



Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer



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ABSTRACT

A mono-component intumescent flame retardant named ethylenediamine-modified ammonium polyphosphate (MAPP) is used in polyethylene-octene elastomer (POE). Insight into the flame-retardant mechanisms of the MAPP is provided from a new perspective. The fire performance of POE/MAPP composites is investigated by oxygen index (OI) and vertical burning (UL-94) tests. POE composite containing 35 wt% MAPP achieves a V-0 rating, and its OI is 29.3 vol%. The thermogravimetric analysis (TGA) and Fourier transform infrared spectra (FTIR) confirm that the incorporation of ethylenediamine changes the thermal decomposition of APP, mainly resulting in the formation of char layer with a thermally stable structure. Cone calorimeter analysis revealed the flame-retardant modes of action of MAPP in POE under forced-flaming conditions. Quantitative analysis illustrates that both the residue due to charring and the fuel dilution/flame inhibition resulting from the release of incombustible products/phosphorus species decrease the total heat release (fire load) by 20–28%. The residue increases linearly with increasing MAPP content, whereas the reduction in effective heat of combustion levels off. Moreover, the flame-retardant effect resulting from the protective properties of the char is discovered to be the dominant mode of action (up to 85% reduction) with respect to the peak heat release rate, leading to the excellent flame retardancy of POE/MAPP.

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1. Introduction

In the past several decades, it has been confirmed that intumescent flame retardants (IFRs) are very effective to flame retard polymeric materials [1–3]. The typical IFR is usually composed of three main components: an acid source, a carbon source, and a gas source. At present, ammonium polyphosphate (APP) has been extensively applied as an acid source and a gas source in IFR [4–7]. However, without a sufficient carbon source APP has low flame-retardant efficiency. APP has hardly any charring ability during thermal decomposition, and the residue it forms is neither continuous nor compact [8]. So a charring agent is necessary in flame retardant polymers using APP. Charring agents such as

pentaerythritol [9], PA6 [10], triazine [11], novolac [12], and so on strongly promote the flame-retardant efficiency of APP. However, there are several disadvantages for these IFRs consisting of several components, including a complicated preparation process, pollution to the environment, and poor compatibility with polymer matrix. To overcome the disadvantages, mono-component IFRs have been proposed, and most of them are based on APP because it combines two typical characteristics of IFR, namely the acid source and the gas source.

There are two types of methods for fabricating mono-component IFRs based on APP, physical coating and chemical modification. For physical coating, the coating layer contains a silane coupling agent [13,14] and various charring agents [15,16]. Experimental results have demonstrated that above mentioned coatings promote the charring ability of APP and achieve highly efficient intumescent flame retardation of polymers. Wang and his coworkers applied two methods to prepare the coated APP, the first one in which APP was coated by UV-curable epoxy acrylate resin [17]; the second in which APP was coated by polysiloxane through

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in situ polymerization [7]. Both categories of prepared APP products significantly improved the flame retardancy of polypropylene, in which the coating on the surface of APP made an obvious contribution to the charring of APP. Yang et al. [18] investigated the effect of APP microencapsulated with *N*-ethyl triazineepiperazine copolymer on the flame retardancy of polypropylene, and the results showed that the polypropylene composite passed the UL-94 V-0 rating with 19 wt% APP microencapsulated for specimen of 3.2 mm thickness.

For the mono-component IFRs prepared through chemical modification, several types of chemically-modified APPs have recently been obtained, including EDA-APP [19], ETA-APP [20], and PA-APP [21]. Experimental results confirmed that they were very efficient in flame retarding polyolefin. For these IFRs, the key point in achieving the highly efficient flame retardation for polyolefin is that they have excellent charring ability. Wang and coworkers [19–21] demonstrated that plenty of thermally stable structures were formed during thermal decomposition of these mono-component IFRs, which must be the leading reason for the excellent flame retardation of these flame-retarded polyolefin composites. The influence of charring by these flame retardants on their flame retardant efficiency was illustrated by analyzing the microstructures of the products formed during thermal decomposition. During burning, properties such as the effective heat of combustion, total heat release, and the residue can be tracked quantitatively with the aid of a cone calorimeter, and the relationship of these quantitative data may directly reveal the flame retardant mechanism of flame retardants from another perspective, which is quite different from the analysis mentioned above. It is very meaningful to quantitatively analyze the burning process of composites filled with mono-component flame retardants in order to more clearly understand the modes of action of these flame retardants.

In this work, ethylenediamine-modified ammonium polyphosphate (MAPP) was used to flame retard flammable POE with excellent mechanical properties and good processability. At present, halogen-free flame-retardants are dominant in flame retarding POE. In Guo et al.'s work [22], ammonium polyphosphate-pentaerythritol (APP-PER) was used to flame retard POE with the aid of organo-montmorillonite, and the result showed that both flame retardancy and mechanical properties of POE composites were improved compared with the corresponding property of neat POE. In addition, Hong et al.'s [23] also studied the flame retardancy of POE through incorporation of magnesium hydroxide, and they found that the magnesium hydroxide coated with polymeric material was very efficient to simultaneously improve the flame retardancy and elongation at break of POE. According to the past work, it is known that intumescent flame retardants (IFRs) is more efficient than the others in flame-retarding POE, so the MAPP was used to flame retard POE in this work. In addition, the aim of this work is to gain insight into the flame retardant modes of action of the mono-component flame retardant MAPP from a new quantitative perspective. POE is used with different concentrations of flame retardants to work out the different dependencies of modes of action when the amount of flame retardant is increased.

2. Experimental section

2.1. Materials

The ethylene-octene elastomer (POE, Engage 8150, 25% octene) was supplied by DOW Co. (USA); ammonium polyphosphate (APP) was supplied by Taifeng New-Type Flame Retardants Co., Ltd. (Shifang, China); ethylenediamine (AR, 99.0%) and ethanol (AR, 99.7%) were purchased from Kelong Chemical Reagent Co., Ltd. (Sichuan, China).

2.2. Preparation of flame-retarded POE composites

POE composites with different weight ratios (25, 30, 35, and 40 wt%) of MAPP were prepared using a Brabender apparatus (XSS-300, Shanghai Kechuang Plastic Machinery Co., Ltd., China) at a temperature of 170 °C. After mixing the POE composites were hot-pressed into different sheets at 170 °C under 10 MPa for various measurements.

2.3. Measurement

The elemental analysis (EA) of MAPP was performed on a CARLO ERBA1106 instrument (Carlo Erba, Italy).

Fourier transform infrared (FTIR) spectra were recorded by a Nicolet FTIR 170 SX spectrometer (Nicolet, America) in the wavenumber range from 4000 to 400 cm^{-1} using KBr disk.

The OI value of all samples with dimensions of 130 mm \times 6.5 mm \times 3.2 mm was measured using a HC-2C oxygen index instrument (Jiangning, China) according to ASTM D2863-97.

The UL-94 vertical burning level of all samples was tested on a CZF-2 instrument (Jiangning, China) according to ASTM D3801. Their dimensions were 130 mm \times 13 mm \times 3.2 mm.

TGA was performed on a thermogravimetric analyzer instrument (209 F1, NETZSCH, Germany) under a N_2 atmosphere at a flow rate of 50 mL/min. The specimen mass was 5 mg; the heating rate was 10 °C/min; the temperature ranged from 40 to 700 °C.

A cone calorimeter (Fire Testing Technology, FTT, UK) was used to characterize the fire behavior under forced-flaming conditions according to ISO 5660. Specimens 100 mm \times 100 mm \times 3.1 mm in size were measured in aluminum trays exposed to an irradiation of 50 kW m^{-2} , and the distance cone-substrate is about 25 mm. The All measurements were done in duplicate, or in triplicate whenever the deviation between the first two measurements was above 10% in any key characteristic such as peak heat release rate (pHRR), total heat evolved (THE) or residue. The values for THE and the residual mass were taken at the time to flame-out. Thus the THE = total heat release at time to flame-out, THR (t_{fo}). Flame-out was defined as the extinguishment of the visible yellow flame.

3. Results and discussion

3.1. Characterization of MAPP

In our previous paper [19], it was confirmed that MAPP was prepared successfully through the analysis of FTIR, scanning electron microscopy, ^1H NMR and X-ray diffraction. In this work, an efficient MAPP was used to flame retard POE. Before analysis, the EA was used to confirm the contents of carbon (C), nitrogen (N) and hydrogen (H) of both APP and MAPP, and the result is shown in Table 1. For APP, the contents of C and H are 0 and 4.10% respectively. For MAPP, the corresponding contents are 5.84% and 4.84% respectively. Obviously, the content of both elements increases after incorporating ethylenediamine into the APP, while the content of N has no significant change before and after the modification of APP.

Table 1
The C, H and N contents of APP and MAPP.

	C (%)	H (%)	N (%)	P (%)
APP	0	4.10	15.12	31.15
MAPP	5.84	4.84	14.93	25.09

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