

## SYNERGISTIC EFFECTS OF NOVOLAC-BASED CHAR FORMER WITH A PHOSPHORUS/NITROGEN-CONTAINING FLAME RETARDANT IN POLYAMIDE 6\*

Wei-cheng Xiong, Li Chen\*\*, De-yi Wang, Fei Song and Yu-zhong Wang\*\*

*Center for Degradation and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China*

**Abstract** The synergistic effect of phosphorus oxynitride (PON) with a novolac-based char former modified by salification (NA-metal salt) on the flame retardance of polyamide 6 (PA6) was investigated. For this purpose, various flame-retardant PA6 systems were melt-compounded with PON, PON/NA, PON/NA- $V_2O_5$  and PON/NA- $Fe_2O_3$ , and their flame retardance was evaluated by measuring the limiting oxygen index (LOI) values and UL-94 vertical burning ratings. The results showed that, compared with the PA6/PON/NA system, the combination of two char formers (NA- $V_2O_5$ , NA- $Fe_2O_3$ ) with PON could obviously improve the char formation and flame retardance of PA6. The flame retardance and cone calorimetric analyses showed the stronger synergism as well as the better flame retardant performance of PON/NA- $Fe_2O_3$  flame retardant system. The effects of different char formers on the flame retardance and thermal stability of this system were also discussed.

**Keywords:** Polyamide; Flame retardance; Novolac resin; Synergistic effect.

### INTRODUCTION

Polyamide 6 (PA6), an engineering thermoplastics with excellent mechanical and electrical properties, was widely used in electronic and electrical equipments. However, the application of PA6 has been limited in some areas due to its flammability. The general method to improve flame retardance of PA6 was the addition of intumescent flame retardants to form a protective layer<sup>[1, 2]</sup>. On heating, intumescent materials could form a foamed surface cellular charred layer, which protected the underlying material from the action of the flame. The proposed mechanism of the action was based on the charred layer which slowed down heat and mass transfer between the gas and condensed phase as a physical barrier.

An ultimate condensation product of melamine and phosphoric acid was a non-melt solid, named as phosphorus oxynitride (PON). PON and its analogues have been widely applied in flame-retardant polymers including PA6<sup>[3–8]</sup>. During the polymer combustion, novolac resin could be used as a good char source and phosphorus-containing compounds could promote the char formation<sup>[9, 10]</sup>. A marginal anti-dripping effect was achieved only by the formulation of PON and novolac resin, which could slightly improve the UL-94 test performance. Thus combination of PON and novolac resin cannot endow PA6 with satisfied flame retardance due to its serious flammable dripping.

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\*\* Corresponding author: Li Chen (陈力), E-mail: l.chen.scu@gmail.com

Yu-zhong Wang (王玉忠), E-mail: yzwang@scu.edu.cn

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In order to increase the flame retardant synergism of novolac resin in PA6/PON, we converted the novolac resin into metal salts, because the effectiveness of the flame retardant agent combination can be generally improved<sup>[11]</sup>. Here two kinds of metal oxides ( $V_2O_5$ ,  $Fe_2O_3$ ) were selected as the examples, which were widely used as carbonization promoter of polymeric materials<sup>[12–14]</sup>. The results showed that the combination of two char formers (NA- $V_2O_5$ , NA- $Fe_2O_3$ ) with PON improved not only the char formation but also the flame retardance of PA6, comparing with PA6/PON/NA composites. It was found that the novolac based char formers could promote char forming and give a better char residue of decomposition products of PA6 during combustion.

## EXPERIMENTAL

### Materials

Novolac resin (RD-104) was provided by Shandong Runda Chemical Engineering Co. Iron oxide and vanadic oxide were purchased from Chengdu Kelong Chemical Reagent Co. PA6 (YH800) was supplied by Yueyang Baling Petrochemical Co. PON flame retardant was prepared according to the former literature<sup>[6]</sup>, and its synthetic route is shown in Fig. 1.

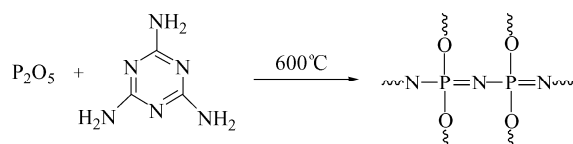


Fig. 1 Synthesis of phosphorus oxynitride

### Synthesis of PON

Phosphorus oxynitride was prepared according to the method suggested by Sommer<sup>[6]</sup>. Phosphorus oxide and melamine were mixed with the weight ratio of 1:2 and heated in a dish made of V4A steel. The temperature was allowed to increase gradually within 45 min to 600°C and keep at 650°C for 30 min. Then the pulverulent mass became more viscous, meanwhile ammonia and carbon dioxide were given off. The reaction product, a white porous mass, can be easily pulverized after cooling. The obtained white, light powders could be dissolved in concentrated sulfuric acid. According to chemical analysis, the phosphorus content corresponded well to that of PON (calcd. 50.8%, found 48.7%).

### Preparation of Novolac-based Char Former

Novolac resin and metal oxides (vanadic oxide and iron oxide) were mixed with the weight ratio of 50:1 and heated at 230°C for 4 h. The novolac resin was reacted with metal oxide and converted into metal salts (NA- $V_2O_5$ , NA- $Fe_2O_3$ ). After casting the finished resins onto a metal plate, they hardened quickly and formed brittle products which could readily be sized within 2 mm to 4 mm diameter.

### Preparation of Flame-retardant PA6

Polyamide 6 (PA6) was mixed with novolac resin and PON in a two-screw extruder (Nanjing ChengMeng Plastics Machinery Industry Co., Ltd, SLJ-30) under the range of 205–230°C. The PA6 composites 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 flammability test.

### Measurements

The limited oxygen index (LOI) values were measured on a oxygen index meter (Nanjing Jiangning Analysis Instrument Co., JF-3) with sheet dimensions of 130 mm × 6.5 mm × 3.2 mm according to ASTM D2863-97. The vertical burning test (UL-94) of samples was conducted on an instrument (Nanjing Jiangning Analysis Instrument Co., CZF-2) according to ASTM D3801 testing procedure. The samples were made to a size of 130 mm × 13 mm × 3 mm. The cone calorimeter tests were carried out by following the procedures indicated in

the ISO 5660 standard with a FTT cone calorimeter (Fire Testing Technology Co., Ltd., UK). Square specimens (100 mm × 100 mm × 30 mm) were irradiated at a heat flux of 35 kW/m<sup>2</sup>.

The thermal decomposition studies were performed at a temperature range of 40–700°C using a thermogravimetric analyzer (NETZSCH, 209F1, GE) under nitrogen environments with heating rates of 20 K/min. The outlet of the TGA was coupled on-line with an FTIR spectrometer through an interface that consisted of a gas cell heated up to 200°C. The gaseous fraction of decomposition products was analyzed by an FTIR (Nicolet, 8700, USA) spectrometer combined with a NETZSCH 209F1 thermogravimetric apparatus. The TG-FTIR measurements were carried out in a nitrogen atmosphere (gas carrier) at a heating rate of 10 K/min up to 650°C with samples weight of about 12 mg. IR spectrum was obtained by eight scans at a resolution of 8 cm<sup>-1</sup>.

The FTIR spectra of residues of flame-retardant PA6 after LOI test were recorded with KBr powder by using a Nicolet FTIR 8700. The surface morphology of char obtained after LOI test was observed by means of a scanning electron microscope (SEM, JEOL1011, JP) at 10 kV accelerating voltage.

## RESULTS AND DISCUSSION

### *Effect of Combined Char Former and PON on the Flammability of PA6*

Various formulations incorporated PON, char former (NA, NA-V<sub>2</sub>O<sub>5</sub>, NA-Fe<sub>2</sub>O<sub>3</sub>) with PA6 were prepared and their LOI values were evaluated. The flame retardant properties of PA6 filled with PON and co-additives were characterized by determining the limiting oxygen index (LOI), and UL-94 vertical burning results. Relevant results are summarized in Table 1. The neat PA6 exhibited LOI value of 22.4. Similar LOI values were obtained for all formulations containing flame retardant PON and char former. On the other hand, when PON was added into PA6 alone, the composite was not rated (NR) in the UL-94 test. UL-94 rating of the PON/NA binary combination was slightly improved to V-2. Adding NA-V<sub>2</sub>O<sub>5</sub> and NA-Fe<sub>2</sub>O<sub>3</sub> to the PON formulation could further increase the UL-94 rating to V-1 and V-0, respectively. Especially, in the PON-containing combination system, NA-Fe<sub>2</sub>O<sub>3</sub> was a more effective synergist than NA-V<sub>2</sub>O<sub>5</sub>. Furthermore, three formulations of PON, and NA or NA-metal salt combination (PA2, PA4 and PA6) were found to give remarkably low UL-94 rating of not rated, in spite of comparatively high LOI values. In order to explain this difference, the influences of novolac based char former and PON (PON/NA, PON/NA-V<sub>2</sub>O<sub>5</sub>, and PON/NA-Fe<sub>2</sub>O<sub>3</sub>) on the flame retardant properties of PA6 matrix were investigated by cone calorimeter as follows.

**Table 1.** Flame retardant formulations and their LOI and UL-94 combustion tests

| Sample code | Additive (wt%) |                                         | UL-94 | LOI  |
|-------------|----------------|-----------------------------------------|-------|------|
|             | PON            | NA or NA-metal salt                     |       |      |
| PA          | 0              | 0                                       | NR    | 22.4 |
| PA1         | 30             | 0                                       | NR    | 32.2 |
| PA2         | 20             | 10 (NA)                                 | NR    | 28.7 |
| PA3         | 12             | 18 (NA)                                 | V-2   | 30.0 |
| PA4         | 20             | 10 (NA-V <sub>2</sub> O <sub>5</sub> )  | NR    | 33.1 |
| PA5         | 12             | 18 (NA-V <sub>2</sub> O <sub>5</sub> )  | V-1   | 33.8 |
| PA6         | 20             | 10 (NA-Fe <sub>2</sub> O <sub>3</sub> ) | NR    | 32.3 |
| PA7         | 12             | 18 (NA-Fe <sub>2</sub> O <sub>3</sub> ) | V-0   | 31.3 |

The HRR and THR of cone calorimeter tests using external heat fluxes of 35 kW/m<sup>2</sup> are illustrated in Fig. 2 and Fig. 3, and the cone calorimeter results are summarized in Table 2.

### *Heat release*

It was clear that a significant flame retardant effect was obtained with treatment on PA6. Neat PA6 burned rapidly after ignition and a sharp heat release rate (HRR) peak appeared at 255 s. When PON/NA was presented, time to ignition ( $t_{\text{ign}}$ ) of PA6/PON/NA samples decreased slightly with a notable reduction of the peak of heat (PHRR) value. The HRR of samples showed two separate peaks during burning, which indicated the gradual

burning of the specimen was formed through the thickness after the initial charred layers. This combustion feature of multiple HRR peaks was intumescent flame retardant peculiarity<sup>[15, 16]</sup>. An approximate 62% reduction in the PHRR of PA6/PON/NA composite may be attributed to the carbonization reaction of the decomposition products from PA6 flame retarded by PON/NA<sup>[17]</sup>. While PA6/PON/NA- $V_2O_5$  and PA6/PON/NA- $Fe_2O_3$  showed lower burning rates with the peak of 278 and 193  $kW/m^2$ , which were only 32% and 22% for PA6, respectively. The results suggested that the addition of NA- $V_2O_5$  and NA- $Fe_2O_3$  can reduce the flammability in terms of PHRR.

Figure 3 showed that the total heat release of PA6 flame retarded with PON. In addition, total heat release (THR) of flame-retardant PA6 composites with reasonable composition reduced by 20%–25% compared to that of neat PA6. The conclusion could be made that such synergistic agents could not only reduce the total heat release but also notably decrease the peak of heat release as well as gradual release of heat.

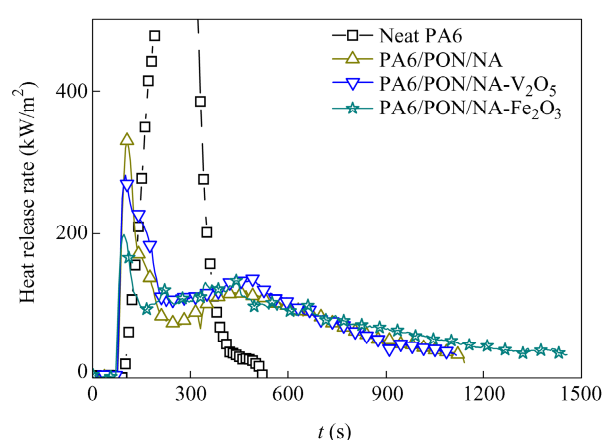


**Fig. 2** The heat release rate (HRR) curves of neat PA6, PA6/PON/NA, PA6/PON/NA- $V_2O_5$  and PA6/PON/NA- $Fe_2O_3$

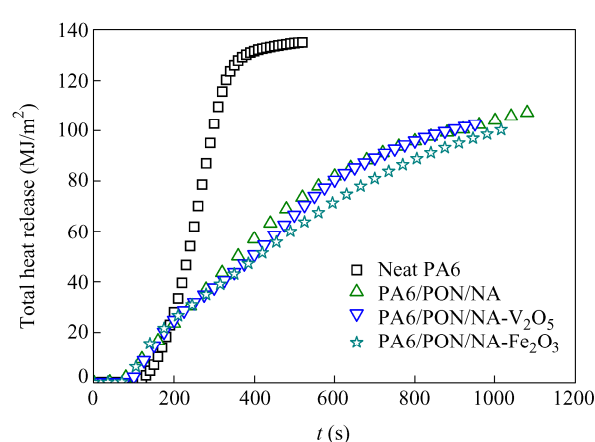


**Fig. 3** The total heat release (THR) curves of neat PA6, PA6/PON/NA, PA6/PON/NA- $V_2O_5$ , and PA6/PON/NA- $Fe_2O_3$

**Table 2.** Cone summary results of pristine PP and its flame retardant composites (35  $kW/m^2$ )

| Sample code | TTI (s) | THR ( $MJ/m^2$ ) | PHRR ( $kW/m^2$ ) | TSP ( $m^2/s$ ) |
|-------------|---------|------------------|-------------------|-----------------|
| PA          | 84      | 135              | 863               | 1               |
| PA3         | 72      | 108              | 331               | 12              |
| PA5         | 71      | 104              | 278               | 15              |
| PA7         | 68      | 101              | 193               | 8               |

#### Mass loss and smokes

Figure 4 shows the mass loss of the samples with combustion time. The slope of curves significantly decreased with the addition of flame retardant into PA6, and the weight of the char residues was higher compared with that of PA6. It demonstrated the presence of PON gave rise to a dramatic change in pyrolysis under external heat radiation, and promoted extensive charring in PA6. For these formulations of PON with other co-additives, the slope of mass loss curves remained similar to that of the addition of 30 wt% PON/NA, in which the slope of curve incorporated with synergistic NA- $Fe_2O_3$  was the lowest. Neat PA6 yielded a residue of 2.7 wt%, while those of flame retardant PA6 (PA6/PON/NA, PA6/PON/NA- $V_2O_5$ , PA6/PON/NA- $Fe_2O_3$ ) upon heating were 40.4 wt%, 43.7 wt% and 38.7 wt%, respectively. The presence of NA- $Fe_2O_3$  had the best flame retardance on both the UL-94 test and cone calorimeter experiment, but it lowered the char yield obviously. The flame retardant effect thus depended on the properties and the rate of forming char. Compared with the cone results, superior burning performance in terms of much lower rate of heat and mass loss could be seen in PA6/PON/NA- $Fe_2O_3$ .

A similar phenomenon was observed in the total smoke product (TSP) and smoke product rate (SPR) of the above samples. From Fig. 5, it is easy to find out that the smoke rate of flame retardant samples was slower than that of neat PA6, although their amounts of smoke were increased. The change of the SPR was similar for the addition of NA- $V_2O_5$  and NA- $Fe_2O_3$ , and the SPR of PA6 flame retarded by PON/NA- $Fe_2O_3$  was the lowest. This meant that the PA6 flame retarded by PON/NA- $Fe_2O_3$  composite could make the residue serve as a better barrier, which showed a more significantly reduced rate of decomposition of the underlying char protection than did equivalent PA6-containing combinations.

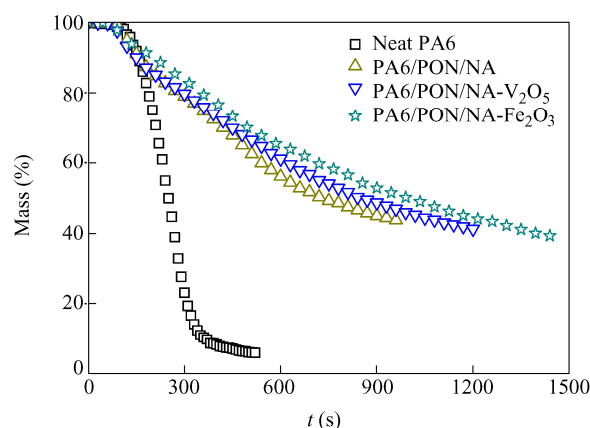


**Fig. 4** The mass loss (ML) curves of neat PA6, PA6/PON/NA, PA6/PON/NA- $V_2O_5$  and PA6/PON/NA- $Fe_2O_3$

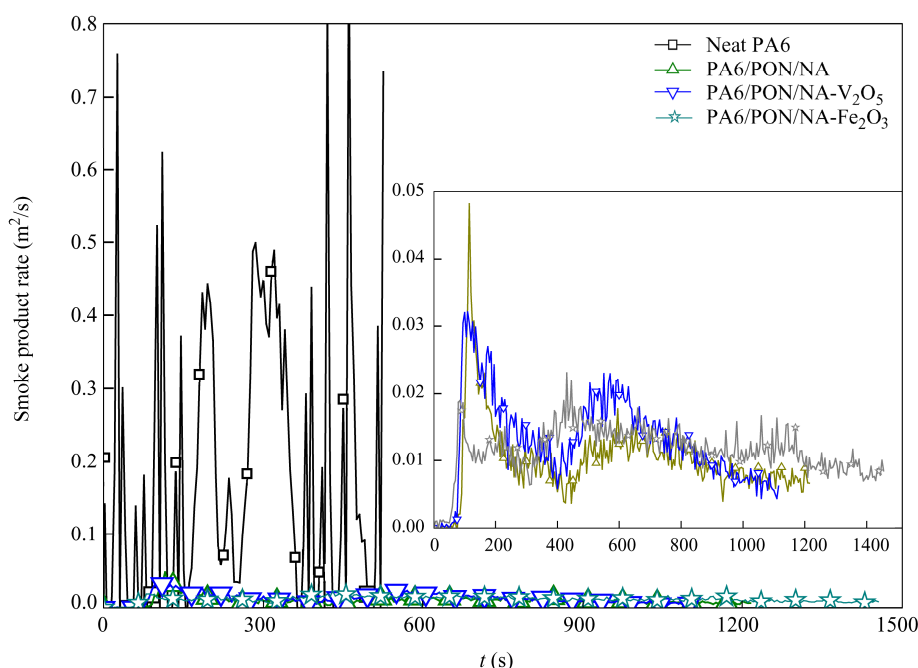


**Fig. 5** The smoke product rate (SPR) curves of neat PA6, PA6/PON/NA, PA6/PON/NA- $V_2O_5$  and PA6/PON/NA- $Fe_2O_3$

### ***Effect of Combined Char Former, PON on the Thermal Stability of PA6***

The TGA and DTG curves of neat PA6 and flame-retardant PA6 in atmosphere of nitrogen, are shown in Fig. 6, and the related data are listed in Table 3. Comparison of these curves showed that between 320°C and 450°C, the mass loss of flame-retardant PA6 began with a fast process followed by a slower process which was

ascribed to the protection against thermal decomposition for PA6 at high temperature stage. The weight loss rate of the second main decomposition step (corresponding to form intumescent carbonaceous layers and charring) was remarkably decreased for all systems with addition of PON, especially for the systems with NA- $V_2O_5$  and NA- $Fe_2O_3$  where the minimal weight loss rate, 0.13%/°C and 0.11%/°C, were found. The residues of PON flame retardant systems with PON at 700°C were higher than that of the neat PA6 system. These data clearly indicated that PON was an efficient char promoter for PA6. The addition of flame retardant seemed to alter the mechanism of thermal decomposition of PA6, since three steps of weight loss were observed. A decrease of the weight loss rate of the second peak could be found in the flame retardant systems with NA-metal salt (see Table 3), relative to the PA6/PON/NA, meaning a promoted crosslink process by addition of NA- $V_2O_5$  or NA- $Fe_2O_3$  to some extent<sup>[18]</sup>. At 700°C, the yield of the residual char was almost similar in these flame-retardant PA6 composites, which indicated that the composites with PON/NA-metal salt promoted the formation of residual char in intermediate stage of combustion albeit with similar yield.

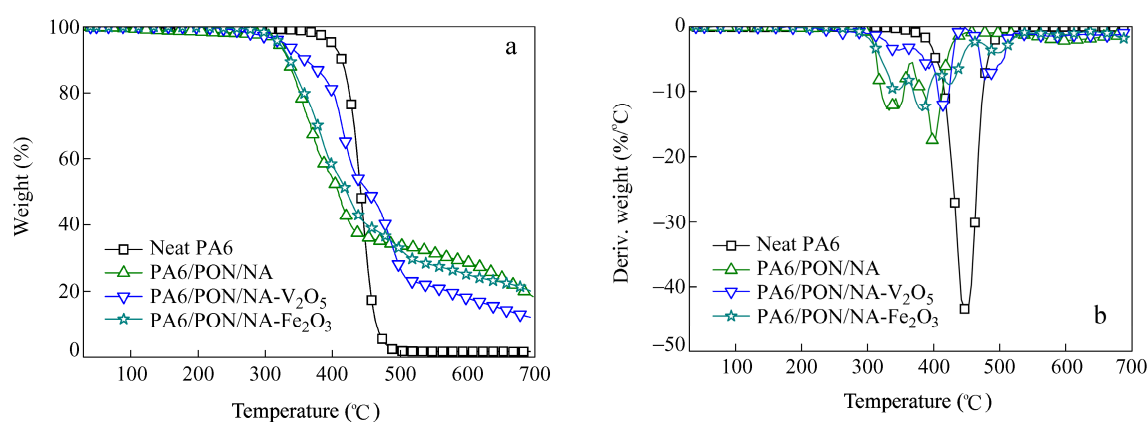


**Fig. 6** Thermogravimetry (a) and derivative thermogravimetry (b) curves of neat PA6, PA6/PON/NA, PA6/PON/NA- $V_2O_5$  and PA6/PON/NA- $Fe_2O_3$  in nitrogen at a heating rate 20 K/min

**Table 3.** Flame retardant TG and DTG experimental results of the analysis

| Sample code | $T_{5\%}^a$ (°C) | $T_{1\text{ peak}}$ (°C) | $T_{2\text{ peak}}$ (°C) | $T_{3\text{ peak}}$ (°C) | Residue yield at 700°C (wt%) |
|-------------|------------------|--------------------------|--------------------------|--------------------------|------------------------------|
| PA          | 397              | 452                      | —                        | —                        | 2                            |
| PA3         | 320              | 332                      | 398                      | 597                      | 20                           |
| PA5         | 327              | 347                      | 409                      | 477                      | 17                           |
| PA7         | 320              | 347                      | 382                      | 422                      | 20                           |

<sup>a</sup> Temperature (°C) for 5% weight loss

### Effect of Combined Char Former and PON on the Evolved Gas

The evolved gas analysis for flame-retardant PA6 by TG-FTIR exhibited characteristic bands of ammonia ( $3332\text{ cm}^{-1}$ ), carbon dioxide ( $2360\text{ cm}^{-1}$ ), hydrocarbons ( $2943$  and  $2879\text{ cm}^{-1}$ ) and amide ( $962$  and  $934\text{ cm}^{-1}$ ), proving the main decomposition products under programming heating process (Fig. 7). These results were comparable to the published studies<sup>[19–23]</sup>. The profile of the amount of various gases released during thermal decomposition of flame-retardant PA6 in nitrogen atmosphere is shown in Fig. 8. The maximum production of all the gases identified occurred in the same temperature region for the flame-retardant PA6. The profile of evolution of three kinds of flame-retardant PA6 indicated these materials could work as flame retardant for PA6 which had the similar decomposition process in the range of 350–650°C. The release and release rate of gas product, hydrocarbon/amide, was reduced in the case of PA6/PON/NA- $Fe_2O_3$  and PA6/PON/NA- $V_2O_5$  as compared to PA6/PON/NA. The addition of PON/NA, PON/NA- $V_2O_5$  and PON/NA- $Fe_2O_3$  probably caused accumulation of char protection in the condensed phase, while suppressing the production of volatile species<sup>[24]</sup>.

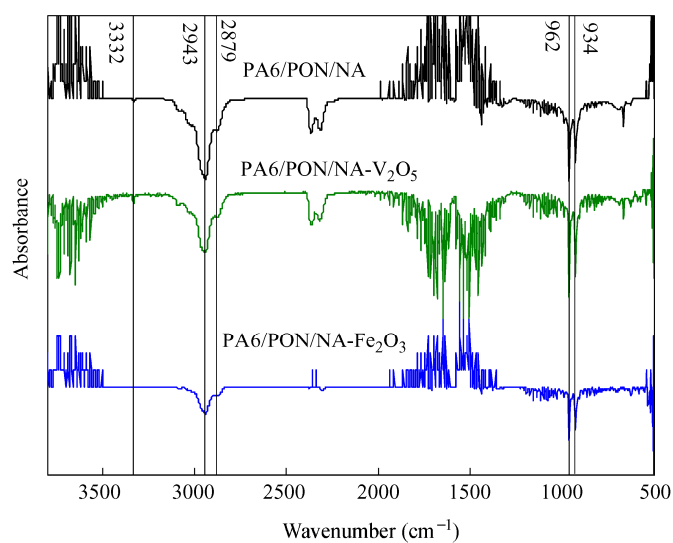


**Fig. 7** Characteristic evolved gas analysis spectra of PA6/PON/NA at 36.5 min, PA6/PON/NA- $V_2O_5$  at 36.5 min and PA6/PON/NA- $Fe_2O_3$  at 37 min

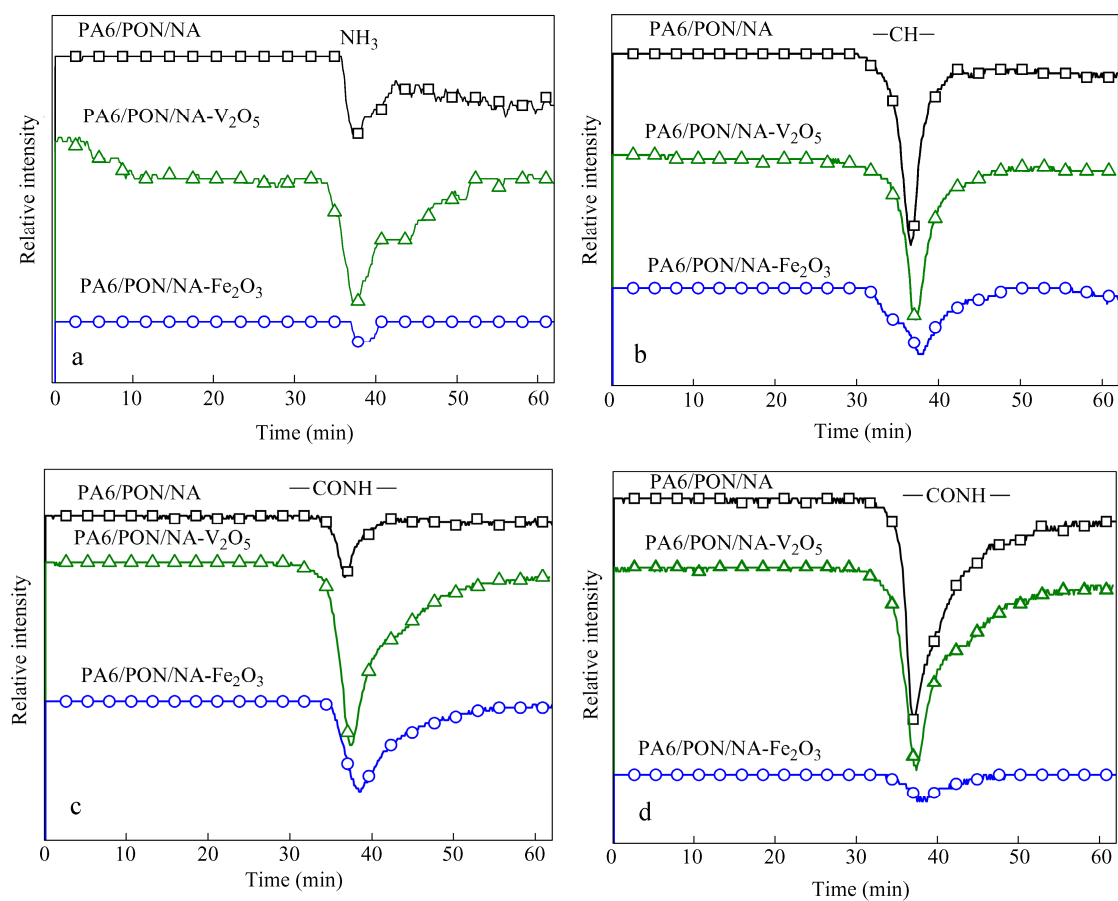


**Fig. 8** Three evolved gases profile of flame retardant PA6 on pyrolysis: (a)  $NH_3$ , (b)  $CH$ , (c) amide at  $962\text{ cm}^{-1}$  and (d) amide at  $934\text{ cm}^{-1}$

### Effect of Combined Char Former and PON on the Char Morphology of PA6

Figures 9 and 10 show the SEM photographs of the internal and external char surfaces of PA6/PON/NA, PA6/PON-NA- $V_2O_5$  and PA6/PON-NA- $Fe_2O_3$  systems obtained after LOI test. It could be seen that the internal surface of the char residue for the flame-retardant PA6 blends all took on an intumescent and bumpy morphology; however, there were obvious differences in the microscopic morphology of char. There were many continuous, small, and closed intumescent blebs in the internal char residues of sample C, and the char residues outside were stacked closely. Figure 9(c) and Fig. 10(c) show that there are much more effective barriers in impeding mass and heat transfer compared to residues without the NA- $Fe_2O_3$  (Figs. 9a, 9b and Figs. 10a, 10b). It revealed that the structure of the barrier effect could be improved with the addition of NA- $Fe_2O_3$  due to the more compact char with few holes formed. The strong nature of the chars formed from PA6/PON-NA- $Fe_2O_3$  composite provided the significant improvements in flame retardance as discussed above.

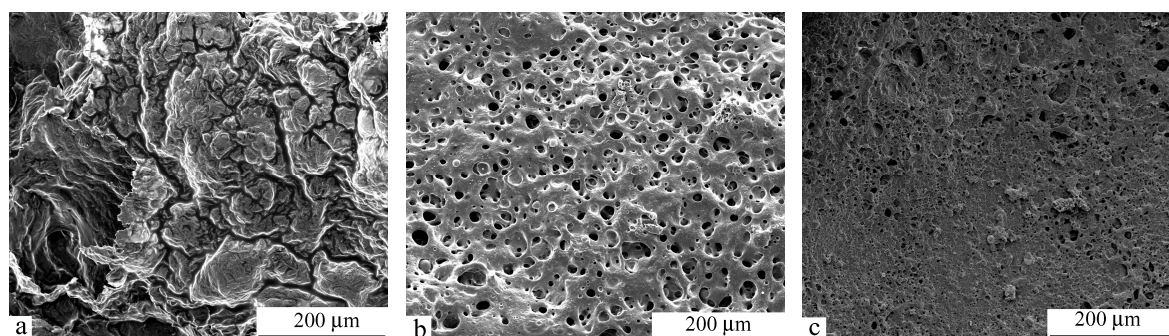


**Fig. 9** SEM micrographs of the internal surface of the char residue for the flame-retardant PA6 blends: (a) PA6/PON/NA, (b) PA6/PON/NA- $V_2O_5$  and (c) PA6/PON/NA- $Fe_2O_3$

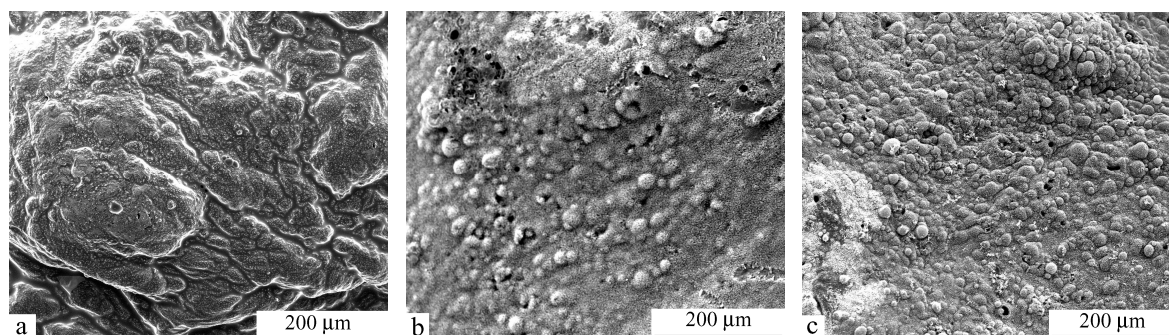


**Fig. 10** SEM micrographs of the external surface of the char residue for the flame-retardant PA6 blends: (a) PA6/PON/NA, (b) PA6/PON/NA- $V_2O_5$  and (c) PA6/PON/NA- $Fe_2O_3$

### Effect of Combined Char Former and PON on the Char Composition of PA6

Figure 11 shows the diffuse reflectance IR spectra for the residue of flame-retardant PA6 (PA3, PA5, PA7) after LOI test. From the spectrum of PA6/PON/NA- $Fe_2O_3$ , it could be seen that the radical increase of the typical absorptions of the amide ( $C=O$ ,  $1630\text{ cm}^{-1}$  and  $NH-C=O$ ,  $1410\text{ cm}^{-1}$ ) indicated the decomposition of the polyamide structure. Also, broad aromatic and olefinic carbon peaks ( $2930$  and  $1440\text{ cm}^{-1}$ ) were due to the main precursors to the aromatic components of the chars. In the fingerprint area characteristic bands developed ( $1110$  and  $990\text{ cm}^{-1}$ ), which were caused by phosphate and phosphate esters<sup>[25, 26]</sup>. Based on the above results, it could be concluded that a lot of phosphoric and polyphosphoric acids were generated during the combustion, which reacted with PA6 producing phosphoric esters. Intumescent char was formed by thermal decomposition of the esters.

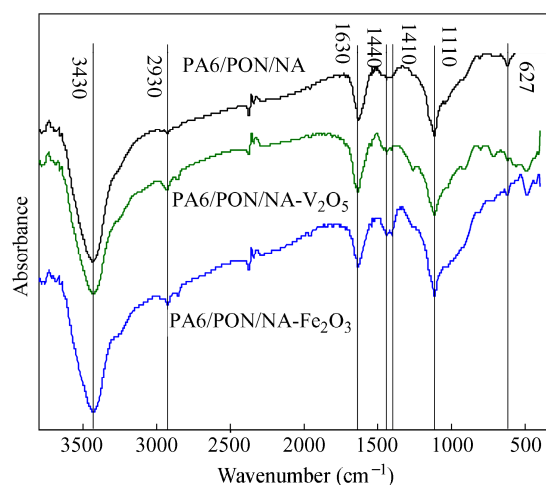


**Fig. 11** The FTIR spectra of the residue of flame retardant PA6 after LOI test: PA6/PON/NA, PA6/PON/NA- $V_2O_5$  and PA6/PON/NA- $Fe_2O_3$

### ***The Mechanism for the Formation of Residual Char with High Yield Based on the Combined Char Former and PON***

Metal oxide, added as such, was described as a char-forming additive by Bayer researchers<sup>[27]</sup>. Ammonium polyphosphate or sodium polyphosphate was in combination with novolac resin, in which these novolac resins were transformed into salts by reacting with metal oxide. Metal-containing products reacted with phosphoric acid, leading to the formation of a special form of metal phosphate, which in turn catalyzed charring of the polymer. It was also shown that these crosslinking reactions improved the stability of the charred layers. This effect might be due to the promotion of charred layer formation by the action of metal-containing products as catalysts.

However, the effect of metal oxide on the carbonization of polymers was more complicated. The presence of metal oxide, novolac resin and PON compounds probably affected not only the decomposition of PA6 but also further reaction of novolac resin, such as addition and condensation. Novolac resin burned in the presence of PON formed a reinforced cross-linking reinforcing char, due to a char forming dehydration reaction of the novolac resin with the acidic species generated from PON. The acids existed during carbonization reaction of the decomposition products catalyzed by metal catalyst, which led to carbon deposition. Therefore, PON transformed into the composite acid source (phosphoric and/or polyphosphoric acids) in PA6/PON-NA-metal salt system, and the cross-linking and charring process was promoted by  $V_2O_5$  and  $Fe_2O_3$ . The difference produced by the iron oxide appeared in the improved quality of the char and possibly in the rapidity with which the char was formed. Therefore, based on the condensed-phase mechanism, the flame retardance of PA6 was improved.

### **CONCLUSIONS**

In this article, PON used as a main flame retardant and metal salt of novolac resin served as a synergistic agent were incorporated to enhance the flame retardance of PA6. It was proved that by introducing 12 wt% of PON and 18 wt% of NA- $Fe_2O_3$ , the flame-retardant PA6 could pass UL-94 V-0 rating, as well as the heat release rates and the rate of smoke production could be effectively suppressed. Both PHRR and PSSR values of the system with NA- $Fe_2O_3$  were obviously decreased by 42% and 52% compared to those of the PA6/PON/NA system. The results of UL-94 test and cone calorimeter showed the sample containing NA- $Fe_2O_3$  had the best flame retardance. It was also indicated that all the metal salt of novolac resin and PON systems possessed obvious synergistic effects by improving char morphology rather than quantity. PA6/PON-NA- $Fe_2O_3$  system exhibited better catalytic effects, and resulted in substantial and compact intumescent chars that protected the matrix from further combustion. Thus, the presence of NA- $Fe_2O_3$  could significantly improve the flame retardance of PA6/PON composites.

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