Flammability Characteristics and Performance of Halogen-Free Flame-Retarded Polyoxymethylene Based on Phosphorus–Nitrogen Synergistic Effects

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ABSTRACT: The flammability characteristics and thermal stability of a novel halogen-free flame-retardant compounding system based on polyoxymethylene (POM) were studied, and a very effective flame retarding formulation for POM was developed from a combination of ammonium polyphosphate (APP), melamine cyanurate (MC), novolak, and dipentaerythritol. The decomposition behavior of POM compounds was evaluated by thermogravimetric analysis. The compound shows optimal flame retardancy with a limiting oxygen index of 52.8 and flammability rating of UL94 V-0, when 27 wt % APP, 9 wt % MC, 4 wt % novolak, and 4 wt % dipentaerythritol are simultaneously incorporated into POM. The presence of novolak and dipentaerythritol as char-forming agents results in a dense and compact multicellular char residue for the test bar after combustion, while Fourier transform infrared spectra confirm a characteristic phosphorous- and carbon-rich char resulting from the APP/MC formulation. The pyrolysis–gas chromatography/mass spectrometry analysis indicates that highly flammable formaldehyde gas, the main pyrolysis product of POM, is annihilated by amide derivatives produced by the pyrolysis of MC, imparting better flame retardancy. The comprehensive flame-retardant mechanisms based on phosphorus–nitrogen synergism promote the high flame retardancy of POM to reach the nonflammability of V-0 rating. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 611–622, 2010

Key words: polyoxymethylene; flame retardancy; halogen-free; synergistic effect; thermal stability

INTRODUCTION

Nowadays, synthetic polymers are used in an ever increasing range of applications and under ever more demanding environmental conditions. However, fire hazards associated with the use of these polymeric materials, which cause the loss of life and property, are of particular concern to governments, consumers, and manufacturers alike.[1–3] The use of flame-retardant additives to reduce combustibility of the polymers, and smoke or toxic fume production, therefore, becomes the main focus of the development and application of new polymeric materials. Amongst the major applications, for which the flame-retardant additives are required, the industries dealing with construction, electrical and electronic appliances, and transportation are of significant importance. A well known approach to achieve nonflammability for polymers is addition of bromine-containing compounds and antimony oxide, which can constitute an effective flame-retardant synergistic system.[4–6] However, such flame-retardant polymeric materials containing bromine might generate possibly toxic compounds, such as dioxin relatives, during their combustion.[7,8] Much effort has being made to eliminate the toxicity and environmental impact of the principal flame-retardant additives currently in use.[9–12] The European Community proposed to restrict the use of brominated diphenyl oxide flame retardants because potentially carcinogenic substance may be formed during combustion.[13,14] It is essential that new halogen-free and environmentally friendly flame-retardant systems are developed to meet the constantly changing demand of new regulations and standards.[15–17]

As one of the most important engineering thermoplastics, polyoxymethylene (POM) exhibits very good mechanical properties, such as high tensile strength, flexural modulus, and deflection temperature. Furthermore, POM possesses high creep and fatigue resistance, resistance to friction and wear, and excellent resistance against heat and solvents.[18,19] However, applications of POM are restricted because of its high combustibility, which

only exhibit an HB rating in terms of the Underwriter Laboratories (UL) 94 standards.[20,21] Moreover, POM is considered as the most difficult flame-retarded thermoplastic polymer because of its special chemical structure as well as its thermal stability and chemical degradation characteristics. It is well known that the backbone of POM chain consists of the simple carbon–oxygen bonds. POM possesses a high oxygen content of 53 wt %, and its ignition temperature is relatively low compared to other synthetic polymeric materials,[22] which result in extremely high flammability with little oxygen supplied from outside during combustion. This means that POM can continuously burn under conditions of low oxygen concentration. In fact, the limiting oxygen index (LOI) of POM is only around 15, while those of many thermoplastics exceed 18.[23] Furthermore, the high flammability of POM is also a result of its "unzipping" degradation mode. POM is an inherently unstable polymer, and it easily depolymerizes starting at its chain ends on thermally unstable hydroxyl groups. This leads to quick decomposition of its carbon–oxygen backbone accompanied by the formation of a great deal of combustable formaldehyde. The produced formaldehyde and its oxide, formyl acid, can further accelerate the degradation of POM's main chains, and thus more small-molecule fuel is released thus intensifying the combustion process.[24–26] In addition, POM catalytically decomposes in the presence of protonic or Lewis acids such as formic acid, hydrogen halide, and antimony halide to generate highly flammable monomeric formaldehyde gas. Therefore, the common halogenated flame retardants are completely ineffective for POM.

In recent years, there has been considerable interest in using phosphorus- and nitrogen-containing flame retardants, as not only do they have a wide range of thermal and chemical stabilities but can also enhance the thermal and flame-retardant properties to POM and its composites.[27–30] Itoh and coworkers[31] investigated the effect of the ternary combination of red phosphorus, novolak, and melamine on flame retardancy of POM and found an effective synergism to enhance the flame resistance of POM. The resulting POM compound achieved the UL94 flammability rating of V–1. Wang and coworkers[32] took advantage of the thermoplastic polyurethane to encapsulate the halogen-free flame retardant, melamine phosphate, hence improving the compatibility of POM with flame retardant powders and achieving a fine dispersion of these powders in the matrix. The prepared POM compounds also obtained a significant improvement in LOI. Although several attempts to develop the flame-retardant POM by incorporating nitrogen- and phosphorus-containing flame retardants have been reported, there has been

little information presented about the more effective flame-resistance techniques for POM to achieve the V–0 rating and the corresponding mechanisms to determine their effects on the flame retardancy.

Phosphorus-containing flame retardants such as ammonium polyphosphate (APP) are becoming increasingly popular because they give rise to environmentally friendly products when incinerated. These additives mainly act in the condensed phase, and their effectiveness is highly dependent on the chemical structure of polymer; they are particularly effective for high oxygen content polymers.[33–35] In this work, APP and melamine cyanurate (MC) were used as phosphorus- and nitrogen-containing flame retardants, respectively, as well as the auxiliary additives for preparing the flame-retarded POM compounds, and their synergistic effect on the flame retardancy of POM was investigated. Thus, the aim of this study is to explore an effective method for improving the fire resistance of POM and to develop the halogen-free POM compounds with a good balance of flame-retardant, thermal, and mechanical properties.

EXPERIMENTAL

Materials

The POM used in this study is purchased from Asahi Kasei Chemicals Co., Japan. It is a polyacetal copolymer (commercial grade: TENAC-C-4520) with a number average molecular weight of 25,000, melt index of 9.0 g/10min, and specific gravity of 1.41). APP (JLS-APP101R) and MC (JLS-MC25) were commercially supplied by Hangzhou JLS Flame Retardants Chemical Co., China. Novolak with the degree of polymerization of around 7 and a softening temperature of 85°C was purchased from Xinxiang Boma Fengfan Industry Co., China. Dipentaerythritol was purchased from Beijing Chemical Reagent Co., China.

Preparation of POM compounds

POM, APP, and MC were dried in a vacuum oven at 80°C overnight to ensure the removal of any moisture. The POM compounds containing various flame retardants were blended using a ZSK-25 twin-screw extruder (screw diameter: 25 mm, L/D: 32, Werner & Pfleidere Co., Germany) with a screw configuration adapted to POM. All the components were premixed in a high-speed mixer and then fed through the throat of the extruder. The temperature along the barrel was set from 170 to 180°C, and the rotating speed of the screw was 250 rpm. The melt was passed through a cooling water bath and subsequently palletized. The extrusion parameters were slightly

varied from one composition to another. The compounds were further dried at 80°C and then were injection-molded into the test bars with the different shapes required for flammability measurements.

Characterization

Vertical burning test

A vertical burning test was performed on a CZF-3 instrument (Jiangning Analysis Instrument Factory, China) to determine the flammability rating of all the compounds in terms of the protocols obtained from Underwriter Laboratory (UL)-94 standard. A test bar with dimensions of 127 mm × 12.7 mm × 3.2 mm was clamped from the upper 6 mm of the bar with the longitudinal axis vertical and hung vertically over some surgical cotton. The lower end of the bar was contacted by a butane flame for 10 s thus initiating burning. A second ignition was made after self-extinguishing of the flame at the sample. The samples were classified depending on time of extinguishment of the flame after each ignition and on whether combustion occurs with dripping of flaming particles capable of igniting surgical cotton placed under the specimen. Five test bars were tested for each sample. The sample achieves the flammability rating of V-0 if total flaming combustion for each test bar stops within 10 s after two applications of 10 s each of a flame to a test bar, and the cotton below the test bar is not ignited by the flaming drips. However, the sample only achieves the V-1 rating when burning stops within 30 s after two applications of 10 s each of a flame to a test bar, and no flaming drips are allowed yet. While the sample can achieve the V-2 rating when burning stops within 30 s after two applications of 10 s each of a flame to a test bar, and the surgical cotton placed under the test bar is ignited by flaming drips produced by combustion of the bar.

LOI measurement

The LOI measurement was carried out using HC-2 oxygen index apparatus (Jiangning Analysis Instrument Factory, China) with a magneto-dynamic oxygen analyzer according to ASTM D2863 standard. The test bar with dimensions of 65 mm × 10 mm × 4 mm was clamped vertically in the center of the combustion chamber and ignited by a butane burner with a mixture of oxygen and nitrogen continuously going through with a flow rate of 171 mL/min. The flammability was determined by the minimum concentration of oxygen supplied for the combustion.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed on a Tensor 27 FTIR spectrometer (Bruker Co., Germany) with a scanning number of 30 using KBr pellets. The spectra of the residual chars after the vertical burning test were obtained at 1 cm^{-1} resolution in the 400–4500 cm^{-1} region.

Scanning electron microscopy

Morphologies of the residual chars after the vertical burning test were observed and photographed using a S-4700 scanning electron microscope (SEM) (Hitachi Co., Japan). The sample surface was coated with a thin layer (10–20 nm) of gold in a high vacuum evaporator and vaporizing the metal held in a heated tungsten basket before the SEM measurement.

Pyrolysis–gas chromatography/mass spectrometry

Pyrolysis–gas chromatography (GC)/mass spectrometry (MS) was performed to detect the pyrolysis products of pure POM and its compounds. A PY-2020iD pyrolyzer (Frontier Lab., Japan) was used to pyrolyze the sample at a desired temperature in static air at atmospheric pressure. The pyrolysis chamber is composed of a stainless steel cell and an electrically heated Ni/Cr/Fe sample holder/filament. The sample holder/filament was cleaned by heating at 800°C to burn off residual material from previous experiments. Preweighed sample amounts of $\sim$ 15 mg were placed in the boat-shaped filament, and the cell was tightly sealed to retain all gaseous products. The pyrolysis temperature was set to a desired value of 600°C and held for 40 s. Pyrolysis gases were slowly drawn up into a preheated gas tight syringe beginning 5 s after initiation of the reaction and continuing for the remaining reaction time of 25 s. Separation of the collected products was accomplished by a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, USA) using a HP-5 capillary column with the following temperature program: initial oven temperature of 40°C, held for 5 min; then raised to 220°C at 20°C/min and held for 10 min. The GC effluents were fed directly into the ion source of a Trace DSQ II mass spectrometer (Thermo Fisher Scientific, USA). Helium with a gas pressure of 5 psi was used as the carrier gas. The mass range from m/z 20 to 540 was scanned. Identification of the pyrolysis gaseous products was achieved by comparing the observed mass spectra to those in the NIST mass spectral library. Because of the lack of an appropriate standard mixture for calibration, percent-fractional yields of gaseous pyrolysis products were calculated from the total integrated area of all products and expressed relative to the total mass lost during pyrolysis.

Differential scanning calorimetry

A differential scanning calorimetry (DSC) measurement was performed using a DSC 200 F3 instrument (Netzsch Co., Germany) at a heating rate of 10°C/min. All measurements were made under N_2 atmosphere with the sample weight of around 10 mg. The first heating scan was carried out from the room temperature to 200°C, and the sample was held at this temperature for 10 min to diminish the thermal and processing histories before the formal test. The melt temperature (T_m) and the enthalpy of fusion (ΔH_m) of the samples were calculated from the maximum and the area of the endothermic peak, respectively.

Thermogravimetric analysis

A thermogravimetric analysis (TGA) measurement was performed on a TG 209 F3 instrument (Netzsch Co.,Germany) at a heating rate of 20°C/min from 40 to 600°C under an N_2 atmosphere with sample weight of ~ 10 mg contained in aluminum sample cup.

RESULTS AND DISCUSSION

Flame-retardant performance

The POM compounds containing various amounts of flame retardants were prepared via a melt blending, and numerous formulations were evaluated on the basis of the LOI and vertical burning tests. We selected several representative compounds for presentation, and their testing results are listed in Table I. It is seen that pure POM resin has a much lower LOI than most general thermoplastics. The vertical burning test also shows that pure POM burns continuously with a smokeless blue flame after vertical ignition accompanied with flammable dripping and a pungent smell due to the release of formaldehyde produced by the thermal decomposition, which indicated the high flammability of pure POM. Nevertheless, the POM compounds containing 24 wt % APP and 8 wt % MC obtained an improvement in the LOI and reached a UL94 flammability rating of V-2 with a few flaming drips. The flame retardancy could be further enhanced with an increase in the APP and MC loadings, and then the compounds achieved the V-1 rating without any drips. These results indicate that the flame retardancy of POM can be improved by incorporating APP and MC. It is known that the combustion of polymeric material may be viewed as a two-step process whereby volatile fragments produced in the thermal degradation of the condensed phase mix with the ambient oxygen in the gas phase where they are combusted. Therefore, the activity of flame retardants is due to their ability to inhibit free-radi-

cal reactions, which propagate gas-phase combustion and/or to their capacity to depress the rate of evolution of volatile compounds from the condensed phase. In the present flame-retardant system, APP can act in both the condensed and the gas phase. In the gas phase, phosphorus results in flame inhibition through radical trapping; in the condensed phase, it initiates the formation of phosphorus-rich and carbon-rich char or inorganic residue. Simultaneously, MC can release nonflammable gases, such as melamine, NH_3, CO_2, N_2, and H_2O, during combustion to dilute the hot atmosphere, cool the pyrolysis zone at the combustion surface, and cut off the supply of oxygen. These products from the decomposition of MC may also in their own respect have changed the decomposition mechanism of POM. As a result, a synergism of the two phosphorus- and nitrogen-containing flame retardants affects in flame retardancy to POM.

However, the flammability of the POM compound could not reach the V-0 rating even when high loadings of the two flame retardants were incorporated. It was also observed that the test bars of these compounds hardly self-extinguish after second ignition during the vertical burning test. These phenomena are attributed to the fact that less char is formed during combustion resulting from the characteristic molecular structure of POM.[36] When dipentaerythritol or novolak as an additive for promoting the char formation (i.e., a char-forming agent) was incorporated into the compounds, the LOIs increased remarkably. Furthermore, the addition of dipentaerythritol or novolak also significantly reduced the total flaming times and maximal flaming time for the single test bar during the vertical burning test, although the flammability of the compounds still did not reach the V-0 rating. Evidently, the presence of novolak or dipentaerythritol, together with phosphorus- and nitrogen-containing flame retardants may lead to the formation of carbon- and phosphorus-rich char, which are very efficient physical and thermal barriers protecting the underlying polymers. The flammability performance shown in Table I also implies that novolak is more effective for char formation than dipentaerythritol. It is noteworthy that, when both novolak and dipentaerythritol were incorporated into POM, the flame-retardant performance was significantly enhanced, and the compounds also achieved the V-0 rating without further increase in the APP and MC loadings. These results indicate that the flame-retardant effect is more significant when using the two char-forming agents together instead of one. Herein, it is found that the combination of novolak and dipentaerythritol displays a very effective enhancement in char formation during combustion, also suggesting the synergism of the two char-forming agents for flame retardancy of

TABLE I
Flame-Retardant Property of the POM Compounds

Sample code	Composition (wt %)					LOI (vol %)	Flammability test of UL94			
	POM	APP	MC	Novolak	Dipentaerythritol		Rating	Flaming drips	Total flaming time (s)	Maximal flaming time (s)
1	100	–	–	–	–	15.5	Failed	Yes	–	–
2	78	24	8	–	–	28.6	V-2	Yes	211.5	28.8
3	64	27	9	–	–	30.5	V-1	None	146.2	29.4
4	56	33	11	–	–	34.7	V-1	None	109.4	25.7
5	56	27	9	–	8	35.9	V-1	None	65.8	19.3
6	56	27	9	8	–	40.5	V-1	None	46.7	12.5
7	56	27	9	4	4	52.8	V-0	None	26.3	3.5
8	56	29	7	4	4	47.5	V-0	None	34.5	8.2
9	56	24	12	4	4	45.3	V-0	None	37.1	7.6

the POM compounds. In addition, the results in Table I also confirm that the 3/1 is an optimal APP/MC weight ratio for flame retardancy of POM, while 36 wt % flame retardants and 8 wt % char-forming agents in the condensed phase are minimal loadings for POM reaching the V-0 rating.

Analysis of residual char

Figure 1 shows the profiles of the test bars after vertical burning test, which demonstrates the status of the char formation after combustion. It is seen that the test bar of pure POM does not char after the first flame application during the vertical burning test, indicating that POM is so flammable that it combusts exhaustively. After APP, MC, and the other additives are incorporated into POM, all the compounds exhibit the char formed on the surfaces of the burned test bars. However, it is also noticed that the surfaces of Sample 2 and Sample 3 are covered with the char in large area. Owing to the lack of the char-forming agent, the two test bars are difficult to be self-extinguished after the second burner flame application, resulting in a great area of char on the surface of the test bar. Furthermore, when the char-forming agent is incorporated into the POM compounds, the char becomes heavier and more compact and is concentrated more in a smaller area, which results from the self-extinguishing after the second burner flame application to the test bars during the vertical burning test. However, it is found that the char of the dipentaerythritol-containing compound is more loose and crumbly compared to the one of the novolak-containing compound in the vertical burning test. Sample 7 demonstrates the heaviest and most compact char with the smallest area compared to the other samples, indicating that a combination of the two char-forming agents effectively enhances the char formation.

The char morphologies of the test bars are confirmed by SEM images shown in Figure 2. For the POM compound only containing APP and MC, the residual char was solid and crushed after the test bar was burned. This phenomenon implies that, based on this formulation, an integrated layer of char cannot be formed on the surface of the test bar during combustion, resulting in poor flame retardancy. After dipentaerythritol or novolak as the char-forming agent was incorporated into the compounds, the monolithic char was formed on the burned test bar. It is observed that this char is loose and multiporous. However, the distribution of the pore size is not homogeneous, and the char of the dipentaerythritol-containing compound looks so frangible and defective compared to that of the novolak-containing one [see Fig. 2(b,c)]. It is also seen in Figure 2(d–f) that the formed char is more dense and compact and exhibits a finely multicellular structure after combustion of the compound containing APP, MC, novolak, and dipentaerythritol, indicating a synergistic effect of novolak and dipentaerythritol on charring. Such a characteristic morphology suggests that the combination of the two char-forming agents as well as APP and MC results in a formation of the well-defined char network, which protects the surface of the test bar from flaming due to the intumescent mechanism to provide
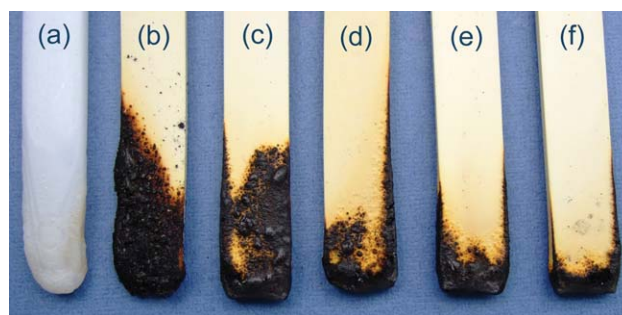

Figure 1 Digital photographs of the test bars of the POM compounds after the vertical burning test: (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 5, (e) Sample 6, and (f) Sample 7; the sample code corresponds to the composition in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
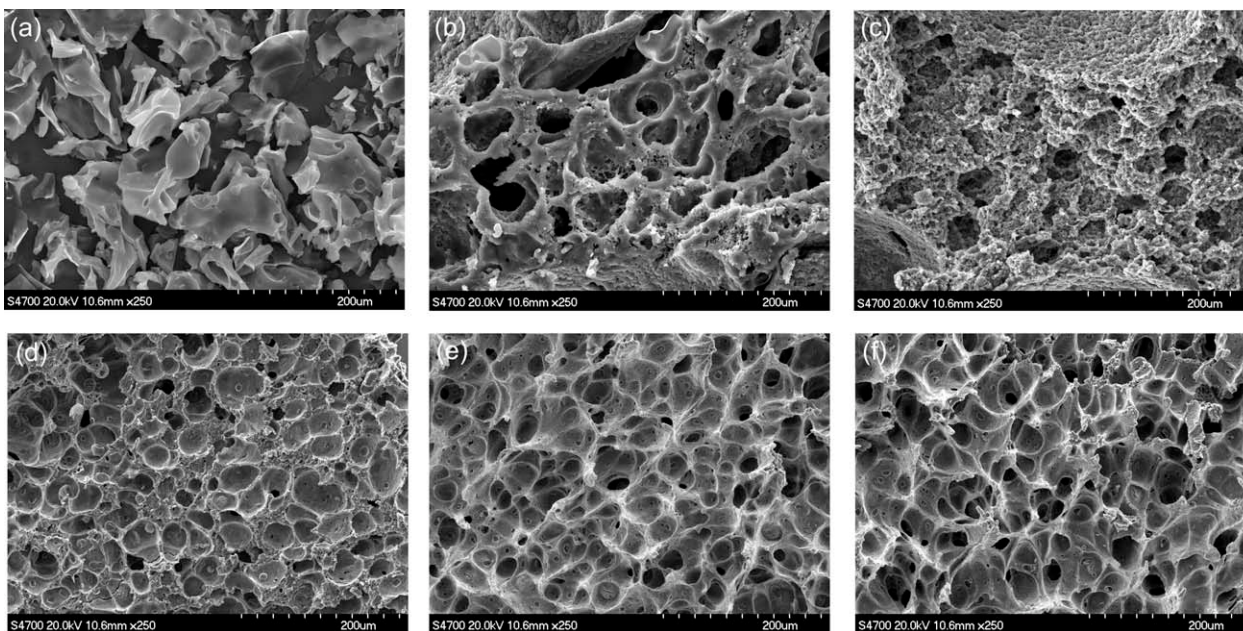
Figure 2 SEM images of the residual chars of the POM compounds after the vertical burning test: (a) Sample 3, (b) Sample 5, (c) Sample 6, (d) Sample 7, (e) Sample 8, and (f) Sample 9; the sample code corresponds to the composition in Table I.

high flame retardancy to POM matrix.[37] As a typical intumescent process for this POM system, it is clear that, when the compound starts to combustion, APP decomposes to yield phosphoric acid which in turn phosphorylates dipentaerythritol and novolak to form the esters. These esters begin to dehydrate and crosslink to char simultaneously with the evolution of gas from MC, which causes the char to swell and hence provides an insulating multi-cellular protective layer. This shield limits at the same time the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source resulting in a conservation of the underlying material, and thus resulting in the extinguishment of fire fast. Furthermore, the holes and pores formed on the surface of char during combustion seem to be accessible to nonflammable volatiles, NH_3, CO_2, N_2, and H_2O produced by the pyrolysis of APP and MC.[38,39] As a result, the three samples achieved a high nonflammability of the UL94 V-0 rating.

The chars obtained from all the samples were also analyzed by FTIR spectroscopy, and their spectra are presented in Figure 3. It is seen that these spectra show a broad absorption band at 3423 cm^{-1} corresponding to the N—H stretching vibration. A strong peak at 487 cm^{-1} is associated with the C—N deformation vibration attached to the triazine ring. These two characteristic bands confirm the pyrolysis products of MC. A series of broad absorption bands between 1159 and 1637 cm^{-1}, corresponding to aromatics and polyaromatics, are characteristic of the carbonized polymers. The intensive absorption
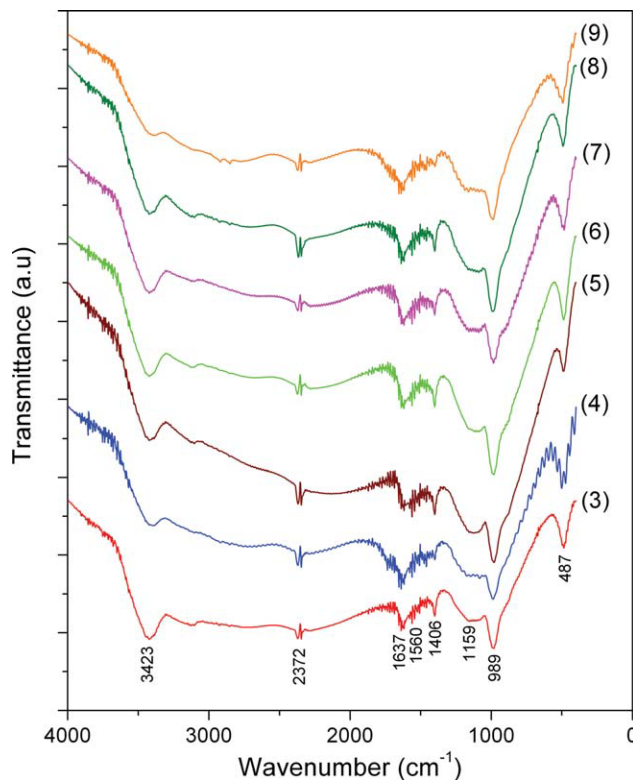

Figure 3 FTIR spectra of the residual chars of the POM compounds after the vertical burning test; the curve number corresponds to the sample code in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Test Results Obtained from Pyrolysis–GC/MS During the Pyrolysis of Pure POM and Its Compound

Sample	Peak no.	Retention time (min)	Molecular weight	Pyrolysis product	Relative yield (%)	Char yield (wt %)
Pure POM	1	1.56	30	Formaldehyde	93.01	0.06
	2	2.94	75	1,2-Propanediol	0.8	
	3	6.46	90	Ethylene glycol monoformin	0.6	
	4	10.09	84	2-Ethoxy propane	1.68	
	5	13.00	90	1,3,5-Trioxane	1.32	
Sample 7	1	1.53	30	Formaldehyde	69.61	26.71
	2	2.68	74	1,3-Dioxolane	3.21	
	3	2.89	72	Tetrahydro furan	2.02	
	4	5.86	84	Dimethylaminol acetoritrile	0.94	
	5	6.61	59	N-Methyl formamide	2.63	
	6	6.81	73	N,N-Dimethyl formamide	1.27	
	7	10.3	–	Unknown	2.81	
	8	11.47	129	Hexahydro-1,3,5-trimethyl-1,3,5-triazine	7.78	
	9	11.94	147	1-Methoxy-3,3-diethyltriazine 2-oxide	4.61	
	10	15.54	–	Unknown	1.39	
	11	19.33	206	2,4-Bis[1,1-dimethylethyl]-phenol	0.79	

bands at 989 and 1159 cm^{-1} are attributed to the stretching vibrations of the P—O—C bonds. The FTIR spectra also reveal a weak band at 2372 cm^{-1} assigned to the P—OH stretching vibration.[40] These results indicate that the chars of the POM compounds after combustion seem to consist of phosphorous- and carbon-rich compounds, and such characteristic phosphorous- and carbon-rich chars resulting from APP/MC formulation as well as the char-forming agents can protect the surface of the test bar from flaming in terms of the intumescent mechanism. The protection offered by the char to the polymer is shown by the increase in the LOIs and reduction in total flaming time and maximal flaming time. It may be explained by the formation of a layer of the phosphorous- and carbon-rich char on the polymer surface when the sample is subjected to heat. The char formation with the multipurpose and compact structure favors fire resistant purposes as the char prevents the entry of flammable gases into the gas phase and insulates the underlying polymer from flame.

Pyrolysis-GC/MS analysis

The effect of flame-retardant additives on the amount and distribution of evolved gaseous products during the pyrolysis of the flame-retarded POM compounds was investigated using isothermal pyrolysis coupled with GC/MS to gain an insight into their degradation mechanisms. This technique provides information about the decomposition behavior of a polymer when exposed to a rapid temperature as a result of the effect of radiation from fire. Identifiable compounds constituted an estimated 72–89% of the evolved gases from the pyrolysis of each sample. In this article, pure POM and its flame-retarded compounds with an optimal composition (i.e., Sample 7) were analyzed using pyrolysis-GC/MS, and their gas chromatograms are shown in Figure 3. An integrated NIST mass spectral library was used to identify the evolved gaseous products and these are listed in Table II.

As is seen in Figure 3(a), the thermal degradation of pure POM is shown to occur mainly as result of bond cleavage in the carbon–oxygen backbone leading principally to formaldehyde as the predominant product. However, because some, although few, random chain scission reactions can occur at the higher pyrolysis temperatures, a whole range of oligomers and substituted trioxanes are to be expected. Table II provides a list of the pyrolysis products of pure POM detected in this study, along with the principal ions detected which were used to identify the products. As previously mentioned, the major product of the pyrolysis of POM is formaldehyde, which accounts for over 93% of the detected volatile products. Two other species of significance (over 1%) are 2-ethoxy propane and 1,3,5-trioxanes with methoxy substituents. All the other compounds detected are less than 1%, and consisted of a wide variety of low molecular methoxy oligomers.

When the POM compound containing APP, MC, novolak, and dipentaerythritol was pyrolyzed, the first observation was the apparent reduction in the chemical species detected that could be attributed to POM as shown in Figure 4(b). The large reduction in the yield of formaldehyde was especially noticeable based upon the data presented in Table II. Interestingly, while the number of methoxy oligomers detected has significantly decreased when POM is pyrolyzed in the presence of the flame-retardant additives, the yields of several new compounds such as 1,3-dioxolane and tetrahydro furan show
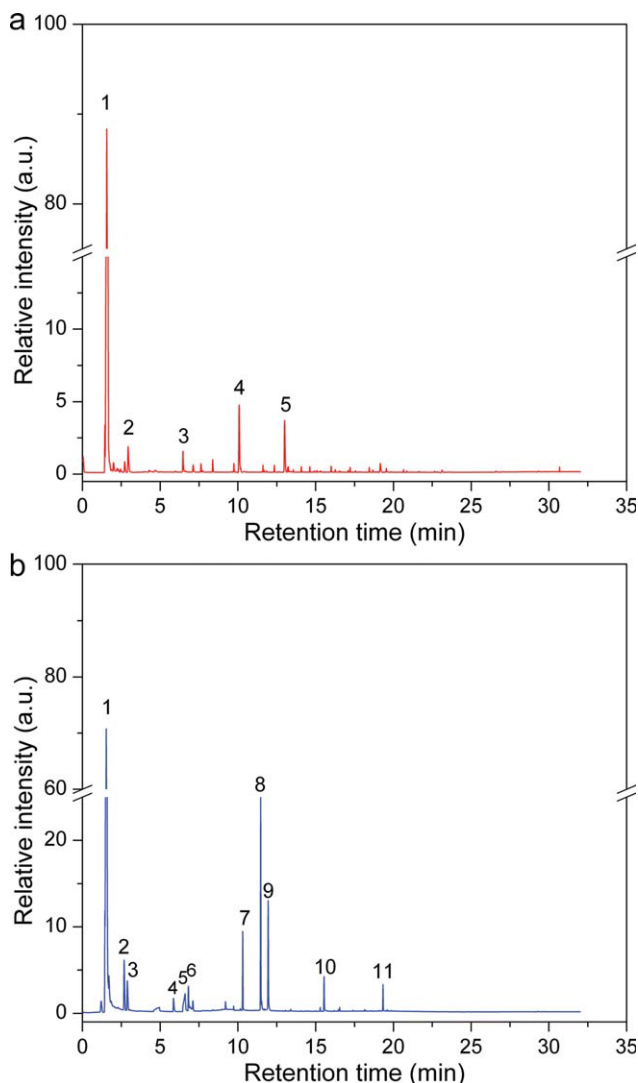
Figure 4 Gas chromatograms of the pyrolysis–GC/MS detection of gaseous products evolved from pyrolysis of (a) pure POM and (b) Sample 7 at 600°C for 40 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

substantial increases. These increases meant that they became relatively important species in the pyrolysis product profile. Meanwhile, a series of nitrogen-containing compounds such as dimethylaminol acetoritrile, N-methyl formamide, N,N-dimethyl formamide, and some triazine-type species were detected, which were attributed to the pyrolysis products of MC. It is noteworthy that the phosphorus-containing species could not be detected; however, notable increments in char formation are observed, which indicates that the pyrolysis products of APP remained in the solid residue. This maybe suggest that APP is effective in the condensed phase at promoting char formation, which concurs very well with the published propositions.[41] The residual char calculated at 26.7% also implies that the combination of the four flame-retardant

additives is effective in preventing depolymerization of POM.

DSC analysis

The melting point (T_m) is an important parameter for determining the heat resistance of the crystalline thermoplastics, and in most cases, their service temperatures are below T_m. Therefore, the investigations on the mechanism of T_m variation and the prediction of T_m decline are critical for the formulation design and application of polymer blends. Thermal behavior of POM compounds was evaluated by DSC, and Figure 5 displayed their thermograms. The T_ms and ΔH_ms corresponding to the POM phase in the compounds are obtained from the DSC analysis and are summarized in Table III, where the ΔH_m is normalized to the POM phase in consideration of the loadings of all the flame-retardant additives. Thermal analysis data confirmed a high crystallinity of POM with a T_m of 165.5°C and ΔH_m of 142.2 J/g. After APP, MC, and the char-forming agents are incorporated into POM, the T_m and ΔH_m of the POM phase decreases slightly. This suggests that the presence of the flame-retardant additives interfere with the crystallization of the POM phase, and thus result in a decrease in the T_m and ΔH_m. However, the T_m is never lower than 163.0°C, indicating that there is no
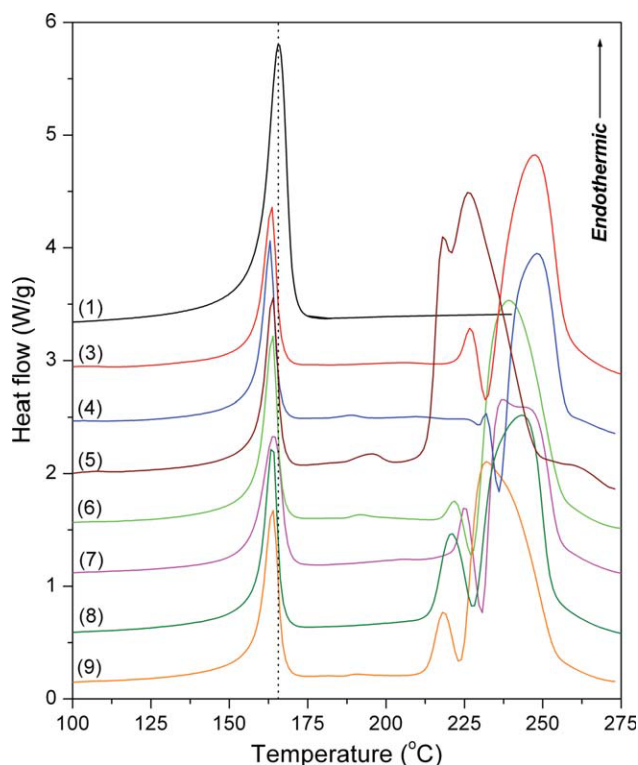

Figure 5 DSC thermograms of the POM compounds; the curve number corresponds to the sample code in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Sample code	$T_{m,POM}$ (°C)	$\Delta H_{m,POM}$ (J/g)	Temperature at characteristic weight loss (°C)		Temperature at rapid weight loss (°C)	Char yield at 600°C (wt %)
			2 wt %	10 wt %		
1	165.5	142.2	306.8	336.1	386.8	0.01
2	164.7	139.7	230.4	241.4	249.5	22.6
3	163.6	135.4	229.3	243.3	251.8	25.8
4	163.0	132.8	228.8	238.9	242.6	26.8
5	164.1	136.5	224.4	235.2	241.7	27.3
6	163.9	134.6	226.4	240.1	248.5	26.4
7	163.7	135.3	227.8	243.5	251.2	25.7
8	163.4	133.9	225.7	241.3	250.3	26.3
9	164.0	134.7	229.9	242.8	250.6	25.6

The sample code corresponds to the composition of the POM compounds in Table I; the ΔH_ms are normalized to the POM phase in consideration of the loadings of all the flame-retardant additives.

deterioration against the heat resistance of the flame-retarded POM. In addition, the DSC thermograms of the POM compounds also exhibit several melting peaks at temperatures of more than 250°C, which are attributed to the fusion of APP, MC, and/or dipentaerythritol. It is evident that most flame-re-tardant additives remain solid until the POM matrix has completely melted in the compound and will not generate a negative effect on the heat resistance of the flame-retarded POM.

Thermal stability

The TGA thermograms of the POM compounds are shown in Figure 6, and their analysis results are presented in Table III. The weight loss profile of pure POM reveals a typical one-stage degradation, in which thermal degradation occurs at a high temperature of 306°C due to the chain scission of the C—O—C bonds. This thermally induced chain rupture leads to a complete unzipping of the damaged chain and thus leaves almost no residual char. The derivative thermogravimetric (DTG) curves in Figure 6(b) also demonstrate that the degradation rate of POM reaches a maximum at 387°C assigned to the temperature of the rapid weight loss. However, the degradation behavior of all the POM compounds shows a two-stage pathway with the first step attributed to the decomposition of the flame-retardant additives (i.e., APP, MC, novolak, and/or dipentaer-ythritol), while the second step is due to the chain scission of the POM to reach full degradation at high temperatures. The onset of the first thermal degradation for these compounds, measured as the temperature at which 2 wt % weight loss occurs, is around 224–230 °C, while the temperature at rapid weight loss is around 241–250 °C.

It is not surprising that the low decomposition temperature of the flame retardants favors flame
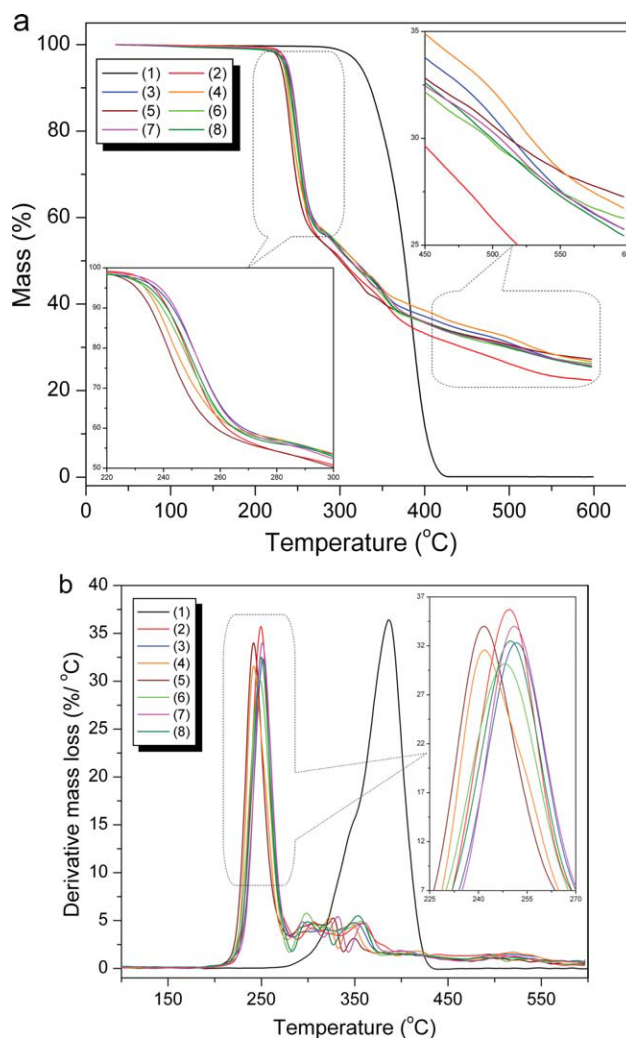

Figure 6 TGA (a) and DTG (b) thermograms of the POM compounds; the curve number corresponds to the sample code in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

retardancy of POM, although the presence of the flame retardants as well as the char-forming agents reduces the thermal stability of compounds remarkably. It can be deduced that the POM compounds first undergo endothermic decomposition of the flame retardants (i.e., APP and MC) releasing melamine, CO_2, and some phosphate derivatives before the pyrolysis of POM during combustion. The melamine subsequently sublimes or decomposes into incombustible NH_3; this process acts as a heat sink cooling the compound. The release of phosphate derivatives may lead to the formation of phosphoric acids, which are known to promote char formation, therefore shielding the condensed combustible POM. As a result, the decomposition of the two flame retardants at low temperature eventually delays the degradation process of POM at high temperatures during combustion, and thus enhances fire resistance of the compounds.

It is also noteworthy that the residual char yields of the POM compounds significantly increase by more than 20 wt %, and furthermore, the char yield increases with increased loading of the flame retardants. During the pyrolysis, the flame retardants (i.e., APP and MC) first decompose to form a phosphorous-rich residue, which prevents further decomposition of the POM resin by acting as an insulation layer on the surface of the compounds to prevent or slow down the transfer of heat and combustible volatiles into the remaining unreacted POM and pyrolysis zone, respectively, thus retarding the combustion process, and consequently resulting in a high char yield.[42] The high char yield has been correlated to denote the flame retardancy and has been widely referenced in studies of the flame-retardant properties of polymers.

Flame-retardant mechanism

It is clear that the high flame retardancy of the POM compounds was due to a combination of APP, MC, novolak, and dipentaerythritol as a phosphorus–nitrogen synergetic effect. However, the flame-retardant mechanism of these POM compounds is still not very clear, although they have considerable potential applications on the basis of their flame-retardant properties. There have been many proposals for the mechanism of the phosphorus–nitrogen flame-retardant systems, such as the gas phase mechanism,[43] the condensed phase mechanism,[44] and the phosphorus–nitrogen synergism mechanism.[45] On the basis of the investigation on the thermal decomposition and flame retardancy of the POM compounds in this article, the flame-retardant level of the flame-retarded POM may be not due to any single mechanism but moreover due to a number of effects.

First, at temperatures above 260°C, APP starts to decompose and produce phosphoric acid or metaphosphoric acid, which then is converted to polyphosphoric acid. These pyrolysis products act in the condensed phase to enhance the crosslinking of polymer fragments, and thus promote the formation of a stable char on the surface as a barrier to inhibit gaseous products from diffusing to the flame, to shield the polymer surface from heat and air, and to prevent or slow down oxygen diffusion as well. The condensed phase flame-retardant mechanism results in the retention of carbon networks hence the observed enhanced residual char. APP also produces the phosphinylidyne free radicals (PO·), which maybe annihilate H· and OH· free radicals on the POM chain scission and therefore terminate the combustion reaction.

Second, MC undergoes an endothermic decomposition to produce melamine and cyanuric acid at above 350°C, thus removing a great deal of combustion heat and leading to quick self-extinguishing of POM compounds. The melamine as a blowing agent could create continuous blowing action over the char-forming temperature range, enhancing the barrier functionality of the char layer. It is observed that there is a great number of formed pores distributed on the residual char surface [see Fig. 2(b–f)], which shows that the test bars experienced intensive expansion due to the generated nitrogen-containing gas from the decomposition of MC at high temperature. MC also acts as a source of the inert diluents because the combustion of MC generates nonflammable gases such as NH_3, CO_2, N_2, and H_2O, which can dilute the hot atmosphere and cool the pyrolysis zone at the combustion surface as well as cut off the supply of oxygen.

Third, it is well understood that the incorporation of nitrogen- and phosphorus-containing flame retardants shows improved flame retardancy compared to the use of the only one, which is called "phosphorus–nitrogen synergism."[46,47] Accordingly, the incorporation of APP and MC has possible complementary and synergistic effects in the present flame-retarded POM compounds. This synergistic action is attributed to the interaction between APP and MC, which retards the loss of one another, capturing their volatile components by formation of macromolecular substances such as $(PNO)_n$ or $(PN)_n$ with high thermal stability to further consolidate the condensed phase. These phosphorus–nitrogen substances that remain in the char provide protection against further degradation. However, the process is quite complicated and so far the detailed mechanisms are not very clear.

Finally, char-forming agents (i.e., novolak and dipentaerythritol) play an important role in current flame-retardant systems. APP and MC are

formulated as the combined acid and carbon source in intumescent systems for POM. However, when dipentaerythritol as a char-forming agent is present in the compound, there is an additional chemical effect of char promotion. This is particularly the case in more complex phosphorus compounds such as pentaerythritol-based phosphates, where the polyol present possesses a built in char-forming tendency.[39] On the other hand, novolak can react with formaldehyde, the main pyrolysis product of POM to form highly cross-linked phenol–formaldehyde copolymers, which provide both thermal stability and char forming ability.[33] As a result, the intumescent char-forming system consisting of dipentaerythritol and novolak can act by combined chemical and physical reactions to form a compact voluminous foamed residue or char, which offers protection to the underlying substrate from further decomposition and also attempts to offset the melt dripping tendency, and therefore imparts better flame retardancy.

In addition, the pyrolysis–GC/MS analysis has confirmed the "unzipping" degradation of POM via main chain scission accompanied with the release of formaldehyde, which is the critical reason leading to its high flammability. The highly flammable formaldehyde gas can further enhance combustion of POM, resulting in a failure in many flame-retardant POM systems. Therefore, a key approach to the flame retardancy of POM is to prevent formaldehyde from diffusing from the condensed phase to the gas phase. In the present flame-retardant system, the pyrolysis products of MC and novolak are a series of phenolic and aminotriazine compounds. Formaldehyde is a highly active chemical compound and can easily react with these nucleophilic compounds. In this case, novolak can easily react with formaldehyde at the remaining free o- and p-positions of phenolic groups to produce the methylol derivatives and their highly crosslinked products, which is well known as phenol–formaldehyde copolymer through the addition-condensation reaction. A main pyrolysis product of MC, melamine is also an aminotriazine compound having three amino groups per molecule and can easily react with formaldehyde without a catalyst to produce methylol melamine and the melamine–formaldehyde copolymer. Furthermore, these compounds may cocondense further to form a dense aminotriazine–phenol–formaldehyde–melamine network, which shows high self-extinguishing performance.[33] These effects have been verified by reduction of the relative intensity of formaldehyde [see Fig. 4(b)] and the significant increase of char yield (see Table II).

In summary, a combination of APP, MC, novolak, and dipentaerythritol could colligate all the flame retarding means for POM both in the condensed and gaseous phase, thus providing POM with a highly flame retardant performance to qualify the UL94 V-0 rating. The nonflammable halogen-free POM compounds developed in this study have potential applications in electric and electronic fields in consideration of the environment and human health.

CONCLUSIONS

The flame-retardant POM system involving APP, MC, novolak, and dipentaerythritol was intensively investigated, and an optimal formulation containing 27 wt % APP, 9 wt % MC, 4 wt % novolak, and 4 wt % dipentaerythritol in the POM matrix was obtained on the basis of the best flame-retardant performance with an LOI of 52.8 and flammability rating of UL94 V-0. A combination of novolak and dipentaerythritol as char-forming agents promoted formation of a dense and compact multicellular char providing the POM with protection against further degradation, while the FTIR spectra confirmed a characteristic phosphorous- and carbon-rich char resulting from the APP/MC formulation. The highly flammable formaldehyde gas released by the pyrolysis of POM was annihilated by the derivatives produced from the pyrolysis of MC and novolak, enhancing the flame retardancy of POM. The comprehensive flame-retardant mechanisms based on phosphorus–nitrogen synergism promote the high flame retardancy of POM leading toward the nonflammable V-0 rating.

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