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Flame Retardancy of Aluminium Dipropylphosphinate in Combination with Melamine Polyphosphate in Polyamide

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In this paper, the flame retardancy of aluminium dipropylphosphinate in combination with melamine polyphosphate in polyamide 6 was studied by the limiting oxygen index measurement, the vertical burning test and the cone calorimeter test and the mechanism was also discussed by residural analysis. It was concluded that there was no synergistic flame retardancy between aluminium dipropylphosphinate and melamine polyphosphate in polyamide 6. The flame retarded polyamide 6 with 15 wt. % aluminium dipropylphosphinate received a V-0 classification in UL 94 tests and had an increased limiting oxygen index value of 30.7 %, while the flame retarded polyamide 6 with 15 wt. % aluminium dipropylphosphinate/melamine polyphosphate (the weight ratios of aluminium dipropylphosphinate to melamine polyphosphate being 65:35) only achieved a V-2 classification with a limiting oxygen index of 27 % and the mass of the former decreased faster and the peak heat release rate, average heat release rate, average effective heat of combustion and total heat release were higher than the later. In addition, aluminium dipropylphosphinate/melamine polyphosphate had greater influence on the thermal stability of the composites than aluminium dipropylphosphinate and melamine polyphosphate. Fortunately, the combination of aluminium dipropylphosphinate and melamine polyphosphate was more economical because melamine polyphosphate was much cheaper than aluminium dipropylphosphinate. The analysis of the residues obtained in cone calorimeter test showed that aluminium dipropylphosphinate played the role of flame retardancy by gaseous and condensed phase mechanisms, on the one hand, aluminium dipropylphosphinate was decomposed into non-volatile aluminum phosphate and promoted the carbonization of polyamide 6 and the formed intumescent layer resulted in flame retardancy by the barrier effect on heat, air and decomposition products. On the other hand, it was decomposed into volatile phosphorus compounds which brought about flame retardancy by flame inhibition. Although the residues amount of polyamide 6 containing aluminium dipropylphosphinate/melamine polyphosphate was significantly increased, but the resulting loose non-intumescent layer by combining melamine polyphosphate weaken the fire retandancy of the materials.

Keywords: Aluminium dipropylphosphinate, Melamine polyphosphate, Flame retardancy, Polyamide 6.

INTRODUCTION

The alkylphosphinates developed by Clariant company (Germany) have some merits such as low toxicity and smoke density, high comparative tracking index (CCT), good thermal stability and efficient flame retardancy, especially used as a flame retardant for polyamides, polyesters and epoxy resin[1-3]. Although the dialkylphosphinate are only moderately efficient in nylons, they were found synergistic effect with some nitrogen-containing products like melamine[4], melamine cyanurate[5,6], melamine phosphate or melamine polyphosphate[7-9]. For example, aluminium phosphinates in glass-fibre reinforced polyamide 6,6 is satisfactorily effective only on rather high loadings of 30 wt. %[10]. The phosphinate dosage can be reduced to about 10 wt % in the presence of melamine polyphosphate[8].

So far, Clariant products and most investigations about the phosphinate flame retardants are based on diethylphosphinates, but they are more difficult to production due to high pressure for ethylene liquefaction which results in storage and transportation difficulties. Taking into account that the propylene is easy liquefaction, so that its storage and transportation are more convenient and its price is cheaper and its supply is more abundant than ethylene. We have developed aluminium dipropylphosphinate and commercialized in Shandong Brothers Science and Technology Co. Ltd., China and found that it has a good flame retardancy in polyamide 6 and an excellent synergistic effect with melamine[4]. However, it has no obvious synergistic flame retardancy with melamine cyanurate[11], even no synergistic effect with melamine polyphosphate. In this work, the flame retardancy and its mechanisms of aluminium dipropylphosphinate in combination with melamine polyphosphate in polyamide 6 were reported.

EXPERIMENTAL

Polyamide 6 (PA6) was provided by Shijiazhuang Refining & Chemical Co. China. The aluminium dipropylphosphinate

(ADPP) was provided by Shandong Brothers Science and Technology Co.LTD.,China. The melamine polyphosphate (MPP) was provided by Shouguang Weidong Chemical Co.LTD.,China. The antioxidants of 1010 and 168 were provided by Beijing Jiyi 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: Polyamide 6, flame retardants, small amount of 1010 and 168 antioxidants were mixed at *ca.* 230 ºC 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 × 4 mm sheets at 220-230 ºC 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 flame retardant test.

Flammability tests: Limiting oxygen index (LOI) was measured according to ASTMD 2863 with a JF-3 oxygen index meter (Jiangning Analytical Instrument Company, China). The specimens with a size of 100 mm × 6.5 mm × 4 mm were used.

The vertical burning test was carried out on a CZF-3 horizontal and vertical burning tester (Jiangning Analytical Instrument Company, China) with specimens with a size of 100 mm × 13 mm × 4 mm according to the UL 94 test standard.

The cone calorimeter 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 × 4.0 mm according to ISO5660.

Thermogravimetric analysis: Thermogravimetric experiments were performed using a SDTQ600 thermogravimetric analyzer (TA company, United States) with a nitrogen flow of 50 mL/min.The samples (*ca.* 10 mg) were heated in150 µL alumina pans at a heating rate of 10 ºC/min.

Morphology analysis of the residues : The morphology of the residue obtained in the cone calorimeter test was observed by a scanning electron microscopy (SEM, Model JSM-6700F Jeol, Japan).

Phosphorous content analysis: The content of phosphorous was measured by the method of gravimetric quimociac method[12].

RESULTS AND DISCUSSION

Limiting oxygen index and UL94 classification: In case of the loading of flame retardants was 25 wt % based on the total weight of the composites, the effect of the formulation of the combinations of aluminium dipropylphosphinate and melamine polyphosphate was investigated and the results were summarized in Table-1. The flame retarded polyamide 6 with aluminium dipropylphosphinate receive a V-0 classification in UL 94 tests and has an increased limiting oxygen index of 33.2 %. The flame retarded polyamide 6 with melamine polyphosphate failed the vertical UL 94 test with a limiting oxygen index of 31.5 %. Thus it was concluded that the flame retardancy of aluminium dipropylphosphinate in polyamide 6 was clearly better than melamine polyphosphate. When aluminium dipropylphosphinate were combined with melamine polyphosphate, the flame retardant effect in polyamide 6 was worse by adding greater the proportion of melamine polyphosphate.

In order to further understand the flame retardancy of a combination of aluminium dipropylphosphinate and melamine polyphosphate, the influence of the loading of flame retardants on the limiting oxygen index and vertical burning classifications was, respectively investigated under the weight ratios of aluminium dipropylphosphinate to melamine polyphosphate of 100:0, 85:15 and 0:100 and the results were shown in Table-2. The limiting oxygen index of polyamide 6 was 22.5 % and the burning test rating was failed. The limiting oxygen index of the flame retarded polyamide 6 alone with aluminium dipropylphosphinate of 15 wt % could be up to 30.7 %, the demanding V-0 classification could be achieved, which indicated that aluminium dipropylphosphinate had a good flame retardancy in polyamide 6. When the weight ratios of aluminium dipropylphosphinate to melamine polyphosphate was 65:35 and the loading of the combination was 15 wt %, the limiting oxygen index only increased to 27 % and V-2 was achieved and adding 20 wt. % the combination increased a limiting oxygen index of 29.1 % and passed the vertical UL94 tests. These results presented that there was no synergistic flame retardancy between aluminium dipropylphosphinate and melamine polyphosphate in polyamide 6.

Cone calorimetry analysis: The heat release rate, mass loss rate, total heat release and mass curve of polyamide 6 and the flame retarded polyamide 6 were, respectively illustrated in Figs. 1-4 and the important cone calorimetry data were tabulated in Table-3. As could be seen in the above figures and table, polyamide 6 burned fastly after ignition, the heat release rate, mass loss rate and total heat release increased rapidly, while the mass decreased rapidly and its heat release rate curve was characterized by a sharp peak with the maximal heat

TABLE-1
EFFECT OF THE WEIGHT RATIOS OF ALUMINIUM DIPROYLPHOSPHITE TO MELAMINE POLYPHOSPHATE ON ITS FLAME RETARDANCY IN POLYAMIDE 6

w(Aluminium dipropylphosphinate): w(melamine polyphosphate)	Limiting oxygen index (%)	UL-94 class	Combustion phenomenon
100:0	33.2	V-0	Difficult ignition, self-extinguishing, no drips
85:15	30.5	V-0	Difficult ignition, self-extinguishing, no drips
75:25	28.5	V-0	Difficult ignition, self-extinguishing, no drips
65:35	29.3	V-0	Difficult ignition, self-extinguishing, no drips
55:45	27.3	V-0	Difficult ignition, self-extinguishing, no drips
45:55	27.7	V-1	Gentle burning, self-extinguishing, no drips
35:65	27.3	V-2	Slightly severe burning, dripping
25:75	27.2	V-2	Slightly severe burning, dripping
15:85	28.0	V-2	Slightly severe burning, dripping
0:100	31.5	No	Severe burning, dripping

TABLE- 2
EFFECT OF THE LOADING OF FLAME RETARDANTS ON ITS FLAME RETARDANCY IN POLYAMIDE 6

w(aluminium dipropylphosphite): w(melamine polyphosphate)	Loading (%)	Limiting oxygen index (%)	UL-94 class	Combustion phenomenon
100:0	0	22.5	No	Severe burning, dripping
	5	26.8	No	Severe burning, dripping
	10	29.8	V-1	Gentle burning, self-extinguishing, no drips
	15	30.7	V-0	Difficult ignition, self-extinguishing, no drips
	20	32.2	V-0	Difficult ignition, self-extinguishing, no drips
	25	33.2	V-0	Difficult ignition, self-extinguishing, no drips
65:35	5	24.3	No	Severe burning, dripping
	10	25.2	No	Severe burning, dripping
	15	27.0	V-2	Slightly severe burning, dripping
	20	29.1	V-0	Difficult ignition, self-extinguishing, no drips
	25	29.3	V-0	Difficult ignition, self-extinguishing, no drips
0:100	5	23.1	No	Severe burning, dripping
	10	24.5	No	Severe burning, dripping
	15	25.4	No	Severe burning, dripping
	20	26.6	No	Severe burning, dripping
	25	31.5	No	Severe burning, dripping

release rate of 1187 kw/m^2 in the burning of 185 s. Compared with polyamide 6, the heat release rate, mass loss rate and total heat release of the flame-retarded polyamide 6 with 25 wt % melamine polyphosphate also increased rapidly after ignition, the mass decreased more rapidly, but the maximum heat release rate, mass lose rate, total heat release and average heat release rate cut down markedly, which showed that polyamide 6 was flammable and melamine polyphosphate had a poor fire retardancy in polyamide 6. The heat release rate, mass loss rate and total heat release of the flame retarded polyamide 6 with 25 wt % aluminium dipropylphosphinate increased slowly after ignition, the mass decreased slowly, the heat release rate maintained at 200-469 kw/m^2 during the burning of 115-445 s and the curves of heat release rate were characterized by a wider peak. The peak heat release rate and average heat release rate were markedly reduced and the time for peak heat release rate and complete combustion increased significantly, which suggested that aluminium dipropylphosphinate had a good fire retardancy, but the total heat release and average effective heat of combustion increased slightly. The fire behaviour of the flame-retarded polyamide 6 with aluminium dipropylphosphinate/melamine polyphosphate was similar to the flame-retarded polyamide 6 with aluminium dipropylphosphinate, but the mass of the former decreased faster and the peak heat release rate, average heat release rate, average effective heat of combustion and total heat release were higher than the later, which further confirmed that there was no synergistic effect between aluminium dipropyl-phosphinate and melamine polyphosphate in polyamide 6.

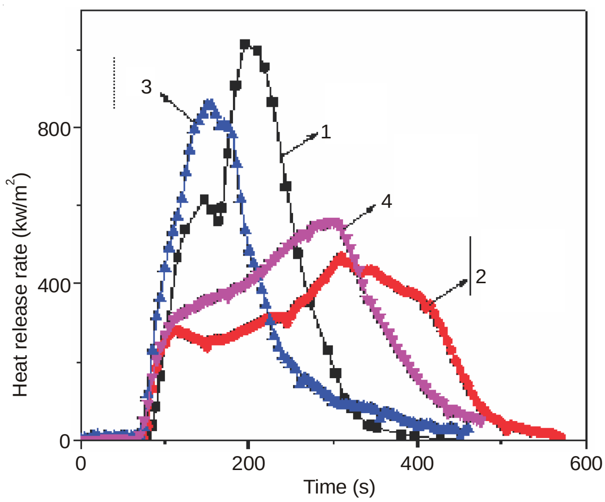

Fig. 1. Heat release rate curves of polyamide 6 and flame-retarded polyamide 6: 1 polyamide 6; 2 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate; 3 flame retarded polyamide 6 with 25 wt % of melamine polyphosphate; 4 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine polyphosphate (the weight ratio of aluminium dipropylphosphinate and melamine polyphosphate being 65/35)

TABLE-3
CONE CALORIMETRY DATA FOR POLYAMIDE 6 AND FLAME-RETARDED POLYAMIDE 6

Term	Polyamide 6	PA6/MPP	PA6/ADPP	PA6/ADPP/MPP
THR (MJ/m^2)	122.01	87.42	127.25	130.66
PHRR (Kw/m^2)	1187.00	864.65	469.00	558.77
PHRR, time (s)	185	135	310	300
MHRR (Kw/m^2)	372.06	194.45	221.32	272.47
PEHC (MJ/kg)	80	80	80	80
MEHC ((MJ/kg)	21.54	28.49	24.35	26.41
MMLR (g/s)	0.10	0.13	0.07	0.09
TTI (s)	75	65	80	80
Combustion time(s)	380	445	570	475

THR: Total heat release; PHRR: peak heat release rate; MHRR: average heat release rate; PEHC: peak effective heat of combustion; MEHC: average effective heat of combustion; MMLR: average mass loss rate; TTI: time to ignition.

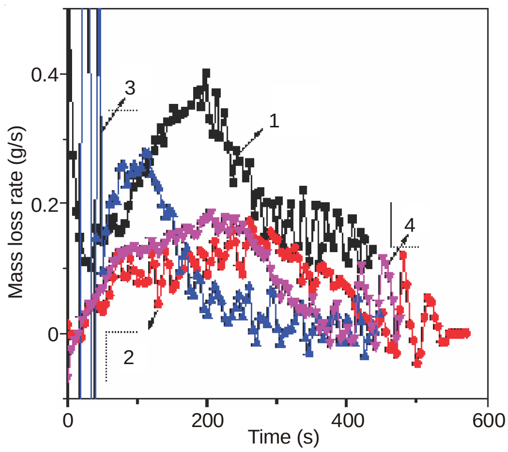

Fig. 2. Mass loss rate curves of polyamide 6 and flame-retarded polyamide 6 1 polyamide 6; 2 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate;3 flame retarded polyamide 6 with 25 wt % of melamine polyphosphate;4 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine polyphosphate (the weight ratio of aluminium dipropylphosphinate and melamine polyphosphate being 65/35)

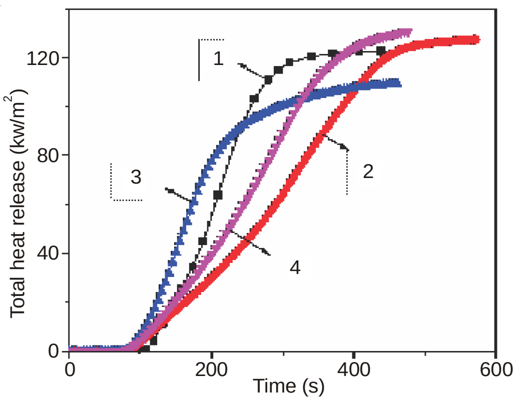

Fig. 3. Total heat release curves of polyamide 6 and flame-retarded polyamide 6 1 polyamide 6;2 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate;3 flame retarded polyamide 6 with 25 wt % of melamine polyphosphate;4 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/ melamine polyphosphate (the weight ratio of aluminium dipropylphosphinate and melamine polyphosphate being 65/35)

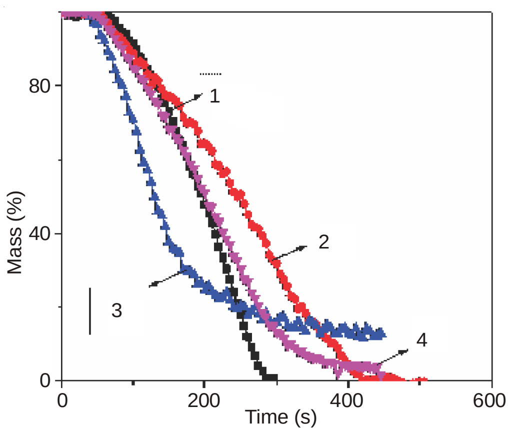

Fig. 4. Mass curves of polyamide 6 and flame-retarded polyamide 6 1 polyamide 6;2 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate;3 flame retarded polyamide 6 with 25 wt % of melamine polyphosphate;4 flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine polyphosphate (the weight ratio of aluminium dipropylphosphinate and melamine polyphosphate being 65/35)

Thermogravimetric analysis: Thermogravimetric results of flame retardants and flame retarded polyamide 6 were presented in Figs. 5 and 6 and Table-4. As could be seen in Fig. 5 and Table-4, the initial thermal decomposition temperature ($T_{2wt\%}$, the temperature at 2 wt % mass loss) of aluminium dipropylphosphinate and melamine polyphosphate were, respectively 315.8 and 344.1 ºC and subsequently the mass loss of melamine polyphosphate was smaller than aluminium dipropylphosphinate under the same temperature and their weight percent of the resulting residues in 500 ºC was, respectively *ca.* 14 and 65 wt. %, which indicated that the thermal stability of melamine polyphosphate was better than aluminium dipropylphosphinate. The thermal decomposition temperature of the 65 wt. % aluminium dipropylphosphinate/35 wt. % melamine polyphosphate was 275.5 ºC, which was lower than aluminium dipropylphosphinate and melamine polyphosphate and the decomposition temperature at 5 and 10 % of mass loss were, respectively 347.5 and 375.1 ºC which was between aluminium dipropylphosphinate and melamine polyphosphate for the same mass loss.

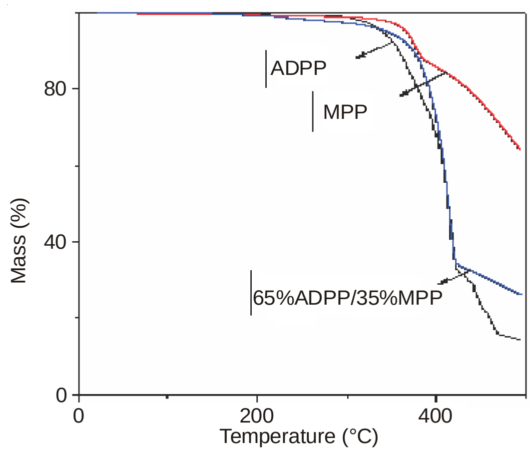

Fig. 5. TG of flame retardants

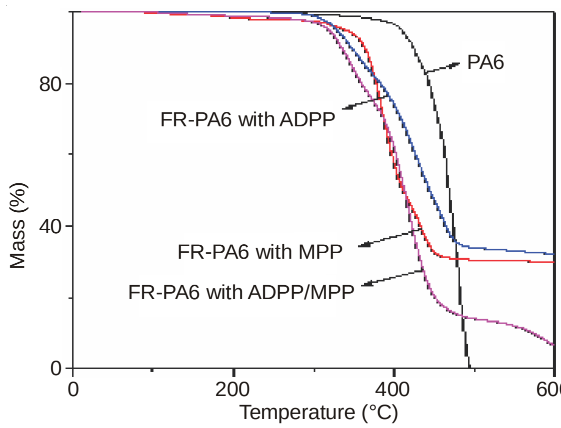

Fig. 6. TG of the flame retarded polyamide 6 with flame retardants

Fig. 6 (Table-4) showed that the polyamide 6 was initially decomposed in 333.9 ºC ($T_{2 wt \%}$), rapidly over 402.6 ºC and almost completed at 500 ºC without any residue, which meant that polyamide 6 was extremely difficult to be carbonized. The flame retarded polyamide 6 with 25 wt % aluminium dipropylphosphinate was initially decomposed in 310 ºC and the $T_{5 wt \%}$ and $T_{10 wt \%}$ were, respectively 328.6 and 347.2 ºC,

TABLE -4
THEMOGRAVIMETRIC RESULTS

Materials	$T_{2\ wt\ \%}$ (ºC)	$T_{5\ wt\ \%}$ (ºC)	$T_{10\ wt\ \%}$ (ºC)	600 ºC (%)
ADPP	315.8	342.3	358.8	14.5 (500 ºC)
MPP	344.1	367.3	379.9	44.3
ADPP/MPP*	275.5	347.5	375.1	23.2
PA6	333.9	386.1	402.6	0.2
PA6/MPP	221.0	338.1	363.4	27.6
PA6/ADPP	310.0	328.6	347.2	32.0
PA6/ADPP/MPP	272.0	318.1	334.7	9.8

*Weight ratio of ADPP/MPP was 65/35.

obviously lower than polyamide 6, which suggested that the addition of aluminium dipropylphosphinate cut down the thermal stability of polyamide 6. The 32 % residual rate in 600 ºC indicated improved charring of polyamide 6 by adding aluminium dipropylphosphinate. The $T_{2\ wt\ \%}$, $T_{5\ wt\ \%}$ and $T_{10\ wt\ \%}$ of the flame retarded polyamide 6 with 25 wt % melamine polyphosphate were, respectively 221.0, 338.1 and 363.4 ºC, clearly lower than polyamide 6 under the same mass loss, which suggested that the addition of the melamine polyphosphate reduced the thermal stability of polyamide 6. The $T_{2\ wt\ \%}$, $T_{5\ wt\ \%}$ and $T_{10\ wt\ \%}$ of the flame retarded polyamide 6 with 25 wt % aluminium dipropylphosphinate/melamine polyphosphate (the weight ratio of aluminium dipropylphosphinate and melamine polyphosphate was 65:35) were, respectively 272.0, 318.1 and 334.7 ºC, significantly lower than polyamide 6 and polyamide 6/aluminium dipropylphosphinate, even $T_{5\ wt\ \%}$ and $T_{10\ wt\ \%}$ was lower than polyamide 6/melamine polyphosphate. This indicated that the aluminium dipropylphosphinate/melamine polyphosphate had more severe impact on the stability of polyamide 6.

Fire retardancy mechanism: The flame retardancy mechanism of aluminium dipropylphosphinate and aluminium dipropylphosphinate / melamine polyphosphate in polyamide 6 was discussed by the analysis of the residues obtained in cone calorimeter test. As could be seen in the photos of residues shown in Fig. 7, the burning behaviour of polyamide 6 and polyamide 6/aluminium dipropylphosphinate/melamine polyphosphate was not accompanied by intumescent char layer formation, whereas polyamide 6/aluminium dipropylphosphinate and polyamide 6/melamine polyphosphate did.

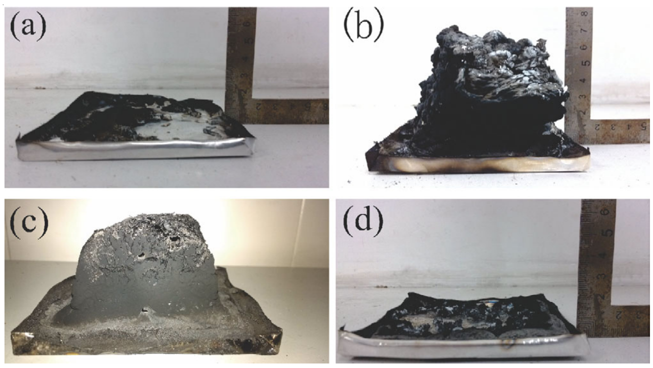

Fig. 7. Photos of the residue obtained in the cone calorimeter test(a) polyamide 6; (b) flame retarded polyamide 6 with 25wt % of aluminium dipropylphosphinate;(c) flame retarded polyamide 6 with 25 wt % of melamine polyphosphate(d) flame retarded polyamide 6 with 25 wt % of 65 wt %aluminium dipropylphosphinate/35 wt % melamine polyphosphate

SEM images of the residues presented in Fig. 8 showed that the smooth and dense layers were formed after the combustion of the flame retarded polyamide 6 with aluminium dipropylphosphinate or melamine polyphosphate, but was not the case for the residue of polyamide 6/aluminium dipropylphosphinate/melamine polyphosphate. On the basis of these results, it was proposed that the flame retardancy was caused by the barrier effect of the smooth and dense layers, while the loose layers formed for polyamide 6/aluminium dipropylphosphinate/melamine polyphosphate weaken the flame retardancy.

The polyamide 6 has a residue of only 0.5 wt %, obviously lower than the values of flame retarded polyamide 6. The residual rate of polyamide 6/aluminium dipropylphosphinate, polyamide 6/aluminium dipropylphosphinate/melamine polyphosphate and polyamide 6/melamine polyphosphate were, respectively 3.5, 6.1 and 12.7 wt. %. Although the residues amount of polyamide 6 containing aluminium dipropylphosphinate/melamine polyphosphate has significantly increased, but the resulting loose non- intumescent layer by combining melamine polyphosphate weaken the fire retandancy of the materials. The phosphorus content in the residues of the flame retarded polyamide 6 with aluminium dipropylphosphinate, melamine polyphosphate and aluminium dipropylphosphinate/melamine polyphosphate was, respectively 18.5, 6.4 and 17.3 %

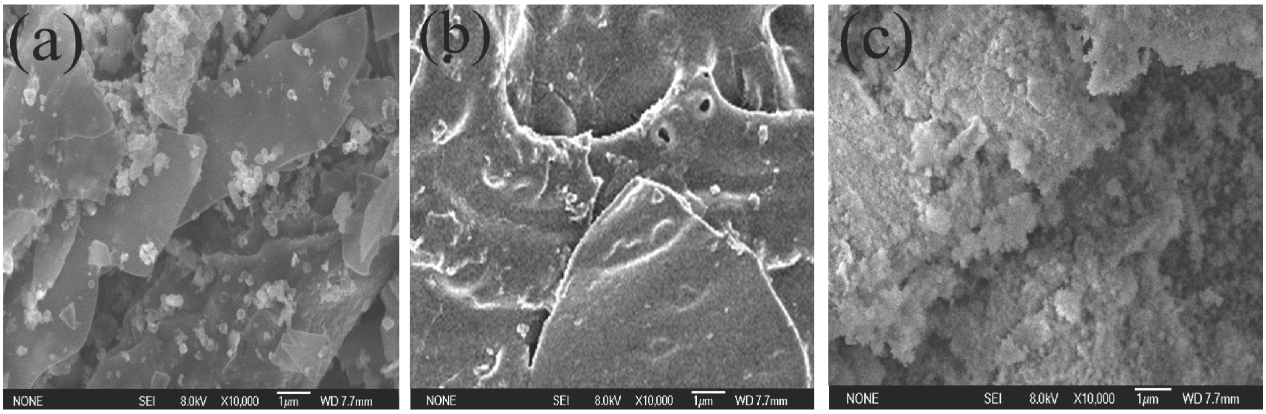

Fig. 8. SEM pictures of the residue obtained in the cone calorimeter: (a) flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate; (b) flame retarded polyamide 6 with 25 wt % of melamine polyphosphate ; (c) flame retarded polyamide 6 with 25 wt %of 65 wt %aluminium dipropylphosphinate/35wt % melamine polyphosphate

and the corresponding phosphorus residual rate was, respectively 13.4, 23.2 and 23.9 %, which implied that most of the decomposition products of aluminium dipropylphosphinate were vaporized to gaseous phase in the process of combustion. The above analysis revealed that aluminium dipropylphosphinate played the flame retardancy by gaseous and condensed phase mechanisms, on the one hand, they were decomposed into non-volatile aluminum phosphate and promoted the carbonization of polyamide 6 and the formed intumescent layer resulted in flame retardancy by the barrier effect on heat, air and decomposition products[13], on the other hand, it was decomposed into volatile phosphorus compounds such as dipropylphosphinic acid which brought about flame retardancy by flame inhibition[13-15].

Conclusion

In this work, no synergistic flame retardancy between aluminium dipropylphosphinate and melamine polyphosphate was found in polyamide 6. The polyamide 6 containing 15 wt. % aluminium dipropylphosphinate received a V-0 classification in UL 94 tests and has an increased limiting oxygen index value of 30.7 %, while the polyamide 6 containing 15 wt. % aluminium dipropylphosphinate/melamine polyphosphate (the weight ratios of aluminium dipropylphosphinate to melamine polyphosphate is 65:35) achieved a V-2 classification with a limiting oxygen index of 27.0 % and the mass of the former decreased faster and the peak heat release rate, average heat release rate , average effective heat of combustion and total heat release were higher than the later. In addition, aluminium dipropylphosphinate/melamine polyphosphate had greater influence on the thermal stability of the composites than aluminium dipropylphosphinate and melamine polyphosphate. Fortunately, the combination of aluminium dipropylphosphinate and melamine polyphosphate was more economical because melamine polyphosphate was much cheaper than aluminium dipropylphosphinate. The analysis of the residues obtained in cone calorimeter test showed that aluminium dipropylphosphinate played the role of flame retardancy by gaseous and condensed phase mechanisms, on the one hand, aluminium dipropylphosphinate was decomposed into non-volatile aluminum phosphate and promoted the carbonization of polyamide 6 and the formed intumescent layer resulted in flame retardancy by the barrier effect on heat, air and decomposition products. On the other hand, it was decomposed into volatile phosphorus compounds which brought about flame retardancy by flame inhibition. Although the residues amount of polyamide 6 containing aluminium dipropylphosphinate/melamine polyphosphate was significantly increased, but the resulting loose non- intumescent layer by combining melamine polyphosphate weaken the fire retandancy of the materials.

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