Combustion Characteristics of Halogen-Free Flame-Retarded Polyethylene Containing Magnesium Hydroxide and Some Synergists

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ABSTRACT: Halogen-free flame-retarded polyethylene materials have been prepared by using magnesium hydroxide (MH) as a flame retardant combined with red phosphorous (RP) and expandable graphite (EG) as synergists. The effects of these additives on the combustion behavior of the filled linear low density polyethylene (LLDPE), such as a limiting oxygen index (LOI), the rate of heat release (RHR), the specific extinction area (SEA), etc., have been studied by the LOI determination and the cone calorimeter test. The results show that RP and EG are good synergists for improving the flame retardancy of LLDPE/MH formulations. In addition, a suitable amount of ethylene and vinyl acetate copolymer (EVA) added in the formulations can increase the LOI values while promoting the char formation and showing almost no effect on the RHR and SEA values. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 206–214, 2001

Key words: combustion characteristics; polyethylene; magnesium hydroxide; halogen-free flame retardation; cone calorimeter test

INTRODUCTION

There is an increasingly concern about the use of poly(vinyl chloride) (PVC) and polyolefins (PO) with halogen-containing flame retardants in the wire and cable industry because they can produce a large amount of smoke and toxic hydrogen chloride gases during combustion.[1] It is therefore worthwhile to investigate the halogen-free flame retardation of PO (HFRPO). There are many kinds of compounds that can be used as flame-retardant additives in HFRPO, such as metal hydroxides, phosphorous-containing compounds, nitrogen-containing compounds, and so on. Metal hydroxides, mainly magnesium hydroxide (MH) and aluminum hydroxide (ATH), are widely used as flame-retardant additives of polymers. MH has a high endothermic decomposition temperature (>340 °C), whereas ATH begins to decompose at ~180 °C, which is usually in the range of PO processing temperature and thus limits the use of ATH in HFRPO.[2] From this point of view, MH is a more promising flame retardant in HFRPO than ATH.

Many investigations have been done on the use of MH as a flame retardant in thermoplastics. Hornsby and co-workers[2–4] have examined thoroughly the flame retarding and smoke suppressing properties of polypropylenes by using MH. The work reported by Larcey et al.[5] has showed

that the flammability of many combustible polymers can be reduced by MH. Jancar and Wang et al.[6-8] have studied the effects of MH on mechanical properties of heavily filled polymer composites. Many researchers have found that >50 wt % MH loading was required to obtain an adequate level of flame retardant property, whereas high loading levels of MH could be detrimental to the mechanical properties of the filled PO materials. MH combined with some HFR synergists, such as red phosphorous (RP), expandable graphite (EG), etc., could increase flame retardancy and decrease its high loading level of MH. However, RP as a flame-retardant additive has some problems; such as, easy spontaneous ignition and absorbing moisture when exposed to air. Microcapsulation of RP is an important way to solve these problems.[9] EG has been found to be a good synergist in flame-retardant polymers in some patents[10, 11] and in our recent work.[12, 13] However, there is no report in the literature on the use of EG as an HFR synergist of MH. EVA, a copolymer of ethylene and vinyl acetate, is often used alone or in combination with low-density polyethylene as cable sheaths and insulated materials.[14] It is well known that EVA can be used to improve the compatibility of polyethylene with high levels of metal hydrates and cable flexibility.[15, 16]

In this paper, attempts have been made to develop MH-based HFRPO materials with satisfactory flame-retardant and mechanical properties, in which the total filler level is limited to <50% by weight. The main purpose is to obtain the optimizing formulations with MRP, EG, and/or EVA as synergists of MH by limiting oxygen index (LOI) and cone calorimeter determination that can be used for halogen-free flame-retardant wires and cables.

EXPERIMENTAL

Materials

Linear low density polyethylene (LLDPE, DFDC 7050) was supplied by Zhongyuan Petrochemical Company, China. Ethylene and vinyl acetate copolymer (EVA, containing 19% VA) was purchased from Yanshan Petrochemical Company, China. Magnesium hydroxide, with a median particle size of ~2 μm and a surface area of 12.5 m^2g^{-1} (Brunauer–Emmett–Teller method), and expandable graphite (EG), with expansion ratios of 100 (EG1) and 150 (EG2), are commercial prod-

ucts used as received. Microcapsulated red phosphorous (MRP) containing ~85% phosphorous was prepared in our laboratory with melamine–formaldehyde resins as coating.

Preparation of Samples

All compositions were melt compounded using a two-roll mill at a temperature of ~120 °C for 15 min. The resulting mixtures were then compression molded at ~130 °C into sheets (1- and 3-mm thickness) under a pressure of 9 MPa for 10 min. The sheets (3 mm) were cut into suitable size specimens for fire testing. The dumbbell-shaped samples for the tests of mechanical properties were cut from the 1-mm sheets. The formulations used in the present work are listed in Table I.

Mechanical Measurements

The tensile strength (σ_b) and elongation at break (ε_b) were measured with a Universal Testing Machine DCS-5000 (Shimadzu, Japan) at the cross head speed of 25 mm/min according to the Chinese Standard GB 2951.6-82 (the test method for determining the mechanical properties of cable sheathing compounds).

Limiting Oxygen Index Measurements

A limiting oxygen index (LOI) is defined as the minimum oxygen concentration required to sustain the downward flame combustion of materials. The LOI measurements were carried out in accordance with ASTM D 2863. The specimens used for the test are of dimensions 100×6.5×3 mm.

Cone Calorimeter Tests

The cone calorimeter (Stanton Redcroft) was used to measure the rate of heat release (RHR), the time to ignition (IT), the specific extinction area (SEA), etc. of polyethylene and its blends. The cone calorimeter tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions of 100×100×3 mm was wrapped in aluminum foil and exposed horizontally to an external heat flux of 35 kW/m^2.

RESULTS AND DISCUSSION

Mechanical Properties of LLDPE/MH Blends

The effect of the concentration of MH additive on the mechanical properties of filled LLDPE is very

Table I   Formulations Containing Different Additive Levels

Sample Code	LLDPE	EVA	MH (phr)	MRP (phr)	EG1 (phr)	EG2 (phr)
A	100	—	0	—	—	—
B	100	—	90	—	—	—
C	100	—	100	—	—	—
D	100	—	110	—	—	—
E	100	—	120	—	—	—
F	100	—	130	—	—	—
G	100	—	150	—	—	—
H	100	—	85	5	—	—
I	100	—	80	10	—	—
J	100	—	70	20	—	—
K	100	—	60	30	—	—
L	100	—	85	—	5	—
M	100	—	80	—	10	—
N	100	—	70	—	20	—
O	100	—	85	—	—	5
P	100	—	80	—	—	10
Q	100	—	70	—	—	20
R	90	10	90	—	—	—
S	80	20	90	—	—	—
T	70	30	90	—	—	—
U	60	50	90	—	—	—

sensitive, as shown in Figure 1. It is expected that the tensile strength (σ_b) and the elongation at break (ε_b) decrease with increasing amount of MH additive. When MH loading increased to 100 phr (parts per hundred resin), the σ_b decreased from ~20 MPa to ~9 MPa, and the ε_b decreased from 1564 to 17%. These results indicate that the mechanical properties of the filled LLDPE were greatly deteriorated, especially at high loading of MH. The reductions in the properties are mainly due to the poor adhesion between the filler and the polymer substrate. Therefore, the amount of additives was controlled to 90 phr (<50% by
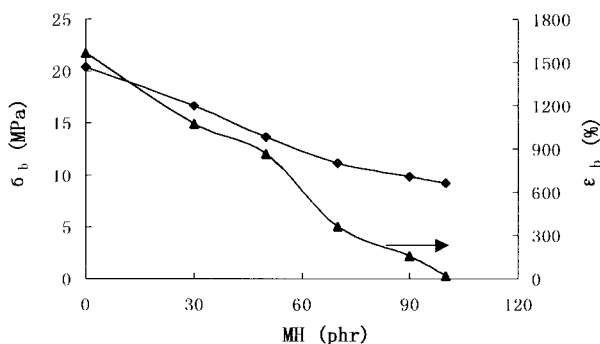

Figure 1   Effect of MH concentration on the mechanical properties of LLDPE blends.

weight) in the present work to avoid causing serious damage to the mechanical properties of the filled LLDPE.

Synergistic Effect of MH Combined with MRP or EG on the LOI Values

The LOI test is still widely used to evaluate flame retardation of materials, especially for screening flame-retarded formulations of polymers, although it has caused much controversy because the flame propagates downward during the LOI test and its results have poor correlation with those obtained from large-scale fire tests.[17, 18] The LOI values of sample (A) to (Q) in this work are listed in Table II. It can be seen from Table II-1 that the LOI values of LLDPE blends increase gradually with increasing MH amount from 90 to 150 phr. The LOI value of LLDPE blends was ~22.5 at 100 phr (50% by weight) of MH, whereas the corresponding value at 150 phr (60% by weight) was only 25.5, as listed in samples (C) and (G) of Table II, respectively. These results illustrate the low flame-retardant efficiency of MH in the LLDPE system.

The LOI values of the samples (H) to (K) containing different amounts of MRP at the same level of additives are shown in Table II-2. It can

Table II   Combustion Behavior of LLDPE/MH/Synergists Blends

Sample Code		LOI	IT (S)	PRHR (kW/m^2)	PSEA (m^2/kg)	Residues (%)
1	A	17.5	106	938	1258	2.2
	B	22.0	117	242	573	36.7
	C	22.5	120	228	455	38.9
	D	23.0	124	198	395	43.6
	E	23.5	132	177	288	44.3
	F	24.0	136	158	263	46.0
	G	25.5	148	153	236	49.2
2	H	23.5	130	159	859	38.6
	I	26.0	153	124	1101	44.8
	J	25.0	120	130	1411	38.7
	K	23.0	96	260	1328	34.0
3	L	26.5	81	267	536	34.2
	M	27.0	75	259	359	38.5
	N	28.0	69	185	352	40.0
	O	26.5	80	255	396	37.8
	P	27.0	77	224	354	39.3
	Q	30.5	61	158	290	41.3

be seen that the addition of MRP into the LLDPE/MH blends increases the LOI values efficiently. It is apparent that MRP provided a synergistic effect on the LOI values of MH-filled LLDPE blends. However, the optimum amount of MRP additive in the LLDPE/MH blends is ~10 phr because its corresponding LOI value has reached the maximum of ~26. This result is in agreement with the report by Hearle and Sparrow.[19]

The data in Table II-3 clearly indicate that EG plays a very important role in raising LOI values of the LLDPE/MH formulations. A remarkable increase of LOI value was observed from 22.0 of the control sample (B) to 26.5 of the samples (L) and (O), as shown in Table II. The LOI values of samples (N) and (Q) containing 20 phr EG were 28.0 and 30.5, respectively; this result indicates that EG2, with an expandable ratio of 150, is more efficient than EG1, with an expandable ratio of 100, in increasing LOI value. The increase of LOI value is probably attributed to the formation of intumescent materials during the combustion of polymer composites with EG, which can prevent the heat transfer from the flame to the burning substrate in the LOI test.

The Cone Calorimeter Studies of the LLDPE/MH/Synergist Blends

The cone calorimeter based on the oxygen consumption principle[20] has widely been used to evaluate the combustion behavior of materials and products since it was developed at the NBS (now NIST) in 1982.[21] The cone calorimeter is a small-scale test, but some of its results have been found to correlate well with those obtained from large-scale fire tests and can be used to predict the behavior of materials in real fires.[22, 23] The peak rate of heat release (PRHR), for example, is a very important parameter, which may be used to express the intensity of fires.[24]

The dynamic RHR of different MH concentrations obtained by the cone calorimeter test from the LLDPE blend samples (A) to (G) is shown in Figure 2. The pure LLDPE resin burned very fast after ignition and appeared as a sharp peak on the RHR curve, whereas the addition of MH into LLDPE resulted in a great decline of RHR and the prolonged combustion process of the blends. The detailed data obtained by the cone calorimeter from the aforementioned series of samples are presented in Table II-1. The PRHR values of the formulations decrease with increasing amount of MH. The PRHR value of sample (C) with the MH additive of 100 phr was 228 kW/m^2, which is only about one-quarter of 938 kW/m^2 for the sample (A) without MH. The PRHR value of sample (G), with the loading of 150 phr MH, was reduced to only about one-sixth of that for the sample (A). The IT values and the residues left after burning also increase with increasing amount of MH, as shown in Table II-1.
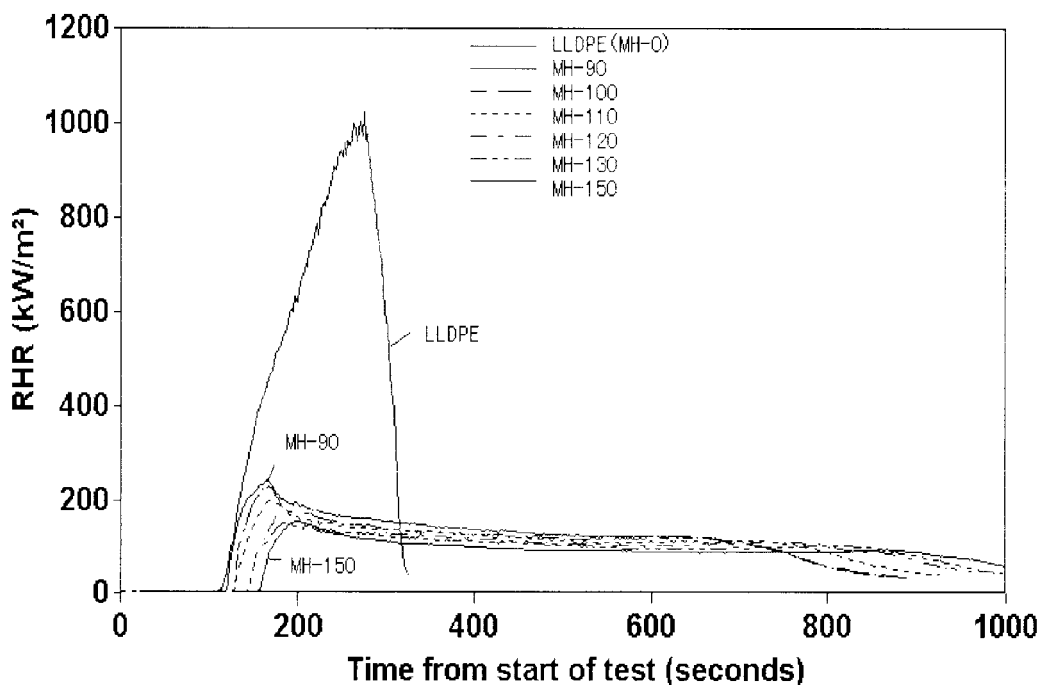
Figure 2 Dynamic RHR curves of the LLDPE blends with different concentrations of MH.

The MH additive exerts its flame-retardant action by the following factors: (i) the endothermic decomposition accompanying the release of water in MH, (ii) the formation of a stable charred layers over the polymer substrate, and (iii) the water vapor dilution of flammable volatiles in the gas phase.[2] It has been reported that the decomposition reaction of MH additive occurs by absorbing much heat (1301 J/g) from the burning polymer.[5] It is apparent that the formation of the charred layers can prevent heat flow from the flame zone to the polymer substrate, thus retarding the thermo-oxidation degradation of the polymer. A lot of water vapor obviously suppresses the combustion occurring in the gas phase due to the concentration decrease of combustible compounds. All these factors suppress the RHR of the MH-filled blends and, hence, enhance their flame retardancy.

Not only is MH an effective RHR reducer, but MH is also a smoke suppressant. It can be seen from Table II-1 that the peak specific extinction area (PSEA) decreases with increasing MH concentration. The PSEA value of sample (C) with the 100 phr MH decreased by a factor of at least 2 compared with sample (A) without MH. The PSEA of sample (G) with the 150 phr MH was only about one-sixth of the sample (A). The magnesium oxide with the high surface area produced

from the combustion of MH-filled LLDPE can catalyze the oxidation of carbon,[2] resulting in smoke reduction. The water released from the decomposition of MH did not provide a preferable effect on smoke suppression.[2, 25, 26] Hirschler and Thevaranjan[25] have confirmed that magnesium oxide is as effective as magnesium hydroxide in the smoke suppression of polystyrenes.

The dynamic RHR changes of the sample (H) to (K) containing different concentrations of MRP additive up to 30 phr, with the total additive level of 90 phr, are shown in Figure 3. The corresponding PRHR data are given in Table II-2. The sample (B) in Figure 3 is used as the control sample at 90 phr MH. The sample (I), with 10 phr MRP, shows the lowest PRHR value and the highest percent residues among all the samples with MPR. The loading of 30 phr MRP resulted in an increase in PRHR compared with the control sample. It is generally accepted that RP exerts its flame retardancy in polymers not only in the gas phase, but also in the condensed phase. In RP-filled hydrocarbon polymers, it is oxidized to phosphoric acids, which can form a protective coating on the burning substrate, limiting fuel volatilization and oxygen penetration to the condensed phase.[27] As for the mode of action of RP in the gas phase, Hastie and McBee[28] have found that phos-
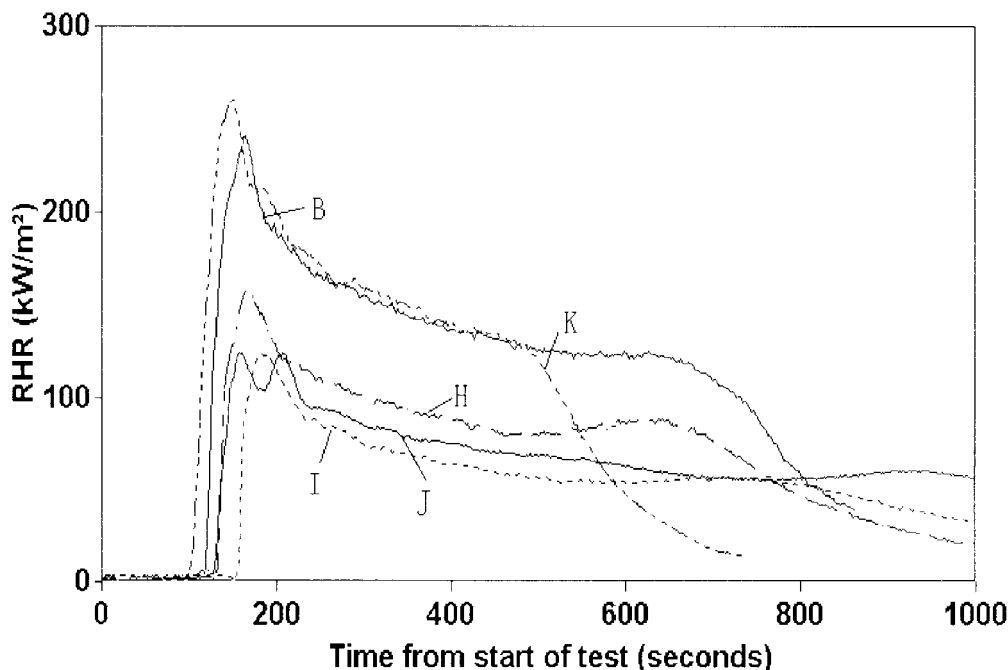
Figure 3 Dynamic RHR curves of the LLDPE/MH blends with different amounts of MRP at the same levels of 90 phr additives. The formulations of samples (B) and (H) to (K) are listed in Table I.

phorus monoxide (PO) was the most predominant species in the flame, and confirmed that several hundred parts per million of phosphorous monoxide in the flame is sufficient to reduce the radical concentration. The addition of a small amount of MRP can decrease the RHR and increase the IT values of the LLDPE/MH formulations, probably because the water produced by MH decomposition may be helpful to the formation of phosphoric acids from phosphorus oxide. The reason why high loading of MRP in the LLDPE/MH formulations increases the flammability compared with the blends of low loading of MRP is still unknown; further research is needed to elucidate this phenomenon. The main problem associated with the use of RP in polymers is that it usually increases the smoke production on burning. The results in Table II-2 also indicate that the PSEA values increase sharply with increasing amount of MRP compared with the formulations without MRP shown in Table II-1.

The effect of EG as a synergist on the RHR of LLDPE/MH formulations is shown in Figure 4. It can be seen that the RHR curves of the sample (L) to (Q) with EG shift to a bit left compared with the curve of sample (B) without EG, which means the formulations with EG caught on fire easily. There is a slight increase in the PRHR of the formula-

tions containing lower parts of EG compared with the control sample (B) containing the same additive level (Table II-3). The PRHR was, however, significantly reduced when EG was added to the formulations at a higher loading, such as samples (N) and (Q) with 20 phr EG. The reason for this result may be that at a higher loading of EG the dense intumescent layers are formed, which can prevent the heat transfer efficiently between the flame zone and the burning substrate and thus retard the pyrolysis of polymers.

The decrease of IT with increasing amount of EG is shown in Table II-3. The result in this work is in agreement with those reported by Chuang et al.,[29] who have found that EG tends to decrease IT in EPDM rubber. It can be seen that the smoke suppression of EG is much better than that of MH because the PSEA data of samples (L) to (Q) with EG in Table II-3 are much lower that that of the control sample (B). Also, the PSEA and the residues in Table II-3 indicate that EG2 is more effective than EG1 in smoke suppression and promoting char formation.

Effect of EVA on the Combustion Characteristics of LLDPE/MH Blends

The RHR curves obtained from the different fractions of EVA added into LLDPE/MH formula-
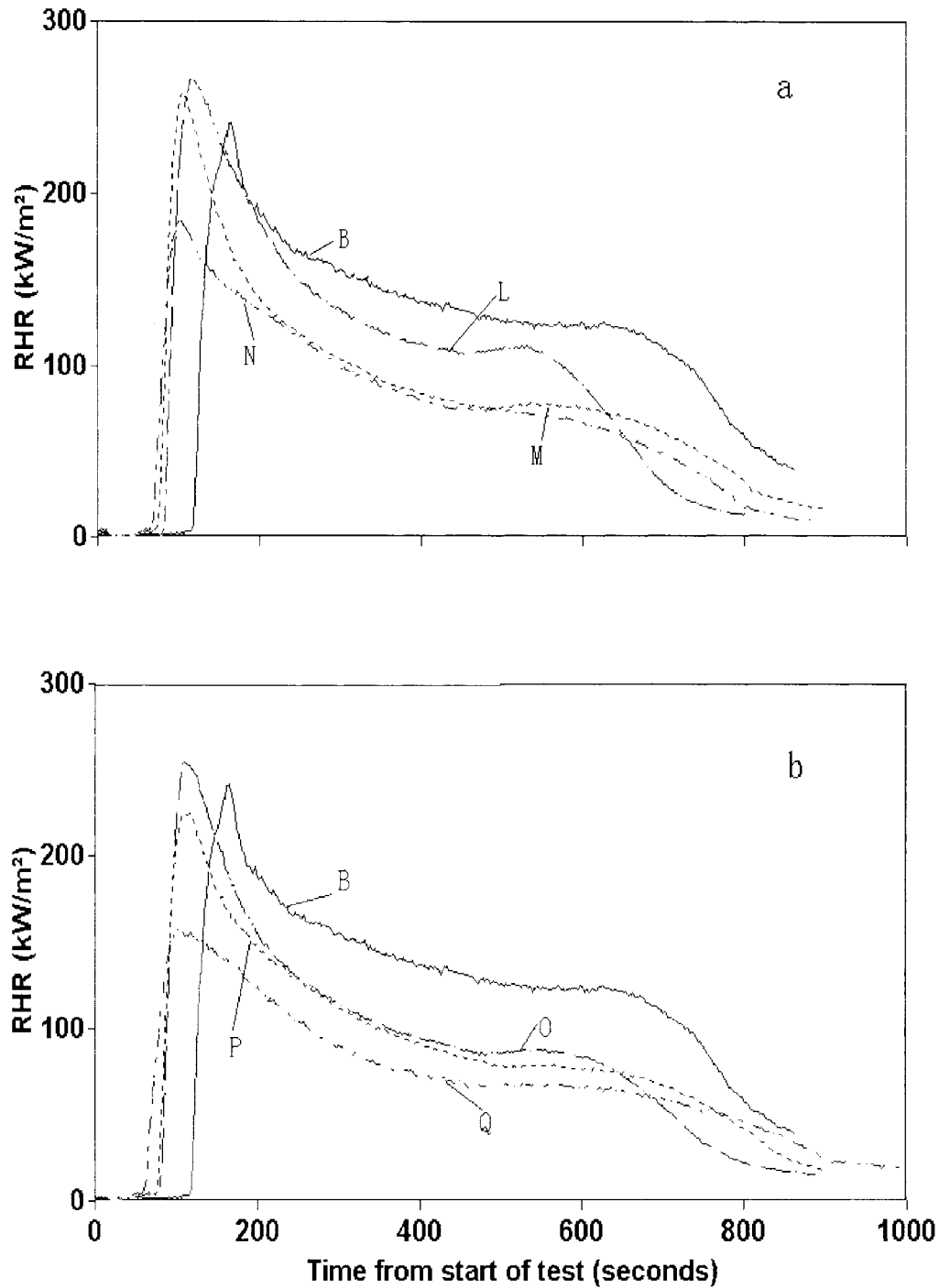
Figure 4 Dynamic RHR curves of the LLDPE/90 phr MH blends with different amounts of EG at the same levels of 90 phr additives: (a) EG1; (b) EG2. The formulations of samples (B) and (L) to (Q) are listed in Table I.

tions, as listed in the samples (R) to (U) of Table I, are shown in Figure 5. The corresponding data of the LOI values and the parameters of flammability are listed in Table III. It can be seen from Figure 5 and Table III that the intensities of

PRHR peaks increase gradually with increasing EVA amounts added into the formulations compared with the control sample (B). The IT and PSEA values of the samples (R) and (S) within the 20 parts of EVA decreased, whereas the corre-
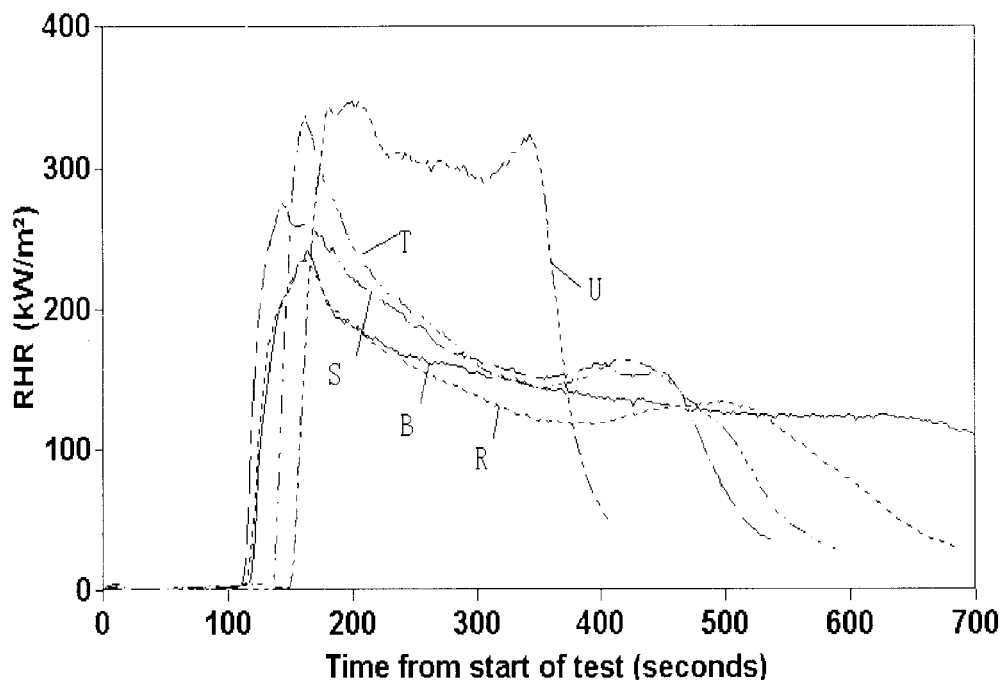
Figure 5 Dynamic RHR curves of the LLDPE/90 phr MH blends with different amounts of EVA at the same levels of 90 phr MH. The formulations of samples (B) and (R) to (U) are listed in Table I.

sponding values of the samples (T) and (U) with >20 parts of EVA increased compared with the control sample (B). The residues left after combustion decreased with increasing EVA fraction, but the residues from the formulations with EVA were higher than that from the formulation without EVA at the same loading level. The LOI values increased at first with increasing EVA fraction up to 30 parts in the formulations, as shown in the samples (R), (S), and (T) of Table III. Then, the value began to decline when EVA reached 50 parts (sample (U)). The conclusion can be drawn that the optimum amount of EVA in LLDPE/MH systems might be in the range 20–30 parts.

CONCLUSIONS

The combustion behavior of LLDPE formulations containing MH, MRP, and EG has been studied using the cone calorimeter and the LOI. When MH as a halogen-free flame retardant is used alone in polyethylene, >60% by weight of MH is usually needed to reach an adequate level of flame retardation of the filled polymer. However, high loadings of MH can be detrimental to the mechanical properties.

Suitable addition of MRP into the LLDPE/MH formulations resulted in a sharp decrease in PRHR and a substantial increase in IT and LOI. However, the formulations containing MRP in-

Table III   Combustion Behavior of LLDPE/EVA/MH Blends

Sample Code	LOI	IT (S)	PRHR (kW/m²)	PSEA (m²/kg)	Residues (%)
B	22.0	117	242	573	36.7
R	23.5	108	237	516	40.9
S	24.5	110	274	458	40.0
T	25.0	134	337	645	39.9
U	24.5	149	347	868	39.0

creased the smoke evolution greatly compared with the only MH-filled LLDPE.

EG is a very effective synergist in raising LOI and reducing PRHR and PSEA of the LLDPE/MH formulations, especially for EG with a higher ratio of expansion. The addition of EG, on the other hand, led to a decrease in IT of the formulations.

EVA is commonly used to improve the compatibility between polyethylene and metal hydrates. Partial replacement of LLDPE by EVA in the LLDPE/MH formulations increased the LOI value and the residue after burning and did not affect the rate of heat release and the smoke evolution greatly.

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