Synergistic Flame Retardancy of Polyamino Cyclotriphosphazene and 1,3,5-*tris*(2-Hydroxyethyl)cyanurate in Polypropylene

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In this paper, the synergistic flame retardancy of polyamino cyclotriphosphazene and 1,3,5-*tris*(2-hydroxyethyl)cyanurate in polypropylene was studied by limiting oxygen index measurement, vertical burning test and cone calorimeter test. Thermal stability of flame retarded polypropylene (FR-PP) was investigated by thermogravimetric analysis and the mechanism was discussed by the residue analysis obtained in cone calorimeter test. The results showed that there was an excellent synergistic flame retardancy between polyamino cyclotriphosphazene (PHACTPA) and 1,3,5-*tris*(2-hydroxyethyl)cyanurate (THEIC) in polypropylene, which resulted in the increased limiting oxygen index, improved vertical burning class and reduced total heat release, peak heat release rate, the mean heat release rate, mean effective heat of combustion and mean mass loss rate. For example, the flame retarded polypropylene alone with 20 wt. % polyamino cyclotriphosphazene or 1,3,5-*tris*(2-hydroxyethyl)cyanurate based on the total weight of the composites had the limiting oxygen index of 25.2 and 18.7 %, respectively and did not pass UL94-0 class of the burning test, while the flame retarded polypropylene with 20 wt. % the combination consisted of 65 wt. % polyamino cyclotriphosphazene and 35 wt. % 1,3,5-*tris*(2-hydroxyethyl)cyanurate had the limiting oxygen index of 27.4 % and passed UL94-0 class. The thermogravimetric results indicated polyamino cyclotriphosphazene or polyamino cyclotriphosphazene/ 1,3,5-*tris*(2-hydroxyethyl)cyanurate improved the thermal stability of polypropylene. The residues obtained in cone calorimeter test showed that polyamino cyclotriphosphazene/1,3,5-*tris*(2-hydroxyethyl)cyanurate played a flame retardancy by a condensed phase mechanism. The polyamino cyclotriphosphazene was decomposed into non-volatile phosphoric acid compounds such as phosphoric acid, metaphosphoric acid and polyphosphoric acid in the process of combustion, which promoted the carbonization of polypropylene and inert gases such as CO_2, N_2 released from the thermal decomposition of polyamino cyclotriphosphazene, polypropylene and 1,3,5-*tris*(2-hydroxyethyl)cyanurate made the char layer foaming, the formed intumescent layer resulted in flame retardancy by the barrier effect on heat, air and decomposition products. Combining 1,3,5-*tris*(2-hydroxyethyl)cyanurate promoted the decomposition of polyamino cyclotriphosphazene to phosphoric acid compounds, so improved the charring of polypropylene and resulted in excellent synergistic flame retardancy.

Keywords: Flame retardancy, Polyamino cyclotriphosphazene, 1,3,5-*tris*(2-Hydroxyethyl)cyanurate, Polypropylene.

INTRODUCTION

Polypropylene (PP) is an important plastic commodity, but its usage is often limited because of its poor flame retardancy, so the studies on flame retarded polypropylene (FR-PP) have attracted considerable interests during the last decades. So far, halogen flame retardants has been broadly used as an effective flame retardant, but its application is more and more limited as they produce poisonous gases and cause second pollution, so there is a trend in the area of flame retardants to shift from halogen flame retardants to more environmentally friendly halogen-free flame retardants[1-3]. and some halogen-free flame retardants such as ammonium polyphosphate (APP), red phosphorus (RP) and metal hydroxides such as aluminium hydroxide and magnesium hydroxides, are more and more extensively used in polypropylene[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 and easy to recycle of the flame retarded material. 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 efficiency bring about the large dosage for better effect, which decreased significantly mechanical properties of materials, so its application is also limited[9,10].

Phosphazene is a class of chemical compound consisted of phosphorus and nitrogen atoms as the main chain with alternating single and double bond[11]. It is characterized by a highly effective flame retardancy and good thermal stability because of its unique phosphorus and nitrogen hybrid structure and high phosphorus and nitrogen content. Furthermore, it also has some merits such as less smoke, non-toxicity and non-corrosive gas when burning and so on[12,13]. So far, a number of phosphazene flame retardants have been developed, for example, *hexakis*(4-nitrophenoxy) cyclotriphosphazene[14], hexaglycidyl cyclotriphosphazene[15], phenoxycyclotriphosphazene[16], hexa(ally 4-hydroxybenzoate) cyclotriphosphazene[17] and so on. Despite all this, but the commercialized phosphazenes are not much because of the difficult synthesis. Hexaamidocyclotriphosphazene has high phosphorus, nitrogen content and good flame retardant effect, so that it has been one of the few commercial phosphazene as flame retardants. However, due to its high solubility in water, its practical application has been strictly limited and only for the textile fibers[18,19]. The literature[20] reported that polyamino cyclophosphazene (PHACTPA) obtained by polycondensing hexaamidocyclotriphosphazene had lower water solubility and good flame retardant effect in poly(vinyl alcohol) fiber. However, the investigation about PHACTPA as a flame retardant for plastics haven't found. For this reason, we have investigated its flame retardancy in polyolefin and found that there was a synergistic effect between PHACTPA and 1,3,5-*tris*(2-hydroxyethyl)-cyanurate (THEIC)[21,22]. In this paper, the synergistic flame retardancy in polypropylene was presented.

EXPERIMENTAL

Toluene was purchased from Wuhan Youji industries Co. LTD., China. The hexachlorocyctriphosphazene was provided by Zibo Lanyin Chemical Co. LTD., China. Ammonia was supplied by Qingdao Pengxin Gas Manufacturing Co. LTD., China. Polypropylene (PP) with trade mark of PPH-T03 was purchased from Petroleum & chemicals Co. Ltd., China. 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 and characterization of polyamino cyclotriphosphazene: To a 250 mL four-necked round-bottomed flask containing 150 mL of toluene equipped with a reflux condenser, the thermometer, mechanical stirrer and gas inlet tube was charged hexachlorocyctriphosphazene (17.40 g, 0.05 mol). The mixture was cooled to -5 – 0 °C with stirring using ice salt bath, then ammonia gas was introduced over a period of 24 h at the temperature range of -5 to 0 °C. The white powder consisted of hexaamidocyclotriphosphazene and the by-product ammonium chloride was obtained by filteration and drying. The above powder was heated in an thermostatic oven in 180-185 °C for 0.5 h, then cooled to the room temperature. The content was dispersed in 30 mL deionized water and stirred for 10 min, then filtered. The cake was washed twice with additional 15 mL × 2 deionized water, then dried to constant weight at 105-110 °C to afford 9.95 g of PHACTPA
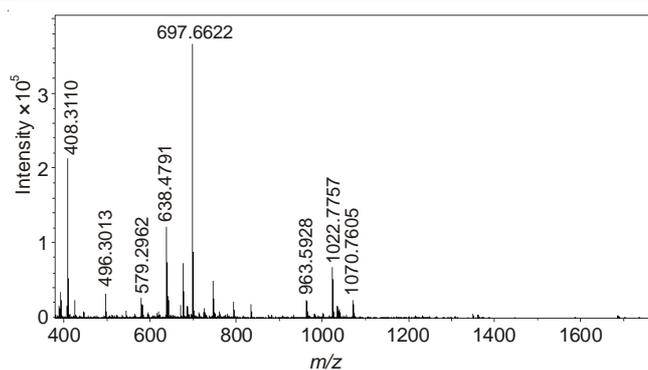

Fig. 1. Mass spectra of polyamino cyclotriphosphazene

as a white solid. Elemental analysis: P, 43.38 %; N, 50.89 %; H, 3.68 %; Cl, 2.05 %, the solubility of PHACTPA was 1.05 g/100 mL water and the hygroscopicity in 50-60 % relative humidity was 5.9 %. Mass spectra shown in Fig. 1 indicated that the product was composed of dimer, trimer, tetramer and pentamer of aminocyclotriphosphazene mainly, with the relative molecular weight of 400-1100.

Preparation of flame-retarded samples: Polypropylene, flame retardants, small amount of 1010 and 168 antioxidants were mixed in 180°-190° 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 $100 \times 100 \times 3.2$ mm³ sheets at 185°-190° under 5 MPa by 2G-10T press vulcanizer (Dongguan Zhenggong Mechanical and Electrical Equipment Technology Co., LTD., China). The sheets were then cut into standard samples for flame retardant test.

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 for the limiting oxygen index test were of dimensions 100 mm × 6.5 mm × 3.2 mm. The flame retardant efficiency (EFF) and synergistic efficiency (SE) were calculated according to literatures[23,24].

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

The cone calorimeter test was conducted with a FTT standard cone calorimeter (FTT company, British) in external heat fluxes of 50 kW/m² with specimens of 100 mm × l00 mm × 3.2 mm according to ISO5660. Each formulation was tested repeatedly for three times.

Thermogravimetric and differential thermal analysis: Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) were performed on a SDTQ600 thermogravimetric analyzer (TA company, United States). Approximately 8 mg samples were examined in an alumina crucible (6 mm in diameter and 13 mm in height)with a heating rate of 10 °C/min and air flow of 50 mL/min in a temperature range from 25 to 700 °C.

Charaterization of the residue and the product: The morphology of the residue obtained in the cone calorimeter test was observed by scanning electron microscopy (SEM, S-4800 Hitachi High-Tech Corporation, Japan).

Infrared spectra of the residue was measured by potassium bromide pellet technology using a TENSOR-27 IR spectrometer (Bruker Corporation, Germany).

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

The mass spectra (MS) analysis was carried out by using SURVEYOR PLUS LC-LTQXL Mass spectrometer (Thermo Electron, United states).

The content of phosphorous was measured by the gravimetric quimociac method according to ISO6598. To a 100 mL iodine flask containing 15 mL 10 % nitric acid solution equipped with a reflux condenser was charged 0.5000 g sample. The content was boiled for a few minutes using a heating jacket, then 35 mL quimociao was added, subsequently cooled to room temperature and stand for 0.5 h for the precipitation. Then the precipitation was followed by the procedure of filtration, drying and weighing. The content of phosphorous was calculated according to the formula presented in ISO6598.

The content of chlorine was measured by mercurimetric method according to ISO2463. To a 100 mL iodine flask containing 10 mL 35 % nitric acid solution equipped with a reflux condenser was charged 1.0000 g sample, the content was boiled with a heating jacket for about 1 h, then the solution was cooled to room temperature and the chlorine ions was titrated with a mercury nitrate solution using diphenylcarbazone as an indicator.

The content of H and N was measured by the automatic analysis by Vairo EL Elemental analysis (Elementar Analysensystem Gmbh, Germany).

RESULTS AND DISCUSSION

Limiting oxygen index tests and UL94 classification: As the loading of the flame retardants was 20 wt. % based on the total weight of the composites, the effect of the formulation of the combinations of PHACTPA and THEIC was investigated.

As could be seen in Table-1, the weight ratios of PHACTPA to THEIC had impact on the limiting oxygen index and vertical burning property of the flame retarded polypropylene (FR-PP). The limiting oxygen index value, flame retardant efficiency and the vertical burning UL94 classification of the flame retarded polypropylene increased first and then decreased with the increasing proportion of PHACTPA. The limiting oxygen index and flame retardant efficiency of the flame retarded polypropylene alone with THEIC was only 18.7 % and 0, respectively and vertical burning test was failed, the limiting oxygen index and flame retardant efficiency of the flame retarded polypropylene alone with PHACTPA was 25.2 % and 0.33 and the demanding V-1 classification could be achieved. while the limiting oxygen index, synergistic efficiency and flame retardant efficiency of the flame retarded polypropylene with the combination consisted of 65 wt. % PHACTPA and 35 wt. % THEIC could be up to 27.4 %, 0.39 and 1.18, respectively and the demanding V-0 classification could be reached. Therefore, it could be concluded that there was an obvious synergistic flame retardancy between PHACTPA and THEIC under appropriate weight ratio.

In order to further study the flame retardancy of the combination, the effect of the dosage of the combination consisted of 65 wt. % PHACTPA and 35 wt. % THEIC on the limiting oxygen index and vertical burning property of the polypropylene was investigated. As could be seen in Table-2, the limiting oxygen index increased gradually with the increasing dosage and the limiting oxygen index could be up to 27.4 and V-0 could be passed as the dosage increased to 20 %.

Cone calorimetry analysis: The heat release rate (HRR), mass loss rate (MLR), total heat release (THR) and the mass curve of polypropylene and the flame retarded polypropylene were respectively illustrated in Figs. 2-5 and the important cone calorimetry data were tabulated in Table-3. It could be seen that the fire behaviour of polypropylene was similar with the flame retarded polypropylene with 20 wt. % THEIC, both of them burned fastly after ignition and the heat release rate (HRR), mass loss rate (MLR) and total heat release increased

TABLE-1
INFLUENCE OF THE WEIGHT RATIO PHACTPA TO THEIC ON ITS FLAME RETARDANCE IN POLYPROPYLENE

w(PHACTPA):w(THEIC)	Limiting oxygen index (%)	UL-94	EFF	SE
0:100	18.7	No	0.00	-
20:80	20.4	No	0.09	-
25:75	22.6	No	0.20	-
35:65	26.4	V-0	0.39	1.18
50:50	27.0	V-0	0.42	1.27
65:35	27.4	V-0	0.44	1.34
75:25	27.4	V-1	0.44	1.34
80:20	26.6	V-1	0.40	1.21
100:0	25.2	V-1	0.33	-

EFF: Flame retardant efficiency; SE: Synergistic efficiency

TABLE-2
INFLUENCE OF THE DOSAGE OF PHACTPA/THEIC ON ITS FLAME RETARDANCE IN POLYPROPYLENE

Dosage (%)	Limiting oxygen index (%)	UL-94 class	Combustion phenomenon
10.0	23.2	No	Severe burning, dripping
12.5	24.8	No	Severe burning, dripping
15.0	26.6	No	Severe burning, dripping
17.5	26.8	V-1	Gentle burning, self-extinguishing
20.0	27.4	V-0	Difficult ignition, self-extinguishing

rapidly, the mass reduced quickly and the curves of HRR and MLR were characterized by a sharp peak, but the peak heat release rate (PHRR), the mean heat release rate (MHRR), total heat release (TRR), the mean effective heat of combustion (MEHC) and the mean mass loss rate (MMLR) of the former were much larger than that of the later, while the time to ignition of the former was less than the later. From above results, it could be seen that polypropylene was flammable and THEIC had a poor flame retardancy in polypropylene. The fire behaviour of the flame retarded polypropylene with 20 wt. % PHACTPA was similar with the flame retarded polypropylene with 20 wt. % PHACTPA/THEIC, both of them burned slowly after ignition and the HRR, MLR and total heat release increased slowly, the mass reduced slowly, the HRR curves were characterized by a broad peak and compared with polypropylene, the total heat release, PHRR, MHRR and MEHC of the flame retarded polypropylene were reduced significantly, for the flame retarded polypropylene with 20 wt. % PHACTPA/THEIC by 57.11, 86.5, 76.59 and 32.87 % respectively, while the flame retarded polypropylene with 20 wt. % PHACTPA

Fig. 4. Total heat release curves of polypropylene and the flame retarded polypropylene: (1) polypropylene; (2) flame retarded polypropylene with 20 % PHACTPA; (3) flame retarded polypropylene with 20 % THEIC; (4) flame retarded polypropylene with 20 % the combination
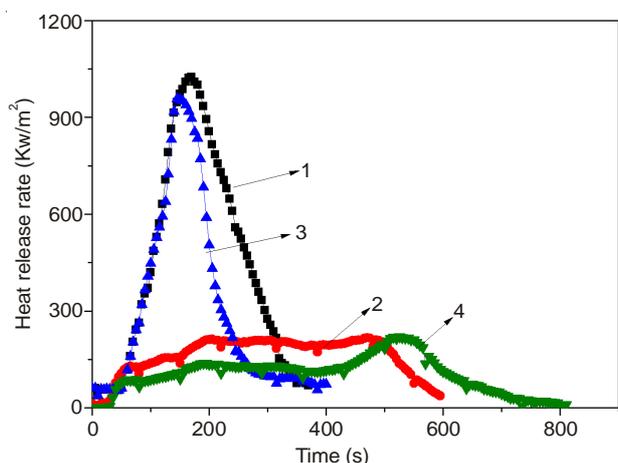

Fig. 2. Heat release rate curves of polypropylene and the flame retarded polypropylene: (1) polypropylene; (2) flame retarded polypropylene with 20 % PHACTPA; (3) flame retarded polypropylene with 20 % THEIC; (4) flame retarded polypropylene with 20 % the combination consisted of 65 and 35 wt. %

Fig. 5. Mass curves of polypropylene and the flame retarded polypropylene: (1) polypropylene; (2) flame retarded polypropylene with 20 % PHACTPA; (3) flame retarded polypropylene with 20 % THEIC; (4) flame retarded polypropylene with 20 % the combination
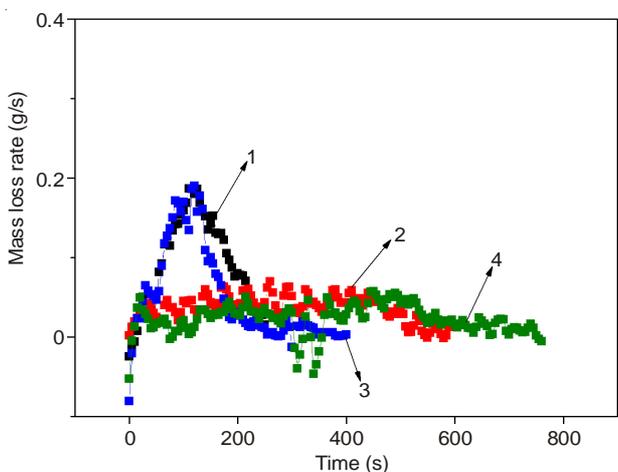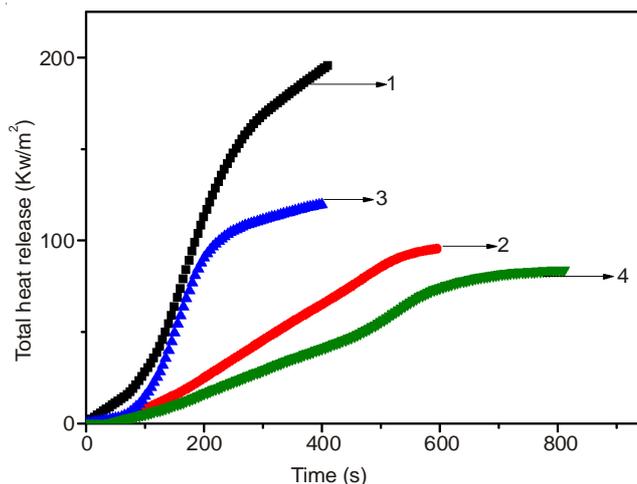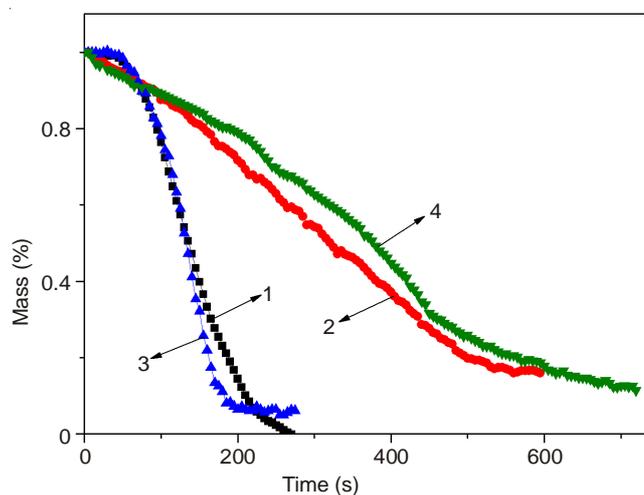

Fig. 3. Mass loss rate curves of polypropylene and the flame retarded polypropylene: (1) polypropylene; (2) flame retarded polypropylene with 20 % PHACTPA; (3) flame retarded polypropylene with 20 % THEIC; (4) flame retarded polypropylene with 20 % the combination

by 51.18, 79.30, 63.75 and 29.63 %, respectively. Furthermore, The mass of the flame retarded polypropylene with PHACTPA/THEIC reduced more slowly than the flame retarded polypropylene with PHACTPA. The above results revealed that PHACTPA/THEIC had better flame retardancy than PHACTPA in polypropylene.

Thermogravimetric analysis and differential thermal analysis: Thermogravimetric results of flame retardants and flame retarded polypropylene were presented in Figs. 6 and 7, respectively and the TGA data were summarized in Table-4. As could be seen in Fig. 6, the decomposition of THEIC was characterized by a single decomposition step and leaving no residue and the initial thermal decomposition temperature (the temperature for 2 % mass loss, $T_{2wt. \%}$) was 237 °C, the temperature of maximum mass loss rate (T_{max}) was 265 °C. Compared with THEIC, PHACTPA had the lower initial thermal decomposition temperature with 70 °C due to the volatilization of absorbed water, but the main decomposition occurred over 300 °C, the T_{max} was up to 656 °C and the residue in 700 °C

TABLE-3
CONE CALORIMETRY DATA FOR POLYPROPYLENE AND FLAME RETARDED POLYPROPYLENE

Term	PP	THEIC/PP	PHACTPA/PP	PHACTPA/THEIC/PP
THR (MJ/m^2)	195.4 ± 3	119.7 ± 1	95.4±2	83.8±1
PHRR (Kw/m^2)	1024 ± 11	956 ± 10	212 ± 6	138 ± 5
PHRR, time (s)	170 ± 3	145 ± 2	205 ± 3	190 ± 3
MHRR (Kw/m^2)	439.2 ± 11	296.3 ± 8	159.2 ± 6	102.8 ± 4
PEHC (MJ/kg)	80 ± 0	80 ± 0	80 ± 0	80 ± 0
MEHC ((MJ/kg)	52.42 ± 7	41.28 ± 2	36.89 ± 2	35.19 ± 2
MMLR (g/s)	0.0678 ± 0.0003	0.0614 ± 0.0003	0.0366 ± 0.0003	0.0349 ± 0.0002
TTI (s)	31 ± 1	40 ± 1	59 ± 1	58 ± 1
Combustion time (s)	370 ± 1	400 ± 2	590 ± 1	810 ± 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
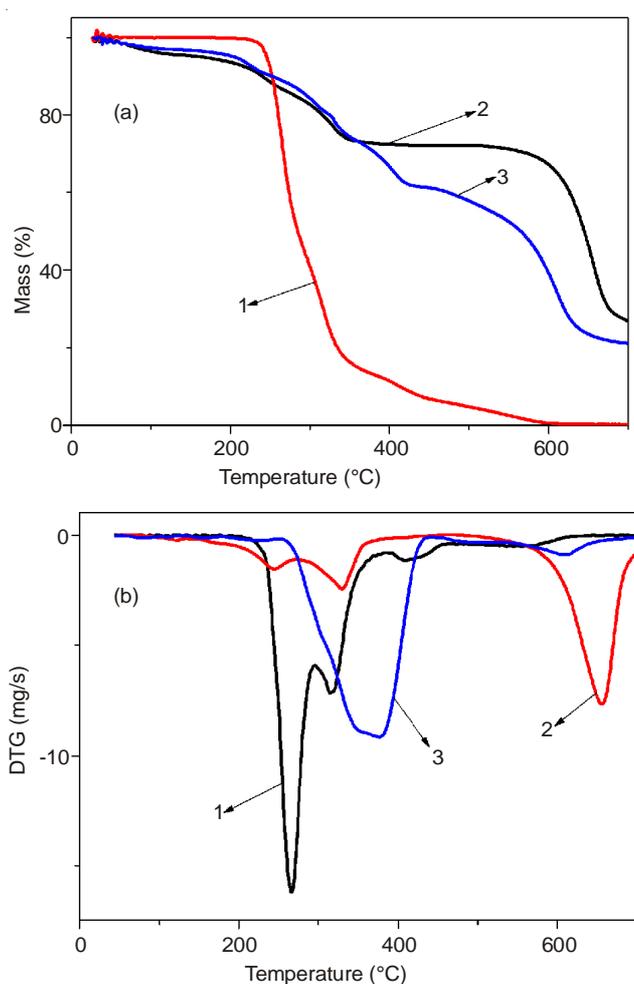

Fig. 6. TGA (a) and DTG (b) curves of the various flame retardants: (1) THEIC; (2) PHACTPA; (3) combination consisted of 65 wt. % PHACTPA/35 wt. % THEIC

was 27 %, which revealed that PHACTPA had better thermal stability. The combination consisted of 65 wt. % PHACTPA and 35 wt. % THEIC also had a good thermal stability with the $T_{2wt. \%}$ of 71 °C and the residue of 21 % in 700 °C and T_{max} of 368 °C.

As could be seen in Fig. 7, polypropylene was initially decomposed in 282 °C and almost completely in 410 °C with negligible residue, which indicated that the polypropylene had a poor charring character. Thermal behaviour of the flame retarded polypropylene with 20 wt. %THEIC was similar with polypropylene, but the addition of 20 wt. % THEIC made the T_{max} of the main decomposition step increase from 369 to 381 °C. Although the addition of 20 wt. % PHACTPA reduced obviously the $T_{2wt \%}$, $T_{5wt \%}$ and T_{max} of polypropylene, but increased markedly its mass residue over 300 °C. The thermal decomposition characteristics of the flame retarded polypropylene with 20 wt. % PHACTPA/THEIC was similar with the flame retarded polypropylene with 20 wt. % PHACTPA, but the $T_{2wt \%}$ and T_{max} of the former was obviously higher than the later. In addition, the mass loss of the flame retarded polypropylene with 20 wt. % PHACTPA/THEIC was higher than polypropylene blow 310 °C, but obviously less than polypropylene over 310 °C, and its T_{max} was 382 °C and the residue in 700 °C was 7.71 %, which were much higher than that of polypropylene. The above results indicated that adding PHACTPA or PHACTPA/ THEIC improved the thermal stability of polypropylene and promoted the charring of polypropylene.

Fire retardancy mechanism: The flame retardancy mechanism of PHACTPA and PHACTPA/THEIC in polypropylene was discussed by the residue analysis of the flame retarded polypropylene.

As could be seen in the images of residues obtained in the cone calorimeter test shown in Fig. 8, the residue of

TABLE-4
THERMOGRAVIMETRIC RESULTS

Materials	$T_{2wt\%}$ (°C)	$T_{5wt\%}$ (°C)	$T_{10wt\%}$ (°C)	T_{max} (°C)	Residue in 700 (°C) (wt. %)
Polypropylene	282 ± 2	292 ± 3	303 ± 3	369 ± 2	0.08 ± 0.6
PHACTPA	70 ± 2	161 ± 2	239 ± 2	656 ± 3	27.00 ± 2
THEIC	237 ± 2	245 ± 3	252 ± 2	265 ± 2	0.30 ± 0.1
Combination*	71 ± 1	203 ± 2	251 ± 3	368 ± 2	21.10 ± 2
Flame retarded PP with 20 wt. % PHACTPA	138 ± 2	282 ± 2	302 ± 3	356 ± 3	7.50 ± 0.8
Flame retarded PP with 20 wt. % THEIC	282 ± 1	294 ± 2	307 ± 2	381 ± 2	0.69 ± 0.1
Flame retarded PP with 20 wt. % the combination	195 ± 2	282 ± 2	299 ± 3	382 ± 2	7.71 ± 0.6

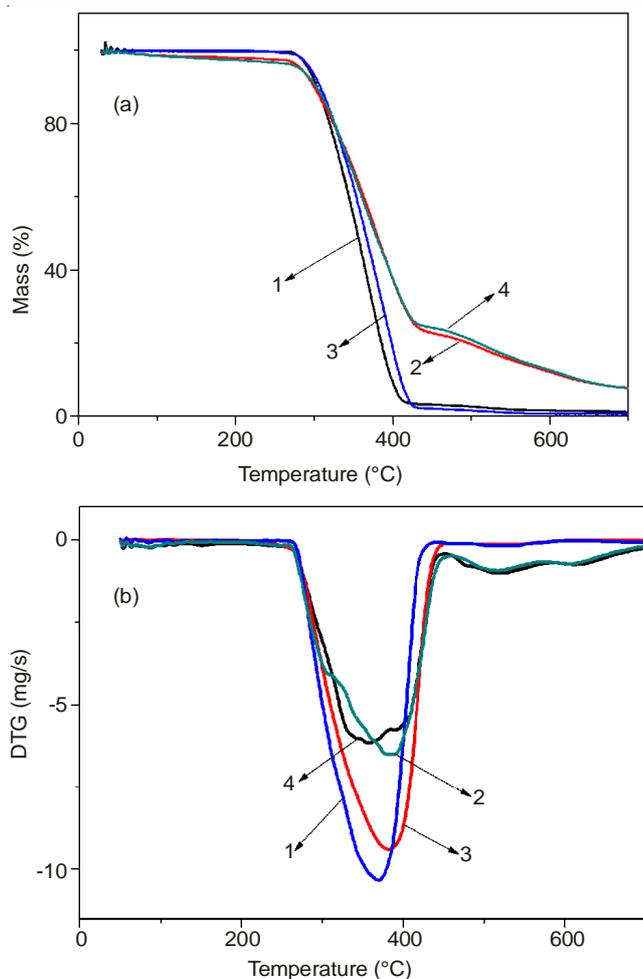*Weight ratio of PHACTPA/THEIC was 65/35

Fig. 7.   TGA (a) and DTG (b) curves of the flame retarded polypropylene: (1) polypropylene; (2) flame retarded polypropylene with 20 wt. % the combination; (3) flame retarded polypropylene with 20 wt. % THEIC; (4) flame retarded polypropylene with 20 wt. % PHACTPA
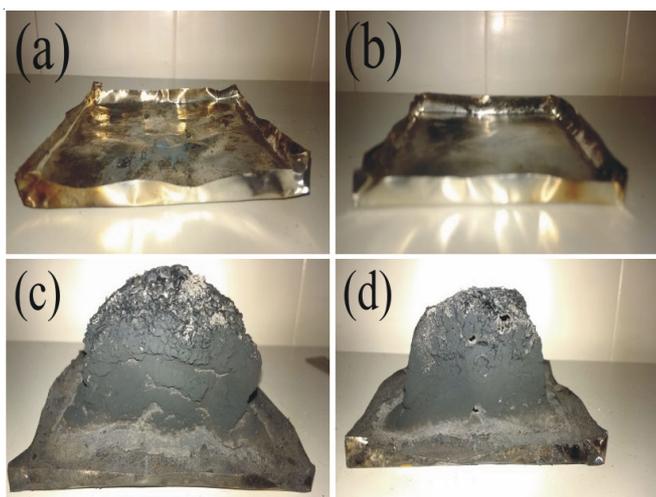

Fig. 8.   Images of the residues obtained in the cone calorimeter test: (a) polypropylene; (b) flame retarded polypropylene with 20 wt. % THEIC; (c) flame retarded polypropylene with 20 wt. % PHACTPA; (d) flame retarded polypropylene with 20 wt. % combination

polypropylene and the flame retarded polypropylene with THEIC were hardly any, while the intumescent residues were formed for flame retarded polypropylene with PHACTPA and with PHACTPA/THEIC.

The SEM pictures of the residues obtained in the cone calorimeter test were shown in Fig. 9, which indicated that the residue of flame retarded polypropylene with the combination was more smooth and dense than the residue with 20 wt. % PHACTPA, On the basis of these results, it was proposed that the flame retardancy was caused by the barrier effect of the intumescent layers and the more smooth and dense layers for the flame retarded polypropylene with PHACTPA/THEIC brought about the better flame retardancy.
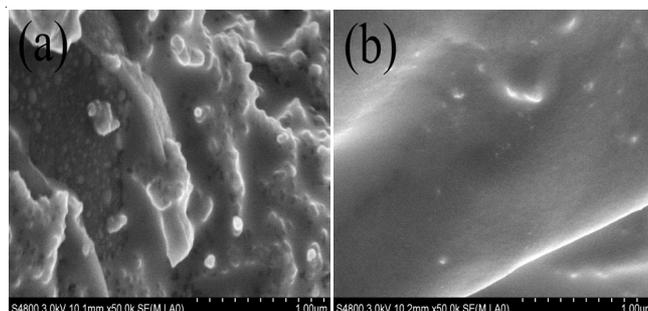

Fig. 9.   SEM of the residues obtained in the cone calorimeter test: (a) flame retarded polypropylene with 20 wt. % PHACTPA; (b) flame retarded polypropylene with 20 wt. % combination

As could be seen in Fig. 10, the ^{31}P NMR spectra of the residue of the flame retarded polypropylene with 20 wt. % PHACTPA was similar with that with 20 wt. % the combination (the residues were dissolved in 10 wt. % sodium hydroxide solution). The main signal around 5.8 ppm points to an dominate product of sodium phosphate (phosphoric acid compounds was converted into sodium phosphate in the presence of sodium hydroxide).
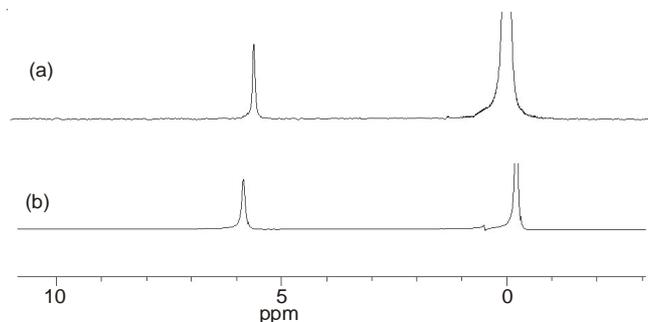

Fig. 10. ^{31}P NMR of the residue of the flame retarded polypropylene:(a) flame retarded polypropylene with 20 wt. % PHACTPA; (b) flame retarded polypropylene with 20 wt. % the combination

The IR spectra of the residues of the flame retarded polypropylene with 20 wt. % PHACTPA and with 20 wt. % the combination showed the nearly same absorption, where the absorption peak at 1000 and 510 cm^{-1} were ascribed to the stretching vibration and bend vibration of P-O, respectively, the absorption peak at 1651cm^{-1} was ascribed to the bonds stretching vibration of P=O, at 1420 cm^{-1} was ascribed to the bend vibration of N-H, the broad peak from 3151 to 3196 cm^{-1} were ascribed to the stretching vibration of N-H, which suggested that the residues contained phosphate radical and amino group.

The above IR spectra and ^{31}P NMR spectra revealed that PHACTPA was converted into phosphoric acid compound such

Sample	Residue (%)	P (%)		N (%)	
		Content	Residue	Content	Residue
Flame retarded polypropylene with PHACTPA	9.04	25.02	21.75	2.96	3.26
Flame retarded polypropylene with the combination	13.79	24.25	48.21	3.07	6.48

TABLE-5
ANALYSIS RESULTS OF THE RESIDUES

as phosphoric acid, metaphosphoric acid and the polyphosphoric acid in the process of combustion.

As shown in Table-5, the residue rate of the flame retarded polypropylene with the combination and with PHACTPA were 13.79 and 9.04 %, respectively. Phosphorus content in the residues were 24.25 and 25.02 %, respectively, the corresponding residue rates were up to 48.21 and 21.75 %, respectively.

It could be concluded that PHACTPA and PHACTPA/ THEIC played a flame retardancy by a condensed phase mechanism, where PHACTPA was decomposed into non-volatile phosphoric acid compounds which promoted the carbonization of polypropylene and THEIC, inert gases such as CO_2 and N_2 released from the decomposition of PHACTPA, polypropylene and THEIC foamed the residues and resulted in the intumescent layers and the intumescent layer resulted in flame retardancy by the barrier effect on heat, air and decomposition products[25,26]. Combining THEIC promoted the decomposition of PHACTPA to phosphoric acid compounds, so improved the charring of polypropylene, which resulted in an excellent synergistic flame retardancy. In addition, the lower residual rate of P implied that the decomposition products of PHACTPA were partially vaporized to gaseous phase in the process of combustion, which resulted in a flame retardancy by flame inhibition[27]. CO_2 and N_2 released from the decomposition of PHACTPA, polypropylene and THEIC also showed some fuel dilution effects[28].

Conclusion

There was an excellent synergistic flame retardancy between PHACTPA and THEIC in polypropylene, which resulted in the increased limiting oxygen index, improved vertical burning class and reduced total heat release, PHRR, MHRR, MEHC and MMLR of the flame retarded polypropylene. For example, the flame retarded polypropylene alone with 20 wt. % PHACTPA or THEIC based on the total weight of the composites had the limiting oxygen index of 25.2 and 18.7 %, respectively and failed UL94-V-0 classification of the burning test, while the polypropylene with 20 wt. % the combination consisted of 65 wt. % PHACTPA and 35 wt. % THEIC had the limiting oxygen index of 27.4 % and passed UL94-V-0 classification. The thermogravimetric results indicated PHACTPA or PHACTPA/THEIC improved the thermal stability of polypropylene. The analysis of the residues obtained in the cone calorimeter test showed that PHACTPA and PHACTPA/ THEIC played a flame retardancy by a condensed phase mechanism, where PHACTPA was decomposed into non-volatile phosphoric acid compounds such as phosphoric acid, metaphosphoric acid and polyphosphoric acid and promoted the carbonization of polypropylene and the formed intumescent layer resulted in flame retardancy by the barrier effect on heat, air and decomposition products. Combining THEIC promoted

the decomposition of PHACTPA to phosphoric acid compounds improving the charring of polypropylene, which resulted in excellent synergistic flame retardancy.

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