

Preparation and flammability of a novel intumescent flame-retardant poly(ethylene-co-vinyl acetate) system

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ABSTRACT

A phosphorus-containing flame retardant, 4-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yloxymethyl)-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane-1-oxide (MOPO), was synthesized successfully and characterized. The flame retardancy and thermal behavior of a new intumescent flame-retardant (IFR) system for EVA, which was made of MOPO and ammonium polyphosphate (APP), were investigated by limiting oxygen index (LOI) test, vertical burning test (UL-94), cone calorimeter, and thermogravimetric analysis (TGA). An LOI value of 28.4 and UL-94 V-0 rating can be achieved when the total loading of MOPO and APP was 30 wt.%. The results from cone calorimeter indicate that both the heat release rate (HRR) and the total heat release (THR) of IFR-EVA decreased significantly compared with those of neat EVA. TG curves showed that the amount of residues increased significantly when intumescent additives were added; it also could be found that the LOI values increased with the increase in char residues. Meanwhile, morphology of the residues obtained from burning IFR-EVA in LOI test was studied through the SEM observations and rich compact char layers could explain the excellent flame retardance.

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1. Introduction

Poly(ethylene-co-vinyl acetate) (EVA) was widely used in the wire and cable industry as insulating materials due to its good mechanical and physical properties [1]. However, it is easily flammable, and this is why flame retardation of EVA is being widely studied. This problem could be solved by using flame-retardant additives, such as halogenated compounds in synergistic combination with antimony trioxide [2]. Unfortunately, their fire retardant action may be accompanied by negative effects such as generation of corrosive, obscuring, toxic smoke. Thus, halogenated flame retardants had been under pressure due to perceived environmental concerns. In addition, the new regulations like the European Directives on WEEE (Waste of Electric and Electronic Equipment) and RoHS (Restrictions of Hazardous Substances) restricted the demand for some brominated flame retardants. Therefore, there was a growing demand for new, environmentally friendly solutions [3]. This had prompted the development of

halogen-free fire retardants [4,5]. In recent years, intumescent flame-retardant (IFR) additives had been widely utilized in the flame retardation of flammable polymers [6–11].

In this paper, a phosphorous-containing flame retardant, 4-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yloxymethyl)-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane-1-oxide (MOPO, see Scheme 1) was synthesized successfully, which was an intumescent additive. The molecular structure of MOPO was characterized by FT-IR and ¹H NMR spectroscopy. Meanwhile, a novel intumescent flame-retardant EVA system (IFR-EVA) had been obtained from EVA, MOPO and APP. Its thermal properties and flame retardancy were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI), UL-94 test and cone calorimeter. The synergism between MOPO and APP in EVA systems was studied; meanwhile, the morphology of the intumescent char layer and its possible mechanism were investigated by scanning electron microscopy (SEM) and FT-IR spectroscopy.

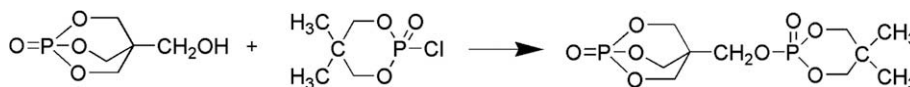
2. Experimental

2.1. Materials

Phosphoryl trichloride (POCl₃) was supplied by Chengdu Jianjie Chemical Reagent Corp. (Chengdu, China). 1,4-Dioxane, hexane,

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Scheme 1. The structure of MOPO.

acrylonitrile, ether absolute, triethylamine and trichloromethane (CHCl_3) were provided by Tianjin Bodi Chemical Corp. (Tianjin, China). Pentaerythritol (PER) was supplied by Tianjin Damao chemical reagent factory (Tianjin, China). Pyridine and 2,2-dimethyl-1,3-propanediol were provided by Chengdu Kelong chemical reagent factory (Chengdu, China). APP was supplied by Zhejiang Longyou GD Chemical Industry Corp. (Longyou, China). EVA (KA-31, AFG552, $\text{MFI} = 7$) contained 28% vinyl acetate was supplied by Sumitomo Chemical Co., Ltd. (Osaka, Japan). 1-Oxo-4-methoxy-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (PEPA) was synthesized according to Refs. [12,13] and 2,2-diethyl-1,3-propanediol phosphoryl chloride (DPPC) was prepared according to Refs. [14,15].

2.2. Synthesis of 4-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl)oxymethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-1-oxide (MOPO) [16]

In a 500 mL round-bottom flask, equipped with a stirrer, thermometer, dropping funnel, condenser and heating bath, 250 mL acrylonitrile, 90 g PEPA, and 92 g DPPC were added with 0.9 mL pyridine as catalyst. Then, the mixture was stirred at about 80°C for 1 h, then 70 mL triethylamine was added into the flask and heavy fume could be seen immediately. Thereafter, the mixture was heated and kept under reflux for about 10 h. Then acrylonitrile was removed to obtain a solid. Successively, the obtained solid was washed three times with deion water and once with acetone. The powdery product was dried at 70°C under vacuum to a constant weight. The melting point of the purified product was $170\text{--}172^\circ\text{C}$.

2.3. Preparation of flame-retardant EVA samples

The total content of MOPO and APP in EVA was kept as 30 wt.%, and EVA samples of various APP/MOPO formulations were prepared using a counter-rotation twin screw extruder under standard conditions: average residence time: 25 s, rotation of screw: 80 rad min^{-1} , mixing temperature: 150°C . After mixing, the samples were hot-pressed under 10 MPa for 5 min at 150°C into a sheet of suitable thickness and size, according to the corresponding test standard.

2.4. Characterization

2.4.1. Characterization of MOPO by FT-IR, ^1H NMR and ^{31}P NMR spectroscopy

The structure of MOPO was determined by ^1H NMR and ^{31}P NMR, which were performed on an FT-80A NMR by using deuterated DMSO as a solvent. The FT-IR spectra of MOPO were recorded with KBr powder by using a Nicolet FTIR 170SX infrared spectrophotometer. From FT-IR spectroscopy, it could be observed that absorption of $\nu_{\text{-CH}_2\text{-}}$ and $\nu_{\text{-CH}_3}$ from DPPC was at about 2897 cm^{-1} and 2980 cm^{-1} , respectively. The peaks at 1317 cm^{-1} , 1282 cm^{-1} and $990\text{--}1070\text{ cm}^{-1}$ were associated with the stretching mode of $\text{P}=\text{O}$ and $\text{P}-\text{O}-\text{C}$ in the phosphate, respectively. The absorptions at 873 cm^{-1} and 835 cm^{-1} were assigned to the skeleton vibration of caged bicyclic phosphates [15,17]. Based on ^1H NMR spectra of MOPO, ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ : 0.83 (s, 3H), 1.14 (s, 3H), 4.13 (d, $J = 10.80\text{ Hz}$, 2H), 3.96 (d, $J = 11.20\text{ Hz}$, 1H), 3.91 (d, $J = 11.20\text{ Hz}$, 1H), 3.94 (d, 2H), 4.71 (d, 6H). Furthermore, ^{31}P NMR revealed two

resonances at -21.2 and -7.1 ppm corresponding to caged P and the other one in the MOPO's structure, respectively.

2.4.2. LOI and UL-94 testing of IFR-EVA

The LOI values were measured on an HC-2C oxygen index meter (Jiangning, China) with sheet dimensions of $130 \times 6.5 \times 3\text{ mm}^3$ according to ASTM D 2863-97.

Vertical burning tests were conducted on a vertical burning test instrument (CZF-2-type) (Jiangning, China) with sheet dimensions of $130 \times 13 \times 3\text{ mm}^3$ according to ASTM D3801.

2.4.3. Cone calorimeter

The signals from the cone calorimeter (FTT Standard Cone Calorimeter, Fire Testing Technology Ltd., UK) were recorded and analyzed by a computer system. All samples ($100 \times 100 \times 5\text{ mm}^3$) were exposed horizontally to an external heat flux of 50 kW/m^2 according to ISO 5660 standard procedures (without the use of the "frame and grid").

2.4.4. Thermogravimetric analysis (TGA) of IFR-EVA

Thermogravimetric analysis (TGA) was performed on a DuPont 1090B thermogravimetric analyzer at a heating rate of $10^\circ\text{C min}^{-1}$. Samples of 7 mg were examined under an air flowing rate of 80 mL min^{-1} at temperatures ranging from room temperature to 600°C .

2.4.5. FT-IR spectroscopy of EVA and char residues

The FT-IR absorption spectra of the original EVA prepared by hot-pressing to sheets of 0.5 mm thickness under 10 MPa for 3 min at 140°C were determined by a Nicolet 560 (USA). Residues obtained from burning IFR-EVA (APP:MOPO = 2:1) in LOI test were characterized with KBr powder by using a Nicolet FTIR 170SX infrared spectrophotometer.

2.4.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) observed on a JEOL JSM-5900LV was used to investigate the residues of the flame-retardant EVA systems. The residue samples for SEM were collected after combustion in their limiting oxygen concentration. The specimens were recorded at 20 kV after gold coating surface treatment.

3. Results and discussion

3.1. Flammability

MOPO synthesized in this work was used as both charring agent and acid source, which was mixed with APP and EVA to produce a new intumescent flame-retardant EVA (IFR-EVA). Based upon a number of formulation investigation, we found that a total loading of 30 wt.% flame-retardant additive was suitable. Therefore, in this study, the total loading of flame-retardant additives for all samples is kept as 30 wt.%. For the investigation of the flame retardancy of IFR-EVA, limiting oxygen index (LOI) values and vertical burning ratings (UL-94) of the IFR-EVA with a total loading of MOPO and APP additives of 30 wt.% were tested, and the results are listed in Table 1. From Table 1, it could be found that the LOI values of the EVA/MOPO system without APP and the EVA/APP system without MOPO were 23.8 and 24.7, respectively; both of their UL-94 ratings were only V-2. Consequently, a single additive flame retardant did not improve significantly the flame retardancy

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