 and 1:2 have excellent water resistance property, after 168 h the samples can still obtain a UL-94 V-0 rating.

Thermal stability

Figure 3 shows the TG curves of pure LDPE and the LDPE/CFA/MCAPP systems. Compared to pure LDPE, the LDPE/CFA/MCAPP systems have poorer thermal stability before 340 °C. Above 340 °C, LDPE/CFA/MCAPP systems show much higher thermal stability and have about 20% char compared with almost nothing for pure LDPE. The ratio of CFA/MCAPP also influences the thermal behavior of the LDPE composite. LDPE/CFA/MCAPP (1:3) has higher thermal stability than LDPE/CFA/MCAPP (2:1) above 400 °C, and at 600 °C the charred residue of LDPE/CFA/MCAPP (1:3) is 20 wt% which is more than that of LDPE/CFA/MCAPP (2:1).
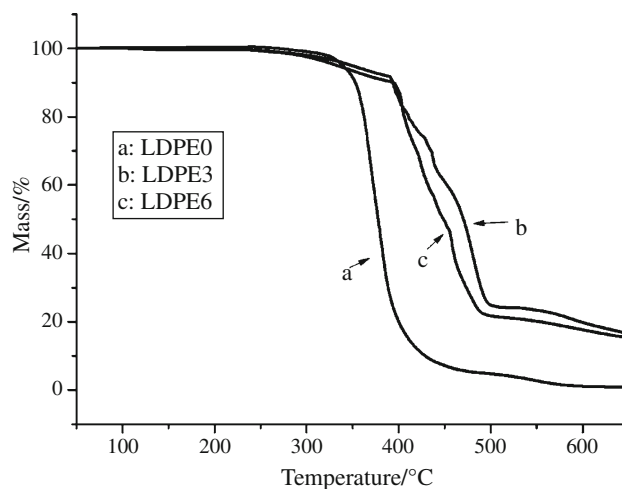
TG–IR was used to further analyze the gas products during the thermal degradation. Figure 4 shows the 3D TG–IR spectrum of gas phase in the thermal degradation of LDPE3 under nitrogen. From this figure, FTIR spectra of all the volatile pyrolysis products evolved at different time can be observed. Some small molecular gaseous species can easily identified by their characteristic absorbance: H_2O (3,400–4,000 cm^{-1}), saturated hydrocarbons (–CH_3 and –CH_2– groups: 2,950–2,850 and 1,515–1,370 cm^{-1}), unsaturated alkane (3,076 and 890 cm^{-1}), CO_2 (2,381 cm^{-1}), and NH_3 (927 cm^{-1}) [15]. In order to clearly understand the change of these formative products, the relationship between intensity of characteristic peak and temperature for volatilized saturated hydrocarbons, unsaturated alkane, H_2O, and NH_3 is plotted in Fig. 5. The Fig. 5 shows that at low temperature the small volatile gas NH_3 appears. Associated with the analysis of TG result, the first step decomposition of flame retardant LDPE
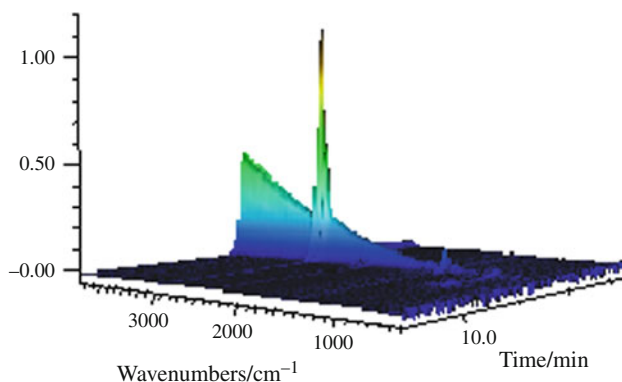

Fig. 4 The 3D TG–IR spectrum of gas phase in the thermal degradation of LDPE3 under nitrogen

Fig. 5 The relationship between intensity of characteristic peak and temperature for volatilized saturated hydrocarbons, unsaturated alkane, H_2O, and NH_3
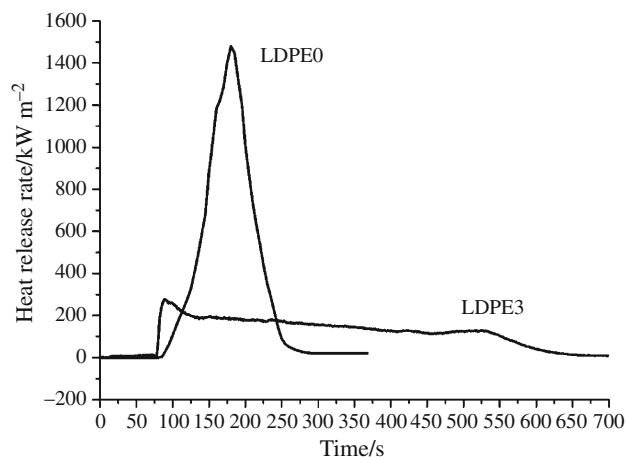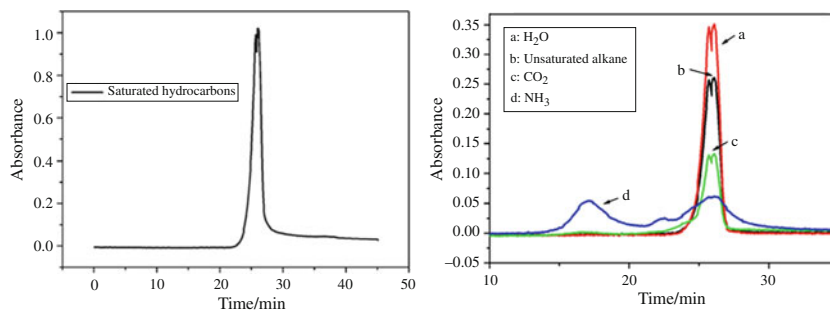
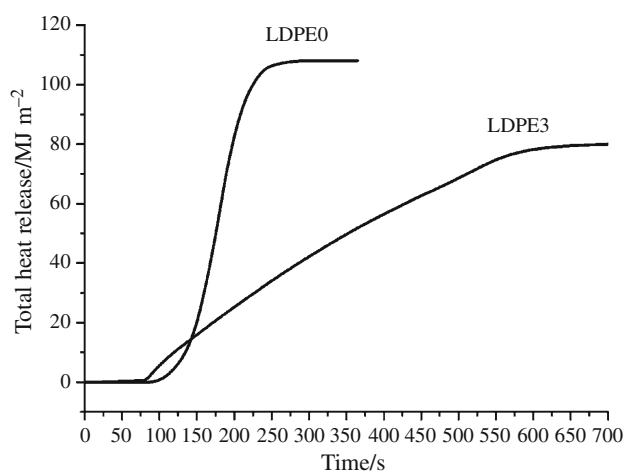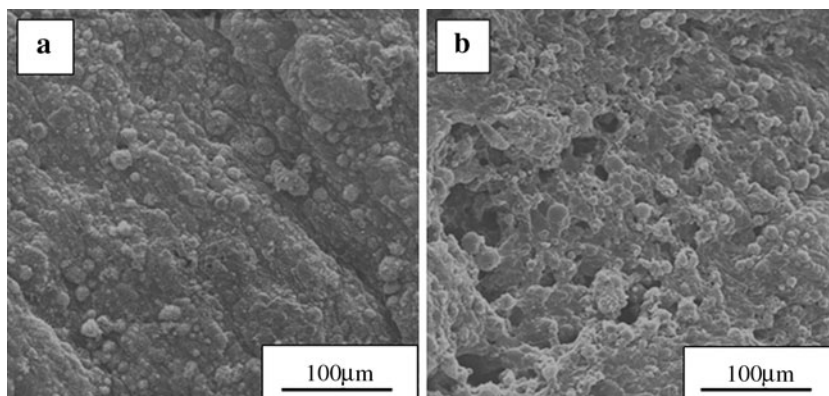**Fig. 6** The HRR curves of pure LDPE and flame retardant LDPE composite

Fig. 7 The THR curves of pure LDPE and flame retardant LDPE composite

composites may be due to the release of such small molecules due to decomposition of MCAPP, which can cause the char to expand and also can dilute the oxygen and flammable gas during the burning. It can be seen that the intensity of characteristic peak for hydrocarbons initially shows a peak value at 23.8 min and then turns into a rapid decrease, and this step is due to the decomposition of LDPE matrix. It can be found that the volatilized products for the thermal degradation of LDPE3 at maximum decomposition are saturated hydrocarbons, unsaturated alkane, CO_2, H_2O, and NH_3, etc.

Cone calorimeter test

Cone calorimetry test provides useful information on fire, and has good correlation with real fire disaster, so it is used to predict the behavior of materials in real fires [16]. Figure 6 shows the HRR curves of pure LDPE and flame retardant LDPE composite (LDPE3). When CFA and MCAPP are combined, the HRR peak of LDPE composite is remarkably decreased. The HRR peak of LDPE3 is 273.5 kW m^{-2}, with a 81.5% decrease compared with that of pure LDPE (1479.6 kW m^{-2}). The curves of the flame

Fig. 8 SEM photographs of outer surface of the chars after LOI test: **a** LDPE3, **b** LDPE6

retardant LDPE3 show two peaks. The first peak is due to the formation of an intumescent shield. With the presence of the efficient intumescent shield, the combustible gas escaping from the matrix and the amount of heat transferred to the polymer matrix decrease greatly, so the further degradation of LDPE is prevented. The second peak is due to the degradation of the shield which exposes the underlying LDPE to the flame and oxygen [17, 18].

Figure 7 presents the total heat release (THR) for pure LDPE and flame retardant LDPE composite (LDPE3). The slope of THR curve can be assumed as representative of fire spread. From Fig. 7, it can be seen that the THR is decreased by the flame retardants. It can be seen from Fig. 6 that the THR drops from 108.0 MJ m^{-2} in LDPE to 80.5 MJ m^{-2} in LDPE/CFA/MCAPP(1:3). As mentioned before, the compact char layer decreases the evolution of combustible gases during the combustion process, which leads to an increase of residue formation and a decrease of PHRR and THR.

SEM analysis of char residue after LOI test

The morphology of char residue after LOI test was investigated by SEM (Fig. 8). The investigation of the morphology of the char is helpful to explain the differences in the flame retardancy among the LDPE/CFA/MCAPP systems, because the different char residues contribute to the FR performance. When CFA and MCAPP are mixed at a 1:3 ratio, the coherent and dense char layer can be formed (Fig. 8a). The formation of the efficient char layer can prevent the heat transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning and retard the pyrolysis of polymers. When the CFA/MCAPP ratio is 2:1, the char layer is swollen and has some big holes (Fig. 8b), and this char layer can not provide a good protection for polymer matrix, so the flame retardant ability of LDPE/CFA/MCAPP (2:1) is not as good as LDPE/CFA/MCAPP (1:3).

Conclusions

CFA and silica-gel MCAPP are selected to form novel IFR system, and then the influence of this novel IFRs on the thermal and flame retardant properties of LDPE has been studied.

When the loading is 30 wt% IFRs (CFA/MCAPP = 1:3), the LOI value can reach 29.0, and can pass UL-94 V-0 rating. The water resistance test proves that the LDPE composites with CFA/MCAPP = 1:3 has the excellent water resistance and can still pass UL-94 V-0 rating after 168 h soaking in water.

The results of cone calorimetry show that the flame retardant properties of LDPE with 30 wt% novel IFR (CFA/MCAPP = 1:3) improve remarkably. The heat release rate peak, THR decreases, respectively, from 1479.6 to 273.5 kW m^{-2} and from 108.0 to 80.5 MJ m^{-2}.

SEM indicates flame retardant LDPE composite with suitable ratio of CFA and MCAPP can form excellent and compact char residue, which can better endure the oxidation of high temperature.

From the above results, we can summarize that the combining of CFA and MCAPP in LDPE matrix can prepare novel flame retardant LDPE composites with good flame retardant properties and with excellent water resistance ability.

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