Expandable Graphite Systems for Halogen-Free Flame-Retarding of Polyolefins. I. Flammability Characterization and Synergistic Effect

RONGCAI XIE, BAOJUN QU

State Key Laboratory of Fire Science and Department of Polymer Science and Engineering, University of Science and Technology of China, 230026 Hefei, Anhui, People's Republic of China

ABSTRACT: The use of some types of expandable graphite (EG) as an intumescent flame-retardant additive in polyolefins was studied using the cone calorimeter test (CCT), thermogravimetric analysis (TGA), the limiting oxygen index (LOI), and the-UL 94 test and through measurement of EG's mechanical and electrical properties. The present study has shown that some suitable EG systems combined with other organic and inorganic halogen-free flame-retardant (HFFR) additives apparently can improve the flame-retardant capacity with good mechanical properties of polyolefin blends. For linear low-density polyethylene and/or ethylene vinyl acetate/EG/HFFR blends the limiting oxygen index can reach a rating above 29, and the UL-94 test can produce a value of V–0. The CCT and TGA data show that the EG and EG/HFFR additives not only promoted the formation of carbonaceous char but also greatly decreased the heat release rate and the effective heat of combustion and increased the residues after burning. The synergistic effect of EG with other HFFR additives, such as zinc borate, the phosphorus–nitrogen compound NP28, and microcapsulated red phosphorus is examined and discussed in detail in this article. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1181–1189, 2001

Key words: expandable graphite; halogen-free flame-retardant; polyolefins; synergistic effect; cone calorimeter test; TGA

INTRODUCTION

Polyolefins (PO) are used extensively in many fields, especially in electrical engineering and electronics as an excellent insulating material with good physical and mechanical properties. However, they are particularly flammable and emit smoke while burning. These defects restrict their application in these fields. Therefore, flame-retardant additives have been developed in order to obtain PO materials with good flame-retardant ability and low emission of smoke and poisonous gases. Most flame-retarded PO materials usually are made by the joint use of a halogen-type fire retardant and antimony trioxide. In recent years there has been much concern worldwide over their use because they give rise to toxic gases and smoke that can choke people exposed to the toxic and acidic fumes and can damage costly equipment.[1] The stringent conditions set by statutory governmental regulations for the use of fire retardant (FR) demand development of halogen-free fire-retardant (HFFR) materials.

Several HFFR intumescent systems for flame-retarded polyolefins have been developed.[2,3] Intumescent FR additive formulations usually consist of a char-forming agent, a carbonization catalyst, and a blowing agent. In case of a fire they provide protection by forming surface-expanded carbonaceous structures between the flames and the polyolefins. These charred layers protect the underlying materials from the action of heat flux in flames. Unfortunately, intumescent fire-retardant additives, such as nitrogen- and phosphorus-containing FRs, which are mostly nontoxic, have been covered to a lesser degree because of such reasons as cost and effectiveness. Recently, some patents have disclosed the use of expandable graphite (EG) as an intumescent flame-retardant additive for manufacturing PO foams.[4–7] However, there has little reported in the literature on the flame-retardant behavior of EG and its interaction with other HFFRs in polyolefin systems. That is to say, EG as an intumescent flame-retardant additive has not been studied in detail.

This article is devoted mainly to reporting on a study—using the cone calorimeter test (CCT), thermogravimetric analysis (TGA), the limiting oxygen index (LOI), and the UL-94 test along with measurement of mechanical and electrical properties—of the function of EG as an intumescent flame-retardant and its synergism with other flame-retardant additives in PO blends. The main interest in the present work was to develop new halogen-free flame-retardant PO materials that can be used in the manufacture of electric engineering materials and electronics, such as wires and cables.

EXPERIMENTAL

Materials

Two kinds of polyolefins were used in the present work: linear low-density polyethylene (LLDPE DFDC-7050), from Zhongyuan Oil Company, and ethylene vinyl acetate copolymer (EVA, 19% containing vinyl acetate), from Yanshan Company. Expandable graphite with a high expansion coefficient of 180 (HEG) and a low expansion coefficient of 40 (LEG) was supplied by Baoding Lianxing Carbide Company, Ltd. The particle size of HEG was 0.2 mm and the pH value 8.5, while the particle size of LEG was 100 mesh and the pH value 7.2. The following HFFR additives were used in this work: ammonium polyphosphate (APP) from Anhui Institute of Chemical Engineering, zinc borate ($2ZnO3B_2O_33.5H_2O$; ZB) from Gaizhou Inorganic Chemicals Company, and the phosphorus–nitrogen compound NP28, containing 15.6% P and 27.5% N with a particle size of 400 mesh, from Weizheng Fine Chemicals Company. A microcapsulated red phosphorus (RP) was made in our laboratory. All the above chemicals except RP are commercial products made in China and used as received.

Sample Preparation

All samples, composed of 100-g batches of PO with the desired amounts of EG and HFFR additives, were mixed with a rubber mill for 15 min at 115–130°C as. After mixing, under 10 MPa for 3 min at 130–150°C the samples were hot-pressed into sheets of suitable thickness. Each sample was then rapidly cooled to room temperature in air. Sheet size and thickness were dependent on the testing methods used in the present study.

Analysis of Sample

Limiting Oxygen Index

The limiting oxygen index (LOI) was measured using a ZRY-type instrument (made in China) on sheets $120 \times 60 \times 3$ mm^3 according to the standard oxygen index test ASTM D2863-77.

UL-94 Test

The vertical test was measured on sheets $127 \times 12.7 \times 3$ mm^3 according to the standard UL-94 test ASTM D635-77.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out in air at a heating rate of 10°C/min using a STA409C thermogravimetric analyzer. In each case a 20-mg sample was examined at an air flow rate of 6×10^{-5} m^3/min at temperatures ranging from room temperature (25°C) to 800°C.

Cone Calorimeter Test

To do the cone calorimeter test (CCT), a cone calorimeter (Stanton Redcroft Type, made in England) was used to measure the flammability characterization under a heat flux of 35 kW/m^2 according to ASTME-1356-90. The parameters of

Table I   Compositions of LLDPE Samples Used for Cone Calorimeter Test

Compositions (phr)	Sample Symbol						
	a	b	c	d	e	f	g
LLDPE	100	70	70	70	70	70	70
LEG	—	10	10	10	10	10	10
RP	—	5	5	5	—	—	—
APP	—	15	—	—	20	—	—
ZB	—	—	15	—	—	20	—
NP28	—	—	—	15	—	—	20

Table II   Effect of EG Additive on the LOI Values of LLDPE/EG Blends

Amount of Additives (%)	LOI Values	
	HEG	LEG
0	17.5	17.5
10	23.6	22.9
15	26.0	24.8
20	27.4	26.5
30	29.6	28.1

these flammability characterization are time to ignition (TTI, s), heat release rate (HRR, kW/m^2), effective heat of combustion (EHC, MJ/kg), toxic gas production (CO, kg/kg), residues (%), and specific extinction area (SEA, m^2/kg) of smoke produced per unit weight of burning sample. Table I shows the seven kinds of LLDPE samples used for cone calorimeter tests in the present work. The instrument has an experimental error rate of about 5% for the CCT data.

Mechanical Measurement

The tensile strength and elongation at break were measured with a DCS 5000 universal test machine using an elongation rate of 25 mm/min.

Bulk Resistivity Measurement

The bulk resistivity measurement (BRM) was taken with a high-resistance meter according to ASTM D257-78.

For all these measurements usually two or three samples were analyzed to determine the average values of the LOI, UL-94, CCT, mechanical, BRM, and other measurements in order to obtain reproducible results.

RESULTS AND DISCUSSION

Effects of EG and EG/FR on LOI Values of LLDPE Blends

The effects of EG additive on the LOI values of the LLDPE blends have been examined in detail, as shown in Table II. It can be seen that LOI values increase with an increasing amount of EG additives. LOI values of the LLDPE blends containing 30% HEG increased rapidly to 29.6 from

17.5 of pure LLDPE. HEG is more efficient than LEG in increasing LOI values possibly because HEG produces more high-volume expanded graphite and results in occupying more space at high temperature than does LEG. This can prevent combustible gases from feeding the flame, and it also separates oxygen from the burning material more efficiently.

Figure 1 presents the effects of four kinds of LEG/HFFR systems on the LOI values of the LLDPE blends. It is obvious that NP28 is more efficient than APP and ZB. The LOI value of LLDPE/EG blend containing 20%/NP28 increased to 29.5 from the original value 22.9. A small amount of RP increases the LOI values very efficiently, but the loading of more than 10% RP leads the LOI values to drop down sharply, as shown in Figure 1. This is because RP is essentially a flam-
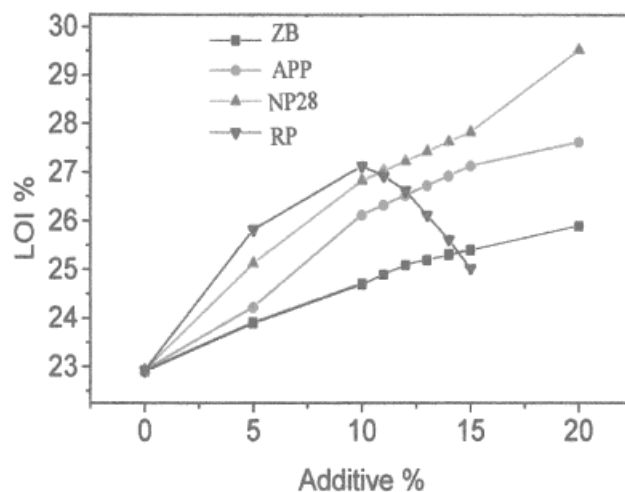

Figure 1   Changes of the LOI values with different level of additives in the LLDPE/10% EG blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table III   Cone Calorimeter Data of Various LLDPE Samples

Sample Symbol	TTI (S)	Peak HRR (kW/m²)	Average EHC (MJ/kg)	Average CO (kg/kg)	Average SEA (m²/kg)	Residues (%)
a	106	938	51.0	0.018	661	1
b	129	217	35.0	0.149	850	28
c	124	180	34.6	0.112	698	36
d	118	179	32.4	0.140	741	34
e	107	272	36.2	0.030	578	24
f	100	195	37.0	0.017	375	37
g	109	208	35.0	0.025	420	30

The compositions are listed in Table I.

mable material, and so at a higher amount RP becomes flammable. When a small amount of RP is filled in hydrocarbon polymers, it can be oxidized to phosphoric acids and phosphorus monoxide (PO) on fire. The former can form a protective coating on the burning substrate, limiting fuel volatilization and oxygen penetration to the condensed phase,[8] while the latter can trap the radicals in the gas phase during burning.[9]

Flammability Characterization of LLDPE/EG/FR Blends

The data of dynamic flammability characterization measured by the cone calorimeter for the LLDPE/LEG/FR samples are listed in Table III. The data show that, compared with the pure LLDPE sample (a), the peak HRR, average EHC, and MLR values at a heat flux of 35 kW/m² decrease dramatically with the addition of EG and other FR additives. Table III shows that pure LLDPE loses its 99% mass because of its complete combustion, while the retarded LLDPE blends (b)–(g) burn incompletely and leave a large amount of residuals (about 70%). For example, sample (f) in Table III has the largest residues (37%) because the residual LEG and ZB contents exist in the condensed phase. The time to ignition (TTI) of the retarded samples at the same heat flux increases in different degrees, except for sample (f), with the addition of EG and other FR additives. These results indicate that compared with the original polymer, the retarded polymer materials had become fireproof. All these dynamic flammability behaviors of LLDPE/LEG/FR blends could be a result of the following: When the retarded polymer materials are burning, a foamed char from the EG composition is formed on the

surface of the retarded material and becomes a thermal-insulation material, preventing combustible gases from feeding the flame and separating oxygen from the burning material. Only when the material absorbs more heat will the carbonaceous char break and the burning continue. The decom-
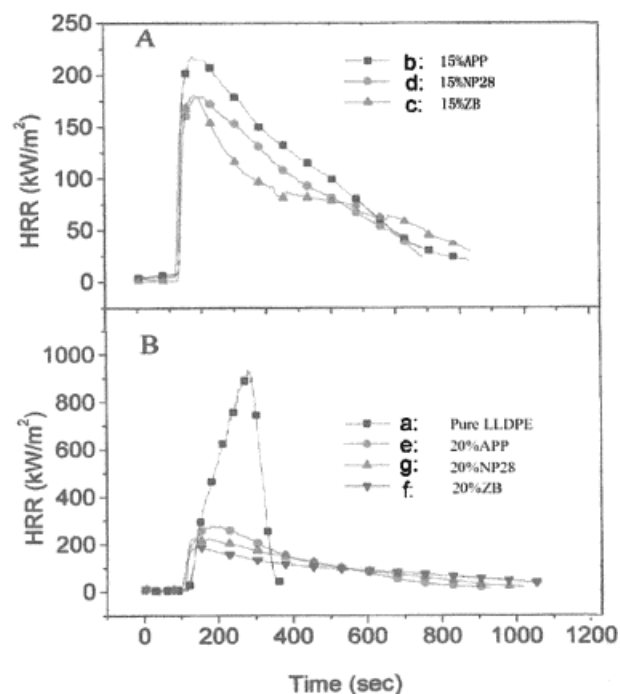

Figure 2 Dynamic curves of the HRR data versus time for the LLDPE and LLDPE/10% LEG sample systems with other FR additives, listed in Table I, at a heat flux of 35 kW/m²: (A) Comparison of the HRR data in the presence of 5% RP; (B) Comparison of the HRR data in the absence of 5% RP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
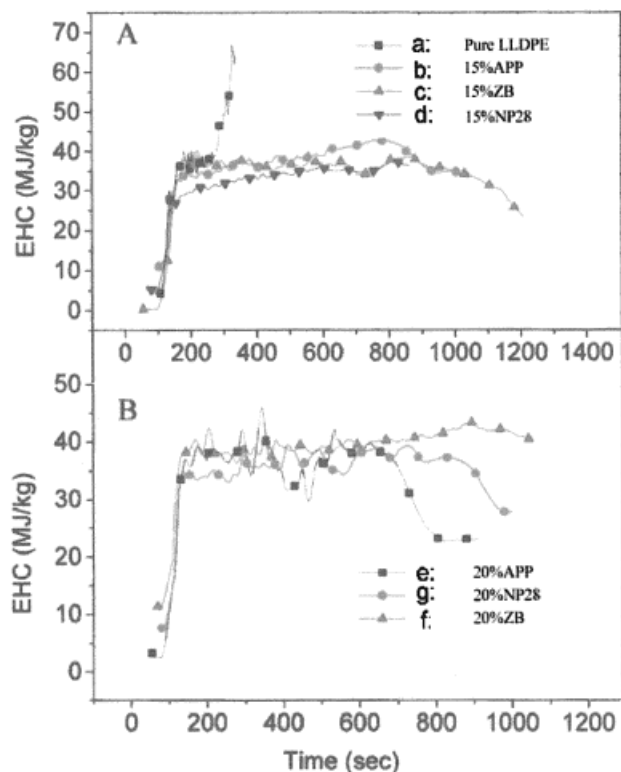
Figure 3 Dynamic curves of the EHC data versus time for the LLDPE and LLDPE/10% LEG sample systems with other FR additives, listed in Table I, at a heat flux of 35 kW/m^2: (A) Comparison of the EHC data in the presence of 5% RP, (B) Comparison of the EHC data in the absence of 5% RP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

position and burning of the material could be retarded in this way. This step-by-step burning process and subsequent flammability improvement can be observed from the following HRR, EHC, CO, and SEA curves, as shown in Figures 2–5.

The dynamic curves of HRR versus time for various samples at a heat flux of 35 kW/m^2 are shown in Figure 2, with Figure 2(a) representing the changes of HRR values of the LLDPE/EG/FR samples with the RP additive and Figure 2(b) representing the same changes without the RP additive. It can be seen from Figure 2 that the burning time of pure LLDPE is 350 s or less while the burning time of all the retarded LLDPE blends is longer than 800 s. The peak HRR values of the retarded samples [(b)–(d) in Fig. 2(a)] decrease to about 200 kW/m^2 from 938 kW/m^2 of the pure LLDPE sample [(a) in Fig. 2(b)]. Moreover,

the HRR curves become relatively smooth and gradual compared with those of the pure LLDPE sample. This is because some elements in the retarded LLDPE blends cannot burn and so some of the blends are transformed to carbonaceous materials, which hardly give off heat. Meanwhile, the retarded LLDPE blends burn slowly.

Compared with samples (b)–(g) in Figure 2, samples (c) and (f), containing ZB, show minimum values of the peak HRR, which could be because of the following two reasons: First, the LLDPE/LEG/ZB blend can release water at the range of 280–400°C, which absorbs a large amount of heat in the burning process. Second, the LLDPE/LEG/ZB blend burns slowly and releases heat smoothly. However, the combustion time of the LLDPE/LEG/ZB blend is longer than that of the LLDPE/LEG/APP and LLDPE/LEG/NP28 blends. It can been seen that the HRR values of sample systems (b)–(d) in the presence of 5% RP are
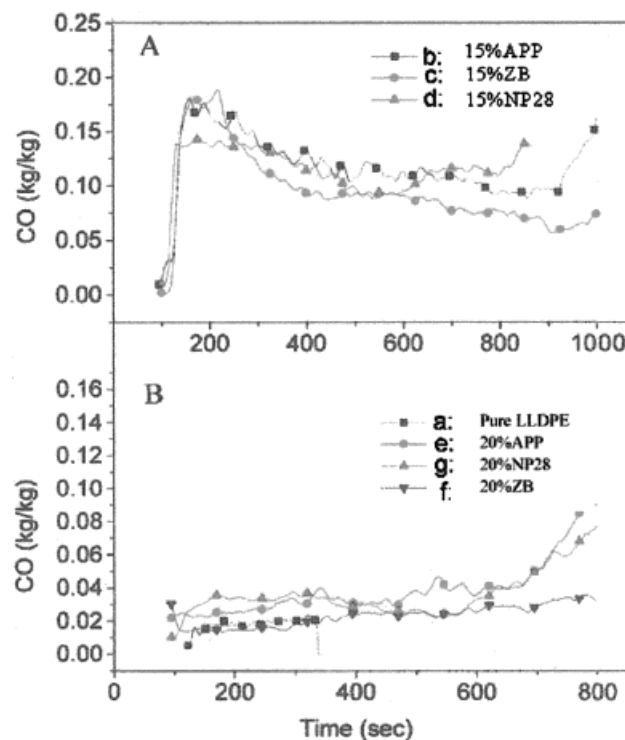

Figure 4 Dynamic curves of the CO amount versus time for the LLDPE and LLDPE/10% LEG sample systems with other FR additives, listed in Table I, at a heat flux of 35 kW/m^2: (A) Comparison of the CO amount in the presence of 5% RP; (B) Comparison of the CO amount in the absence of 5% RP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
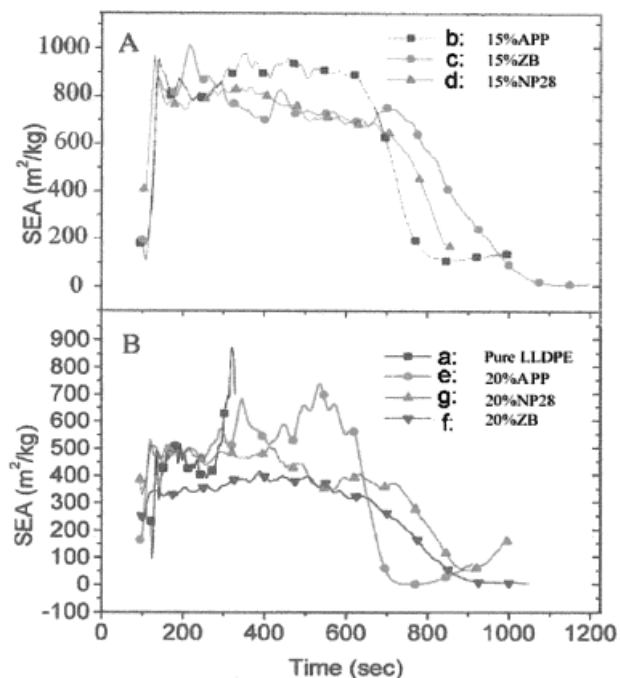
Figure 5 Dynamic curves of the SEA data versus time for the LLDPE and LLDPE/10% LEG sample systems with other FR additives, listed in Table I, at a heat flux of 35 kW/m^2: (A) Comparison of the SEA data in the presence of 5% RP; (B) Comparison of the SEA data in the absence of 5% RP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

smaller than those of samples (e)–(g) without the RP additive, especially for sample (d), which contains 15% NP28 and 5% RP, as shown in Figure 2(a).

The dynamic curves of EHC versus time for various samples at a heat flux of 35 kW/m^2 are shown in Figure 3. It can be seen from Figure 3(a) that the EHC value of pure LLDPE, sample (a), reaches a peak value of 66 MJ/kg at about 320 s. This is because the carbon atoms in pure LLDPE react with oxygen in air to convert into carbon dioxide and the hydrogen atoms react with oxygen to produce water, release a large amount of heat during the burning of the pure LLDPE sample. The average EHC values of LLDPE/LEG/FR samples (b)–(g) apparently decrease as compared with that of sample (a), as shown in Figure 3(a,b). There are several explanations for the EHC decrease of the retarded polymer materials. First, some elements or compounds such as P, N, and H$_2$O in the retarded LLDPE blends cannot release heat when they decompose into the gaseous

phase. Second, it is difficult for the carbon atoms in the retarded LLDPE to be transformed completely into carbon dioxide; instead, some carbon atoms stay in the carbon monoxide. And finally, some hydrogen atoms or free radicals of hydrogen are trapped by the polymer itself and by other traps[10] and thus cannot react immediately with oxygen in order to release heat.

Apparently, samples (d) and (g), which have the NP28 additive, have the lowest average EHC values whether or not the samples contain the RP additive, as shown in Table III. The average EHC values provide additional evidence that, among the FR systems in the present study, NP28 is a more efficient flame-retardant synergistic additive with EG.

The CO curves of various samples versus time at a heat flux of 35 kW/m^2 are shown in Figure 4. The data show that samples (c) and (f) [Figure 4(a,b)], which have the ZB additive, release relatively low values of CO. This means that ZB is an efficient smoke suppressant. It was also found that the amount of carbon monoxide of the LLDPE-FR sample systems (b)–(d) with RP [Fig. 4(a)] is much higher than that of sample systems (e)–(g) without RP [Fig. 4(b)].

The SEA curves of various samples versus time at a heat flux of 35 kW/m^2 are shown in Figure 5. The results show that the SEA values of samples (b)–(d) with RP [Fig. 5(a)] are much higher than those of samples (e)–(g) without RP [Fig. 5(b)]. This may be because of the action of RP in the gaseous phase, which interrupts the transformation of C$_2$ free radicals into C$_1$ free radicals, so that C$_2$ free radicals may condense into polycyclic aromatic hydrocarbons. This material has a strong extinction of light and thus apparently increases the SEA values. Similarly, red phosphorus can trap very active OH · and other free radicals so that carbon monoxide cannot easily change into carbon dioxide and remarkably causes the increasing amount of carbon monoxide.

According to the above studies, the synergistic effects of EG with different HFFR additives in the LLDPE/EG/FR blends can be described as follows: NP28 > ZB > APP.

Thermogravimetric Behavior of LLDPE/LEG/FR Blends

Figure 6 shows the thermogravimetric (TG) behavior of pure LLDPE and LLDPE/LEG/FR
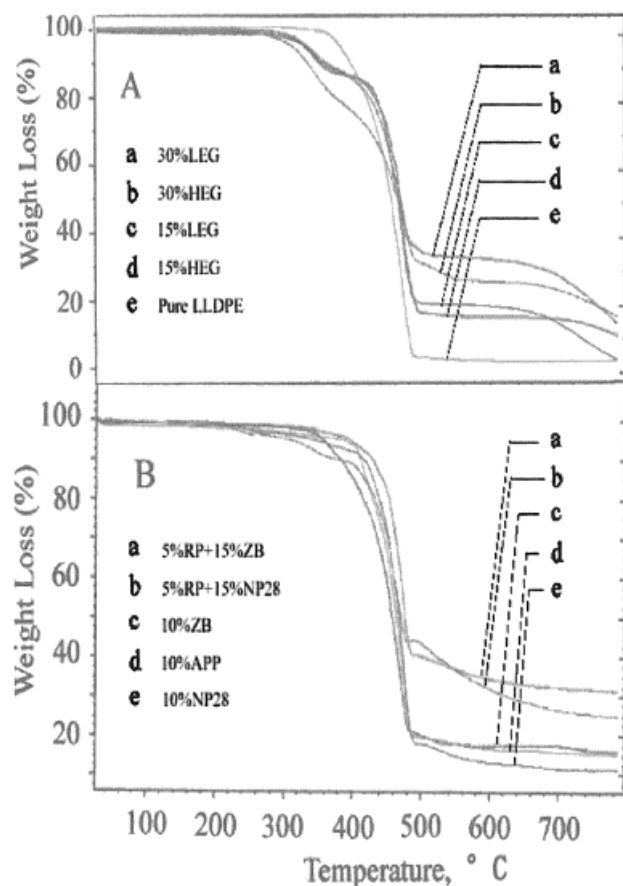
Figure 6 TG curves of different LLDPE blends: (A) LLDPE resin with different levels of EG additives; (B) LLDPE/10% LEG blends with the other FR additives. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

blends under a flow of air. Figure 6(a,b) presents the TG curves from the LLDPE/LEG and LLDPE/ LEG/FR blends, respectively. TG curve (e) in Figure 6(a) shows one step of total weight loss of pure LLDPE, in which the thermo-oxidative degradation of pure LLDPE takes place in the range of 320–480°C.

All the LLDPE/LEG blends under a flow of air have similar TG behavior, with a first step of about a 10% weight loss from the volatilization of some EG volatile and a small amount of thermo-oxidative degradation of LLDPE blends between 280–340°C. Second, there is about a 60–70% weight loss between 340–480°C. Finally, there is about a 5% weight loss between 500–700°C because of further decomposition of residual carbonaceous materials. Figure 6(a) also shows the effect of EG on thermal stability of LLDPE blends, which apparently increases with increasing concentrations of EG. These results are in good agreement with those of the LOI values in Table II. However, it can be seen from Figure 6(a) that the char yields of different EG formulas are quite different. The effective order of their char formation is as follows: $C_{LEG\ 30\%} > C_{HEG\ 30\%} > C_{LEG\ 15\%} > C_{HEG\ 15\%}$. As expected, the thermal stability of the LLDPE/EG blends is superior that of pure LLDPE. For example, the LLDPE blend [curve (d) in Fig. 6(a)] containing 15% HEG has a weight loss of about 73% at 480°C, while the pure LLDPE [curve (e) in Figure 6(a)] loses about 99% weight. Normally, EG itself will lose about 20% by weight after expanding at high temperature because of

Table IV   Mechanical and Electrical Properties of Polyolefin Blends

Additives (%)	LLDPE Blends			EVA Blends	
	T[a]	E[b]	V[c]	T[a]	E[b]
0% EG	20.2	1565	9.2×10^{15}	17.6	1331
5% EG	12.6	780	4.3×10^{15}	13.6	990
10% EG	11.2	64	1.0×10^{15}	12.5	980
15% EG	10.2	13	2.7×10^{14}	12.3	983
20% EG	9.4	10	8.9×10^{12}	10.5	950
30% EG	7.6	9	5.0×10^{12}	5.9	480
10% EG + 20% APP	6.5	14	3.0×10^{13}	—	—
10% EG + 20% ZB	9.3	18	3.2×10^{14}	—	—
10% EG + 20% NP28	10.4	26	6.5×10^{14}	—	—
10% EG + 4% RP + 15% NP28	—	—	1.8×10^{13}	13.7	842
10% EG + 3% RP + 20% ZB	—	—	2.2×10^{13}	12.9	790

[a] T: tensile strength, MPa; [b] E: elongation (%); [c] V: volume resistivity (Ω-cm).

Table V   Formulas of PO/LEG/HFFR Blends that Passed the UL-94 V–0 Ratings

Formulations (phr)	Sample Symbol							
	1	2	3	4	5	6	7	8
EVA	72	70	—	—	—	—	—	—
LLDPE	—	—	70	70	71	67	65	69
LEG	10	10	10	10	10	10	10	10
RP	5	0	5	5	5	0	0	0
APP	0	0	0	15	0	23	0	0
ZB	0	0	15	0	0	0	25	0
NP28	13	20	0	0	14	0	0	21

the volatilization of low-molecular-weight components. However, the char residues of these sample systems with EG additive after thermal degradation are larger than the EG content of corresponding samples. For example, the LLDPE/15% LEG blend has 18% residues. Those data provide positive evidence that EG can promote the formation of carbonaceous materials in the condensed phase.

Figure 6(b) shows the TG curves of the LLDPE/10% LEG sample systems with different FR additives. It was found by comparison that the thermal stability of LLDPE/LEG/NP28 is higher than that of LLDPE/LEG/ZB blends. As expected, thermal stabilization of the LLDPE blends can be improved by the addition of 5% red phosphorus and 15% ZB or NP28 [curves (a) and (b) in Fig. 6(b)]. About 30% residual char yields are obtained from the samples [curve (a) and (b)], which are much higher than the approximately 20% char yields of samples with an individual FR additive of 10% ZB [(curve (c)], 10% APP [curve (d)], or 10% NP28 [curve (e)].

Mechanical and Electrical Properties and UL-94 Ratings of PO/EG/HFFR Blends

Table IV lists the mechanical and electrical properties of different LLDPE and EVA/LEG/HFFR formulation systems. The data show that the addition of LEG significantly reduces the tensile and elongation properties of LLDPE blends. The tensile strength of an LLDPE/LEG blend decreases almost 50%, while the elongation becomes very small, even if only 10% LEG is added into LLDPE, which may be because of the large particle size of EG and its poor compatibility with LLDPE. It can also be found in

Table IV that the tensile strength values of the LLDPE/LEG/HFFR blends are not improved by the addition of ZB, APP, and NP28 of a small particle size. The mechanical properties of EVA/LEG/HFFR blends are much better than those of the LLDPE/EG/FR systems. The results show that the addition of 15% LEG does not affect the mechanical properties adversely, especially for the elongation property.

The effects of EG and the other HFFR additives on the bulk resistivity of PO blends are also listed in Table IV. Apparently, bulk resistivity decreases quickly with an increasing amount of EG and HFFR additives. However, by optimizing the formulation system, the PO/EG/HFFR blends with good mechanical and electrical properties can pass the UL-94 test of V–0 rating and be satisfactory for practical use of flame-retardant wire and cable.

The several PO formulas that were 10% LEG-based combined with about 20% HFFR additives, which can pass the UL-94 V-0 ratings, are shown in Table V.

CONCLUSIONS

1. Expandable graphite, a novel type of intumescent flame-retardant additive for polyolefin materials, acts as both a carbonization compound and a blowing agent. EG or EG combined with other HFFR additives not only increases the LOI values but also promotes the formation of carbonaceous char and improves the thermal stability of the retarded PO materials remarkably.

2. The data on flammability characterization

from the cone calorimeter tests show that the EG combined with the other HFFR additives decreases significantly the HRR and EHC values of LLDPE/EG/FR blends. The flame-retardant mechanism might be mainly a result of the formation of intumescent charred layers in the condensed phase, which slow down heat and mass transfer between the gas and the condensed phases and limit the diffusion of oxygen to the polymer bulk.

3. The synergistic effect of EG with the other HFFR additive plays an important role in the polyolefin systems. The studies of the present work show that phosphorus-containing compounds, such as NP28 and/or a suitable amount of microcapsulated RP, are the most efficient synergistic agents of the EG-based flame-retardant systems.

4. By optimizing the formulation system, PO/LEG/HFFR blends with good mechanical and electric properties can pass the V−0 rating of the UL-94 test and be satisfactory for the practical use of flame-retardant wire and cable.

REFERENCES

1. Sen, A. K.; Mukheriee, B.; Bhattacharya, A. S.; Sanghi, L.K.; De, P. P; Bhowmick, K. J Appl Polym Sci 1991, 43, 1674.
2. Montaudo, G.; Scamporino, E.; Vitalini, D. J Polym Sci, Polym Chem 1983, 21, 3361.
3. Bertelli, G.; Camino, G.; Marchetti, E.; Costa, L; Casorati, E.; Locatelli, R. Polym Degrad Stab 1985, 25, 277.
4. Kenji, I.; Masakij, T.; Bunji, Y. Jpn. Pat. 09,208,731 (1997).
5. Kazuyoshi, I.; Masakij, T.; Kenji, I. Jpn. Pat. 08,295,753 (1996).
6. Kazuyoshi, I. Jpn. Pat. 09 77,894 (1997).
7. Masaru, T. Jpn. Pat. 09,316,257 (1997).
8. Brauman, S. K. J Fire Retard Chem 1977, 4, 38.
9. Edward, E. N. Peters. J Appl Polym Sci 1978, 24, 1165.
10. Aseeva, R. M.; Zaikov, G. E. Combustion of Polymer Materials; Fabrikant, T., translator; Academic Press: Hamser, 1985.