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POLYAMIDE 6 WITH A FLAME RETARDANT ENCAPSULATED BY POLYAMIDE 66: FLAME RETARDATION, THERMO-DECOMPOSITION AND THE POTENTIAL MECHANISM*

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Abstract A novel encapsulated flame retardant containing phosphorus-nitrogen (MSMM-Al-P) was prepared by encapsulating with polyamide 66 (PA66-MSMM-Al-P) for the flame retardation of polyamide 6 (PA6). The structure and thermal properties of PA66-MSMM-Al-P were characterized by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis. The flammability of PA6 containing flame retardants (MSMM-Al-P and PA66-MSMM-Al-P) was investigated by the limiting oxygen index test, vertical burning test and cone calorimeter. The flame retardancy and cone calorimetric analyses suggested a synergistic effect between PA66 and MSMM-Al-P in the flame-retardant PA6. Thermal stability of the flame-retardant PA6 was also investigated.

Keywords: PA6; Thermo-decomposition; Encapsulation; Flame retardance.

INTRODUCTION

Polyamide 6 (PA6) has been one of the widely used engineering plastics for a long time; however, it is easy to be ignited (LOI value of only 22) with serious melt-dripping during combustion[1]. The poor flame retardancy restricted its applications in many fields such as transport, construction, electrical industry, *etc*. Thus, flame retardation for PA6 is extremely necessary. Recently, various halogen-free flame retardants were used due to the environment consideration. Among them, nitrogen- or phosphorus-containing flame retardants have been used for distinct advantages such as environment-friendly, low smoke release and low toxicity. Melamine phosphate (MP) and its analogs were widely applied in flame-retardant polymers including PA6 for their abundant nitrogen and phosphorus contents[1–6]. However, MP utilized as flame retardant would easily accelerate the decomposition of PA6 during processing, and morphology of the char residues generated during burning was loose and porous, thus the char layer could not provide an expected physical obstruct for the underlying material against combustion[7, 8].

To improve the performance of anti-oxidation or fire-resistance of the intumescent char, synergistic agents such as metal salt and metal oxide were employed[9–13]. In the literature, sulfonic acid showed synergistic effects with melamine polyphosphate (MPP) in flame-retardant PA6[14]. A multicomponent synergistic flame retardant-

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modified MP with aluminum ion (MSMM-Al-P) was prepared through sulfonation and salification for PA6[15]. The mixed acid sources (phosphoric and sulfonic acid) generated from the decomposition of MSMM-Al-P, exhibited better catalytic effect for char forming, while aluminum ion crosslinked with phosphoric acids may improve the morphology of the intumescent char. Using polyamide as a carbonization agent in association with MP have already been reported[16, 17]. As an encapsulating material, polyamide could isolate the flame retardants from the polymer matrix, decrease the decomposition of flame retardants during processing and improve the thermal stability of the flame-retardant system. The encapsulating polyamide could also act as a compatibilizer and synergist to encourage the flame retardants to be dispersed homogeneously in the polymer matrix and increase the flame-retardant performances.

In this study, a novel encapsulated flame retardant containing phosphorus-nitrogen (MSMM-Al-P) was prepared by encapsulating with polyamide 66 (PA66-MSMM-Al-P) for the flame retardation of polyamide 6 (PA6). The structure and thermal stability of PA66-MSMM-Al-P were first characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The flame retardancy and fire risk evaluation of flame-retardant PA6 containing flame retardants (MSMM-Al-P and PA66-MSMM-Al-P) were investigated by the limiting oxygen index test (LOI), vertical burning test (UL-94) and cone calorimeter. Thermal stability and potential flame-retardant mechanism of the flame-retardant PA6 were also investigated.

EXPERIMENTAL

Materials

Formic acid (85%) was purchased from Chengdu Kelong Chemical Reagent Co. PA6 and PA66 were kindly supplied by Baling Petrochemical Co. Monosulphomethylmelamine phosphate (MSMM-Al-P) was synthesized in our laboratory through sulfonation and salification[15].

Preparation of Encapsulate PA66-MSMM-Al-P

The encapsulation (PA66-MSMM-Al-P) was conducted by using a phase separation method (PSM)[18]. PA66 resin was first dissolved in formic acid solution, and flame retardant MSMM-Al-P was added to form a suspension. Ultrasonic vibration was conducted to prepare an even-distributed liquid mixture. Then water was introduced into the reaction vessel. The pH value increased, and the dissolved PA66 gradually precipitated on the surface of flame retardant to obtain the encapsulated flame retardant (PA66-MSMM-Al-P), which was filtrated and dried before being filled into PA6.

Preparation of Flame Retarded PA6 Samples

Flame-retardant PA6s were first prepared by compounding PA6 with the flame retardant of MSMM-Al-P or PA66-MSMM-Al-P through a twin-screw extruder (Nanjing Chengmeng Plastics Machinery Industry Co., Ltd., SLJ–30) at 205–230°C. Extruded strips were cut into pellets, and then dried in a vacuum oven at 100°C for 6 h. The obtained pellets were injection molded (Terromatik Milacron Co., K–TEC 40, GE) at 235°C into specimens for subsequent tests.

Measurements

FTIR and XPS spectra of the flame-retardant microspheres were obtained by an FTIR spectrophotometer (Nicolet 8700, USA) and an XPS spectrum spectrometer (Perkin–Elmer Physics Electronics Co., PHI 5300, USA), respectively. For XPS analysis, MSMM-Al-P and PA66-MSMM-Al-P were ball-milled into powder first, and then they were compressed into thin pellet. Binding energies were calibrated using C_{1s} line (285.0 eV) from hydrocarbon contaminants.

LOI values were measured on an oxygen index meter (Nanjing Jiangning Analysis Instrument Co., JF-3) with sheet dimension of 130 mm × 6.5 mm × 3.2 mm according to ASTM D2863-97. UL-94 test was conducted on an instrument (Nanjing Jiangning Analysis Instrument Co., CZF-2) according to the ASTM D3801 testing procedure with sheet dimension of 130 mm × 13 mm × 3.2 mm. Cone calorimetric analysis was carried out by

following the procedures indicated in the ISO 5660 standard with an FTT cone calorimeter (Fire Testing Technology Co., Ltd., UK). Square specimens (100 mm × 100 mm × 6 mm) were irradiated at an external heat flux of 35 kW/m^2, corresponding to a mild fire scenario.

Thermo-decomposition studies were performed in a temperature range of 40–700°C using a thermogravimetric analyzer (NETZSCH, 209F1, GE) under nitrogen flow of 50 mL/min at a heating rate of 20 K/min. All samples were run in duplicate. The temperature of the instrument was reproducible to within ±0.1°C, and the mass was reproducible to within ±1 wt%. XPS spectra of the thermal decomposed product were recorded on an XPS spectrum spectrometer (PHI 5300, USA).

Surface morphology of char obtained after the LOI test was observed by SEM (JEOL1011, JP) at 10 kV accelerating voltage. Before electronic microscopy scan, surface of the samples was gold plated for 30 min. The magnification of the SEM images was 2000 times.

RESULTS AND DISCUSSION

Preparation of PA66-MSMM-Al-P

PA66 was an acid-soluble resin which could be dissolved in formic acid; while the flame retardant MSMM-Al-P was tested to be inert and insoluble with the solvent. The sample was diluted with water, and the acidity of the system decreased during the neutralizing process, thus leading to the dissolved PA66 precipitating on the surface of the flame retardant particles. Figure 1 shows the FTIR spectra of MSMM-Al-P and PA66-MSMM-Al-P. MSMM-Al-P showed two absorption peaks at 1500 and 810 cm^{-1}, which corresponded to the vibrations of the heteroaromatic structure in the melamine (ME) group. The characteristic absorptions at 3369 and 1680 cm^{-1} resulted from the stretching and bending vibrations of —NH_2 in the ME group. The spectra of PA66-MSMM-Al-P showed absorption bands for the ME and NH groups, and bands at 3410 and 1640 cm^{-1} for —NH stretching vibration in PA66 polymer, which meant the flame retardant was successfully encapsulated by PA66[19]. The XPS spectra of the MSMM-Al-P and PA66-MSMM-Al-P samples were shown in Fig. 2, and the peaks at 134.7, 168.2, and 190.9 eV were attributed to P_{2P}, S_{2S}, and S_{2P}, respectively. The characteristic peaks of P_{2P}, S_{2S}, and S_{2P} disappeared in the XPS spectra, while the intensity of the peaks in the C_{1s}, N_{1s}, and O_{1s} increased. The changes in the characteristic peaks were due to the encapsulating PA66 outside the MSMM-Al-P particles[20]. These results further confirmed that the encapsulation method was effective. Potential schematic diagram of PA66-MSMM-Al-P was summarized in Scheme 1.

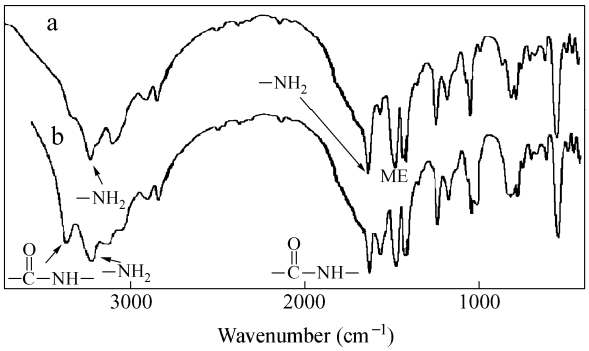


Fig. 1 FTIR spectra of (a) MSMM-Al-P and (b) PA66-MSMM-Al-P

The TG curves of MSMM-Al-P and PA66-MSMM-Al-P were shown in Fig. 3. An endothermic maximum was associated with about 30% mass loss, which corresponded to —$CH_2SO_3Al_{1/3}$ group decomposition (weight fraction 30.4%)[21]. Slower mass loss appeared till the temperature reached 353°C, which was probably a result of releasing melamine and phosphoric acid. At higher temperature, phosphoric acid was transformed into polyphosphoric acid, and the triazine ring in the melamine groups was decomposed. Comparing the thermo-

decomposition behaviors of PA66-MSMM-Al-P and MSMM-Al-P, it showed that both of them were similar at the temperature region below 350°C. The weight loss of both flame retardants became slow with raising temperature over 400°C, and PA66-MSMM-Al-P retained more residues than MSMM-Al-P, indicating MSMM-Al-P might act as a crosslinking agent between the degradation products of PA66 and catalyze the formation of the char. This protective layer suppressed the decomposition of MSMM-Al-P at higher temperatures.

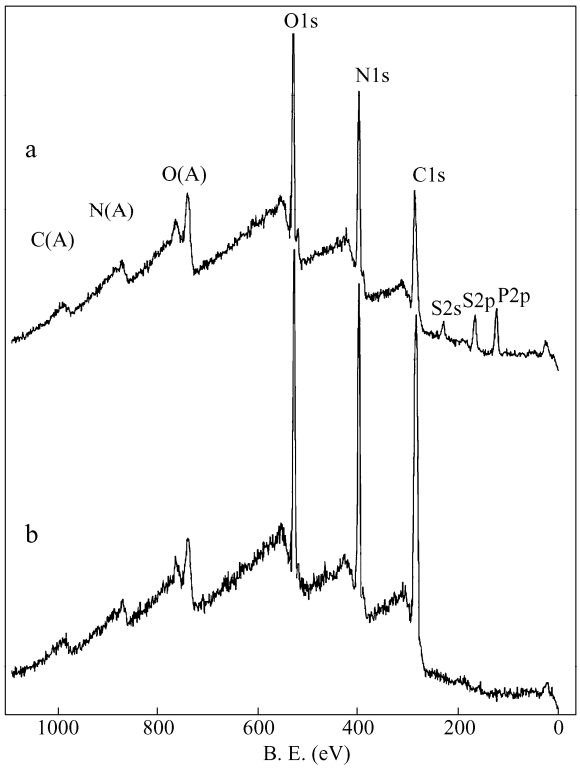
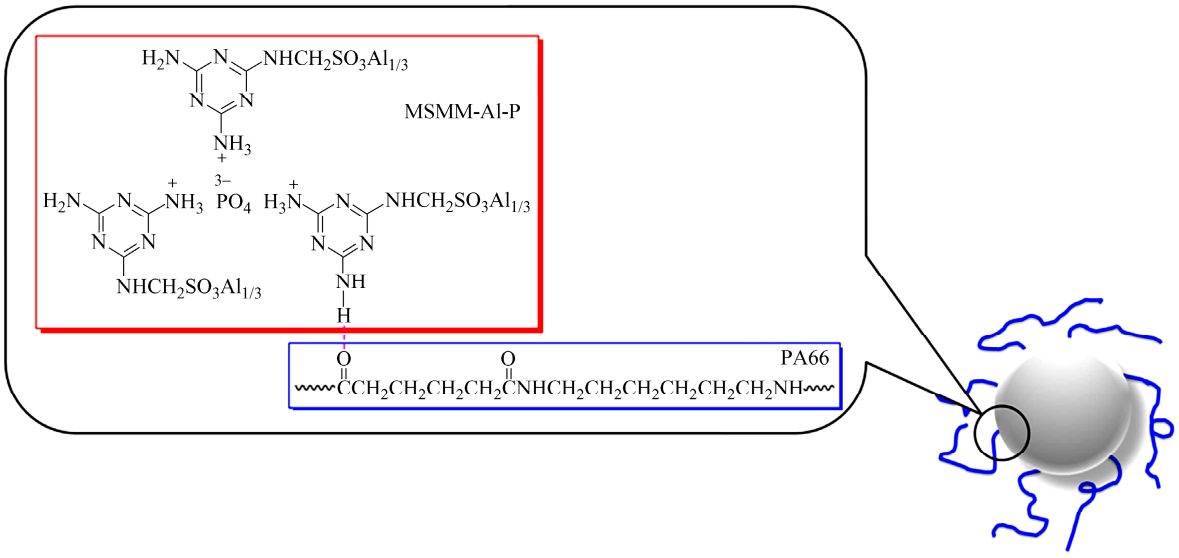


Fig. 2 XPS spectra of (a) MSMM-Al-P and (b) PA66-MSMM-Al-P



Scheme 1 Schematic diagram of polyamide 66 encapsulated flame retardant (PA66-MSMM-Al-P)

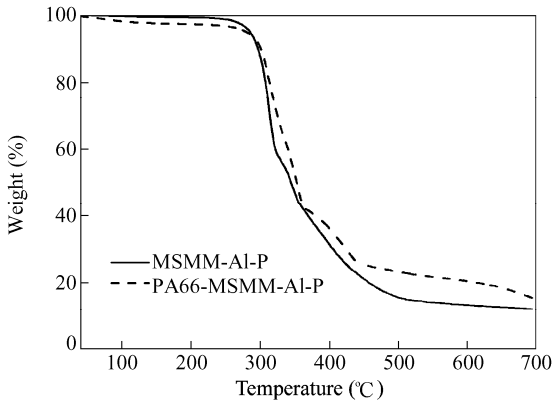


Fig. 3 TG curves of MSMM-Al-P and PA66-MSMM-Al-P at nitrogen flow of 50 mL/min and heating rate of 10 K/min

Effect of PA66 Encapsulated MSMM-Al-P on the Flammability of PA6

LOI test, UL-94 classification and cone calorimetric analysis were carried out to evaluate the flame-retardant performances of flame-retardant PA6 with MSMM-Al-P and PA66-MSMM-Al-P, and related results are summarized in Table 1. LOI value of the flame-retardant PA6 containing 30 wt% of MSMM-Al-P reached 29.6% from 22.4% of neat PA6; while the value arrived at 32.2% when the flame retardant was encapsulated *via* PA66. Also, when MSMM-Al-P was added into PA6, the composite was only V-2 in the UL-94 test; by adding PA66-MSMM-Al-P instead of MSMM-Al-P, the UL-94 rating of the flame-retardant PA6 increased to V-0, suggesting an obvious synergistic effect between PA66 and MSMM-Al-P.

Table 1. LOIs and UL-94 rates of neat PA6 and flame-retardant PA6 blends

Sample	Flame retardant content (wt%)	PA6 (wt%)	LOI (%)	UL-94
Neat PA6	–	100	22.4	NR
PA6/MMSM-Al-P	30	70	29.6	V-2
PA6/PA66-MMSM-Al-P	30	70	32.2	V-0

The cone calorimeter provided insights into intrinsic material properties and monitored fire risks *via* parameters such as heat release rate (HRR), total heat release (THR), carbon dioxide production rate (CO_2PR), time to ignition (TTI), and so on, as Fig. 4 illustrated. Parameters for fire risks summarized in terms of THR, peak of heat release rate (PHRR), TTI and peak of mass loss rate (PMLR) are listed in Table 2. Compared with PA6/MSMM-Al-P, PA6/PA66-MSMM-Al-P showed decreased PHRR, PMLR and THR by 11.3%, 20%, and 5.4%, respectively. The results showed that flame-retardant PA6 with PA66-MSMM-Al-P exhibited a slower burning rate and was less flammable than PA6/MSMM-Al-P.

Table 2. Data of cone calorimetry for neat PA6 and flame-retardant PA6 blends

Sample	THR (MJ/m^2)	PHRR (kW/m^2)	TTI (s)	PMLR (g/s)	PHRR/TTI ($kW/(m^2 \cdot s)$)
PA6	135	863	84	0.81	10.3
PA6/MMSM-Al-P	110	681	100	0.30	6.8
PA6/PA66-MMSM-Al-P	104	604	86	0.24	7.0

Flashover was one of the most terrifying combustion phenomena, which had significant risk in causing major injuries or illness to people, or damaging buildings, cargo and other properties of the environment. Flashover propensity, as defined by PHRR/TTI, combined with THR, gave a better assessment of full-scale fire hazards[22, 23]. Combining the two parameters including THR value and flashover propensity, the fire risk of materials could be rated as follows[22, 23]:

(1) Low grade: flashover propensity = 0.1–1.0, THR = 1.0–10;

(2) Intermediate grade: flashover propensity = 1.0–10, THR = 10–100;

(3) High grade: flashover propensity = 10–100, THR = 100–1000.

Table 2 showed that the flashover propensity of the two kinds of flame-retardant PA6 systems were respectively shorter by 34% and 32% than that of neat PA6, and fire risk reduced from high to intermediate grade. Generally, higher values of flashover propensity and THR were associated with a greater tendency to flashover. This indicated that the flame retardancy of PA6 was promoted, and the incorporation of PA66-MSMM-Al-P was proved to be the best.

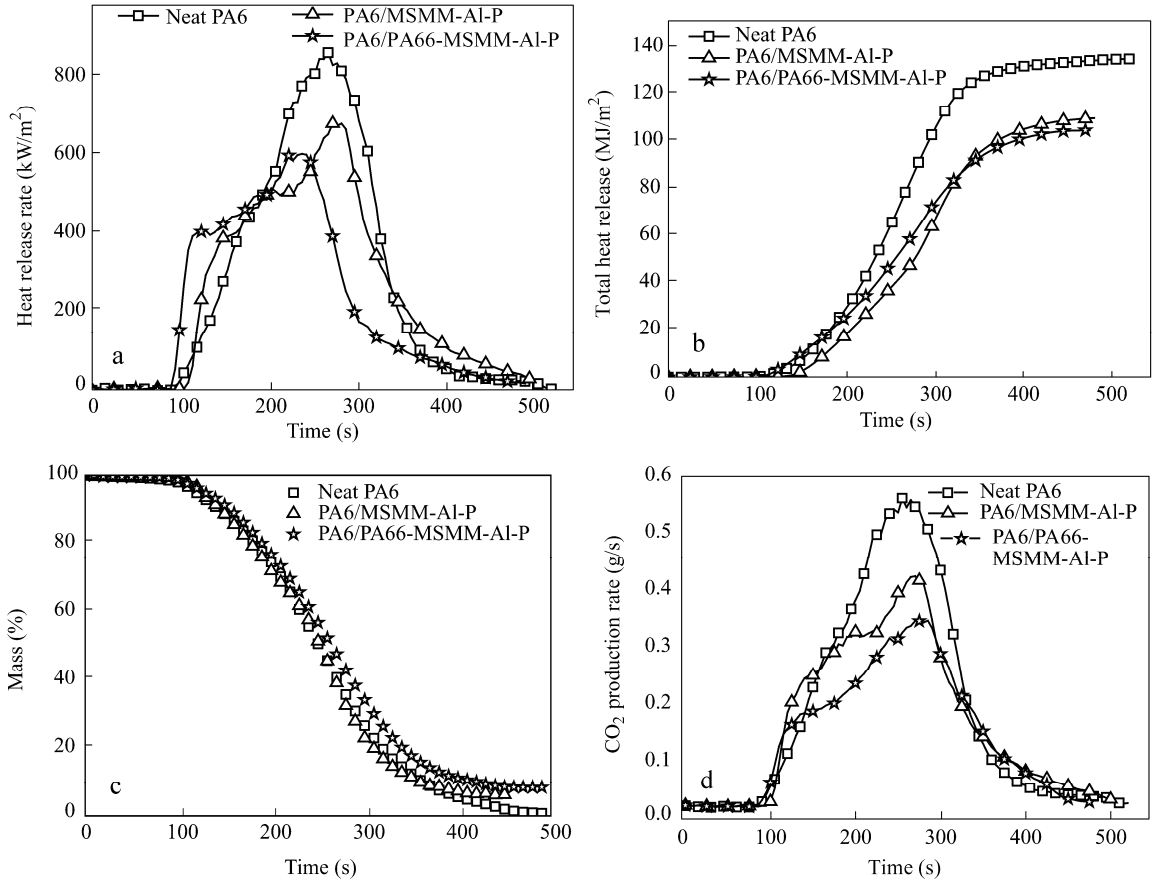


Fig. 4 Cone calorimetric results for neat PA6, PA6/MSMM-Al-P and PA6/PA66-MSMM-Al-P: (a) HRR, (b) THR, (c) mass and (d) CO_2PR curves as function of combustion time

Effect of PA66 Encapsulated MSMM-Al-P on the Thermal Stability of PA6

TG curves of PA6/MSMM-Al-P and PA6/PA66-MSMM-Al-P under nitrogen flow are shown in Fig. 5, and related data are listed in Table 3. Two kinds of flame-retardant PA6 exhibited similar thermostability at lower temperatures, while PA6/PA66-MSMM-Al-P showed higher thermal stability at elevated temperatures. At 400°C, PA6/PA66-MSMM-Al-P significantly increased char residue by about 25% compared with PA6/MSMM-Al-P, which could be explained as PA66 having different charring characteristics over 400°C compared with PA6[1]. The final char yield increased from 5.4% of PA6/MSMM-Al-P to 8.6% of PA6/PA66-MSMM-Al-P. Consequently, the high char residue limited the production of flammable gases, decreasing pyrolysis reactions, thus the flame retardancy of PA6/PA66-MSMM-Al-P was improved.

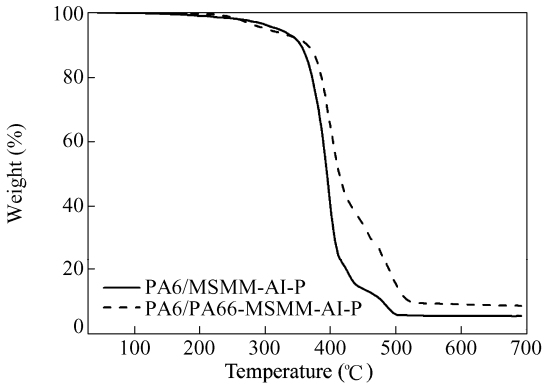


Fig. 5 TG curves of PA6/MSMM-Al-P and PA6/PA66-MSMM-Al-P at heating rate of 10 K/min

Table 3. Data of TG analyses for PA6/MSMM-Al-P and PA6/PA66-MSMM-Al-P

Sample	$T_{5\%}$[a] (°C)	$T_{1,\,peak}$ (°C)	$T_{2,\,peak}$ (°C)	Residual (700°C)
PA6/MSMM-Al-P	295	392	490	5.4%
PA6/PA66-MSMM-Al-P	320	397	482	8.6%

[a] Temperature (°C) for 5% weight loss

Effect of PA66 Encapsulated MSMM-Al-P on the Charring Properties of PA6

The quantitative XPS analysis of the residue of flame-retardant PA6 formulation at a series of temperatures is summarized in Tables 4 and 5, revealing the accumulation of char and the degree of crosslinking during thermo-decomposition. Sherwood and Mcfeely[24, 25] reported that the C_{1s} binding energy of pure graphite was at 283.5–284 eV and a graphite-like char remained in the condensed phase, which could provide thermal protection to the polymer. It can be seen from XPS spectra (C_{1s}, Table 4) that a graphite-like layer is formed on the surface of PA6/MSMM-Al-P at a certain stage of heating process. The analysis of main element of the residue indicated that carbon was shown by the lines with binding energies C_{1s} 285, 286, 288, and 289.4 eV[26, 27], which corresponded to PA6 resin fragments C—H and C—C, CH_2—NH, carbonyl group (C=O) and COOR (C=O),

Table 4. Binding energies (E_b) of C_{1s}, O_{1s}, N_{1s}, and P_{2p} lines and atomic content (AC) during the pyrolysis of PA6/MSMM-Al-P

Temperature (°C)	C_{1s}		O_{1s}		N_{1s}		P_{2p}	
	E_b (eV)	AC (%)	E_b (eV)	AC (%)	E_b (eV)	AC (%)	E_b (eV)	AC (%)
25	285.0	43.9	531.5	13.2	399.5	13.9	134.3	2.9
	286.0	9.0	532.9	3.2	400.0	6.3		
	288.1	7.6						
350	284.8	52.0	531.5	13.4	399.5	3.9	134.3	2.3
	286.0	7.8	532.9	5.1	400.0	1.8		
	288.1	8.3			401.0	0.9		
	289.0	4.5						
400	284.8	54.6	531.8	9.2	398.4	0.9	134.4	2.1
	285.8	9.9	533.0	3.7	400.0	2.2		
	288.1	7.8			401.0	0.9		
	289.4	7.1			401.6	1.6		
450	284.8	46.9	532.0	11.7	400.0	2.6	134.4	3.9
	285.8	7.0	533.0	8.8	401.0	1.6		
	288.1	6.3			401.9	2.8		
	289.4	8.4						
650	284.8	49.2	532.2	9.0	400.0	2.4	134.5	3.2
	286.0	7.2	533.0	11.9	401.0	1.8		
	288.1	6.6			401.9	2.8		
	289.6	3.8						

respectively. Two lines, 400–400.2 eV (N=C group) and 401.1 eV (N−H group)[28], were observed in the nitrogen spectrum. Upon heating, the nitrogen deconvolved into four components at binding energies of 398.4, 400, 401, and 401.9 eV, which were attributed to the C=N (carbon nitride/melamine condensation product), C=N (triazine ring), N−H and NOP groups, respectively[29–32]. Phosphorus was shown in the spectra by the lines with binding energies P_{2p} 134.3–134.5 eV (O=P−O), which was characteristic of phosphorus with maximum oxidation[33].

Table 5. Binding energies (E_b) of C_{1s}, O_{1s}, N_{1s}, and P_{2p} lines and AC during the pyrolysis of PA6/PA66-MSMM-Al-P

Temperature (°C)	C_{1s}		O_{1s}		N_{1s}		P_{2p}	
	E_b (eV)	AC (%)	E_b (eV)	AC (%)	E_b (eV)	AC (%)	E_b (eV)	AC (%)
25	285.0	46.4	531.5	10.3	399.5	13.7	134.3	2.8
	286.0	9.4	532.9	2.3	400.0	6.2		
	288.1	8.9						
350	284.8	51.7	531.5	11.3	399.5	5.4	134.3	2.9
	286.0	8.6	532.9	3.5	400.0	3.2		
	288.1	8.6			401.0	0.9		
	289.0	3.9						
400	284.8	52.6	531.8	9.7	398.4	2.1	134.4	2.6
	285.8	9.3	533.0	3.9	400.0	2.2		
	288.1	8.8			401.0	1.3		
	289.4	5.5			401.6	2.0		
450	284.8	47.1	532.0	10.7	400.0	2.6	134.4	3.9
	285.8	7.1	533.0	8.8	401.0	1.7		
	288.1	4.4			401.9	2.9		
	289.4	10.8						
650	284.0	4.3	532.2	5.0	400.0	2.8	134.5	4.2
	284.8	52.4	533.0	9.6	401.0	2.1		
	286.4	9.0			401.9	3.2		
	288.1	4.2						
	289.4	3.2						

C_{1s} relative intensity and binding energy of PA6/PA66-MSMM-Al-P are listed in Table 5. Increased carbon content in foam coke led to a considerable change in the character of heat capacity dependence on temperature. Graphite-like char was accumulated on the surface of the polymer and increased nitrogen concentration on the surface, indicating that the structure and elements of char layers had been improved.

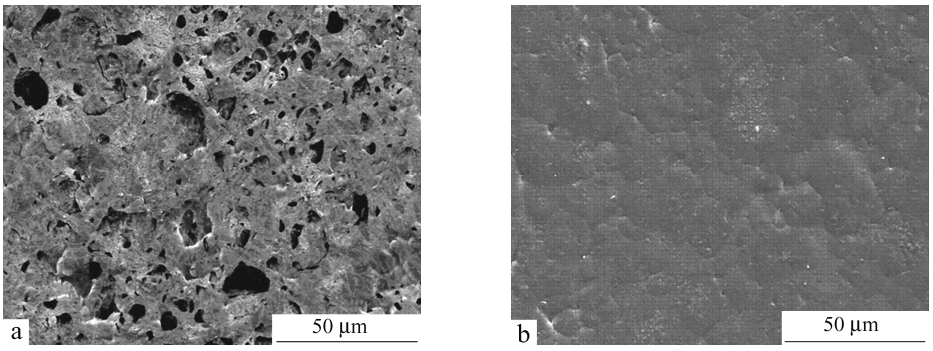


Fig. 6 SEM micrographs of the internal surface of the char residue for (a) PA6/MSMM-Al-P and (b) PA6/ PA66-MSMM-Al-P

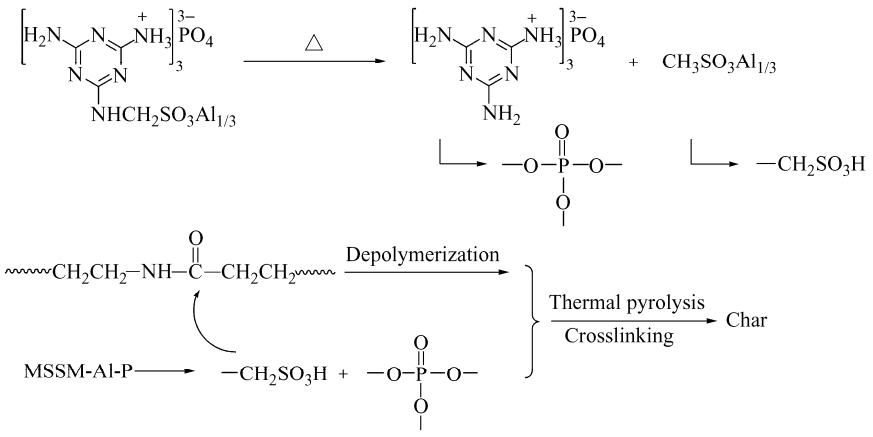
SEM photographs of the morphological structures of the residual char of the systems proved the better charring performance of PA6/PA66-MSMM-Al-P compared with PA6/MSMM-Al-P. From Fig. 6, a porous char could be observed in Fig. 6(a); however, a consolidated, crack-free, and coherent structure was seen in Fig. 6(b), indicating an effective char yield. The more coherent char layer of PA6/PA66-MSMM-Al-P could provide a better barrier to prevent heat and fuel gas from transferring during the burning process.

The Mechanism for the Formation of Residual Char Based on PA66-MSMM-Al-P

The pyrolysis and combustion of PA6 and flame-retardant ones had a close relationship with their thermal degradation process. The mechanism involving the formation of the char was clearly related to the releasing of acid sources (phosphoric acid and sulfonic acid) formed from the acid moieties of PA66-MSMM-Al-P. The decomposition of MSMM-Al-P could be divided into three temperature regions, 260–290°C, 290–370°C, and 370–500°C. According to Costa and Camino[34], the weight loss at 260–290°C could be ascribed to the dehydration reaction of the formed MP and the thermo-decomposition of the $-CH_2SO_3Al_{1/3}$ group, in which the decomposed product of MSMM-Al-P was sulfonic acid. Serving as a synergist, sulfonic acid was the strong acid source, which could promote more condensed and compact char layers. The weight loss at 290–370°C was then contributed by the dehydration of the formed melamine pyrophosphate (MPyP). The dehydration product was MPyP, and MSMM-Al-P generated phosphoric acid during decomposition.

Phosphoric and sulfonic acid acted as acid precursors, which induced charring and performed crosslinking with decomposition products of PA6 and PA66. Due to the strong oxidizing, hydrolyzing and carbonizing effect, the sulfonic acid would perform rapid sulfonation of the PA6 degradation product. In the case of the mixed acid source (phosphoric and sulfonic acid), the char was more compact and was formed more quickly. Due to the existence of encapsulating PA66, the flame retardant played a positive role in a wider range of temperatures, and the effect of phosphoric and sulfonic acid matched PA6 more appropriately. Therefore, the mixed acid source (phosphoric and sulfonic acid) in PA6/MSMM-Al-P system exhibited better catalytic effects in accelerating the formation of char layers.

Several studies[1, 3] had shown that adding flame retardant to PA66 and PA6 showed different but complementary charring mechanisms. Compared with PA6, PA66 resulted in greater quantity of solid residues that could be attributed to a more efficient crosslinking reaction. PA6 decomposed at higher temperatures, and less char was produced. Thus, encapsulating PA66 was easier to crosslink, char precursor was produced earlier, and higher-quality char protecting layer was formed together with PA6 char residue formed later. Therefore, the char yield of PA6/PA66-MSMM-Al-P increased from 5.4% to 8.6 % compared with PA6/MSMM-Al-P, and the thermal stability of the charred layer was improved, which was verified by the thermal-decomposition analysis. Thus, the condensed phase flame-retardant function of the flame-retardant PA6 was promoted. Potential flame-retardant mechanism of PA6/PA66-MSMM-Al-P is summarized in Scheme 2.



Scheme 2 A proposed char-forming mechanism of flame-retardant PAc6 with PA66-MSMM-Al-P

CONCLUSIONS

In summary, MSMM-Al-P as acid and vapour sources which as encapsulated by PA66 (as the carbon source) was applied in flame-retardant PA6. As a macromolecular charring agent, PA66 could effectively enhance the thermal stability and charring performance of the intumescent system as well as the flame retardancy of PA6. The heat release rate, mass loss rate, CO_2PR and THR of PA6/PA66-MSMM-Al-P were obviously lower compared with PA6/MSMM-Al-P. In addition, the flashover time of two kinds of flame-retardant PA6 systems were respectively shorter by 34% and 32% than that of neat PA6, and the fire risk was reduced to intermediate grade comparing with the high grade of the neat PA6. The encapsulation of MSMM-Al-P by PA66 effectively delayed the decomposition of MSMM-Al-P at high temperatures, and the effect of phosphoric and sulfonic acid matched PA6 more appropriately. Due to the different charring tendencies between PA66 and PA6, higher quality protecting char layer was generated. Thus, the flame retardancy of PA6 was improved after MSMM-Al-P was encapsulated by PA66.

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