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Synergistic Flame Retardancy of Polyaminocyclotriphosphazene and 1,3,5-*Tris*(2-hydroxyethyl)cyanurate in Polyethylene

LINSHENG TANG*, WEI BI, LI LI, YANG KE, HONG BIN SONG and JINGWEI YANG

College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, P.R. China

*Corresponding author: E-mail: linshengt62@163.com

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In this paper, the synergistic flame retardancy of polyaminocyclotriphosphazene (PHACTPA) and 1,3,5-*tris*(2-hydroxyethyl)cyanurate (THEIC) in polyethylene (PE) was studied by limiting oxygen index (LOI) measurement, vertical burning test and cone calorimetry test. Meanwhile, the thermal stability of flame-retarded polyethylene (FR-PE) was investigated by thermogravimetric analysis and the mechanism was discussed by the analysis of residues obtained in cone calorimetric test. The experimental results reveal that there is an excellent synergistic flame retardancy between PHACTPA and THEIC in polyethylene, which results in the increased limiting oxygen index, improved vertical burning class, reduced peak heat release rate (PHRR), mean heat release rate (MHRR), slowed mass loss in polyethylene during combustion. For example, FR-PE alone with 20 wt. % PHACTPA or THEIC based on the total weight has the limiting oxygen index of 24.4 and 17.4 % respectively and the vertical burning test is failed, while FR-PE with 20 wt. % the combination consisted of 50 wt. % PHACTPA and 50 wt. % THEIC has the 25.4 % of limiting oxygen index and passes UL94 V-0 classification. Thermogravimetric analysis results indicate that PHACTPA or PHACTPA/THEIC improves the thermal stability of polyethylene. The analysis of residues reveals that PHACTPA plays flame retardancy mainly by condensed phase mechanism, where PHACTPA is decomposed into non-volatile phosphoric acid compounds which promote the charring of polyethylene, the formed intumescent layer results in flame retardancy by the barrier effect on heat, air and decomposition products. 1,3,5-*Tris*(2-hydroxyethyl)cyanurate promotes the decomposition of PHACTPA to phosphoric acid compounds, so improves the charring of polyethylene and results in excellent synergistic flame retardantcy.

Keywords: Polyaminocyclotriphosphazene, 1,3,5-*Tris*(2-hydroxyethyl)cyanurate, Polyethylene, Synergistic flame retardancy.

INTRODUCTION

Polyethylene (PE) is the first major in varieties of thermoplastic. However, as polyethylene belongs to flammable materials with the limiting oxygen index of only 17.4 % and burns with a droplet, it is easy to cause a fire that will create huge threat on people's lives and properties. The fatal defect restricts its field of application. Therefore, the studies on flame retarded polyethylene (FR-PE) have attracted considerable interests in recent decades. So far, halogen-containing flame retardants, particularly those based on bromine, have played a large part in FR-PE. Nevertheless, mainly because of environmental concerns and end-of-life issues, there has been a growing interest in halogen-free solutions[1-3] and some halogen-free flame retardants such as ammonium polyphosphate, red phosphorus and metal hydroxides such as aluminium hydroxide and magnesium hydroxides, are more and more extensively used in polyethylene[4].

Both of ammonium polyphosphate and red phosphorus have some advantages such as less corrosive gases and smoke formed during combustion, high efficiency, low dosage, low-cost price and ease to recycle of the flame retarded materials. However, they also have some disadvantages. For example, ammonium polyphosphate has poor water and moisture resistance and the ammonium polyphosphate-containing material appears sticky[5,6], while red phosphorus is easy to absorb moisture, oxidize, explode and emit poisonous gases and its dark red colour is the largest handicap for its widespread application[7,8]. In recent years, metal hydroxides as a low smoke, low toxic, low cost and low corrosion additive have become one of the most widely used flame retardants. However, its low fire retardant efficiency bring about the large dosage for better effect, which decreases significantly mechanical properties of materials, so its application is also limited[4,9,10].

The unique phosphorus and nitrogen hybrid structure and high phosphorus and nitrogen content of phosphazene make it a good flame retardancy and thermal stability[11]. Furthermore, it also has some merits such as less smoke, non-toxicity and non-corrosive gas formed when burning. So it has attracted widespread attention in academic community[12,13]. So far, a lot of phosphazene flame retardants have been developed, *e.g.*, *hexakis*(4-nitrophenoxy)cyclotriphosphazene[14], hexaglycidylcyclotriphosphazene[15], phenoxycyclotriphosphazene[16], hexa(ally4-hydroxybenzoate)cyclotriphosphazene[17], *etc*. Despite all this, but the commercialized phosphazenes are not much because of the difficult synthesis. Hexaamidocyclotriphosphazene is one of a few commercialized phosphazene flame retardants due to its good flame retardant effect and ease to preparation. However, due to its high solubility in water, its practical application has been strictly limited and only for the textile fibers[18]. The literature[19] reported that polyaminocyclophosphazene (PHACTPA) obtained by polycondensing hexaamidocyclotriphosphazene had lower water solubility and good flame retardant effect in poly(vinyl alcohol) fiber. However, the investigations about PHACTPA as a flame retardant for plastics haven't found. Many compounds containing phosphorus and nitrogen such as ammonium polyphosphate[20,21], melamine phosphate or melamine polyphosphate[22] have good flame retardancy in polyolefin. The phosphorus and nitrogen contents of PHACTPA are up to 40 and 50 % respectively, so it might also have a good flame retardancy in polyolefin. Therefore, we have investigated its flame retardancy in polyolefin and found that there is a synergistic effect between PHACTPA and 1,3,5-*tris*(2-hydroxyethyl)cyanurate (THEIC) as a charring agent[23,24]. In this paper, the synergistic flame retardancy in polyethylene was presented.

EXPERIMENTAL

Polyaminocyclotriphosphazene was prepared according to the lierature[25]. Polyethylene (PE) with trade mark of F600 was purchased from Petrochemical Ind, Co. Ltd., South Korea. The antioxidants of 1010 and 168 were provided by Beijing Jiyi Chemical Co. Ltd., China. 1,3,5-*Tris*(2-hydroxyethyl)-cyanurate was provided by Wuxi Kangaite Chemical Co. Ltd., China. All materials used in this work were of technical grade and were used without further purification.

Preparation of flame-retarded samples: Polyethylene, flame retardants, small amount of 1010 and 168 antioxidants were mixed in 170-180 °C in a JS30A twin-screw extruder (Yantai City Qitong Machinery Co. Ltd., China) with a rotor speed of 20-30 rpm. The well-mixed ingredients were cooled to ambient temperature and were mould-pressed into 100 mm × 100 mm × 3.2 mm sheets in 175-180 °C under 5 MPa by a 2G-10T press vulcanizer (Dongguan Zhenggong Mechanical and Electrical Equipment Technology Co., Ltd., China). The sheets were then cut into standard samples for the tests.

Flammability tests: Limiting oxygen index (LOI) was measured according to ASTM D 2863 with a JF-3 oxygen index meter (Jiangning Analytical Instrument Company, China). The specimens used were of dimensions 100 mm × 6.5 mm × 3.2 mm.

The vertical burning test was carried out as the procedure explained in UL 94 test standard with a CZF-3 horizontal and vertical burning tester (Jiangning Analytical Instrument Company, China) with specimens of 100 mm × 13 mm × 3.2 mm.

The cone calorimetric test was conducted with a FTT standard cone calorimeter (FTT Company, British) in external heat fluxes of 50 KW/m^2 with specimens of 100 mm × l00 mm × 3.2 mm according to ISO5660.

Thermogravimetric analysis and differential thermal analysis: Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) were conducted on a SDTQ600 thermogravimetric analyzer (TA Company, United States). Approximately 10 mg sample were examined in 150 μL alumina pans with a heating rate of 10 °C/min and air flow of 50 mL/min in a temperature range of 25 to700 °C.

Morphology analysis of the residues: The morphology of the residues obtained in the cone calorimeter test (CCT) was observed by a scanning electron microscopy (SEM, S-4800 Hitachi High-Tech Corporation, Japan).

^{31}P NMR spectra measurement: ^{31}P NMR spectra were acquired with an Advance 500 spectrometer (Bruker Corporation, Germany) with D_2O as a solvent, the sample was dissolved in 10 % sodium hydroxide solution with phosphoric acid as an internal standard, ^{31}P chemical shifts were referenced to phosphoric acid ($\delta = 0$ ppm).

Phosphorous content analysis: The content of phosphorous was measured by a gravimetric quimociac method[26].

RESULTS AND DISCUSSION

Limiting oxygen index and UL94 classification: As the loading of the flame retardants was 20 wt. % based on the total weight of the composites, effect of the formulation of the combinations of PHACTPA and THEIC was investigated. As can be seen in Table-1, the weight ratios of PHACTPA to THEIC have impact on the limiting oxygen index and vertical burning rating of the FR-PE. The limiting oxygen index value and the vertical burning UL 94 classification of the polyethylene increase first and then decrease with the increasing proportion of PHACTPA, when the weight ratio of PHACTPA and THEIC is 50:50, the limiting oxygen index is only 25.4 %, but the demanding V-0 classification can be reached, which reveals that there is a good synergistic effect between PHACTPA and THEIC.

In order to further study the flame retardancy of the combination, the effect of the dosage of the combination consisted of 50 wt. % PHACTPA and 50 wt. % (PHACTPA/THEIC) on

TABLE-1
INFLUENCE OF THE WEIGHT RATIO OF PHACTPA TO THEIC ON ITS FLAME RETARDANCY IN POLYETHYLENE

w(PHACTPA):w(THEIC)	Limiting oxygen index (%)	UL-94 class	Combustion phenomenon
0:100	17.4	No class	Severe burning, dripping
35:65	23.6	No class	Severe burning, dripping
50:50	25.4	FV-0	Difficult ignition, self-extinguishing, no drips
65:35	26.0	FV-1	Gentle burning, self-extinguishing, no drips
75:25	26.6	FV-2	Slightly severe burning, dripping
100:0	24.4	No class	Severe burning, dripping

TABLE-2
INFLUENCE OF THE DOSAGE OF PHACTPA/THEIC ON ITS FLAME RETARDANCY IN POLYETHYLENE

Dosage (wt. %)	Limiting oxygen index (%)	UL 94 class	Combustion phenomenon
0.0	17.4	No class	Severe burning, dripping
10.0	22.6	No class	Severe burning, dripping
15.0	23.7	No class	Severe burning, dripping
17.5	24.5	FV-2	Self-extinguishing, slow burning
20.0	25.4	FV-0	Difficult ignition, self-extinguishing

the limiting oxygen index and vertical burning classification of polyethylene was tested. As can be seen in Table-2, the limiting oxygen index increases gradually with the increasing dosage and the limiting oxygen index can be up to 25.4 % and the UL 94-V-0 can be passed as the dosage increases to 20 wt. %.

Cone calorimetric analysis: The typical heat release rate (HRR), total heat release (THR) and the mass curve of polyethylene and the FR-PE were given in Fig. 1 and the important cone calorimetry data were tabulated in Table-3. The results show that the fire behaviour of polyethylene is similar with the FR-PE with 20 wt. % THEIC, both of them burn fast after ignition and the typical heat release rate, mass loss rate and total heat release increase rapidly, the mass reduce quickly and the curve of heat release rate is characterized by a sharp peak, but the peak heat release rate (PHRR), the mean heat release rate (MHRR), total heat release and the mean effective heat of combustion (MEHC) of the former are much larger than that of the later, while the time to ignition of the former is less than the later. From above results, it can be seen that polyethylene is flammable and THEIC has poor flame retardancy in polyethylene. The fire behaviour of the FR-PE with 20 wt. % PHACTPA is similar with the FR-PE with 20 wt. % PHACTPA/THEIC. Compared with polyethylene, the total heat release, the peak heat release rate, the mean effective heat of combustion, mean mass loss rate and the mean heat release rate are reduced significantly, for the FR-PE with 20 wt. % PHACTPA by 46.07, 74.80, 38.74, 25.03 and 57.67 % respectively, while the FR-PE with 20 wt. % PHACTPA/THEIC by 48.17, 79.50, 37.71, 21.31 and 59.37 % respectively, the time to ignition is prolonged for 23 s and 21 s, respectively. From this, it can be concluded that PHACTPA and PHACTPA/THEIC have good flame retardancy in polyethylene. Furthermore, the mass of the FR-PE with PHACTPA/THEIC reduce more slowly than the FR-PE with PHACTPA, which reveals that PHACTPA/THEIC has better flame retardancy than PHACTPA.

Thermogravimetric analysis and differential thermal analysis: The thermogravimetric analysis and differential thermal analysis curves of flame retardants and the FR-PE were presented in Figs. 2 and 3 and the important TGA data were summarized in Table-4. As can be seen in Fig. 2, the initial thermal decomposition temperature ($T_{2\ wt.\ \%}$, the temperature at 2 % weight loss) of THEIC is 237 °C, the temperature of maximum weight loss rate (T_{max}) is 265 °C and no residue leaves in 700 °C. In spite of the $T_{2\ wt\ \%}$ of PHACTPA is only 70 °C due to the volatilization of absorbed water, the main decomposition occurres over 300 °C, the T_{max} is up to 656 °C and the residue in 700 °C is up to 27 %, which reveals that PHACTPA has better thermal stability. The $T_{2\ wt\ \%}$ of PHACTPA/THEIC consisted of 50 wt % PHACTPA and 50 wt % THEIC is 71 °C, the T_{max} is 335 °C, 17 % residue leaves in 700 °C.

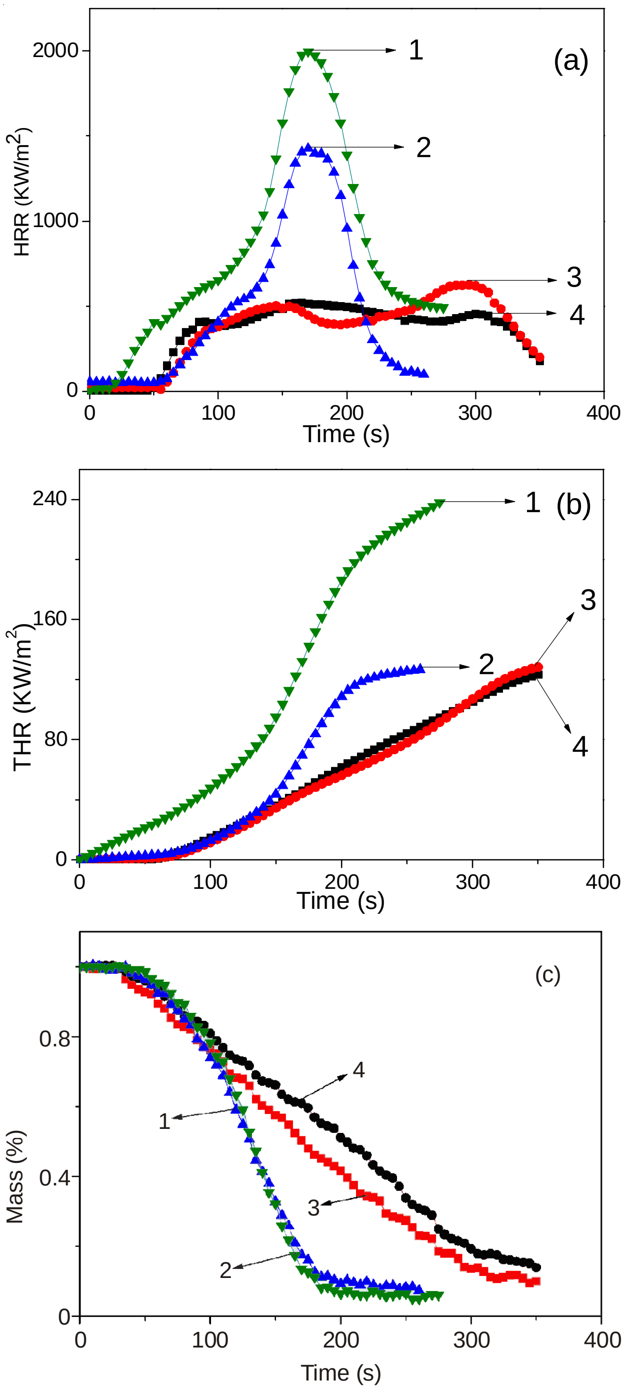

Fig. 1. Typical heat release rate (a), total heat release (b) and Mass (c) curves of polyethylene and the flame retarded polyethylene: (1) polyethylene, (2) the flame retarded polyethylene with 20 wt. % 1,3,5-*tris*(2-hydroxyethyl)cyanurate, (3) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene and (4) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene/1,3,5-*tris*(2-hydroxyethyl)cyanurate (50 wt. % PHACTPA and 50 wt. % THEIC)

TABLE-3
IMPORTANT CONE CALORIMETRIC DATA FOR POLYETHYLENE AND FLAME-RETARDED POLYETHYLENE

Term	PE	THEIC/PE	PHACTPA/PE	PHACTPA/THEIC/PE
THR (MJ/m^2)	237.9 ± 3	126.6 ± 1	128.3 ± 1	123.3 ± 2
PHRR (Kw/m^2)	1995 ± 11	1425 ± 10	502 ± 6and 625 ± 5	408 ± 5 and 521 ± 6
PHRR time (s)	170 ± 3	170 ± 2	145 ± 2 and 295 ± 3	165 ± 3 and 310 ± 3
MHRR (Kw/m^2)	858.0 ± 11	479.3 ± 8	363.2 ± 4	348.6 ± 6
PEHC (MJ/kg)	80 ± 0	80 ± 0	80 ± 0	80 ± 0
MEHC (MJ/kg)	58.6 ± 7	36.8 ± 2	35.9 ± 2	36.5 ± 2
MMLR (g/s)	0.0887 ± 0.0003	0.0952 ± 0.0003	0.0665 ± 0.0002	0.0698 ± 0.0003
TTI (s)	35 ± 1	52 ± 1	58 ± 1	56 ± 1
Combustion time (s)	275 ± 1	260 ± 2	350 ± 1	350 ± 1

THR = Total heat release; PHRR = Peak heat release rate; MHRR = Mean heat release rate; PEHC = Peak effective heat of combustion; MEHC = Mean effective heat of combustion; MMLR = Mean mass loss rate; TTI = Time to ignition

TABLE-4
THERMOGRAVIMETRIC RESULTS

Materials	$T_{2wt\,\%}$ (°C)	$T_{5wt\,\%}$ (°C)	$T_{10wt\,\%}$ (°C)	T_{max} (°C)	Residue in 700 °C (wt. %)
Polyethylene	284 ± 2	312 ± 3	353 ± 3	457 ± 2	1.1 ± 0.6
PHACTPA	70 ± 2	161 ± 2	239 ± 2	656 ± 3	27.0 ± 2
THEIC	237 ± 2	245 ± 3	252 ± 2	265 ± 2	0.3 ± 0.1
PHACTPA/THEIC*	71 ± 1	213 ± 2	271 ± 3	335 ± 2	17.0 ± 2
FR-PE with 20 wt. % PHACTPA	205 ± 2	335 ± 2	404 ± 3	462 ± 3	6.7 ± 0.8
FR-PE with 20 wt. % THEIC	281 ± 1	300 ± 2	336 ± 2	471 ± 2	0.8 ± 0.1
FR-PE with 20 wt. % PHACTPA/THEIC	207 ± 2	292 ± 2	338 ± 3	465 ± 2	5.2 ± 0.6

*Wight ratio of PHACTPA and THEIC was 50:50

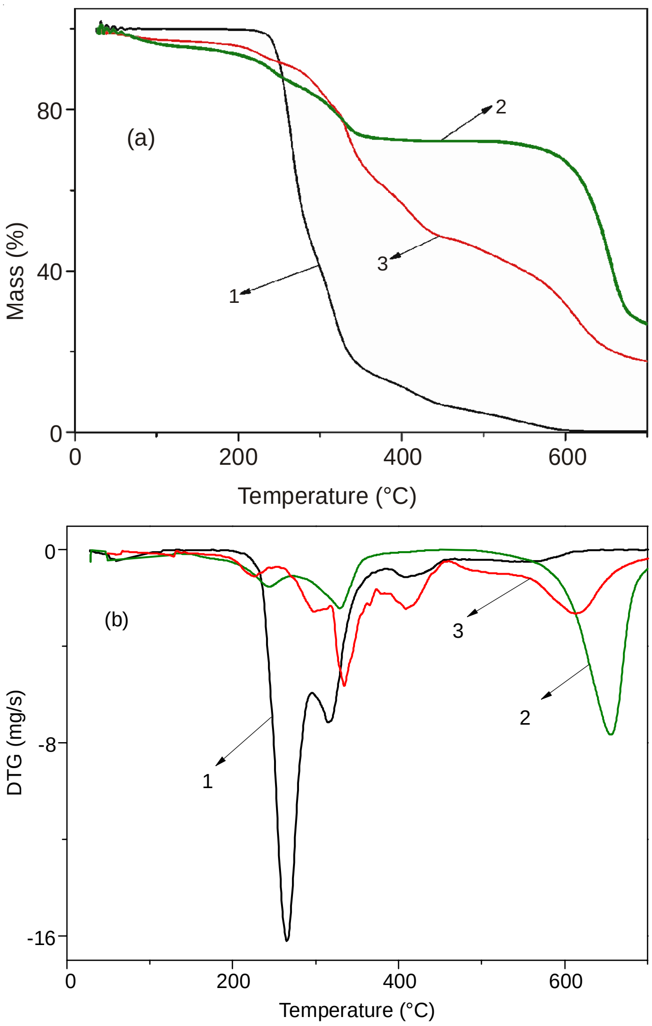

Fig. 2. Thermogravimetric analysis (a) and differential thermal analysis (b) curves of the various flame retardant: 1 1,3,5-*tris*(2-hydroxyethyl)-cyanurate, 2 polyaminocyclotriphosphazene and 3 polyaminocyclotriphosphazene/1,3,5-*tris*(2-hydroxyethyl)cyanurate

As can be seen in Fig. 3, polyethylene is initially decomposed in 284 °C and almost completely in 600 °C, which reveals that polyethylene has a bad char-forming character. The decomposition process of the FR-PE with 20 wt. % 1,3,5-*tris*(2-hydroxyethyl)cyanurate is similar with polyethylene, but the addition of 20 wt. % 1,3,5-*tris*(2-hydroxyethyl)cyanurate make the T_{max} of the main decomposition step increase from 457 °C to 471 °C. The mass loss of the FR-PE with 20 wt. % PHACTPA is much less than the polyethylene over 290 °C, 6.7 % residue leaves in 700 °C and the T_{max} of 462 °C for the main decomposition step is slightly higher than that of polyethylene (457 °C). The mass loss of the FR-PE with 20 wt. % PHACTPA/THEIC is higher than polyethylene blow 370 °C, but obviously less than polyethylene over 370 °C and the T_{max} of the main decomposition step is 465 °C, higher than that of polyethylene (457 °C) and the residues in 700 °C is 5.2 %. The above results indicate that adding PHACTPA or PHACTPA/THEIC improves the thermal stability of polyethylene and promotes the charring of polyethylene.

Fire retardancy mechanisms: The flame retardancy mechanism of PHACTPA and PHACTPA/THEIC in polyethylene was discussed by the analysis of residues of the FR-PE.

As can be seen in the photos of residues obtained in the cone calorimeter test shown in Fig. 4, the residues of polyethylene and the FR-PE with THEIC are hardly any, while the residues of FR-PE with PHACTPA and with PHACTPA/THEIC are much more and appear intumescent.

The SEM images of residues presented in Fig. 5 indicate that the smooth and dense layers are formed after the combustion of the FR-PE respectively with PHACTPA and the combination, but the residue with 20 wt. % the combination shows a more smooth and dense layer than that with 20 wt. % PHACTPA. On the basis of these results, it is proposed that the flame retardancy is caused by the barrier effect of the

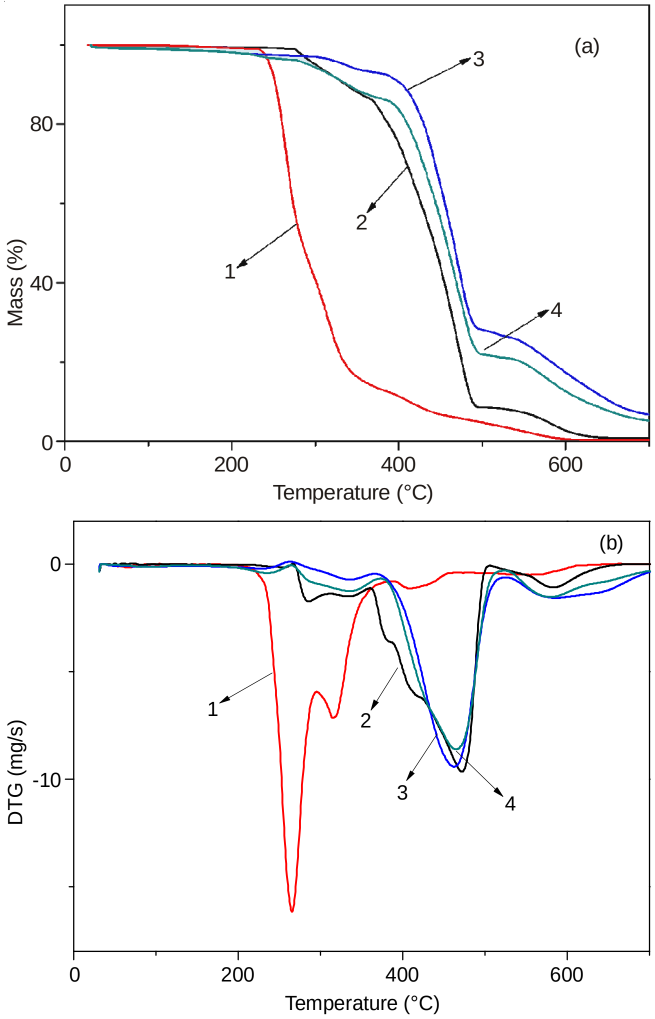

Fig. 3. Thermogravimetric analysis (a) and differential thermal analysis (b) curves of the flame retarded polyethylene: (1) polyethylene, (2) the flame retarded polyethylene with 20 wt. % 1,3,5-*tris*(2-hydroxyethyl)cyanurate, (3) the flame retarded polyethylene with 20 wt. % the polyaminocyclotriphosphazene and (4) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene/1,3,5-*tris*(2-hydroxyethyl)cyanurate

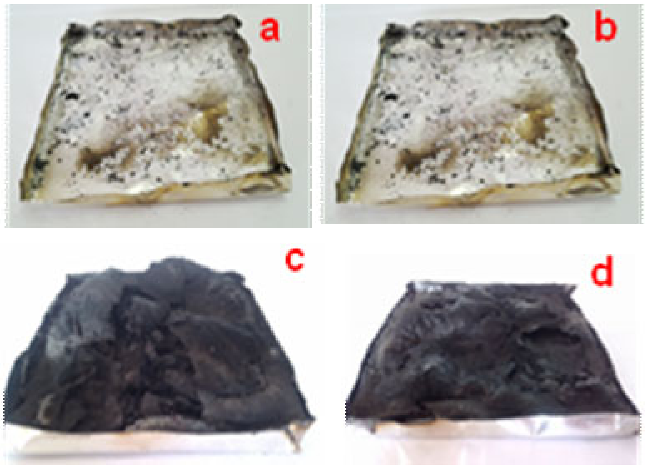

Fig. 4. Photos of the residues obtained in the cone calorimeter test: (a) polyethylene, (b) the flame retarded polyethylene with 20 wt. % 1,3,5-*tris*(2-hydroxyethyl)cyanurate, (c) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene and (d) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene/1,3,5-*tris*(2-hydroxyethyl)cyanurate.

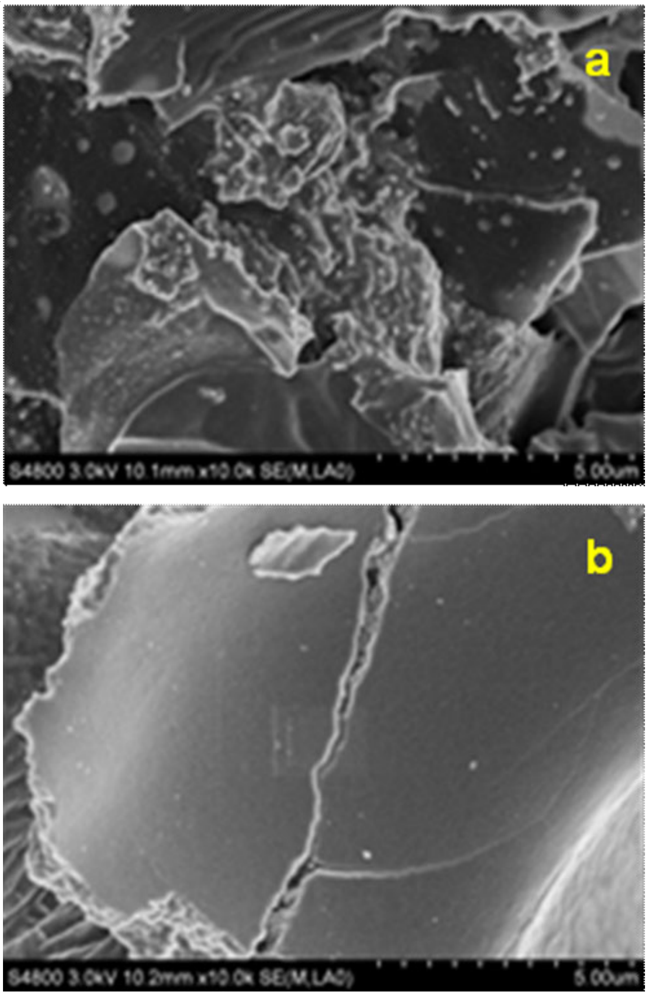

Fig. 5. Scanning electron microscope of the residues obtained in the cone calorimeter test: (a) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene and (b) the flame retarded polyethylene with 20 wt. % polyaminocyclotriphosphazene /1,3,5-*tris*(2-hydroxyethyl)cyanurate.

smooth and dense intumescent layers and the smoother and dense layers of the FR-PE with PHACTPA/THEIC bring about the better flame retardancy.

The residues of the FR-PE respectively with PHACTPA and the combination (the residues were dissolved in 10 wt. % sodium hydroxide solution) were characterized by ^{31}P NMR. Both of the main chemical shifts are around 5.8 ppm, which points to the dominant product of sodium phosphate (phosphoric acid compounds were converted into sodium phosphate in the presence of sodium hydroxide). The ^{31}P NMR spectra reveal that PHACTPA is converted into phosphoric acid compound such as phosphoric acid, metaphosphoric acid and the polyphosphoric acid in the process of combustion, which is consistent with the thermal degradation behavior of poly(diphenoyphosphazene)[27].

Based on the above results, it can be concluded that PHACTPA and PHACTPA/THEIC play a flame retardancy by a condensed phase mechanism, where PHACTPA is decomposed into non-volatile phosphoric acid compounds which promotes the carbonization of polyethylene and THEIC, inert gases such as CO_2 and N_2 released from the decomposition of polyaminocyclotriphosphazene, polyethylene and 1,3,5-

tris(2-hydroxyethyl)cyanurate foam the residues and result in the intumescent layers, which results in flame retardancy by the barrier effect on heat, air and decomposition products[28]. Combining THEIC promotes the decomposition of PHACTPA to phosphoric acid compounds, so improves the charring of polyethylene, which results in an excellent synergistic flame retardancy.

Conclusion

There is excellent synergistic flame retardancy between PHACTPA and THEIC in polyethylene, which results in the increased limiting oxygen index, improved vertical burning class, reduced peak heat release rate and heat release rate and slow mass loss of the FR-PE during the combustion. For example, the FR-PE alone with 20 wt. % PHACTPA or THEIC based on the total weight of the composites has the limiting oxygen index of 24.4 % and 17.4 %, respectively and vertical burning tests are failed, while the FR-PE with 20 wt. % PHACTPA/THEIC has the limiting oxygen index of 25.4 % and passes UL94 V-0 classification. Thermogravimetric analysis shows that adding PHACTPA or PHACTPA/THEIC can improve the thermal stability of polyethylene. The analysis of the residues obtained in the cone calorimeter test reveals that PHACTPA and PHACTPA/THEIC play flame retardancy mainly by a condensed phase mechanism, where PHACTPA is decomposed into non-volatile phosphoric acid compounds, which promotes the carbonization of polyethylene and the formed intumescent layer results in a flame retardancy by the barrier effect on heat, air and decomposition products. Combining THEIC promotes the decomposition of PHACTPA to phosphoric acid compounds and improves the charring of polyethylene, which results in an excellent synergistic flame retardancy.

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