Effect of Ultrafine Zinc Borate on the Smoke Suppression and Toxicity Reduction of a Low-Density Polyethylene/Intumescent Flame-Retardant System

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ABSTRACT: The production of smoke, carbon monoxide (CO), and carbon dioxide (CO_2) were investigated with cone calorimetry testing when low-density polyethylene (LDPE), LDPE treated with an intumescent flame retardant (IFR), and LDPE treated with an IFR and ultrafine zinc borate (UZB) combusted under irradiation. The results of the testing showed that UZB could depress smoke production and reduce the amount of CO and CO_2. The components of the pyrolytic gas and its contents were identified and measured with pyrolysis–gas chromatography/mass spectrometry (Py–GC–MS) when LDPE, LDPE/IFR, and LDPE/IFR/UZB were pyrolyzed at 400°C for 20 s. The Py–GC–MS results implied that UZB had an important influence on the components and contents of the pyrolytic gas of LDPE/IFR. UZB mechanisms of smoke suppression and toxicity reduction with respect to LDPE/IFR are proposed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 443–449, 2010

Key words: composites; degradation; fillers; polyethylene (PE); pyrolysis

INTRODUCTION

Compared with fire and heat, smoke and toxic gas can do great harm to people's lives during a disastrous fire.[1–3] Toxic gas can choke people, and smoke can decrease visibility; this makes it more difficult for people to escape from the fire and hinders firemen trying to rescue them. Carbon monoxide (CO) and carbon dioxide (CO_2) are frequently found in the gas when a polymer combusts. Generally, CO_2 is regarded as a nontoxic substance, but people will lose consciousness and life when the concentration of CO_2 reaches 7–10%. The combined force of CO and hemoglobin is 260 times that of oxygen and hemoglobin, so CO is regarded as the main toxic substance leading to death in disastrous fires. People will lose consciousness and die within 3 min if the concentration of CO is greater than 1.28%.[4] According to statistics for disastrous fires, 70–80% of the dead are choked by smoke and toxic gas.[5,6]

Halogen-containing flame retardants once were the most used organic flame retardants because of their high flame-retarding efficiency and cost performance. However, dense smoke and hydrogen halide (corrosive and toxic gas) are produced during the combustion or pyrogenation of materials treated with halogen-contained flame retardants, and this cause fatal injuries to people in disastrous fires. Therefore, the research and application of halogen-free flame retardants and high-efficiency smoke suppressants have become a hot issue.[7–11] Intumescent flame retardants (IFRs) and inorganic flame retardants are effective halogen-free flame retardants. Zinc borate is an effective inorganic flame retardant and possesses the characteristics of flame retardancy, smoke suppression, drip extinction, char promotion, and so forth.[12–15] Although the smoke-suppressant activity of zinc borate and its char-promoting ability have been discussed quite intensively in the past 2 decades, the mechanisms of smoke suppression and toxicity reduction activity still need to be further investigated. Particle size reduction is necessary for improving the compatibility, which is related to the mechanical properties of composites. The effects of ultrafine zinc borate (UZB) and IFRs on the mechanical and flame-retarding properties of low-density polyethylene (LDPE) have been described elsewhere.[16,17] It is essential to investigate the effects of UZB on the smoke and toxicity of LDPE/IFR systems because of the great harm of smoke and toxicity during combustion.

Many studies have demonstrated that a combination of cone calorimetry and pyrolysis–gas

chromatography/mass spectrometry (Py–GC–MS) is an excellent method for studying the smoke and toxicity of gases involved in the combustion of polymers.[18–21]

The Py–GC–MS technique combines the high separation capability of gas chromatography (GC) and the highly sensitive identification capability of mass spectrometry (MS). The components of pyrolytic gas can be separated and identified qualitatively and quantitatively.[22,23] Rich information on the chemical structure and composition of the gases evolving during the fast pyrolysis of a polymer treated with various flame retardants can be obtained.

This work is devoted mainly to studying the influence of UZB on the smoke suppression and toxicity reduction of an LDPE/IFR system and is based on the smoke production rate, total smoke release (TSR), and concentration and total amount of CO and CO_2 when LDPE, LDPE/IFR, and LDPE/IFR/UZB are burning under radiation. The effect of UZB on the composition of the gases evolving during fast pyrolysis has been investigated by isothermal pyrolysis coupled with GC–MS. The UZB mechanisms of smoke suppression and toxicity reduction for the LDPE/IFR system are proposed.

EXPERIMENTAL

Materials

LDPE (1F7B) was supplied by Beijing Yanshan Petrochemical Co. (Beijing, China). Ammonium polyphosphate (APP; average particle distribution = 10–55 μm, degree of polymerization >1500) was supplied by Zhejiang Longyou GD Chemical Co. (Longyou, China) Pentaerythritol (PER) was obtained from Shanghai Chemical Agent Station (Shanghai, China). The IFR (an APP/PER blend with an APP/PER mass ratio of 3 : 2) and UZB ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) were prepared in our laboratories (average diameter = 73 nm, 90% of particle diameters < 100 nm).[24]

Sample preparation

On the basis of the limiting oxygen index (LOI) test, the UL-94 rating and mechanical properties of different additive concentrations of UZB in the LDPE/IFR system were determined.[16,17] The compositions of typical samples are listed in Table I; the IFR or the IFR and UZB combination were mixed with LDPE in a two-roll mixer (SK-160B, Shanghai Rubber Mechanical Factory, Shanghai, China) at 120–130°C for 20 min. The mixed samples were pressed into 3-mm sheets in a vulcanizing press machine (DLB 500 × 500, Wuxi Jinhe General Equipment Factory, Wuxi, China) at 130–140°C, and samples of various sizes were obtained according to the testing standard.

TABLE I
Composition of the Samples[a] and the Results of LOI and UL-94 Testing

Sample	LDPE	UZB	IFR	LOI	UL-94 rating
LDPE	100	0	0	17.8	Burning
LDPE/IFR	100	0	30	24.5	V-1
LDPE/IFR/UZB	100	4.2	25.8	26.2	V-0

[a] The mass ratios of the compositions.

Measurements

The LOI test was performed according to ISO 4589 in an oxygen index tester (JF-3, Nanjin Jiangning Analytical Apparatus Factory, Nanjin, China); the sample was 130 mm × 6.5 mm × 3.0 mm. The UL-94 test was performed according to ANSI/UL-94-1985 in a vertical burning tester (CZF-2, Nanjin Jiangning Analytical Apparatus Factory, Nanjin, China); the sample was 130 mm × 13 mm × 3.0 mm.

Cone calorimetry testing was performed with a Stanton Redcroft cone calorimeter (Fire Testing Technology Ltd., UK) according to the procedure defined in ASTM E 1354. The samples were put in a horizontal orientation at an incident flux of 35 kW/m². The sample size was 100 mm × 100 mm × 3 mm, and the samples exposed to the incident irradiance were 88.4 cm². The results were the average values of three tests, and the variation of each test was less than 15%.

Py–GC–MS was performed with an R200 pyrolyzer (Shanghai Kechuang Chromatograph Instrument Co., Ltd., Shanghai, China) and by gas chromatography/mass spectrometry (GC–MS; QP2010, Shimadzu, Japan). Samples of approximately 1 mg were pyrolyzed at 400°C for 20 s; the pyrolyzed gas was sent into the GC injector. The injector temperature was 250°C, and the injector was in a split mode (split ratio = 1 : 50). The flow rate of helium was 0.5 mL/min. The analysis of the pyrolyzed gas was performed with a DB-5MS (Agilent Technologies, USA) column (30 m × 250 μm × 0.25 μm); the oven temperature was programmed from 40 to 250°C at 10°C/min with an initial isothermal period of 5 min and a terminal isothermal period of 4 min. The MS ion source was 70 eV, and the scan range (m/z) was 10–600. The components of the pyrolytic gas were identified by the comparison of the observed mass spectra with those in the NIST147 mass spectra library.

RESULTS AND DISCUSSION

LOI values and UL-94 testing

The data presented in Table I indicate that the flame retardancy of LDPE increased substantially when the IFR (30%) was introduced into LDPE. The LOI value of LDPE/IFR was 24.5. Although the LOI value of LDPE/IFR/UZB (26.2) increased only a little in comparison with that of LDPE/IFR, the UL-94
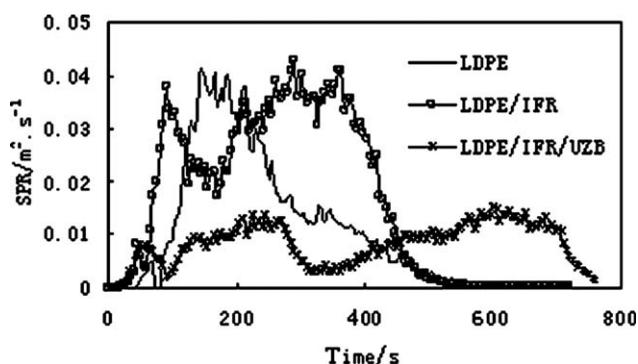
Figure 1 SPR curves of the untreated and treated LDPE.

test of LDPE/IFR/UZB demonstrated a V-0 rating versus the V-1 rating of LDPE/IFR.

Smoke production rate (SPR) and TSR

Smoke suppression is essential for the selection of an ideal flame retardant.[25] The SPR and TSR values of LDPE treated with different flame retardants are illustrated in Figures 1 and 2. The peak SPR value of LDPE/IFR (0.0427 m^2/s) was nearly equal to that of neat LDPE (0.0415 m^2/s); however, the TSR value of the former (1340.95) at combustion termination was greater than that of the latter (879.56), and this indicates that the total amount of smoke increased when the IFR was introduced into LDPE. The peak SPR value and the TSR value of LDPE/IFR/UZB were 0.0151 m^2/s and 719.6, respectively. The time to the peak SPR value of LDPE/IFR/UZB (605 s) was longer than that for LDPE/IFR (290 s) or LDPE (145 s). The results imply that UZB produces obvious smoke suppression in the LDPE/IFR system by decreasing the peak SPR value, TSR, and delay time to the peak SPR value. Smoke suppression by UZB can be explained as follows: zinc borate can promote charring and enhance the quality of char, which can protect the inner matrix and reduce the amount of combustible gas and smoke-forming materials in the gas phase during combustion. Moreover, UZB can absorb smoke particles because of its small particle size and large specific area. Therefore, UZB
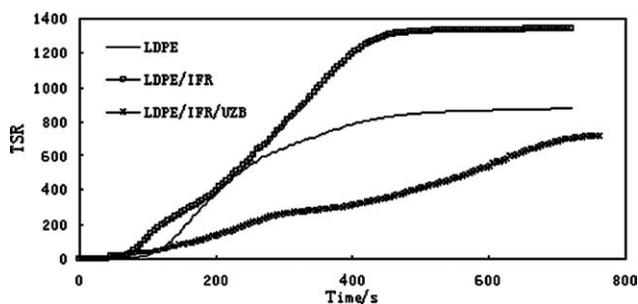
Figure 2 TSR curves of the untreated and treated LDPE.
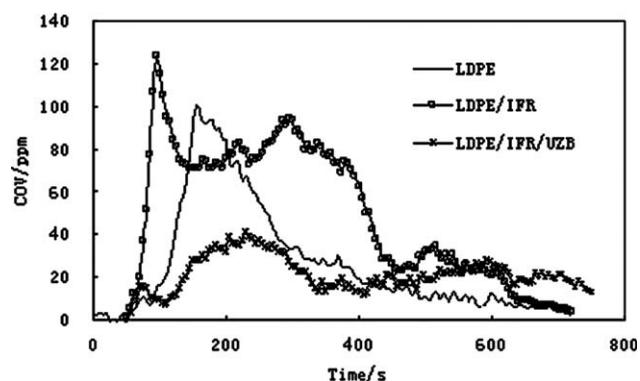
Figure 3 COV curves of the untreated and treated LDPE.

produces strong smoke suppression in addition to the synergistic flame retardancy of LDPE/IFR.[17]

CO

The carbon monoxide concentration (COV), carbon monoxide yield (COY), and total carbon monoxide (T_{CO}) of LDPE, LDPE/IFR, and LDPE/IFR/UZB are presented in Figures 3–5, respectively. Figure 3 shows that the peak COV value of LDPE/IFR and the time to the peak value were 123.8 ppm and 95 s, respectively, and these values corresponded to the LDPE values of 100.7 ppm and 155 s. The results indicate that the peak COV value increased and the peak COV value occurred early when the IFR was introduced into LDPE; this would make it more difficult for people to escape from a disastrous fire and make it easy for them to be choked by CO. An interesting result is that the COV decreased substantially when UZB was incorporated into the LDPE/IFR system. The peak COV value of LDPE/IFR/UZB and the time to the peak value were 41.2 ppm and 230 s, respectively. The COY [the CO mass produced per polymer mass loss (kg/kg)] can be seen in the COY curves of Figure 4; the order was LDPE/IFR > LDPE/IFR/UZB > LDPE. The T_{CO} curve in Figure 5 shows that T_{CO} for LDPE/IFR was greatest and that for LDPE/IFR/UZB was lowest during the
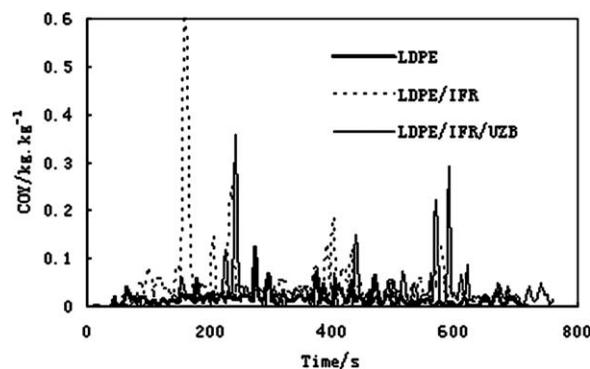
Figure 4 COY curves of the untreated and treated LDPE.
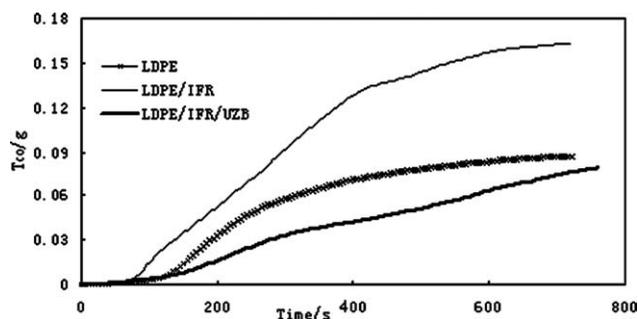
Figure 5 T_{CO} curves of the untreated and treated LDPE.

combustion process. The T_{CO} values for LDPE/IFR, LDPE, and LDPE/IFR/UZB were 0.1629, 0.0869, and 0.0791 g during the whole combustion process, respectively. CO is an important parameter for estimating the toxicity of a gas evolving from a polymer during combustion.[26,27] The results imply that UZB can reduce the toxicity of the involved gas and favor the escape of people from a disastrous fire. There are two reasons that UZB can reduce the COV and total amount of CO in LDPE/IFR. First, zinc borate can promote charring and improve the quality of char, which can protect the inner matrix from degradation and reduce the combustible gas, which is responsible for the production of CO_2 and CO. Second, UZB possesses a strong absorption ability because of its small particle size, high surface energy, and high specific area. CO and oxygen can be absorbed into the outer layer of UZB and may react to produce CO_2 through the catalysis of zinc compounds. The catalytic mechanism will be further investigated.

CO_2

The CO_2 concentrations (CO_2V) of LDPE, LDPE/IFR, and LDPE/IFR/UZB are presented in Figure 6. Figure 6 shows that only one peak of CO_2V appeared when LDPE was burning; the peak value for LDPE and the time to the peak value were 0.65% and 180 s,
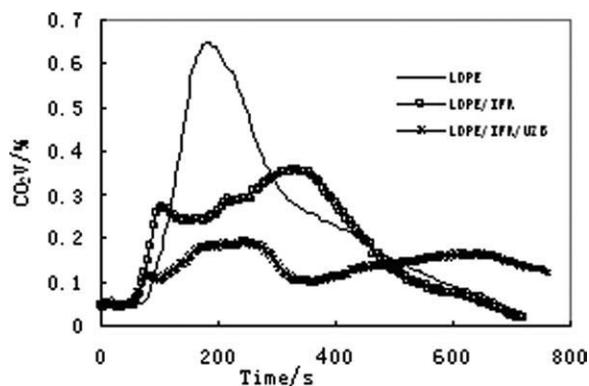
Figure 6 CO_2V curves of the untreated and treated LDPE.

respectively. There were two peaks of CO_2V when LDPE/IFR and LDPE/IFR/UZB were burning. The peak values of LDPE/IFR were 0.265% (110 s) and 0.355% (350 s). The peak values of LDPE/IFR/UZB were 0.195 (245 s) and 0.166% (630 s). The results showed that the peak value of LDPE was greatest because of its complete degradation and combustion. The reduction of the CO_2V peak values of LDPE/IFR and LDPE/IFR/UZB could be attributed to the reduction of combustible gas resulting from the protection of charring; in particular, the quality of charring improved when UZB was introduced into the LDPE/IFR system. The second peak value of LDPE/IFR/UZB decreased substantially in comparison with that of LDPE/IFR, and this implied that anti-oxidation increased sharply at high temperatures when UZB was introduced into the LDPE/IFR system.

Py–GC–MS analysis

On the basis of the thermogravimetric analysis of LDPE, LDPE/IFR, and LDPE/IFR/UZB,[17] samples of LDPE, LDPE/IFR, and LDPE/IFR/UZB were
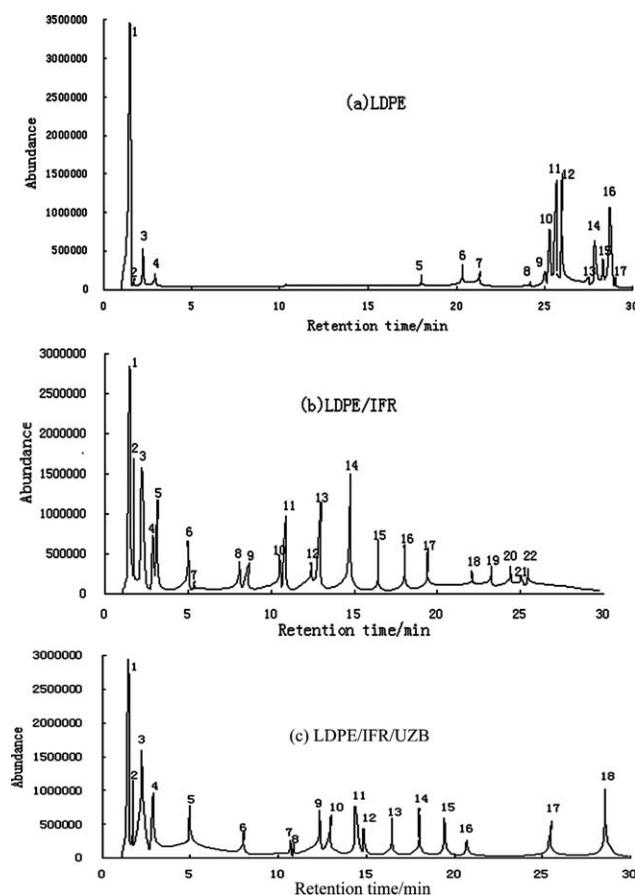
Figure 7 GC of the pyrolysis products of the samples pyrolyzed at 400°C for 20 s: (a) LDPE, (b) LDPE/IFR, and (c) LDPE/IFR/UZB.

TABLE II
GC–MS Results for the Pyrolysis Products of LDPE at 400°C for 20 s

Peak	Retention time (min)	Ratio (%)	Compound	Formula
1	1.489	23.56	Ethylene	C_2H_4
2	1.737	0.91	Water	H_2O
3	2.215	5.43	2-Propenal	C_3H_4O
4	2.892	1.15	Butyraldehyde	C_4H_8O
5	18.000	1.36	1-Dodecene	$C_{12}H_{24}$
6	20.342	4.35	1-Hexadecene	$C_{16}H_{32}$
7	21.360	2.94	n-Hexadecane	$C_{16}H_{34}$
8	24.207	1.35	2-Ethyl-1-decanol	$C_{12}H_{26}O$
9	25.030	3.72	Octadecanal	$C_{18}H_{36}O$
10	25.297	7.12	Octadecyl vinyl ether	$C_{20}H_{40}O$
11	25.699	10.81	Dibutyl phthalate	$C_{16}H_{22}O_4$
12	26.004	10.35	Tridecanedial	$C_{13}H_{24}O_2$
13	27.490	3.13	—	Similarity < 50%
14	27.847	7.17	Cyclododecylmethanol	$C_{13}H_{26}O$
15	28.332	5.11	8-Hexylpentadecane	$C_{21}H_{44}$
16	28.553	11.24	Diisooctyl phthalate	$C_{24}H_{38}O_4$
17	29.049	1.35	cis-1,2-Cyclododecanediol	$C_{12}H_{24}O_2$

The similarity of all compounds identified in Tables II–IV is greater than 85%.

pyrolyzed at 400°C for 20 s; the GC results for the pyrolytic gas are presented in Figure 7. The results of the GC–MS analysis are listed in Tables II–IV. The Py–GC–MS results showed that the main components of the pyrolytic gas of neat LDPE were ethylene, 2-propenal, octadecyl vinyl ether, dibutyl phthalate, tridecanedial, cyclododecylmethanol, 8-hexylpentadecane, and diisooctyl phthalate. The main components of the pyrolytic gas of LDPE/IFR were ethylene, 2-propenal, 1-hexanol, 3-methyl-butanal, 1-nonene, 1-decene, and 4-aminostyrene. The main components of the pyrolytic gas of LDPE/IFR/UZB were ethylene,

2-propenal, butyraldehyde, methoxydiethyl borane, 4-aminostyrene, decanal, 1-dodecene, octadecanal, and diisooctyl phthalate.

The distinction of the components and the corresponding contents of the pyrolytic gas were obvious. The number of components of the pyrolytic gas of neat LDPE was lowest (only 16 components with a concentration no less than 1%), the number of components of the pyrolytic gas of LDPE/IFR was highest (22 components with a concentration no less than 1%), and the number of components of the pyrolytic gas of LDPE/IFR/UZB was between them (18 components with a

TABLE III
GC–MS Results for the Pyrolysis Products of LDPE/IFR at 400°C for 20 s

Peak	Retention time (min)	Ratio (%)	Compound	Formula
1	1.493	16.75	Ethylene	C_2H_4
2	1.735	3.23	Water	H_2O
3	2.218	16.26	2-Propenal	C_3H_4O
4	2.892	4.88	Butyraldehyde	C_4H_8O
5	3.173	7.69	1-Hexanol	$C_6H_{14}O$
6	4.987	6.30	Butanal, 3-methyl	$C_5H_{10}O$
7	5.374	1.59	1-Heptene	C_7H_{14}
8	8.058	3.33	Hexanal	$C_6H_{12}O$
9	8.691	3.18	Octane	C_8H_{18}
10	10.458	2.43	2-Heptanone	$C_7H_{14}O$
11	10.908	5.12	1-Nonene	C_9H_{18}
12	12.404	1.63	Furan, 2-butyltetrahydro	$C_8H_{16}O$
13	13.016	4.74	1-Decene	$C_{10}H_{20}$
14	14.764	5.90	4-Aminostyrene	C_8H_9N
15	16.451	2.23	Decanal	$C_{10}H_{20}O$
16	18.000	3.30	1-Dodecene	$C_{12}H_{24}$
17	19.428	2.63	1-Hexadecene	$C_{16}H_{32}$
18	22.048	1.58	Tetradecanal	$C_{14}H_{28}O$
19	23.250	1.83	Hexadecanal	$C_{16}H_{32}O$
20	24.384	1.90	2-Ethyl-1-decanol	$C_{12}H_{26}O$
21	25.017	1.56	Octadecanal	$C_{18}H_{36}O$
22	25.465	1.73	1,2-Epoxynonadecane	$C_{19}H_{38}O$

Peak	RT (min)	Ratio (%)	Compound	Formula
1	1.491	15.43	Ethylene	C_2H_4
2	1.735	3.87	Water	H_2O
3	2.246	15.32	2-Propenal	C_3H_4O
4	2.933	9.65	Butyraldehyde	C_4H_8O
5	5.007	7.38	Butanal, 3-methyl	$C_5H_{10}O$
6	8.068	3.40	Hexanal	$C_6H_{12}O$
7	10.392	2.78	3-Heptanone	$C_7H_{14}O$
8	10.697	1.25	n-Heptaldehyde	$C_7H_{14}O$
9	12.323	4.45	Methoxydiethylborane	$C_5H_{13}BO$
10	13.018	3.55	Octanal	$C_8H_{16}O$
11	14.349	4.65	4-Aminostyrene	C_8H_9N
12	15.041	2.52	Nonanal	$C_9H_{18}O$
13	16.450	4.66	Decanal	$C_{10}H_{20}O$
14	18.001	4.10	1-Dodecene	$C_{12}H_{24}$
15	19.420	3.54	1-Hexadecene	$C_{16}H_{32}$
16	20.736	2.47	3,5-Dimethylcyclohexanol	$C_8H_{16}O$
17	25.541	4.82	Octadecanal	$C_{18}H_{36}O$
18	28.548	6.41	Diisooctyl phthalate	$C_{24}H_{38}O_4$

concentration no less than 1%); therefore, the number of components of the pyrolytic gas became higher when LDPE was treated with flame retardants. Moreover, a nitrogen-containing compound (4-aminostyrene) was detected in the pyrolytic gas of LDPE/IFR, and a nitrogen-containing compound (4-aminostyrene) and a boron-containing compound (methoxydiethyl borane) were detected in the pyrolytic gas of LDPE/IFR/UZB. Although some components of the pyrolytic gas of LDPE, LDPE/IFR, and LDPE/IFR/UZB were identical, the relative contents of each components were different. The concentration of 2-propenal was more than 15% in the pyrolytic gas of LDPE/IFR and LDPE/IFR/UZB, and it was the second major component after ethylene. However, the concentration of 2-propenal was only 5.43% in the pyrolytic gas of neat LDPE. The concentration of the components whose retention time exceeded 25 min was about 60%, and no component whose retention time was between 3 and 18 min was detected in the pyrolytic gas of neat LDPE. Only two components whose retention time exceeded 25 min were detected, and the concentration was low in the pyrolytic gas of LDPE/IFR. Two components whose retention time exceeded 25 min were detected, and the concentration was about 11% in the pyrolytic gas of LDPE/IFR/UZB. The concentration of ethylene was highest (23.56%) and the concentration of water was very low (0.91%) in the pyrolytic gas of neat LDPE, but the concentration of ethylene decreased and that of water increased obviously in the pyrolytic gas of LDPE/IFR. In particular, the concentration of ethylene reaches its lowest point (15.43%) and the concentration of water reached its highest point (3.87%) in the pyrolytic gas of LDPE/IFR/UZB versus those of neat LDPE and LDPE/IFR; this implies that the IFR could promote dehydration and charring, and this action

could be strengthened when UZB was introduced into LDPE/IFR. The Py–GC–MS results demonstrate that a catalytic effect of UZB on the dehydration and charring of LDPE/IFR exists.

CONCLUSIONS

The results of cone calorimetry testing show that the depression effect of UZB on smoke and CO, which is regarded as one of the most important parameters describing the toxicity of the involved gas, is obvious. The effect has two aspects. First, UZB improves the quality of the char, which can prevent inner matrix degradation and reduce the amounts of combustible gas and smoke-forming materials in the gas phase under combustion, which are responsible for producing the smoke and CO. Second, smoke particles and CO can be absorbed by UZB because of its small particle size, high surface energy, and high specific area. The CO and O_2 absorbed in the outer layer of UZB may react and produce CO_2 via the catalysis of zinc compounds. Therefore, UZB imparts strong smoke suppression and toxicity reduction in addition to the synergistic effect of the flame retardancy of the LDPE/IFR system.[17] A reduction of ethylene and an increase in water can be observed in the pyrolytic gas of LDPE/IFR by Py–GC–MS; this trend is extended when UZB is introduced into LDPE/IFR. These facts provide positive evidence that UZB can promote LDPE dehydration and charring, and this is also an important reason that UZB possesses properties of smoke suppression and toxicity reduction for the LDPE/IFR system.

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