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A Novel Intumescent Flame-Retardant System for Flame-Retarded LLDPE/EVA Composites

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ABSTRACT: A new intumescent flame retardant (IFR) system consisting of ammonium polyphosphate (APP) and charing-foaming agent (CFA) and a little organic montmorillonite (OMMT) was used in low-density polyethylene (LLDPE)/ethylene-vinyl acetate (EVA) composite. According to limiting oxygen index (LOI) value and UL-94 rating obtained from this work, the reasonable mass ratio of APP to CFA was 3 : 1, and OMMT could obviously enhance the flame retardancy of the composites. Cone calorimeter (CONE) and thermogravimetric analysis (TGA) were applied to evaluate the burning behavior and thermal stability of IFR-LLDPE/EVA (LLDPE/EVA) composites. The results of cone calorimeter showed that heat release rate peak (HRR-peak) and smoke production rate peak (SPR-peak) and time to ignition (TTI) of IFR-LLDPE/EVA composites decreased clearly compared with the pure blend. TGA data showed that IFR could enhance the thermal stability of the composites at high temperature and effectively increase the char residue. The morphological structures of the composites observed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) demonstrated that OMMT could well disperse in the composites without exfoliation, and obviously improve the compatibility of components of IFR in LLDPE/EVA blend. The morphological structures of char layer obtained from Cone indicated that OMMT make the char layer structure be more homogenous and more stable. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3626–3635, 2009

Key words: polyethylene (PE); ethylene-vinyl acetate (EVA); montmorillonite; intumescent flame retardant; flammability

INTRODUCTION

Linear low-density polyethylene (LLDPE) is a commodity plastic, which is widely used in wire and cable, building pipe, film aspects because of its mechanical durability, good chemical resistance, low density, low toxicity, good electric insulation, and good processability. Ethylene-vinyl acetate (EVA) is a copolymer that can be used as thermoplastics and elastomer depending on vinyl acetate (VA) content in the copolymer. Nowadays, the blend of LLDPE and EVA is widely used in wire and cable industry. However, the fire retardancy of the blend is required and investigated due to its easy burning.

There are mainly three categories of flame retardants for polyethylene and EVA, such as bromine-containing flame retardants, metal hydroxides and intumescent flame retardants (IFRs).[1] Bromine-containing flame retardants are the most effective and show a good ratio of property to price, however, their uses have been limited for the consideration of life safety and environmental problems due to a large amount of smoke and hydrogen bromide produced during burning.[2,3] Metal hydroxides are nontoxic and smoke-suppressing additives, however, the loading of more than 60 wt % metal hydroxides is required to meet the flame retardancy. Therefore, the main disadvantages of metal hydroxides are mechanical properties and processing ability of polymeric materials destroyed seriously by the high loading.[4,5] The IFRs, as effective flame retardants, have been studied and used more and more widely.[6] In general, IFRs are consisted of three components: acid source, carbonization agent, and blowing agent.[7,8] IFRs swell to form a char layer with cellular structures during heating by a series of chemical reactions and physical functions. And only the "three sources" reasonable match can promote the IFR systems to form a stable swell char layer.[9–13] The char layer acts as a physical barrier to block the transfer of radiant heat and oxygen and reduces the evolution of fuel. Therefore, it protects the underlying materials from the influence of heat and flame. To enhance the efficiency of IFRs, some synergistic agents have been used in IFR systems, such as

zeolites,[14] organoboron siloxane,[15] and some transitional metal oxides[16,17] and montmorillonite (MMT),[4,18,19] whose contribution involves the formation of a carbonaceous silicate char with a high performance.[20–22] MMT, as a kind of clay with high surface area, is commonly used in polymer composite. However, it can not be well dispersed in polymer due to its water affinity and polarity. Therefore, MMT needs to be modified by organic modifier, such as hexadecyl trimethyl ammonium bromide (CTAB), et al. And organic montmorillonite (OMMT) can be well dispersed in polymeric materials compared with MMT, and exfoliated to be nanolaminated structures clay in polymers.[23]

In this article, a novel effective IFR system consisted of ammonium polyphosphate (APP), charing-foaming agent (CFA),[10] and OMMT is applied in LLDPE/EVA blend, and the flame retardancy, mechanical properties, and morphological structure were investigated.

EXPERIMENTAL

Materials

LLDPE resin (LLDPE-7042) was supplied by Daqing Petroleum Company. EVA (VA-18%) supplied by Samsung Company. APP (GD-101, Crystalline form II, $n > 1500$) having a soluble fraction in water below 0.2 g/100 mL H_2O and average particle size of 15 μm was purchased from Zhejiang Longyou GD Chemical Industry Co, Ltd. CFA (a triazine polymer) was synthesized in our laboratory,[10] and its average particle size is 5–10 μm. Na-MMT having the average particle size of 30–50 μm and a cation exchange capacity of 100 meq/100 g is supplied by zhejiang San Ding group Co, Ltd. OMMT was synthesized with Na-MMT and CTAB in our laboratory. Its average particle size is 30–50 μm, and the content of CTAB in OMMT is 31.5 wt % based on its mass loss at 800°C in an oven.

Preparation of samples

IFR LLDPE/EVA composites (IFR-LLDPE/EVA) were prepared by blending of 54–58 wt % LLDPE, 15–16 wt % EVA, 20–30 wt % IFR, 0.4 wt % lubricant (EBS), 0.3 wt % antioxidant 1076, and 0.3 wt % polypropylene wax. New IFR consists of APP, CFA, and OMMT or MMT, which of the mass ratio of APP to CFA was changed from 0 : 1 to 5 : 1 at 8 wt % loading of OMMT in the IFR, and then the loading of OMMT was changed at 0 wt %, 5 wt %, 6 wt %, 7 wt %, and 9 wt %, respectively at the fixed the mass ratio of APP to CFA (3 : 1) in the IFR. All samples were prepared by using a high-speed mixer, and then extruded by a twin-screw extruder (D: 20 mm, L/D: 32, model: SLJ-20 Nanjing Jieya Chemical Engineering Equipment Company, China) at a temperature profile of 160, 170. 190, 190, 205, 185°C, and cut into pellets. The pellets were mixed by a two-roll mill (Harbin plastic Company, China) at a temperature range of 145–155°C for 5 min, then pressed to form sheets on a curing machine at 150°C for 2 min.

Flame retardancy tests

The flame retardancy of all samples was characterized by limiting oxygen index (LOI) and UL-94 methods. LOI data of all samples were obtained at room temperature on an oxygen index instrument (JF-3) produced by Jiangning Analysis Instrument Factory, China, according to GB/T2406-93 standard. The dimensions of all samples were 130 × 6.5 × 3 mm. LOI is an important parameter for evaluating the flame retardancy of polymeric materials in the same condition. It denotes the lowest volume concentration of oxygen sustaining candle burning of materials in the mixing gases of nitrogen and oxygen. Vertical burning ratings of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, China, with sample dimensions of 125 × 12.5 × 1.6 mm according to ISO1210-1992.

Cone calorimeter test

The cone calorimeter, manufactured by Fire Testing Technology (FTT), is a standard apparatus used for fire retardancy tests (ISO 5660-1). The polymer sample ($100 \times 100 \times 4$ mm^3) is placed horizontally on a balance and irradiated at 50 kW m^{-2}.

Thermogravimetry analysis test

All thermogravimetric analysis (TGA) tests were carried out by a PerkinElmer Pyris 1 Thermal Analyzer at a linear heating rate of 10°C min^{-1} under pure nitrogen within the temperature range from ambient to 800°C. The weight of the every sample was kept within 2~4 mg.

Mechanical properties test

Determination of tensile strength and elongation of all samples was performed by a RGD-20A material test machine (produced by Shenzhen Regear Instrument Cooperation (Shenzhen, China), according to GB/T16421-1996.

TABLE I
LOI and UL-94 Data of IFR-LLDPE/EVA Composites

Sample No.	IFR			LOI (%)	UL-94 test (1.6 mm)				
	Loading (wt %)	Mass ratio of APP to CFA	OMMT in IFR (wt %)		t_1 (s)	t_2 (s)	t_{1+2} (s)	Dripping	Rating
LLDPE/EVA	0	No IFR	No IFR	17.6	–	–	–	Yes	No rating
A	25	0 : 1	8	21.2	>50	–	–	Yes	No rating
B	25	1 : 1	8	30.8	2.7	12.1	14.8	No	V1
C	25	2 : 1	8	32.0	2.0	11.5	13.5	No	V1
D	25	3 : 1	8	34.5	1.4	6.4	7.8	No	V0
E	25	4 : 1	8	33.8	1.6	6.8	8.4	No	V0
F	25	5 : 1	8	33.6	2.5	>50	–	Yes	No rating
G	25	3 : 1	0	28.2	>50	–	–	Yes	No rating
H	25	3 : 1	5	32.8	1.5	12.8	14.3	Yes	No rating
I	25	3 : 1	6	33.2	1.5	8.2	9.7	No	V0
J	25	3 : 1	7	33.8	1.6	7.3	8.9	No	V0
K	25	3 : 1	9	33.5	1.4	6.6	8.0	No	V0
L	25	3 : 1	(MMT)8	31.3	2.9	>50	–	Yes	No rating
M	20	3 : 1	8	30.8	1.6	–	–	Yes	No rating
N	22	3 : 1	8	31.2	2.3	7.9	10.2	Yes	V1
O	28	3 : 1	8	36.3	1.2	5.6	6.8	No	V0
P	30	3 : 1	8	39.0	1.1	3.9	5.0	No	V0

Scanning electron microscopy test

Scanning electron microscopy (SEM) was used to examine the morphological structures of IFR-LLDPE/EVA composites and their char residue surfaces. The IFR-LLDPE/EVA composites were fractured under liquid nitrogen, and the char residue surfaces were obtained from cone calorimeter test. The accelerating voltage was set to 15 kV. The sample surfaces were sputter coated with gold layer.

X-ray diffraction test

X-ray diffraction (XRD) experiments were performed directly by using a Japan Rigaku D/max-rA. XRD meter (40 kV, 30 mA) with Cu (k = 1.54λ) irradiation at a rate of 20° min^{-1} in the range of 2–9°.

RESULTS AND DISCUSSION

Flame retardancy of the IFR-LLDPE/EVA composite by LOI and UL-94

A triazine polymer, CFA, has been proved to be a very effective component in IFR for polypropylene.[10,16] In this contribution, the new IFR contained CFA, APP and a synergistic agent was used in the blend of LLDPE and EVA, and OMMT and MMT was used as synergistic agents in IFR. The effects of the mass ratio of APP to CFA and the content of OMMT on LOI values and UL-94 ratings of the LLDPE/EVA composites are shown in Table I. It is seen that LOI values increased clearly at first, and

then reduced gradually with increasing the mass ratio of APP to CFA at the existence of 8 wt % OMMT (see Samples A to F in Table I). When the mass ratio of APP to CFA was 3 : 1 (Sample D), LOI of the composite reached the highest value (34.5%). UL-94 results show the same tendency like LOI results. The LLDPE/EVA composites passed UL-94 V-0 rating at the mass ratio of APP to CFA, 3 : 1 or 4 : 1. When no synergistic agents existed in IFR, LOI value of the IFR-LLDPE/EVA composite was only 28.2% and the composite could not pass UL-94 ratings, while a small quantity of the synergistic agent, such as OMMT and MMT, could effectively enhance LOI values of the IFR-LLDPE/EVA composite. However, the composite with OMMT could pass UL-94 V-0 rating, whereas the composite with MMT could not pass UL-94 ratings. That is, OMMT presents more effective synergism in the IFR-LLDPE/EVA composite than MMT. From Table I, the loading of OMMT is another factor influencing the flame retardancy of IFR in the composites. When the loading of OMMT was between 6 wt % and 9 wt %, the composites could pass UL-94 V-0 rating, their LOI values were more than 33%. Burning time of the composites was the shortest at the loading of 8 wt % in the IFR according to UL-94 test.

LOI and UL-94 experimental results demonstrate that when the mass ratio of APP to CFA was 3 : 1 and the loading of OMMT was 8 wt % in IFR, the intumescent flame retardant is very effective for the flame retardancy of LLDPE and EVA blend. The three components in IFR could form a stable

TABLE II
Flammability Performance of IFR-LLDPE/EVA
Composites at an Incident Heat Flux of 50 kW m^{-2}

Properties	Sample No.			
	LLDPE/EVA	G	L	D
TTI (s)	38	20	20	23
Peak 1-HRR (kW m^{-2})	1249.6	231.8	219.1	187.9
Peak 2-HRR (kW m^{-2})	–	–	191.6	236.8
THR (MJ m^{-2})	156.9	146.7	137.9	143.3
Peak 1-SPR (m^2 s^{-1})	0.091	0.029	0.022	0.02
Peak 2-SPR (m^2 s^{-1})	–	0.028	0.027	0.029
TSP (m^2)	15.1	18.3	13.3	18.1
Final residue (%)	1.5	14.7	15.4	19.2

intumescent char layer and show good interactions proved by following sections.

Combustion behavior of the IFR-LLDPE/EVA composites by cone calorimeter

The cone calorimeter is a performance-based bench scale fire testing apparatus and provides a wealth of information on on combustion behavior. Heat release rate (HRR), total heat release (THR), smoke production rate (SPR), and time to ignition (TTI) are important parameters for evaluating flame retardancy and flammability of polymeric materials.

Table II and Figures 1–5 give combustion data and plots of LLDPE/EVA blend and IFR-LLDPE/EVA composites with different synergistic agent, which
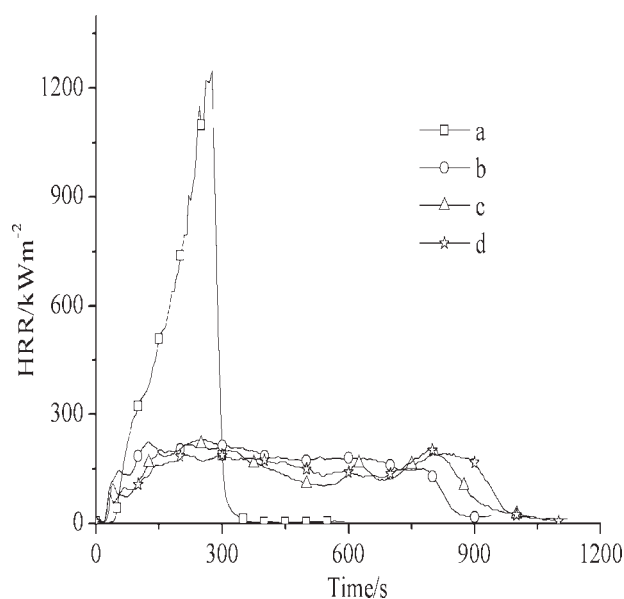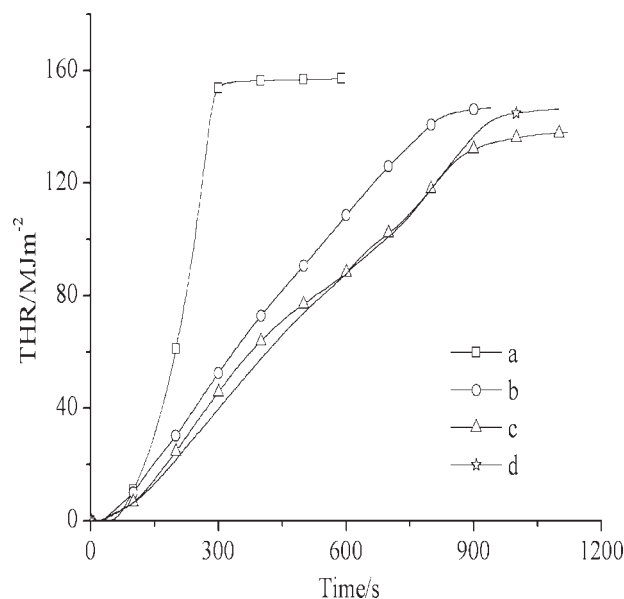

Figure 2 THR curves of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) none, (b) synergistic agent—0 wt %, (c) MMT—8 wt %, and (d) OMMT—8 wt %.

were obtained from the cone calorimeter test at an incident heat flux of 50 kW m^{-2}. From Figure 1, the blend of LLDPE and EVA burned very rapidly after ignition and a sharp HRR peak (1249.6 kW m^{-2}) appeared at 275 s. With the addition of new IFRs, the flammability of the composites was obviously restrained, HRR-peaks of IFR-LLDPE/EVA composites were dramatically reduced to about 219–237 kW m^{-2}.
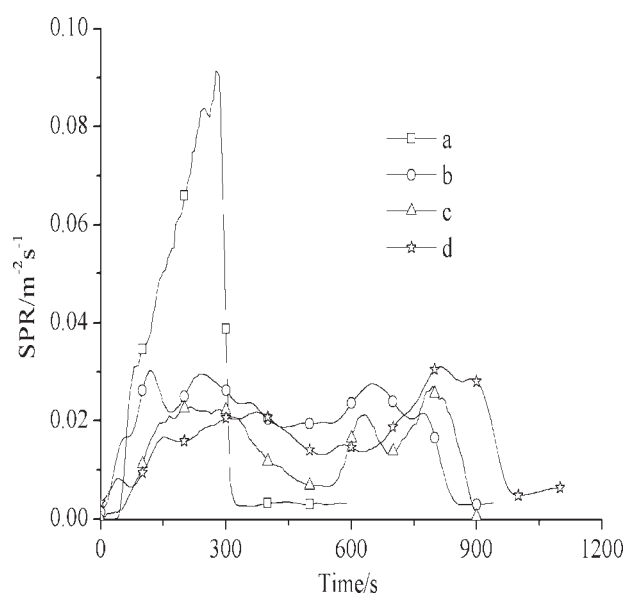

Figure 1 HRR curves of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) none, (b) synergistic agent—0 wt %, (c) MMT—8 wt %, and (d) OMMT—8 wt %.

Figure 3 Smoke production rate curves of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) none, (b) synergistic agent—0 wt %, (c) MMT—8 wt %, and (d) OMMT—8 wt %.
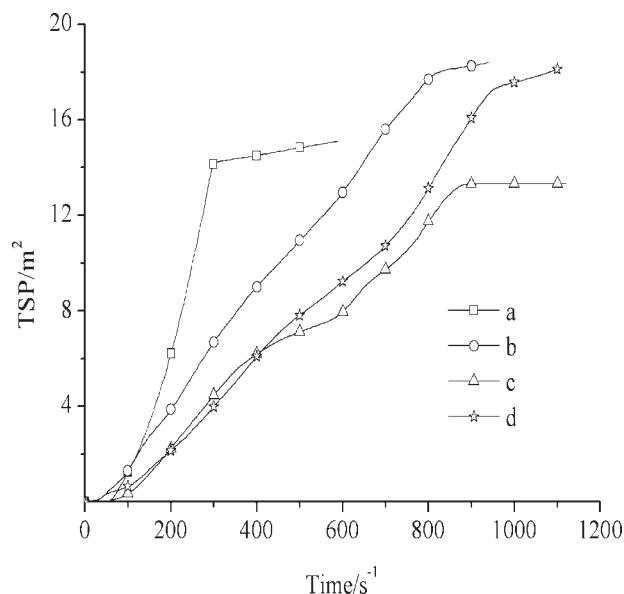
Figure 4 Smoke production curves of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) none, (b) synergistic agent—0 wt %, (c) MMT—8 wt %, and (d) OMMT—8 wt %.

OMMT is beneficial to the decrease of the first HRR peaks of all IFR-LLDPE/EVA composites.

The IFR-LLDPE/EVA composite with OMMT gave the lowest HRR peak value (187.9 kW m^{-2}). It is also found that IFR obviously reduced the ignition time of IFR-LLDPE/EVA composites (Table II). This is attributed to the rapid formation of char layer on the surface of composites that prevented heat from transferring into the polymeric material interior, resulting in the increase of surface temperature, therefore accelerating the decomposition of the polymeric material. The curves of the total heat release (THR) were influenced by IFR, as shown in Figure 2. For all composites, the value of THR was not changed so much, but their total heat release time was obviously delayed compared with that of the pure blend.

The emission of smoke is considered as another important parameter for the flame-retarded materials. The curves of smoke production rate (SPR) and smoke production (SP) via time are seen in Figures 3 and 4. LLDPE/EVA blend and IFR-LLDPE/EVA composites all presented low smoke emission during burning, and their smoke production (SP) all did not exceed 19 m^2. Based on Figure 4 and Table II, IFRs without synergistic agent and with OMMT made the total smoke production of the composites increase, whereas IFR with MMT retarded the total smoke production. However, all IFR systems could effectively reduce the smoke production rate (SPR) of the composites and delayed smoke the whole emission process. MMT is more beneficial to the smoke suppression of the composites than OMMT. This is

probably attributed to the amount of organic modifier cation (hexadecyl trimethyl ammonium ion) contained in OMMT, hexadecyl trimethyl ammonium ion may produce some of smoke during burning and retard the absorption of MMT to smoke at some extent.

Figure 5 shows the curves of mass loss rate (MLR) vs. combustion time for LLDPE/EVA blend and IFR-LLDPE/EVA composites. It is seen that IFRs could effectively prohibit the decomposition of the composites, and form an amount of char on the surface. The mass loss behavior of the composites is in agreement with the heat release behavior and the smoke emission behavior of them.

Effect of MMT and OMMT on the thermal degradation IFR and the composites

Table III and Figure 6 show TGA data and curves of the different IFR systems and their components. The IFR system without synergistic agent is consisted of 25 wt % CFA and 75 wt % APP. From Figure 6 Curve c and Table III, its thermal degradation behavior showed three steps (the first peak at 314.8°C, the second peak at 439.5°C, and the last peak at 585.7°C), and the IFR system presented high char residue at 700°C compared with pure APP (seen in Figure 6 Curve a) and CFA (seen in Figure 6 Curve b). Like the reaction mechanisms of pentaerythritol and APP discussed in literature,[24,25] the first step is probably attributed to the water-elimination reactions of polyhydroxyl triazine macromolecule promoted by APP due to a lot of hydroxyl
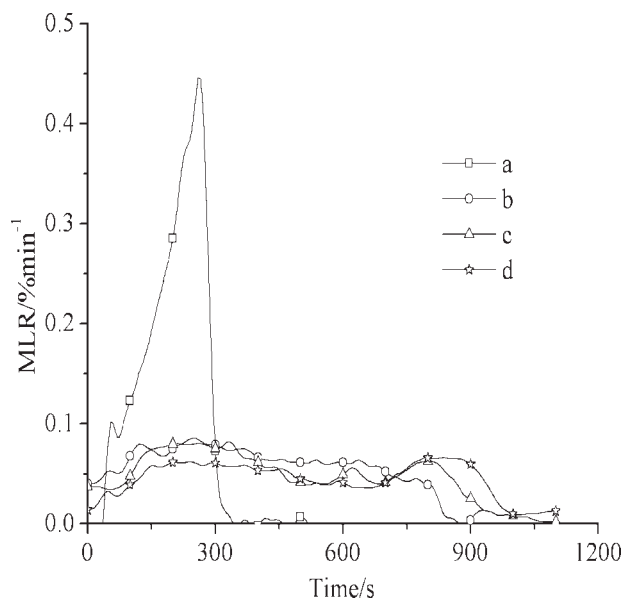

Figure 5 MLR curves of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) none, (b) synergistic agent—0 wt %, (c) MMT—8 wt %, and (d) OMMT—8 wt %.

TABLE III
Thermal Degradation and Char Residue Data Under Pure Nitrogen by TGA

Sample No.	$T_{initial}$ (°C)	R_1peak/T_1peak (% min^{-1}/°C)	R_2peak/T_2peak (% min^{-1}/°C)	R_3peak/T_3peak (% min^{-1}/°C)	Char residue (%) 500°C	Char residue (%) 700°C
APP	289	1.74/324.0	11.14/622.3	–	81.5	13.5
CFA	281	3.99/325.3	5.41/449.0	–	51.9	37.9
MMT	279	1.94/335.1	2.01/410.1	–	67.4	48.4
OMMT	198	2.01/309.1	2.69/432.7	1.95/557.1	60.5	32.9
IFR-synergistic agent—0 wt %	258	2.13/314.8	2.83/439.5	4.25/585.7	65.5	31.6
IFR-MMT—8 wt %	248	2.38/292.6	2.76/432.3	–	62.0	53.4
IFR-OMMT—8 wt %	250	1.52/289.7	2.78/428.9	–	57.2	50.3
LLDPE/EVA	310	0.93/374.0	24.66/471.0	–	2.7	1.6
A	275	0.61/365.3	21.33/488.0	–	17.4	9.7
B	277	0.97/355.5	24.97/487.1	–	17.9	12.6
C	276	0.89/371.9	22.68/488.3	–	19.7	12.8
D	275	0.93/374.3	24.27/487.8	–	20.8	15.3
E	274	1.02/365.1	24.79/487.2	–	20.0	13.5
F	276	1.02/373.2	20.46/483.9	–	17.0	13.5
G	275	1.01/380.0	18.00/478.4	–	16.1	12.9
L	272	0.25/317.7	20.36/490.0	–	23.4	16.5

groups in CFA macromolecule. The second step is considered to be the decomposition and crosslinking reactions of triazine chains. The last step is attributed to the decomposition of P—O bonds in APP, which is similar to the decomposition of APP, can be seen in Figure 6 Curves a. The addition of OMMT and MMT as synergistic agents in IFR can obviously change the thermal degradation behavior of IFR, that is, OMMT and MMT lower the initial temperature ($T_{initial}$) of thermal degradation of IFR, promote IFR to form more char residue. This

experimental fact indicates that OMMT and MMT catalyze water-elimination, crosslinking, and decomposition reactions between CFA and APP. Because of 31.5 wt % CTAB in OMMT, IFR containing 8 wt % OMMT shows lower temperature of thermal degradation and lower char residue than IFR containing 8 wt % MMT.

The posterior part of Table III and Figure 7 give the thermal degradation data and curves for LLDPE/EVA and different IFR-LLDPE/EVA composites. The pure LLDPE/EVA showed two
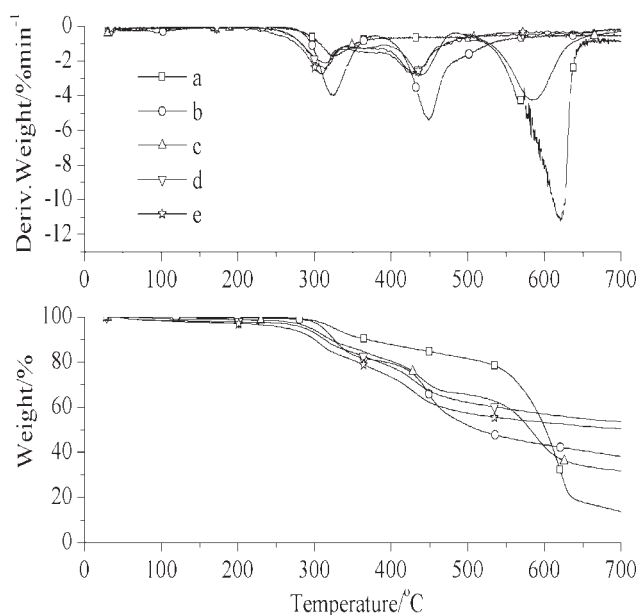

Figure 6 TGA and DTG curves of IFR systems with different synergistic agent (a) APP, (b) CFA, (c) synergistic agent—0 wt %, (d) MMT—8 wt %, and (e) OMMT—8 wt %.
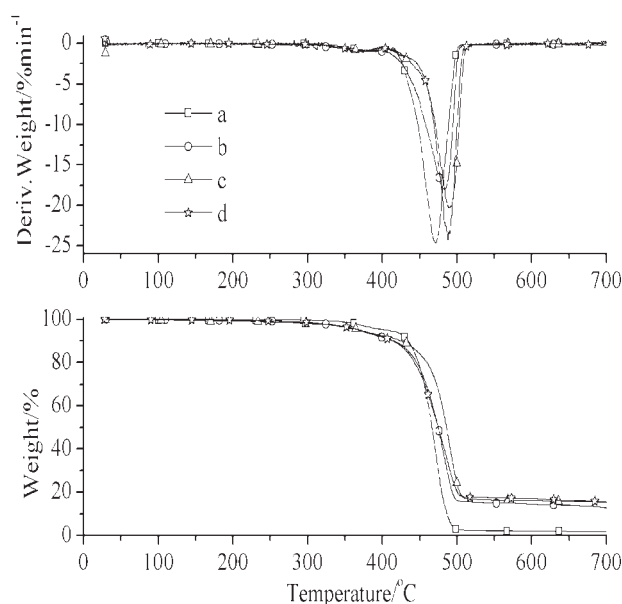

Figure 7 TGA and DTG curves of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) none, (b) synergistic agent—0 wt %, (c) MMT—8 wt %, and (d) OMMT—8 wt %.

TABLE IV
Mechanical Properties of the Composites

Sample No.	Tensile strength (MPa)	Elongation (%)
LLDPE/EVA	11.5	986
A	9.2	367
B	7.3	618
C	7.5	624
D	7.7	628
E	7.8	638
F	8.0	635
G	7.7	606
H	7.6	638
I	7.7	628
J	7.5	623
K	7.5	616
L	6.8	590
M	8.1	754
N	7.8	694
O	7.7	628
P	7.6	620

decompositions at 374°C and 471°C respectively, and nearly no char residue remained over 500°C. It is clearly seen that the different IFR-LLDPE/EVA

composites presented similar thermal degradation. However, their char residues at high temperature increased gradually at first and then reduced with the mass ratio of APP to CFA increased. For example, the char residue of Sample A (0/1) was only 17.4 wt % at 500°C and 9.7 wt % at 700°C, and the char residue of Sample D (3/1) reached 20.8 wt % at 500°C and 15.3 wt % at 700°C. But the char residue of Sample F (5/1) decreased to 17.0 wt % at 500°C and 13.5 wt % at 700°C. IFR-LLDPE/EVA composite with OMMT and MMT clearly increase the content of the char residue.

Effect of IFRs on mechanical properties

The tensile strength and elongation of LLDPE/EVA and IFR-LLDPE/EVA composites are showed in Table IV. The tensile strength and elongation of LLDPE/EVA bend were 11.5 MPa and 986%, respectively. However, the tensile strength and elongation of IFR-LLDPE/EVA composites all declined compared with pure blend. When the IFR was only composed of CFA and OMMT, the tensile strength of
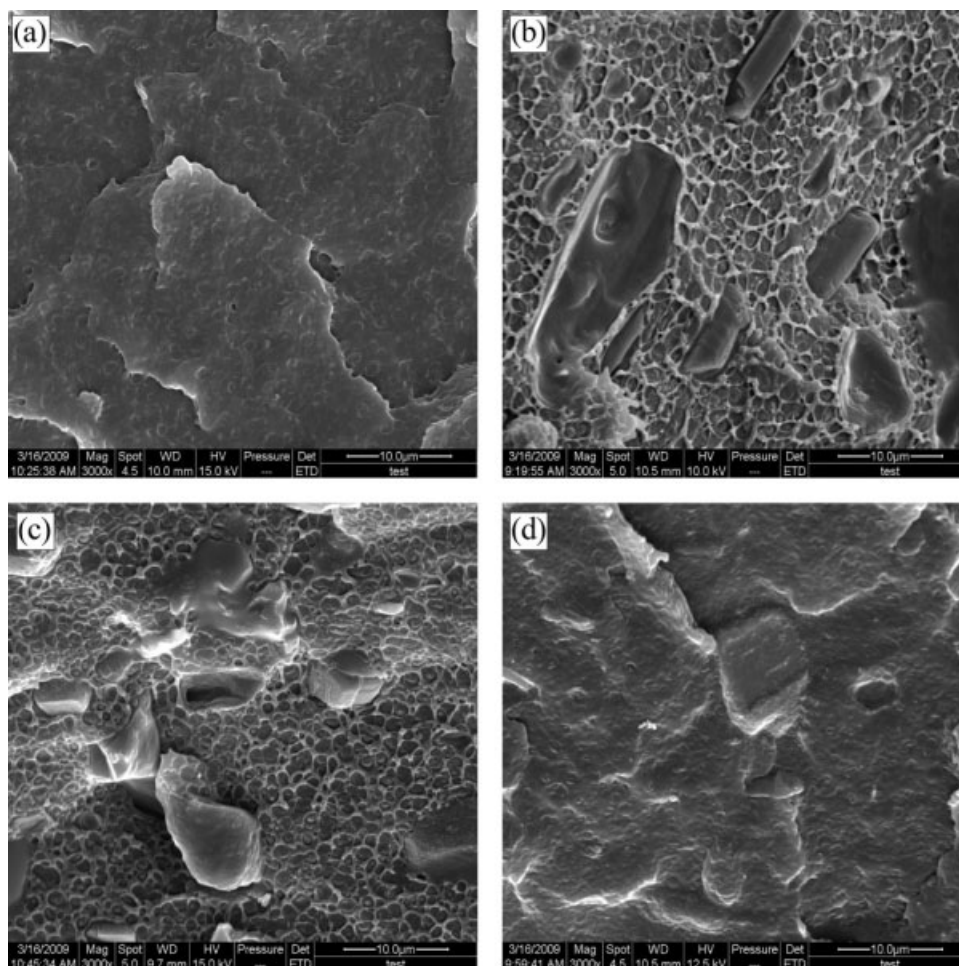

Figure 8 SEM of fracture surface of IFR-LLDPE/EVA composites (a) LLDPE/EVA ×3000, (b) IFR-LLDPE/EVA ×3000, (c) IFR- LLDPE/EVA MMT—8 wt % ×3000, (d) IFR-LLDPE/EVA OMMT—8 wt % ×3000.
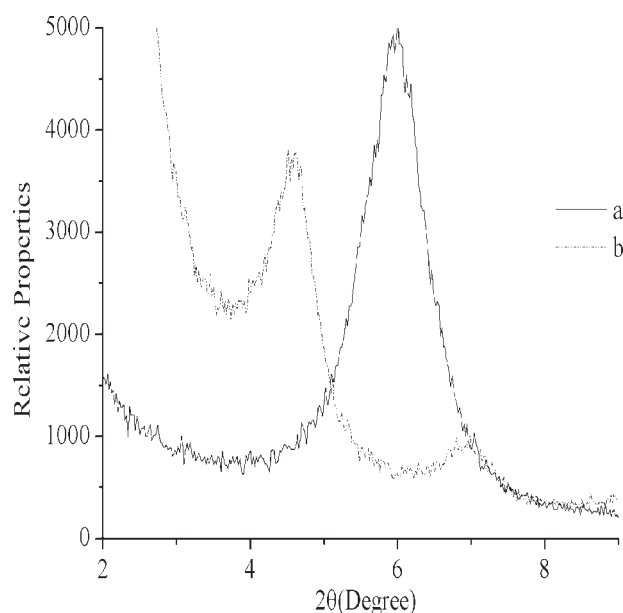
Figure 9 XRD patterns of MMT and OMMT (a) MMT and (b) OMMT.

Figure 10 XRD patterns of LLDPE/EVA with different synergistic agent (a) MMT—2 wt %, (b) OMMT—2 wt %.

IFR-LLDPE/EVA composite was higher than the other composites, whereas the elongation of IFR-LLDPE/EVA composite was the lowest (Table IV Sample A). Mechanical properties of IFR-LLDPE/EVA composites showed a little change with the mass ratio of APP to CFA increased. Compared with IFR-LLDPE/EVA composite with MMT, the tensile strengths and elongation of IFR-LLDPE/EVA composites with OMMT were higher. This is attributed to good dispersion of OMMT in the composites, which was proved by morphological structure characterization (see next section). However, the effect of OMMT content on mechanical properties of IFR-LLDPE/EVA composites was little, mechanical properties slightly decreased with the increase of OMMT (see Table IV Samples D, H–K). The tensile strength and elongation of the composites reduced gradually with increasing the content of IFR (Table IV Samples M–P).

Morphological structures of the composites and char layer

Figure 8 gives SEM micrographs of LLDPE/EVA blend and different IFR-LLDPE/EVA composites. It is seen that EVA and LLDPE showed good compatibility based on Figure 8(a). The fracture surface of IFR-LLDPE/EVA composites without any synergistic agent and with MMT was very rough and the interface between polymers and components of IFR was clear according to Figure 8(b,c). This is because CFA, APP, and MMT are polar materials, whereas LLDPE and EVA are nonpolar polymers. However, the frac-
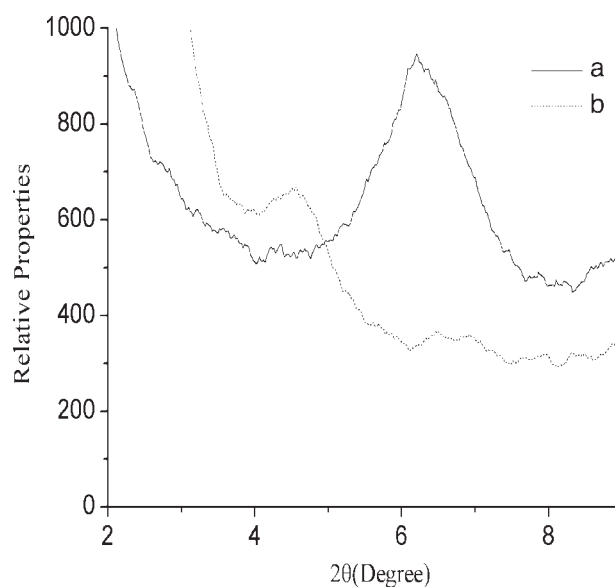
ture surface of IFR-LLDPE/EVA composite with OMMT was smooth, and the interface was not clear. OMMT obviously improved interfacial compatibility among components in the composite, which is attributed to the contribution of CTAB on the compatibility. This result is further proved by the experimental results of mechanical properties. Based on XRD patterns of MMT, OMMT, LLDPE/EVA-MMT (2 wt %) composite, LLDPE/EVA-OMMT (2 wt %) composite, IFR-LLDPE/EVA-MMT (2 wt %) composite, and IFR-LLDPE/EVA-OMMT (2 wt %) composite showed in Figures 9–11, the interlayer spacing of MMT increased from 1.47 to 1.91 nm, this fact
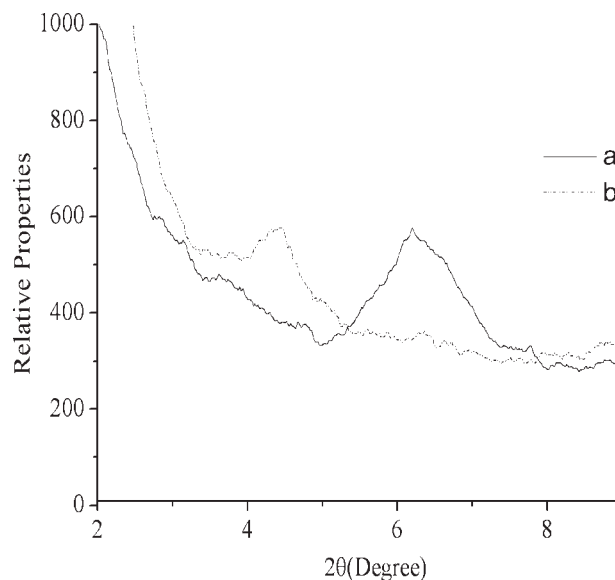

Figure 11 XRD patterns of IFR-LLDPE/EVA composites (a) MMT—8 wt %; (b) OMMT—8 wt %.
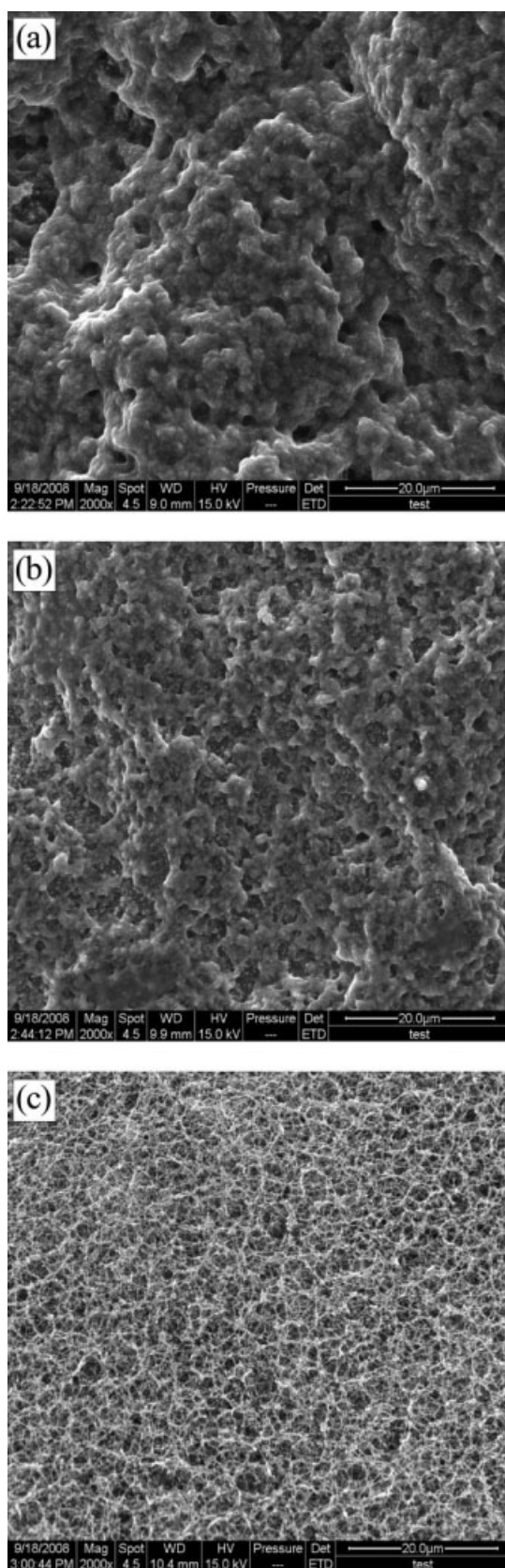
Figure 12 SEM of char residue of LLDPE/EVA blend and IFR-LLDPE/EVA composites (a) IFR-LLDPE/EVA ×2000, (b) IFR-LLDPE/EVA-MMT—8 wt % ×2000, (c) IFR-LLDPE/EVA-OMMT—8 wt % ×2000.

illustrates that hexadecyl trimethyl ammonium bromide (CTAB) was intercalated into interlayer of MMT, and effectively modified surface property of MMT. According to and Figures 8(c) and 11, OMMT is only dispersed into LLDPE/EVA blend, it is not exfoliated to form nano layers of MMT, due to the existence of diffractive peaks.[26]

Figure 12 gives SEM micrographs of the char residue of the composites. To elucidate the relationship between the microstructure of protective char layer and the flame retardancy, three different kinds of char residues were collected from the cone calorimetry experiments. There were many crevasses and holes on the surface of char residue without synergistic agent, Figure 12(a), therefore, heat and flammable volatiles could easily penetrate the char layer into the flame zone during the process of burning. On the contrary, the char residue surface morphology containing MMT was improved based on Figure 12(b), and the microstructure of the char layer seemed to be thicker and solider than the former. However, the microstructure of char residue containing OMMT [Fig. 12(c)] was distinctly different from above two samples, which char layer microstructure was fine and intertwined each other, like a carpet. It has been proved that synergistic agents in IFR, such as zeolites, organoboron siloxane, and MMT, may effectively catalyze dehydration and crosslinking reactions between polyhydroxyl compounds and APP to form stable char layer containing $Si\!-\!O\!-\!P\!-\!O\!-\!C$ and $Al\!-\!O\!-\!P\!-\!O\!-\!C$ bonds.[27–29] Because of the good dispersion of OMMT itself, the compatibility of components of IFR in the blend is obviously improved and is beneficial to the chemical actions among components of IFR in the blend. Therefore, a small amount of OMMT can produce more homogenous char layer and improve its structure. This is an important reason that the novel IFR system containing OMMT presents the efficient flame retardancy in the LLDPE/EVA composites based on cone calorimeter, LOI, and UL-94 results.

CONCLUSIONS

A novel high performance IFR-LLDPE/EVA-OMMT formulation was suggested in this contribution, satisfying with UL-94 V0 rating (1.6 mm) and 34.5% LOI value when the addition of IFR was 25 wt % in the composite and IFR contained 8 wt % OMMT. Based on experimental results of the flame retardancy and the flammability obtained from Cone, UL-94 and LOI tests, new IFR system composed of CFA, APP, and OMMT shows remarkable flame retardancy on LLDPE/EVA blend. OMMT could enhance the tensile strength and elongation of IFR-LLDPE/EVA composites compared with MMT. These factors are because that the addition of OMMT could obviously

improve the compatibility among components in IFR-LLDPE/EVA-OMMT composites, make the char layer structure be more homogenous and more stable.

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