Synergistic Flame Retardancy of Aluminium Dipropyl-Phosphinate and Melamine Cyanurate in Polyamide-6

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The synergistic flame retardancy of aluminium dipropylphosphinate (ADPP) and melamine cyanurate (MCA) in polyamide 6 (PA6) was studied by the limiting oxygen index (LOI) measurement, the vertical burning test, the cone calorimeter test and the mechanism was also discussed by residual analysis. It was found that there was no obvious synergistic flame retardancy between aluminium dipropylphosphinate and melamine cyanurate in polyamide 6. Compared with the flame-retarded polyamide 6 (FR-PA6) with aluminium dipropylphosphinate, the limiting oxygen index of the FR-PA6 with aluminium dipropylphosphinate/melamine cyanurate with appropriate weight ratios increased slightly, but vertical burning class, heat release rate (HRR), peak heat release rate (PHRR), mass loss rate (MLR) and total heat release (THR) were similar. Additionally, aluminium dipropylphosphinate/melamine cyanurate had a greater influence on the thermal stability of the composites than aluminium dipropylphosphinate and melamine cyanurate. 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 one hand, aluminium dipropylphosphinate 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, on the other hand, it was decomposed into volatile phosphorus compounds which brought about flame retardancy by flame inhibition.

Keywords: Aluminium dipropylphosphinate, Melamine cyanurate, Synergistic 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 resin¹⁻³. Although the dialkylphosphinate are only moderately efficient in nylons, they were found synergistic effect with some nitrogen-containing products like melamine⁴, melamine cyanurate^{5,6}, melamine phosphate, or melamine polyphosphate⁷⁻⁹. 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 polyphosphate⁸. Despite of their increasing use, publications on the fire-retardancy mechanism of these phosphinate have been limited. The literature¹¹ claimed that aluminium phosphinate in polyamide 6, 6 acted mainly by flame inhibition. Melamine polyphosphate shows some fuel dilution and a significant barrier effect. Using a combination of aluminium diethylphosphinate and melamine polyphosphate results in some

charring and a dominant barrier effect. These effects are improved in the presence of zinc borate due to the formation of boron-aluminium phosphates instead of aluminium phosphates. The literature^{12,13} also claimed that aluminium diethylphosphinate in glass-fiber reinforced poly(butylene-terephthalate) acted mainly by flame inhibition due to the release of the phosphinic acid in the gas phase. Additional charring influenced the flammability. The literature¹⁴ reported that the addition of organoclay increased the barrier effect of formed char in poly(ethyleneterephthalate). However, investigations about aluminium phosphinate and melamine polyphosphate as flame retardants in poly(methylmethacrylate) showed that the fire retardancy mechanism was mainly based on a condensed phase action¹⁵.

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 very 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 low 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 melamine⁴. However, it has no obvious synergistic flame retardancy with melamine cyanurate and melamine polyphosphate. In this work, the flame retardancy and its mechanisms of aluminium dipropylphosphinate in combination with melamine cyanurate in polyamide 6 were reported.

EXPERIMENTAL

Polyamide 6 was provided by Shijiazhuang Refining & Chemical Co. China. The aluminium dipropylphosphinate and the melamine cyanurate were provided by Shandong Brothers Science and Technology Co. Ltd., China. The antioxidants of 1010 and 168 were provided by Beijing Jiye 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 about 230 °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 × 4 mm sheets at 220-230 °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 flame retardant test.

Flammability tests: Limiting oxygen index was measured according to ASTM D 2863 with a JF-3 oxygen index meter (Jiangning Analytical Instrument Company, China). The specimens with a size of 100 × 6.5 × 4 mm³ 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 × 13 × 4 mm³ 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/m² with specimens of 100 mm × 100 mm × 4 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 (about 10 mg) were heated in 150 µL alumina pans at a heating rate of 10 °C/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 method¹⁶.

RESULTS AND DISCUSSION

Limiting oxygen index and UL94 Classification: As 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 cyanurate was investigated. As could be seen in Table-1, the weight ratios of aluminium dipropylphosphinate to melamine cyanurate had impact on the limiting oxygen index and vertical burning ratings of the FR-PA6. The limiting oxygen index of the FR-PA6 increased first and then decreased and vertical burning UL94 classification unchanged first and then decreased with the increase of the proportion of melamine cyanurate. The limiting oxygen index of the FR-PA6 alone with aluminium dipropylphosphinate could be up to 33.2 % and the burning test could pass the demanding V-0 classification, while the limiting oxygen index of the FR-PA6 with melamine cyanurate was 27 % and only the demanding V-2 classification could be reached, which revealed that the flame retardancy of aluminium dipropylphosphinate in polyamide 6 was much better than melamine cyanurate.

In order to further confirm the synergistic effect between aluminium dipropylphosphinate and melamine cyanurate, the influence of the loading of flame retardants on the limiting oxygen index and vertical burning classification was respectively investigated under the weight ratios of aluminium dipropylphosphinate to melamine cyanurate 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 FR-PA6 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. As the weight ratios of aluminium dipropylphosphinate to melamine cyanurate was 85:15 and the loading of the combination was 15 wt %, the limiting oxygen index could be up to 31.3 % and V-0 could also be achieved. The limiting oxygen index of the FR-PA6 alone with melamine cyanurate of 15 wt %

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

w (Aluminium dipropylphosphinate): w (melamine cyanurate)	Limiting oxygen index (%)	UL-94 class	Combustion phenomenon
100:0	33.2	V-0	Difficult ignition, self-extinguishing, no drips
90:10	36.3	V-0	Difficult ignition, self-extinguishing, no drips
85:15	37.0	V-0	Difficult ignition, self-extinguishing, no drips
75:25	35.5	V-0	Difficult ignition, self-extinguishing, no drips
65:35	33.8	V-0	Difficult ignition, self-extinguishing, dripping
55:45	32.6	V-0	Difficult ignition, self-extinguishing, dripping
45:55	30.7	V-1	Gentle burning, self-extinguishing, no drips
0:100	27.0	V-2	Slightly severe burning, dripping

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

w (Aluminium dipropylphosphinate): w (melamine cyanurate)	Loading (%)	Limiting oxygen index (%)	UL-94 class	Combustion phenomenon
100:0	0	22.5	No rating	Severe burning, dripping
	5	26.8	No rating	Severe burning, dripping
	10	29.8	V-1	Gentle combustion, 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
85:15	5	28.2	No rating	Severe burning, dripping
	10	30.1	V-1	Gentle burning, self-extinguishing, no drips
	15	31.3	V-0	Difficult ignition, self-extinguishing, no drips
	20	33.3	V-0	Difficult ignition, self-extinguishing, no drips
	25	37.0	V-0	Difficult ignition, self-extinguishing, no drips
0:100	5	23.1	No rating	Severe burning, dripping
	10	24.5	No rating	Severe burning, dripping
	15	25.4	No rating	Severe burning, dripping
	20	26.6	No rating	Severe burning, dripping
	25	27.0	V-2	Slightly severe burning, dripping

was only 25.4 % and the burning test rating was failed. Thus it could be found that there was not obvious synergistic flame retardancy between aluminium dipropylphosphinate and melamine cyanurate, which wasn't consistent with that reported in literature^{5,6}. This might be due to different phosphinates and polymers used. Fortunately, the combination of aluminium dipropylphosphinate and melamine cyanurate was more economical because melamine cyanurate was of low-cost than aluminium dipropylphosphinate.

Cone calorimetry analysis: The heat release rate (HRR), mass loss rate (MLR), total heat release (THR), mass curve of polyamide 6 and the FR-PA6 were, respectively illustrated in Figs. 1 to 4 and the important cone calorimetry data were tabulated in Table-3. As observed, the fire behaviour of polyamide 6 was similar with the FR-PA6 with 25 wt % melamine cyanurate, both of them burned fastly after ignition, heat release rate, mass loss rate and total heat release increased rapidly, while the mass decreased rapidly, but the mass of the later decreased more rapidly and the curves of heat release rate and mass loss rate were characterized by a sharp peak. However, peak heat release rate (PHRR), total heat release, average heat release rate (MHRR), peak effective heat of combustion (PEHC), average effective heat of combustion (MEHC) were obviously reduced by adding melamine cyanurate. The above results showed that polyamide 6 was flammable and melamine cyanurate had a poor fire retardancy in polyamide 6. The heat release rate, mass loss rate and total heat release of the FR-PA6 alone 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 115-445s 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 slower combustion, in other words, aluminium dipropylphosphinate had a good fire retardancy, but the total heat release and average effective heat of combustion increased slightly. The fire

TABLE-3
CONE CALORIMETRY DATA FOR
POLYAMIDE 6 AND FR- PA6

Term	Polyamide 6	MCA/PA6	ADPP/PA6	ADPP/MCA/PA6
THR (MJ/m^2)	122.01	87.29	127.25	130.01
PHRR (Kw/m^2)	1187.00	1013.31	469.00	403.25
PHRR, time(s)	185	145	310	280
MHRR (Kw/m^2)	372.06	239.24	221.32	220.54
PEHC (MJ/kg)	80	67.65	80	78.12
MEHC (MJ/kg)	21.54	14.19	24.35	28.26
MMLR (g/s)	0.10	0.07	0.07	0.07
TTI (s)	75	75	80	80
Combustion time (s)	380	360	570	585

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. 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 cyanurate; 4. flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine cyanurate (the weight ratio of aluminium dipropylphosphinate and melamine cyanurate being 85/15)

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 cyanurate; 4. flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine cyanurate (the weight ratio of aluminium dipropylphosphinate and melamine cyanurate being 85/15)

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 cyanurate; 4. flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine cyanurate (the weight ratio of aluminium dipropylphosphinate and melamine cyanurate being 85/15)

Fig. 4. Mass curves of polyamide 6 and flame-retarded polyamide 6: 1. polyamide 6; 2. flame retarded polyamide 6 with 25wt % of aluminium dipropylphosphinate; 3. flame retarded polyamide 6 with 25 wt % of melamine cyanurate; 4. flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate/melamine cyanurate (the weight ratio of aluminium dipropylphosphinate and melamine cyanurate being 85/15)

behaviour of the FR-PA6 with aluminium dipropylphosphinate/melamine cyanurate was similar with the FR-PA6 with aluminium dipropylphosphinate, which further confirmed that there wasn't obvious synergistic flame retardancy between aluminium dipropylphosphinate and melamine cyanurate in polyamide 6.

Thermogravimetric analysis: Thermogravimetric results of flame retardants and FR-PA6 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 ($T_{i-2\text{ wt \%}}$, the temperature at 2 wt % mass loss) of aluminium dipropylphosphinate and melamine cyanurate were 315.8 and 321 °C, respectively and subsequently the mass loss of aluminium dipropylphosphinate was smaller than melamine cyanurate under the same temperature. The complete pyrolysis temperature of aluminium dipropylphosphinate and melamine cyanurate were 500 and 400 °C, respectively and their resulting residues under the above temperature was about 14 and 0 wt %, respectively. The $T_{i-2\text{ wt \%}}$ of the combination (aluminium dipropylphosphinate/melamine cyanurate) consisted of 85 wt % aluminium dipropylphosphinate and 15 wt % melamine cyanurate was 321 °C which was higher than aluminium dipropylphosphinate and melamine cyanurate and the decomposition temperature at

Fig. 5. TG of flame retardants

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

TABLE-4
THEMOGRAVIMETRIC RESULTS

Materials	$T_{i-2wt\%}$ (°C)	$T_{i-5wt\%}$ (°C)	$T_{i-10wt\%}$ (°C)	Residue at 600 °C (wt. %)
PA6	333.6	386.1	402.6	0.2
ADPP	315.8	342.3	358.8	14.5 (500 °C)
MCA	321.0	334.6	350.1	0.2 (500 °C)
85 % ADPP/15 % MCA	321.0	334.6	350.1	18.9 (500 °C)
Flame retarded PA6 with 25 wt % ADPP	309.7	328.4	346.9	27.1
Flame retarded PA6 with 25 wt % MCA	308.9	333.9	345.8	0.2
Flame retarded PA6 with 25 wt % ADPP/MCA*	293.8	326.5	345.2	13.2

*Weight ratio of ADPP/MCA was 85/15

at 5 and 10 wt % mass loss ($T_{i-5wt\%}$ and $T_{i-10wt\%}$) were, respectively 334.6 and 350.1 °C which was between aluminium dipropylphosphinate and melamine cyanurate.

As could be seen in Fig. 6 and Table-4, polyamide 6 was initially decomposed in 333.6 °C ($T_{i-2wt\%}$), rapidly over 402.6 °C and almost completely in 500 °C without any residue, which meant that polyamide 6 was extremely difficult to be carbonized. The FR-PA6 with 25 wt % aluminium dipropylphosphinate was initially decomposed in 309.7 °C and the $T_{i-5wt\%}$ and $T_{i-10wt\%}$ were, 328.4 and 346.9 °C, respectively, obviously lower than polyamide 6, which suggested that the addition of aluminium dipropylphosphinate cut down the thermal stability of polyamide 6. The 27 % residual rate in 600 °C indicated improved charring of polyamide 6 by adding aluminium dipropylphosphinate. The $T_{i-2wt\%}$, $T_{i-5wt\%}$ and $T_{i-10wt\%}$ of the FR-PA6 with 25 wt % of melamine cyanurate were 308.9, 333.9 and 345.8 °C, respectively, obviously lower than that of the FR-PA6 with 25 wt % aluminium dipropylphosphinate, which suggested that the addition of melamine cyanurate more seriously reduced the thermal stability of polyamide 6 than aluminium dipropylphosphinate. The $T_{i-2wt\%}$, $T_{i-5wt\%}$ and $T_{i-10wt\%}$ of the FR-PA6 with 25 wt % aluminium dipropylphosphinate/melamine cyanurate were 293.8, 326.5 and 345.2 °C, respectively, which was lower than polyamide 6 and FR-PA6 with

aluminium dipropylphosphinate or melamine cyanurate, which indicated that aluminium dipropylphosphinate/melamine cyanurate had greater influence on the thermal stability of the materials. The 13 % resulting residues in 600 °C was much more than the additive value of 5 %, which revealed improved charring of polyamide 6 by adding aluminium dipropylphosphinate/melamine cyanurate.

Fire retardancy mechanism: The flame retardancy mechanism of aluminium dipropylphosphinate and aluminium dipropylphosphinate/melamine cyanurate 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 residue of polyamide 6 and the FR-PA6 with melamine cyanurate did not form the intumescent char layer and their residual rate were respectively 0.5 and 0.8 wt %, while the FR-PA6 with aluminium dipropylphosphinate and aluminium dipropylphosphinate/melamine cyanurate formed the intumescent char layer and their residual rate were respectively 3.5 and 2.9 wt %, which indicated that the charring of the latter two was better than that of the former two.

The SEM pictures of the residues presented in Fig. 8 showed that the smooth and dense layers were formed after the combustion of the FR-PA6 with aluminium dipropylphosphinate and aluminium dipropylphosphinate/melamine cyanurate, which

Fig. 7. Photos of the residue obtained in the cone calorimeter test: (a) polyamide 6; (b) flame retarded polyamide 6 with 25 wt % of aluminium dipropylphosphinate; (c) flame retarded polyamide 6 with 25 wt % of melamine cyanurate; (d) flame retarded polyamide 6 with 25 wt % of 85 wt % aluminium dipropylphosphinate/15 wt % melamine cyanurate

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 85 wt % aluminium dipropylphosphinate/15 wt % melamine cyanurate

brought about the flame retardancy by the barrier effect on heat, air and decomposition products¹².

The phosphorus content in the residues of the FR-PA6 with aluminium dipropylphosphinate and aluminium dipropylphosphinate/melamine cyanurate was respectively 18.5 and 19.1 % and all the phosphorus residual rate of the both was only 13.4 %, 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 and aluminium dipropylphosphinate/melamine cyanurate played the flame retardancy by gaseous and condensed phase mechanisms, on the one hand, they were decomposed into non-volatile aluminum phosphate¹² 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 products¹², on the other hand, it was decomposed into volatile phosphorus compounds such as dipropylphosphinic acid which brought about flame retardancy by flame inhibition¹²⁻¹⁴. Melamine cyanurate was decomposed into volatile compounds such as CO₂ and NH₃ which showed some fuel dilution effects^{13,14}.

Conclusion

There was not obvious synergistic flame retardancy between aluminium dipropylphosphinate and melamine cyanurate in polyamide 6. Compared with the FR-PA6 with aluminium

dipropylphosphinate, the limiting oxygen index of FR-PA6 with aluminium dipropylphosphinate/melamine cyanurate with the appropriate weight ratios increased slightly, but vertical burning rating, heat release rate, peak heat release rate, average heat release rate, mass loss rate and total heat release were similar. For example, the limiting oxygen index of the FR-PA6 alone with 15 wt % aluminium dipropylphosphinate was 30.7 %, while the limiting oxygen index of the FR-PA6 with 15 wt % aluminium dipropylphosphinate/melamine cyanurate could be up to 31.3 % and all the both could pass the demanding V-0 classification of the burning test. In addition, aluminium dipropylphosphinate/melamine cyanurate had greater influence on the thermal stability of the composites than aluminium dipropylphosphinate and melamine cyanurate. Fortunately, the combination of aluminium dipropylphosphinate and melamine cyanurate was more economical because melamine cyanurate was much low-cost than aluminium dipropylphosphinate. The analysis of the residues obtained in cone calorimeter test showed that aluminium dipropylphosphinate and aluminium dipropylphosphinate/melamine cyanurate played the role of flame retardancy by gaseous and condensed phase mechanisms.

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REFERENCES

1. S. Hörold, B. Naß, O. Schacker and W. Wanzke, A New Generation of Flame Retarded Polyamides Based on Phosphinates, Proceedings of Flame Retardant, Interscience Publisher, London (2004).
2. S. Hoerold, Flame Retarding Thermosetting Compositions, US Patent 6,420,459 (2002).
3. J.R. Campbell, B. Duffy, J.R. Rude, P. Susarla, M.A. Vallance, G.W. Yaeger and K.P. Zarnoch, Flame-Retardant Thermosetting Composition and Method, WO2005/033179 (2005).
4. L.S. Tang, Z.G. Yuan, L. Xu, X. Li and Y.Z. Ge, *Adv. Mater. Sci. Eng.*, Article ID 960914 (2013).
5. E. Jenewein, H.-J. Kleiner, W. Wanzke and W. Budzinsky, Synergistic Flame Protection Agent Combination for Rheromoplastic Polymers, US Patent 6,365,071 (2002).
6. M. Klatt, B. Leutner, M. Nam and H. Fisch, Flame-Retardant Polyester Molding Compositions Containing Flame-Retardant Nitrogen Compounds and Diphosphinates, US Patent 6,503,969 (2003).
7. E. Schlosser, B. Nass and W. Wanzke, Flame-Retardant Combination, US Patent 6,255,371 (2001).
8. B. Nass and W. Wanzke, Synergistic Flameproofing Composition for Polymers, US Patent 6,207,736 (2001).
9. L.S. Tang, Q.M. Liu, Y.Q. Li and S. Zhang, *China Plastics Ind.*, **39**, 110 (2011).
10. H.-J. Kleiner, W. Budzinsky and G. Kirsch, Low-Fammability Polyamide Molding Materials, US Patent 5,773,556 (1998).
11. U. Braun, B. Scharfel, M.A. Fichera and C. Jäger, *Polym. Degrad. Stab.*, **92**, 1528 (2007).
12. U. Braun and B. Scharfel, *Macromol. Mater. Eng.*, **293**, 206 (2008).
13. U. Braun, H. Bahr, H. Sturm and B. Scharfel, *Polym. Adv. Technol.*, **19**, 680 (2008).
14. M. Dogan, S. Erdogan and E. Bayramli, *J. Therm. Anal. Calorim.*, **112**, 871 (2013).
15. A. Laachachi, M. Cochez, E. Leroy, M. Ferriol and J.M. Lopez-Cuesta, *Polym. Degrad. Stab.*, **92**, 61 (2007).
16. Association of Official Analytical Chemists, Official Methods of Analysis, edn. 10, p. 12 (1965).