

## Flame retardant polyoxymethylene with aluminium hydroxide/melamine/novolac resin synergistic system

Zhang-Yu Wang, Yuan Liu, Qi Wang\*

State Key Laboratory of Polymer Materials Engineering Polymer Research Institute of Sichuan University, Chengdu 610065, China

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### ABSTRACT

Polyoxymethylene (POM), having the lowest limiting oxygen index (LOI) (only ~ 15%), is well known as the most difficult to be flame retarded plastic among all the polymers. In this paper, a novel synergistic flame retardant system composed of aluminium hydroxide (ATH), melamine (ME) and novolac resin was designed and successfully applied to flame retard POM. ATH took effects through heat absorption and water release. Both ME and novolac could react with the decomposition product of POM, formaldehyde, thus improving the flame retardancy. Particularly, novolac resin and ME played the roles of macromolecular charring agent and gas source, enhancing the flame retarding actions in the condensed and gaseous phases, respectively. This ternary synergistic system exhibited fine flame retardancy for POM (UL94 V-1 rating for 1.6 mm bar), and the obtained flame retardant POM also showed good processability and mechanical properties due to the lubrication, compatibilization and aid-dispersion effects of novolac resin.

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### 1. Introduction

Polyoxymethylene (POM) is a kind of polyacetal resins, which possesses good mechanical properties, lubricating performance, fatigue resistance, corrosion resistance, and processability [1]. Moreover, it is one of the few polymers synthesized through non-petroleum route at low cost. Therefore, POM has been widely used in industry, such as automobiles, electrical and electronic products, medical devices, and precision machines, etc.

However, the thermal stability of POM resin is poor due to its rapid thermal depolymerization mechanism (unzipping reaction [2]). It has the lowest limiting oxygen index (LOI) (~ 15%) compared to all the other polymers, and is therefore extremely flammable [3]. POM resin burns violently in blooming blue flame, producing a large number of flaming molten drops which makes the fire easily spread. This has restricted POM's applications in more fields.

Adding flame retardants, a convenient and efficient way to flame retard polymer materials, however, is relatively difficult for POM. Firstly, as POM chains are very sensitive to acidic or basic substances, many flame retardants easily aggravate the decomposition of POM during thermoplastic processing, resulting in the molding of flame retardant POM difficult and its mechanical properties seriously deteriorated. Secondly, the compatibility

between POM resin and most additive fillers is relatively poor, and it is hard to realize a good dispersion of flame retardants in the resin. Thirdly, to achieve satisfactory flame retardancy, high loading level of flame retardant is generally needed due to the high inherent flammability of POM, which obviously will sabotage the original performances of POM resin.

Therefore, it is a big challenge worldwide to prepare flame retardant POM with high flame retardancy while maintaining other good comprehensive properties. Up to now, there have been very few literatures related to flame retardant POM [2,4–8]. In the 1960s, several USA patents referred to flame retardant POM containing halogen flame retardants [4,5], however, halogen flame retardants easily catalyzed the decomposition of POM due to the presence of the halide groups [2]. Moreover, the environment and safety problems arose from the pyrolysis of halogen flame retardants also restricted their applications. Recently, an alternative type of flame retardants, phosphorus-nitrogen synergistic flame retardants, has been used in flame retardant POM [2,6–8]. Du Pont Co. (US) [2] employed an ammonium salt of amidopolyphosphate named as "Victamide" to flame retard POM. Hatsuhiko Harashina, etc. [6] melt-blended red phosphorus, ME, and novolac with POM resin by a twin screw co-extruder under the protection of nitrogen gas, and the resulting flame retardant POM achieved UL94 V-1 rating. Asahi Kasei Co. (JP) [7] adopted a flame retardant system including red phosphorus, phenol resin, polycarbonate resin, and a metal salt of fatty acid to flame retard POM, and the obtained materials possessed relatively satisfactory properties. Polyplastics

\* Corresponding author. Tel./fax: +86 28 85405133.

E-mail address: [qiawang@scu.edu.cn](mailto:qiawang@scu.edu.cn) (Q. Wang).

Co., Ltd. (JP) [8] also reported a compound flame retardant for POM, which is composed of a nitrogen-containing compound, an aromatic compound and a phosphorus-containing compound. However, the flame retardant POM compositions with phosphorus-nitrogen systems were still difficult to possess high flame retardancy, good mechanical properties and fine processability simultaneously.

Compared with phosphorus-nitrogen flame retardant systems, inorganic flame retardants, such as magnesium hydroxide (MTH) and aluminum hydroxide (ATH) have the advantages of low cost, good smoke suppression effects, and environment-friendliness. As a result, they have been increasingly applied in flame retarding polymer materials [9–15]. However, at present there have been very few reports about the application of this kind of flame retardants in POM due to too high loading level. Therefore, developing some effective synergists for MTH or ATH to reduce the loading level of the flame retardants is significant for preparing flame retardant POM with better comprehensive performance.

In this paper, a novel synergistic flame retardant system consisting of ATH, ME and novolac resin was applied to POM resin. The prepared flame retardant POM composites showed satisfactory flame retardancy and good mechanical properties. The synergistic effects of each component and the flame retardant mechanism were investigated.

## 2. Experimental

### 2.1. Materials

POM pellet (M90, acetal copolymer) was purchased from Yunnan Yuntianhua Limited Corporation, China. ATH, with an average particle size of 1250 mesh, was obtained from Yingkou Universal Powder Engineering Limited Corporation, China. ME was supplied by Sichuan Chemical Limited Corporation, China. Linear novolac resin, with a weight-average molecular weight of 650 and a melt temperature of 100 °C, was provided by Henan Bangde Chemical Engineering Company, China. Antioxidant (Ciba® IRGANOX® 245) was a kind of hindered phenol supplied by Ciba, Switzerland.

### 2.2. Equipment

Co-rotating twin screw extruder (TSSJ-25/33) with the screw diameter ( $\phi$ ) of 25 mm and the aspect ratio (L/D) of 33 was manufactured by KQCEC of Chenguang Research Institute of Chemical Industry, China. Injection-molding machine (K-TEC 40) used in this work was manufactured by Terromatik Milacron Corporation, Germany.

### 2.3. Preparation of flame retardant POM

Weighted amounts of POM pellets, ATH powder, synergistic agents and antioxidant were pre-mixed, and then melt-blended by a twin screw extruder at 170–185 °C with a screw rotation speed of 150–180 rpm. The extruded pellets were molded into standard bars for combustibility and mechanical performance tests through an injection-molding machine with a plasticizing temperature of 170–195 °C.

### 2.4. Measurements and characterization

#### 2.4.1. Burning experiments

The vertical burning tests were conducted on a CZF-3 horizontal and vertical burning tester with specimen dimensions of

$127 \times 12.7 \times 3.2 \text{ mm}^3$  and  $127 \times 12.7 \times 1.6 \text{ mm}^3$  according to UL94-2006 standard.

The LOI values were measured by an LFY-605 limiting oxygen index instrument with specimen dimensions of  $120 \times 6.5 \times 3 \text{ mm}^3$  according to ASTM D2863-2009 standard.

#### 2.4.2. SEM analysis

The injection-molding bars were frozen in liquid nitrogen for 20 min, and then were broken off. The ruptured surfaces and the residual chars of the burnt bars were gilt under vacuum before observed by a HITACHI S3400 scanning electron microscope (SEM) instrument, with an accelerate voltage of 10 kV.

#### 2.4.3. FTIR analysis

The Fourier Transform Infrared (FTIR) spectra of ATH, ME, novolac and the char residue of the flame retardant POM after vertical burning test were recorded by a Nicolet 20SXB FTIR spectrometer through KBr disk method.

#### 2.4.4. Cone calorimetry

An FT cone calorimeter was used to evaluate the flammability of samples under an external heat flux of  $35 \text{ kW/m}^2$ , with specimen dimensions of  $100 \times 100 \times 3 \text{ mm}^3$  according to ISO 5660 standard. Time to ignition (TTI), total heat release (THR), heat release rate (HRR), mass loss rate (MLR) and other quantifiable parameters were recorded simultaneously.

#### 2.4.5. Thermal analysis

The thermogravimetry (TG) analyses were carried out on a TA Q-500 TGA thermal analyzer, with a heating rate of  $10 \text{ }^\circ\text{C/min}$  from 30 to 700 °C and an air or nitrogen flow rate of 100 ml/min.

#### 2.4.6. Mechanical properties

The tensile strengths were measured by a REGEER material tester according to ISO527/1-1993 standard. The test specimens were dumb-bell-shaped of type 1A with width of 10 mm (narrow portion) and thickness of 4 mm, and the test speed was 50 mm/min.

The bending strengths were also examined by a REGEER material tester with sheet dimensions of  $80 \times 10 \times 4 \text{ mm}^3$  according to ISO178-2001 standard. The test speed was 2 mm/min.

The charpy notched impact strengths were measured using a ZBC-4B impact testing machine with specimen dimensions of  $80 \times 10 \times 4 \text{ mm}^3$  according to ISO179/1-2000 standard.

## 3. Results and discussion

### 3.1. Decomposition of POM

The flammability of POM resin can be explained by its decomposition and combustion behaviors [2,16]: the macromolecular chain of POM, mainly composed of  $-\text{CH}_2-\text{O}-$  units, is extremely easy to depolymerize into formaldehyde in the presence of heat and oxygen. The resulting formaldehyde can be further oxidized to formic acid, which catalyzes the decomposition of POM. As combustible gases, the rapidly produced formaldehyde and formic acid provide fuel to the intense combustion of POM resin.

Fig. 1 showed the thermogravimetry curves of POM resin in different atmospheres. The onset decomposition temperature of POM was 365 °C in  $\text{N}_2$  atmosphere. While in air, the existence of  $\text{O}_2$  obviously accelerated the decomposition of POM, reducing the decomposition temperature to 312 °C and raising the maximum velocity of weight-loss to a greater extent. However, in both atmospheres, the residue weight ratio was close to zero, meaning that POM completely turned into small molecular products and

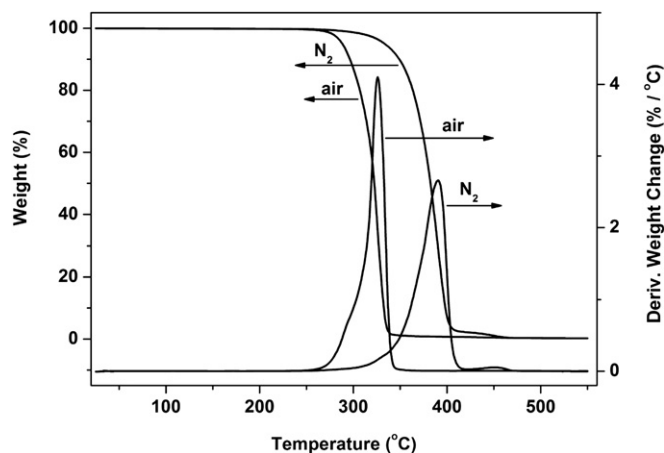


Fig. 1. TG and DTG curves of POM under  $N_2$  and air atmosphere.

that POM resin itself could not form char residues with cross-linked structure at high temperature.

### 3.2. Thermoplastic processability of flame retardant POM

Because of its flame retardant effects such as heat absorption, water release, and isolation, ATH is usually employed in flame retardant polymer materials [13–15]. However, when ATH was used alone to flame retard POM resin, there were pungent gases, including formaldehyde and formic acid, released during the extrusion and injection-molding processes of the ATH/POM system. This could be explained as follows. On one hand, the decomposition temperature of ATH is relatively low (200–300 °C), making it easy to decompose and generate water vapor at the processing temperature of POM. On the other hand, ATH is a kind of amphoteric hydroxide, having two ionization ways in water, which showed alkalinescence and subacidity respectively. With a high loading level of ATH, the produced water is sufficient for the ionization of some ATH. The ionized ATH could catalyze the decomposition of POM, and therefore, reducing the stability of POM resin.

By contrast, there was no detectable decomposition in our designed ATH/ME/novolac/POM system during melt processing, indicating that the synergists could effectively enhance the thermo-oxidative stability of POM. This improvement should be attributed to the formaldehyde-absorbing effects of ME and novolac resin (i.e. the addition and condensation reactions between their reactive hydrogen atoms and aldehyde groups of

formaldehyde), as well as the reactivity of alkalinescent ME with formic acid. Accordingly, compared to the ATH/POM system, the ATH/ME/novolac/POM system showed much better processability, which could be melt-mixed and molded by conventional thermoplastic processing methods, e.g., extrusion and injection-molding, without protective nitrogen or other inert gases.

### 3.3. Flame retardancy

Table 1 listed the UL94 vertical burning test results and LOI values of POM resin and the flame retardant POM samples. It was observed that POM resin (No. 1) burnt violently with blooming flame and a large number of burning molten drops, moreover, the fire could not self-extinguish until the resin burnt-out. Meanwhile, POM resin showed low LOI value of 16%, which also indicated very poor flame retardancy. In the presence of 55 wt% ATH (No. 2), the molten drops were inhibited, and the LOI value increased to 31%, showing an obvious improvement in the flame retardancy. However, the UL94 flame retardancy of this POM/ATH system was still unsatisfactory. When a relatively small amount (5 wt%) of ME or novolac resin was introduced into ATH/POM system (Nos. 3–4), higher LOI values (44.5–46%) were obtained, which indicated that both ME and novolac possessed synergistic actions with ATH on flame retarding POM. However, the LOI values of the ATH/ME flame retardant POM samples slightly decreased (from 45.5% to 44%) with increasing the proportion of ME (from 5 wt% to 15 wt%), because excess ME could not exert satisfactory effects with decrease of the amount of ATH. For the ATH/novolac flame retardant POM samples, the LOI values showed a serious decrease (from 46% to 34%) with increasing the amount of novolac (from 5 wt% to 15 wt%). This could be explained by the following reason. The relatively low melting temperature ( $\sim 100$  °C) and low melt viscosity of novolac resin made the molten blends easier to flow down, and therefore more fuel was provided to support the burning of materials in the LOI test. The massive drops of No. 6 and No. 8 in the vertical burning test also showed that excess novolac was not suitable for ATH flame retardant POM systems.

As shown in Table 1, when both ME and novolac resin were added into ATH/POM (Nos. 9–12), the UL94 flame retardancy of the obtained composites was greatly improved, and all the samples of Nos. 9–12 passed V-1 rating for 3.2 mm bar. In particular, the sample of No. 11 (with 1/1 of ME/novolac weight ratio) exhibited better UL94 flame retardancy (V-1 rating for 1.6 mm bar), and the LOI value achieved 43%, showing a remarkable improvement in the flame retardancy for POM resin. In addition, this sample (No. 11) also possessed good mechanical performance as shown later.

Table 1  
Flame retardancy of POM and the flame retardant POM samples.

Specimen	POM/ATH/ME/novolac (wt%)	UL94 vertical burning test			LOI (%)
		3.2 mm	1.6 mm	Drop	
1.	100/0/0/0	NR <sup>a</sup>	/	Yes	16
2.	45/55/0/0	NR <sup>a</sup>	/	No	31
3.	45/50/5/0	NR <sup>a</sup>	/	No	45.5
4.	45/50/0/5	NR <sup>a</sup>	/	No	46
5.	45/45/10/0	NR <sup>a</sup>	/	No	44.5
6.	45/45/0/10	NR <sup>a</sup>	/	Yes (massive drops)	37.5
7.	45/40/15/0	NR <sup>b</sup>	NR <sup>a</sup>	No	44
8.	45/40/0/15	NR <sup>a</sup>	/	Yes (massive drops)	34
9.	45/45/5/5	V-1	NR <sup>a</sup>	No	/
10.	45/40/5/10	V-1	NR <sup>b</sup>	No	/
11.	45/40/7.5/7.5	V-1	V-1	No	43
12.	45/40/10/5	V-1	NR <sup>b</sup>	No	/

<sup>a</sup> The test bars burnt-out.

<sup>b</sup> The test bars can self-extinguish.

It should be pointed out that the flame retardancy results of the samples from LOI test and UL94 vertical burning test were somehow different, which may be due to the different ignition modes adopted, as reported in some references [17,18].

### 3.4. Char layer observation

It is well known that the char layers of the burnt bars are directly related to the flame retardancy of the corresponding materials. The photos of test bars (1.6 mm) of the different flame retardant POM samples after the vertical burning test were shown in Fig. 2 for comparison.

The test bar of the ATH/POM sample (Sample a) softened and deformed heavily, and there were hardly any chars formed on the surface, showing poor flame retardancy. For the ATH/novolac/POM (Sample b), the softening of the test bar was even more severe, leading to bulky molten drops. However, there were abundant chars formed on the surface of the burnt materials, indicating a good char-forming effect for novolac resin. For the ATH/ME/POM (Sample c), the shape of the test bar kept well, but the obtained chars were brittle and easily curled, thus resulting in many visible cracks on the char layers. By contrast, the char layers of the ATH/ME/novolac/POM (Sample d) became more compact and smooth, and therefore this sample possessed better UL94 flame retardancy.

SEM analysis further revealed the micro-morphology of the residual chars of the above samples (Fig. 3). The residue of the ATH/POM (Sample a) was loose and brittle, accordingly, the char layer was extremely easy to be broken and could not effectively protect the burning materials. As still lacking of charring agent, the residue of the ATH/ME/POM system (Sample c) was also very slimy. On the other hand, serving as a macromolecular charring agent, novolac resin could greatly increase the charring amount, as shown in the ATH/novolac/POM and ATH/ME/novolac/POM systems (Sample b and d). For the two systems containing novolac, the char layer of Sample d was more smooth and compact than that of Sample b.

The improved char structure of Sample d was attributed to the following reasons. 1) Novolac resin melted at  $\sim 100$  °C, and its charring and adhesive actions were beneficial to get a more continuous and compact barrier layer conglomerating  $\text{Al}_2\text{O}_3$  particles (solid residue of ATH), thus reinforcing the flame retardant action in the condensed phase. 2) As a typical gas source, ME endothermically sublimated and decomposed into incombustible volatiles and gases, which could dilute the flammable gases and slow down the burning of materials, enhancing the flame retardant action in the gaseous phase. As a result, the consolidated char layers of Sample d were more effective in protecting the inner materials, accordingly, the corresponding ATH/ME/novolac ternary combination flame retardant POM performed the best flame retardancy (UL94 V-1 rating for 1.6 mm bar) among all the samples.

### 3.5. FTIR analysis

In order to qualitatively investigate the char structure of the POM/ATH/ME/novolac system, FTIR spectrum of the char residue on the surface of the burnt bar (after the vertical burning test) was presented in Fig. 4, where the spectra of original ATH, ME and novolac were also shown for comparison. In the FTIR spectrum of the char residue, the broad peak ranging from  $3200$  to  $3600$   $\text{cm}^{-1}$  should be the mixture peaks assigned for the NH and OH groups. The weak peaks at  $2922$  and  $2851$   $\text{cm}^{-1}$  represented the asymmetric and symmetric C–H stretching vibrations in methylene groups, respectively. While the peak at  $1468$   $\text{cm}^{-1}$  might be assigned to the deformation vibration of C–H in methylene groups, or the semicircle stretching vibration of triazine rings [19,20]. The skeletal vibration of benzene rings appeared at  $1620$   $\text{cm}^{-1}$ , and the peaks at  $758$  and  $599$   $\text{cm}^{-1}$  should belong to the stretching and deformation vibrations of Al–O groups, respectively. According to the FTIR characteristics of the char residue and the decomposition of ATH, the obtained char residue probably included  $\text{Al}_2\text{O}_3$  particles, methylene groups, benzene rings, as well as the molecular fragments and reaction products of novolac, melamine and formaldehyde.

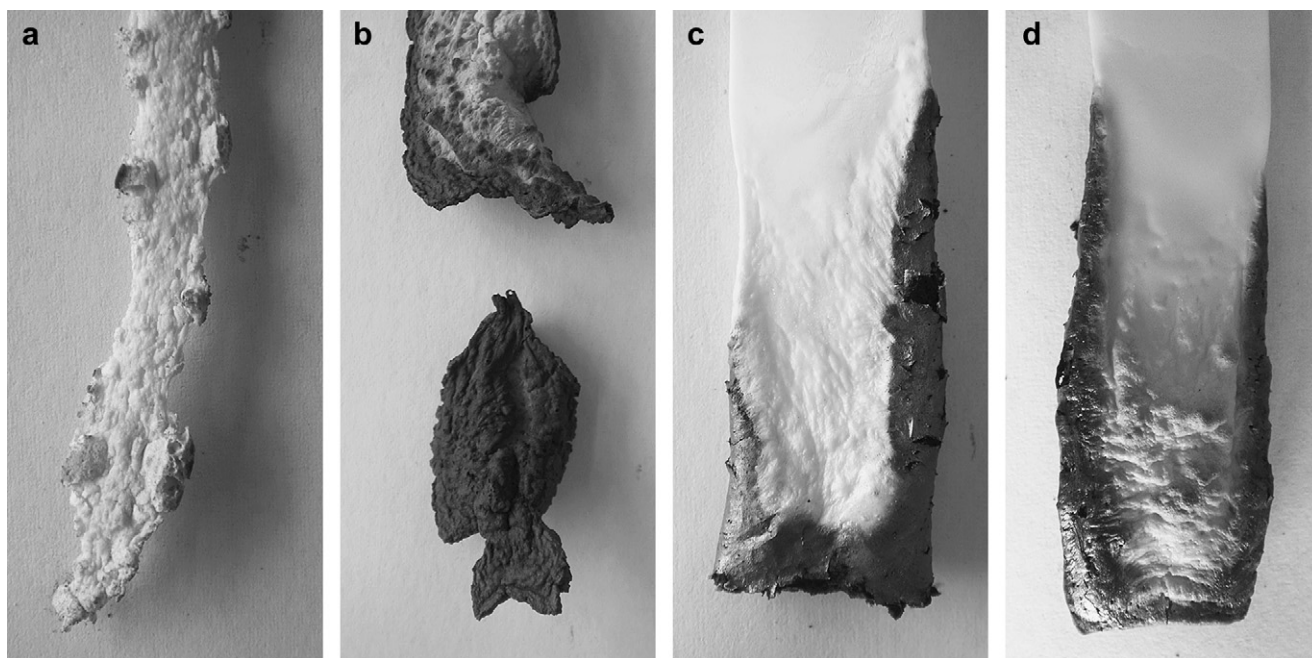
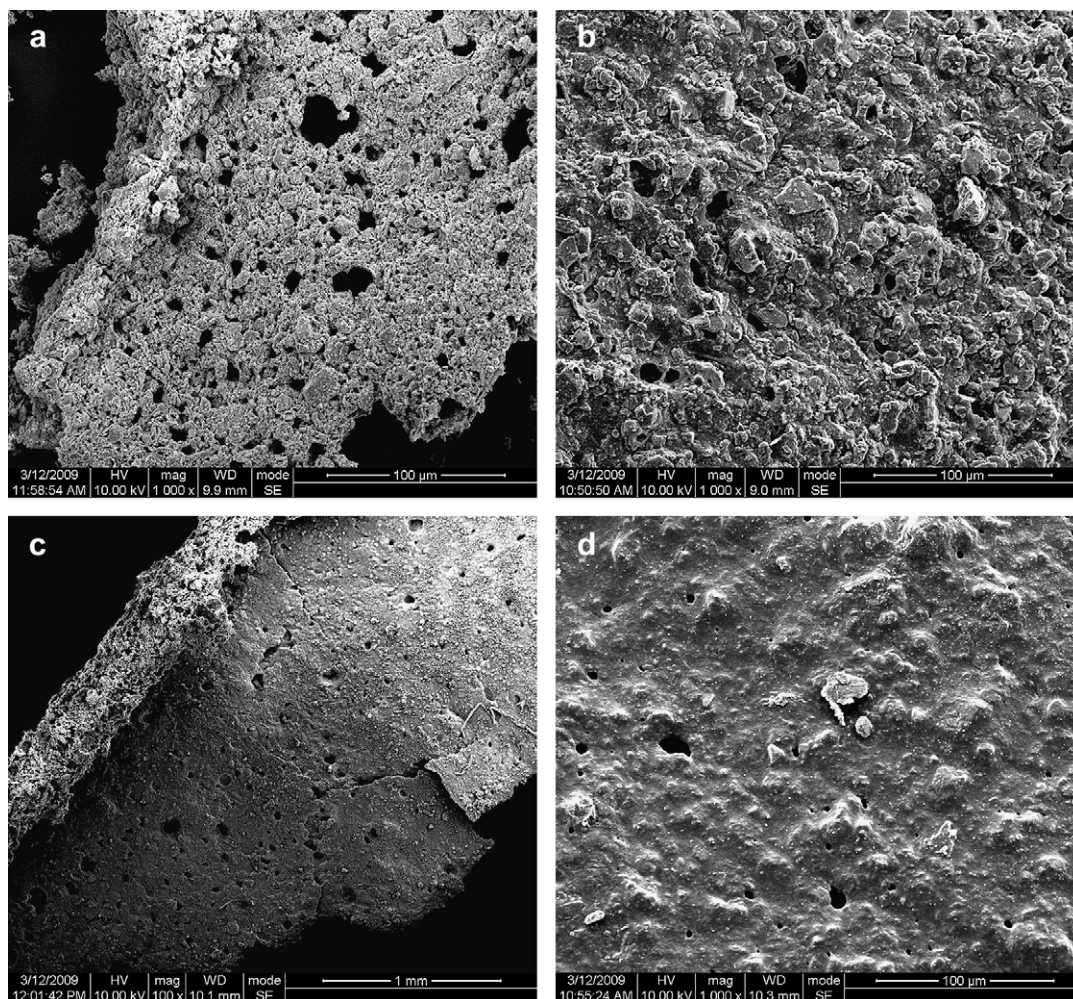


Fig. 2. Photographs of test bars (1.6 mm) of the flame retardant POM samples after vertical burning test: (a) POM/ATH = 45/55 (wt%), (b) POM/ATH/novolac = 45/40/15 (wt%), (c) POM/ATH/ME = 45/40/15 (wt%), (d) POM/ATH/ME/novolac = 45/40/7.5/7.5 (wt%).





**Fig. 3.** SEM microphotographs of residual charred layers of the flame retardant POM system: (a) POM/ATH = 45/55 (wt%), (b) POM/ATH/novolac = 45/40/15 (wt%), (c) POM/ATH/ME = 45/40/15 (wt%), (d) POM/ATH/ME/novolac = 45/40/7.5/7.5 (wt%).

### 3.6. Cone calorimetry

Cone calorimetry is usually used to predict the combustion behaviors and fire safety of polymer materials in a real fire condition [21,22]. The quantitative analysis results of the ATH/ME/novolac ternary flame retardant POM (No. 11) were compared with those of POM. The heat release rate (HRR) curves and mass curves were shown in Figs. 5 and 6, respectively. The cone calorimetry test data, including time to ignition (TTI), total heat release (THR), peak heat release rate (PHRR), time to peak heat release rate ( $t_{\text{Peak HRR}}$ ), average heat release rate (Av-HRR) and average mass loss rate (Av-MLR) were summarized in Table 2.

From HRR curves in Fig. 5 and test data in Table 2, it was found that POM resin burnt rapidly once ignited, and burnt-out within 450 s. The THR, PHRR and Av-HRR were 63.2 MJ/m<sup>2</sup>, 268.8 kW/m<sup>2</sup> and 175.3 kW/m<sup>2</sup>, respectively. While the ATH/ME/novolac ternary flame retardant POM exhibited remarkably lower THR, PHRR and Av-HRR values, which were 35.6 MJ/m<sup>2</sup>, 133.0 kW/m<sup>2</sup> and 61.9 kW/m<sup>2</sup>, respectively. In HRR curve of the flame retardant POM, the relatively low HRR values in the range of ~120–400 s revealed that there was a stable and compact char layer formed after ignition and initial relatively fast burning. The obtained char layer could act as a protective layer to inhibit the release of flammable decomposition volatiles, as well as to restrain the heat transmission into the

test samples. The decreases on heat release and heat release rates, as well as the formation of protective char layer were beneficial to improving the flame retardancy.

From the onsets of HRR curves, the TTI values could be obtained (Table 2). With the ATH/ME/novolac flame retardant, this value increased by 12%, from 66 s for POM resin to 74 s for the flame retardant POM. Before reaching its  $t_{\text{Peak HRR}}$ , HRR curve of the flame retardant POM was similar to that of POM resin, indicating that the initial thermal decomposition of POM was not affected by this ternary flame retardant system. However, a protective char layer was rapidly formed in the flame retardant POM.

Fig. 6 showed the mass curves of POM and the ATH/ME/novolac flame retardant POM, and the photos of their burnt residues after cone calorimetry measurements were shown in Fig. 7. It was found that POM resin almost burnt-out, with only 0.4% mass remained, while the flame retardant POM remained 36.9% mass. Meanwhile, the Av-MLR of the flame retardant POM was half that of POM resin, decreasing from 0.1 g/s to 0.05 g/s (Table 2). The char residue of the flame retardant POM was composed of the thermal decomposition product of ATH (i.e., Al<sub>2</sub>O<sub>3</sub>, which weighted only 26.2% mass by calculation) and the reaction products of ME, novolac and formaldehyde. The results of the cone calorimetry measurements further confirmed that the combination of ATH, ME and novolac could effectively improve the flame retardancy of POM.

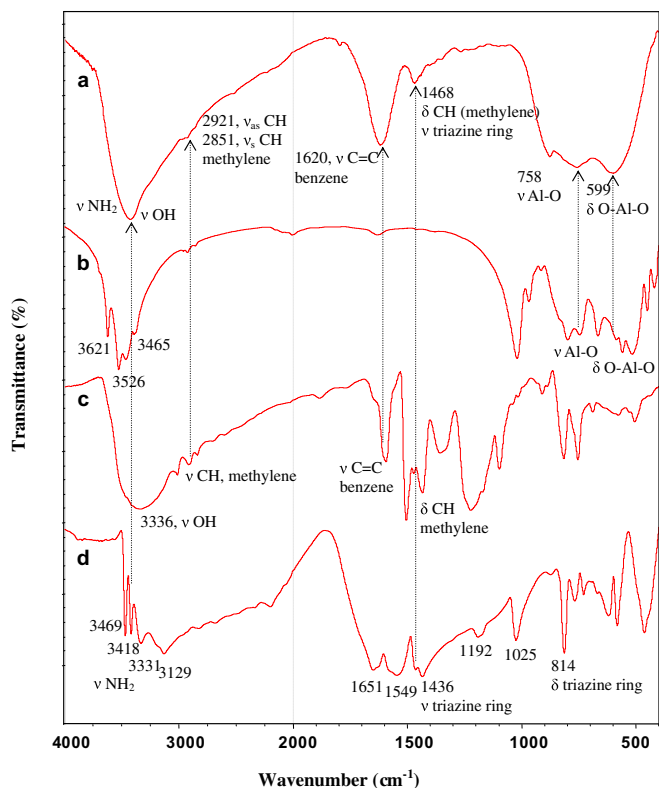


Fig. 4. FTIR spectrums of the samples: (a) char residue of the POM/ATH/ME/novolac sample (No. 11) after the vertical burning test, (b) ATH, (c) novolac and (d) ME.

### 3.7. Thermogravimetric analysis (TGA)

The TGA curves of POM resin and the flame retardant POM samples under air and nitrogen conditions were shown in Figs. 8 and 9 respectively. The onset decomposition temperatures of all the flame retardant systems were lower than that of POM resin in both atmospheres, indicating that the presence of the flame retardants more or less deteriorated the thermal or thermo-oxidative stability of POM.

In the oxidative environment (Fig. 8, air condition), the POM/ATH (Sample b) showed the lowest onset decomposition temperature among all the samples, because the ionized ATH promoted

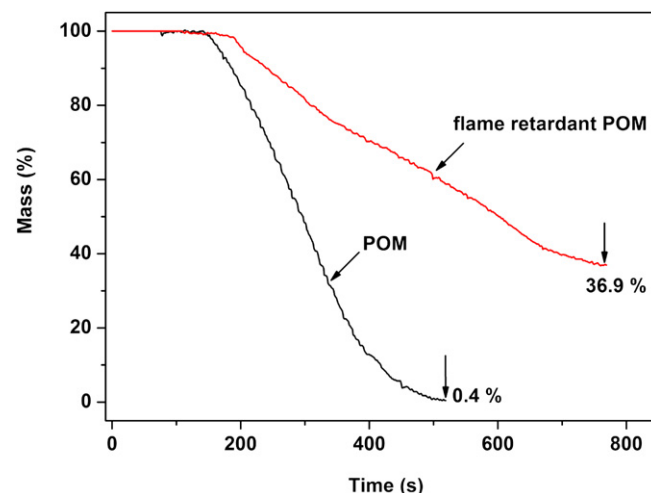


Fig. 6. Mass curves of POM and the ATH/ME/novolac flame retardant POM (No. 11).

the thermo-oxidative decomposition of POM as explained in Section 3.2. The ATH/novolac/POM and ATH/ME/POM systems (Samples c and d) demonstrated slightly elevated onset decomposition temperatures as compared to the POM/ATH system, due to the formaldehyde-absorbing capacity of novolac and ME. The rapid weight-loss of the ATH/ME/POM sample at about 300 °C represented the decomposition of POM as well as the sublimation and thermal decomposition of ME, which also indicated the lack of an efficient shield for the volatile products in this system. On the other hand, novolac resin showed good char-forming ability in the ATH/novolac/POM system. The char-like residue formed quickly below 300 °C and exhibited relatively high thermo-oxidative stability, showing good isolation effect at the temperature range from 300 to 450 °C. In the POM/ATH/ME/novolac system (Sample e), it took the advantages of both novolac resin and ME. The decomposition temperature at the maximum weight-loss rate was much higher than those of other flame retardant systems, even a little higher than that of POM resin. Moreover, the weight-loss rate was dramatically decreased as compared to POM resin, showing an improvement in the thermo-oxidative stability of POM.

While in the non-oxidative environment (Fig. 9, N<sub>2</sub> condition), the situation was more alike to factual combustion [23,24]. In N<sub>2</sub>, the ATH/POM (Sample b) also showed much lower decomposition temperature as compared to POM resin (Sample a), and the temperature difference was larger than that for POM resin in the two different atmospheres, indicating that ATH had even a greater influence on the decomposition of POM than oxygen did. For the POM/ATH/novolac (Sample c), the weight-loss processes at relatively low temperature as well as the char yield at 300 °C was similar in both atmospheres. However, the char yield at 600 °C in N<sub>2</sub> was much higher than that in air, showing that the formed char structure was much more stable in the non-oxidative environment, without obvious oxidation and chain scission at higher temperature. The POM/ATH/ME (Sample d) showed a greatly dropped maximum weight-loss rate in N<sub>2</sub>. Besides the slowed decomposition of POM, the N<sub>2</sub> atmosphere also inhibited the rapid thermal decomposition of ME to produce N<sub>2</sub> and other nitrogenous gases/volatiles. Obviously, the combination of ME and novolac could further improve the thermal stability of the ATH/ME/novolac flame retardant POM (Sample e), which possessed the highest decomposition temperature and lowest weight-loss rate among all the mentioned flame retardant POM systems. As a result, this sample also showed satisfactory UL94 flame retardancy (V-1 rating for 1.6 mm bar) as described in the vertical burning tests.

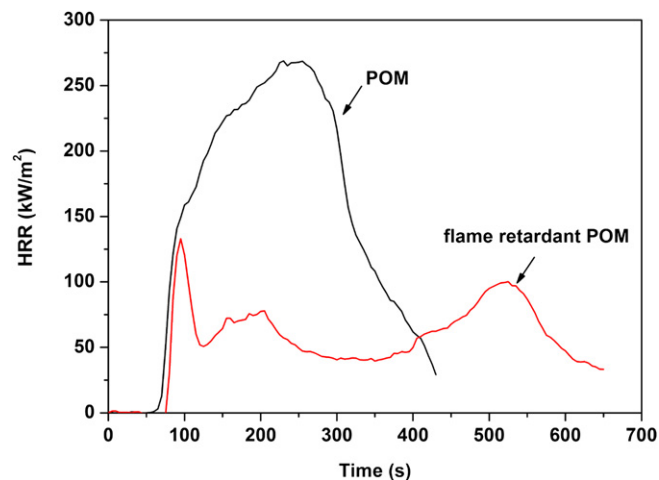


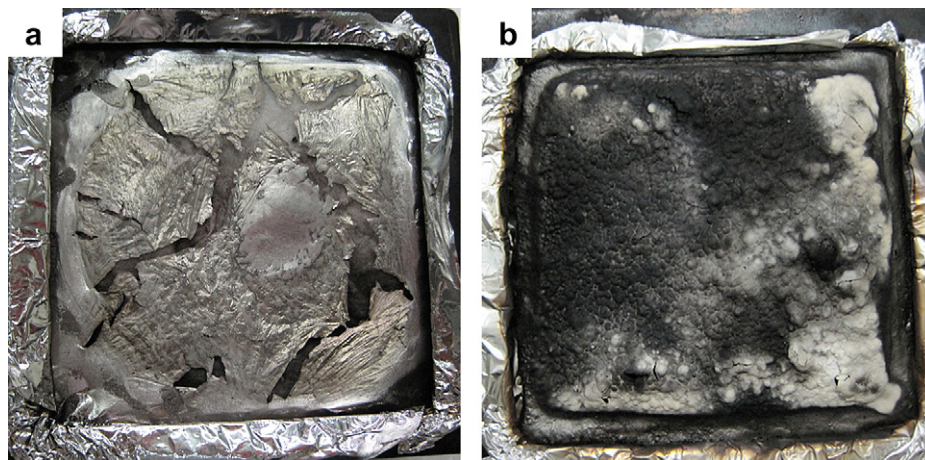
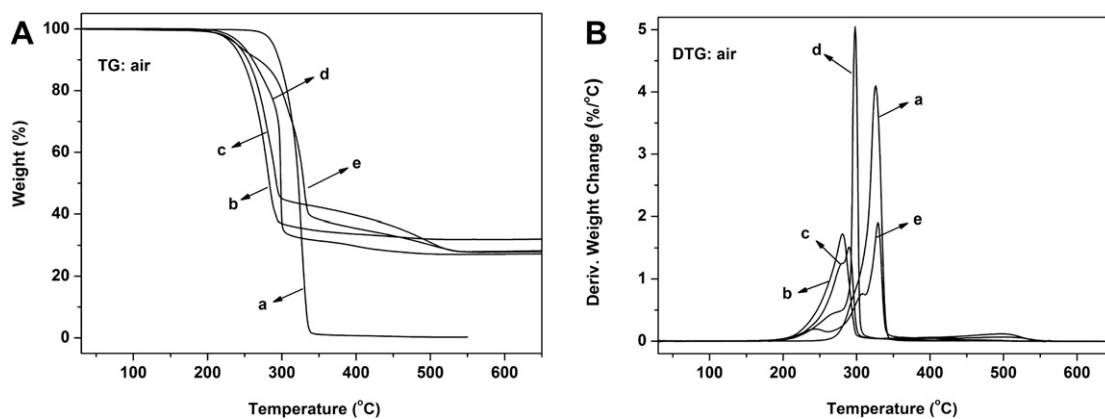
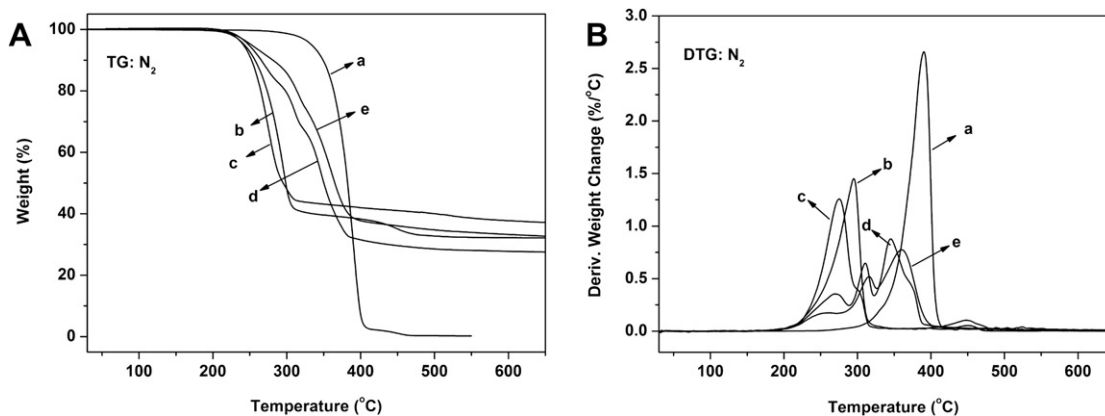
Fig. 5. HRR curves of POM and the ATH/ME/novolac ternary combination flame retardant POM (No. 11).

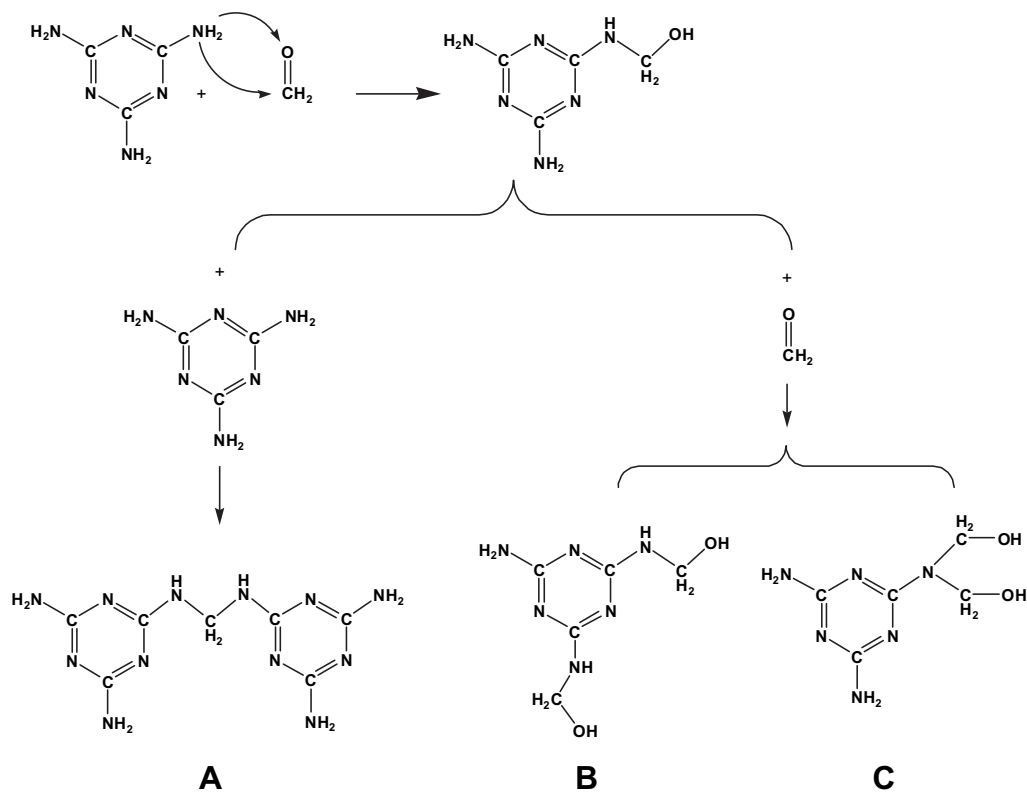


**Table 2**

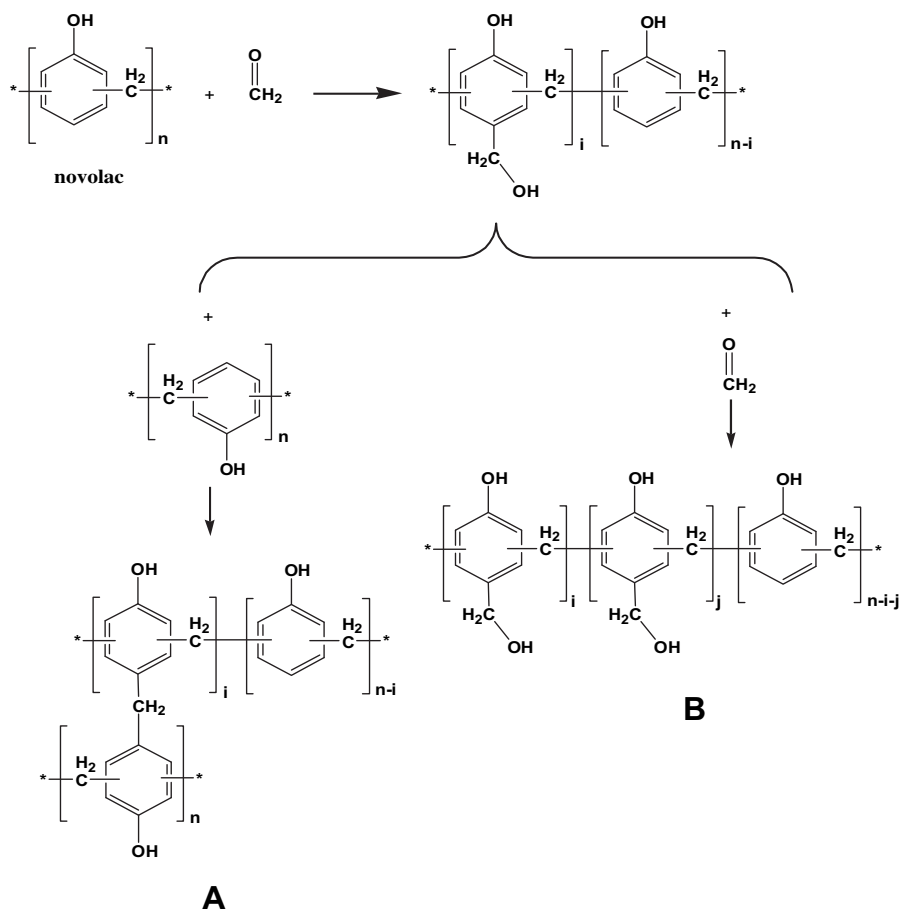
Cone calorimetry data of POM and the ATH/ME/novolac ternary combination flame retardant POM (No. 11).

Samples	TTI (s)	THR (MJ/m <sup>2</sup> )	PHRR (kW/m <sup>2</sup> )	t <sub>Peak HRR</sub> (s)	Av-HRR (kW/m <sup>2</sup> )	Av-MLR (g/s)
POM	66	63.2	268.8	230	175.3	0.10
Flame retardant POM	74	35.6	133.0	95	61.9	0.05

**Fig. 7.** Digital photos of burnt residues of specimens after cone calorimetry: (a) POM and (b) the ATH/ME/novolac flame retardant POM (No. 11).**Fig. 8.** TG and DTG curves of POM and the flame retardant POM systems under air atmosphere: (a) POM, (b) POM/ATH = 45/55 (wt%), (c) POM/ATH/novolac = 45/40/15 (wt%), (d) POM/ATH/ME = 45/40/15 (wt%), (e) POM/ATH/ME/novolac = 45/40/7.5/7.5 (wt%).**Fig. 9.** TG and DTG curves of POM and the flame retardant POM systems under N<sub>2</sub> atmosphere: (a) POM, (b) POM/ATH = 45/55 (wt%), (c) POM/ATH/novolac = 45/40/15 (wt%), (d) POM/ATH/ME = 45/40/15 (wt%), (e) POM/ATH/ME/novolac = 45/40/7.5/7.5 (wt%).



Scheme 1. Reactions between ME and formaldehyde.



Scheme 2. Reactions between novolac and formaldehyde.



### 3.8. Flame retardant mechanism

From above tests and analyses, the synergistic flame retardant mechanism in the ATH/novolac/ME flame retardant POM could be proposed as follows. ATH was the main flame retardant in this system, which could absorb heat and release water, playing roles in reducing temperature of the burning zone and diluting oxygen and fuel gases. In addition, the decomposition residue of ATH, i.e.,  $\text{Al}_2\text{O}_3$  particles, could serve as a shield against the fire due to its high temperature resistance. However, with ATH alone, the discontinuity of this shield (as a result of the non-charring property of POM matrix and the deficiency of adhesive in the POM/ATH system) led to poor protective effects for the materials. Both ME and novolac could absorb formaldehyde through the addition and condensation reactions between their reactive hydrogen atoms and formaldehyde, as presented in Scheme 1 and Scheme 2. The products [(A), (B), (C) in Scheme 1 and (A), (B) in Scheme 2] might further react with ME, novolac or formaldehyde to form cross-linked char structures. Additionally, novolac resin and ME played the roles of macromolecular charring agent and gas source, respectively. Firstly, the carbonized products of novolac resin could conglutinate the  $\text{Al}_2\text{O}_3$  particles to form more continuous and consolidated char layers. Secondly, endothermic sublimation and decomposition of ME could further decrease the temperature of the burning zone. Thirdly, the produced nitrogen-containing gases from ME as well as

the vapors from ATH could effectively dilute oxygen and fuel gases. With remarkably enhanced flame retarding actions in the condensed and gaseous phases, the flame retardancy of the ATH/ME/novolac synergist flame retardant POM was therefore greatly improved.

### 3.9. Mechanical properties

Fig. 10 compared the SEM microphotographs of transverse sections (injection molded specimens) of the POM/ATH (a) and the POM/ATH/novolac (b) systems. In the former system, distinct interfacial spaces were visible due to poor interactions between the laminated ATH particles and the polymer matrix (Fig. 10 a-2), which obviously sabotaged the mechanical performance of materials. However, in the latter system, the adoption of novolac resin significantly improved the compatibility of ATH particles in POM matrix, and the gaps between the two phases could hardly be observed (Fig. 10 b-2). Unique characteristics of novolac resin, such as relatively low melting temperature ( $\sim 100^\circ\text{C}$ ), fine wetting effect on the ATH particles based on the interactions between the phenolic hydroxyl groups of novolac and hydroxyl groups of ATH, as well as intermolecular hydrogen bonds between novolac resin and POM matrix, enabled the novolac resin to assist the ATH particles to be well dispersed in the POM matrix. Accordingly, the multi-effects of the novolac resin, i.e., lubrication, aid-dispersion and

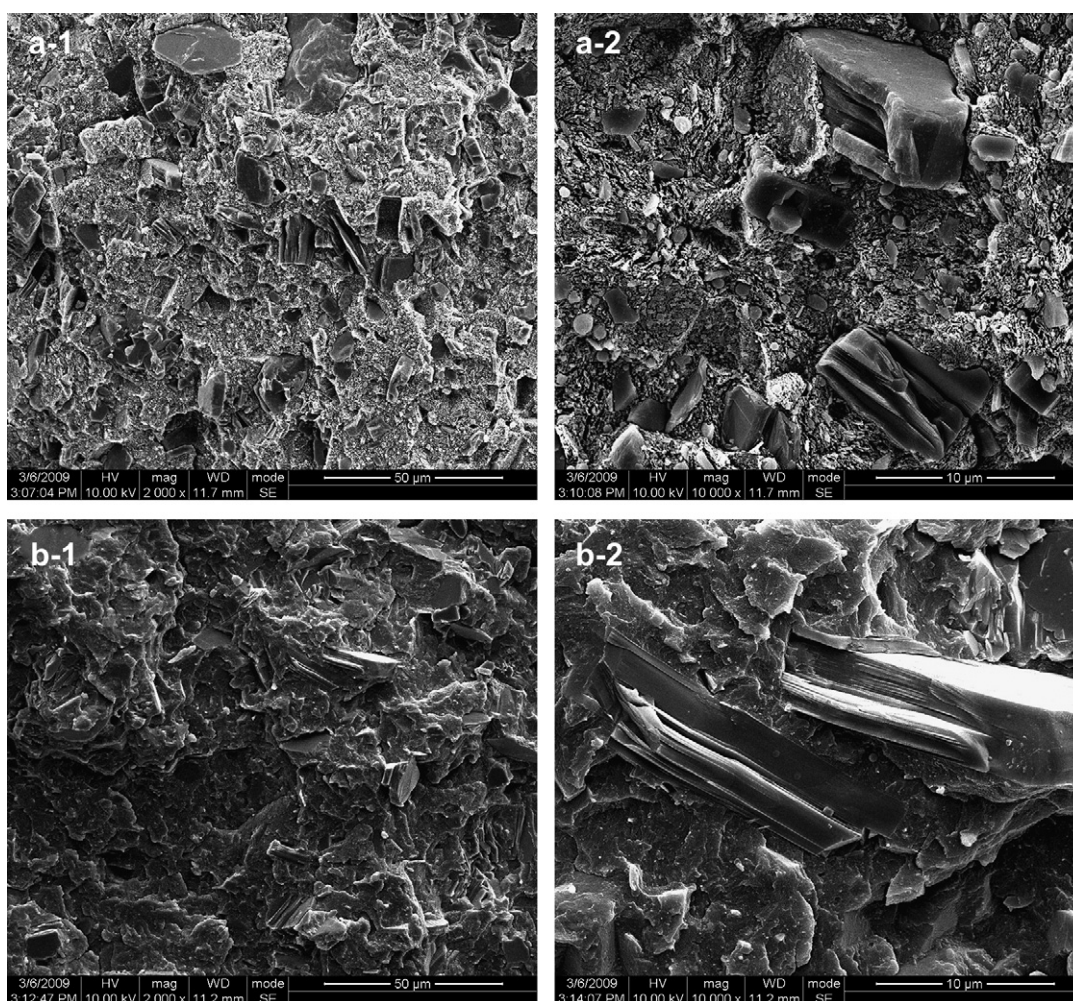


Fig. 10. SEM microphotographs of the flame retardant POM samples: (a) POM/ATH = 45/55 (wt%), (b) POM/ATH/novolac = 45/40/15 (wt%).

**Table 3**  
Mechanical performance of POM and the flame retardant POM (No. 11).

Specimens	Mechanical Properties		
	Tensile Strength (MPa)	Bending Strength (MPa)	Notched Charpy Impact Strength (kJ/m <sup>2</sup> )
POM	57.7	72.0	6.9
Flame retardant POM	50.6	81.0	2.2

compatibilization endowed the flame retardant blends with enhanced combustion performance and better mechanical properties.

Table 3 compared the mechanical properties of POM and the ATH/ME/novolac flame retardant POM (No. 11 in Table 1). The flame retardant POM showed good tensile strength and bending strength. However, its notched impact strength was obviously decreased. In practical applications, appropriate coupling treatments on filler particles might be beneficial to improving the mechanical properties of materials.

#### 4. Conclusion

The ATH/ME/novolac flame retardant POM composites were successfully prepared and the flame retardancy could achieve UL94 V-1 rating for 1.6 mm bar at a suitable composition (POM/ATH/novolac/ME = 45/40/7.5/7.5 wt%). It was also proved that the ATH/novolac/ME system performed synergistic actions in both the gaseous and condensed phases, resulting in improved flame retardancy for POM as compared to either the ATH/ME or ATH/novolac systems. Due to the lubrication, compatibilization and aid-dispersion multi-effects of the novolac resin, the ternary ATH/ME/novolac flame retardant POM presented good processability and mechanical properties, with tensile strength, bending strength and notched charpy impact strength being 50.6 MPa, 81.0 MPa, and 2.2 kJ/m<sup>2</sup>, respectively. Moreover, this established technology provided an effective and convenient way to prepare halogen-free flame retardant POM, showing a promise in the future commercial application.

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