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Synthesis of a novel phosphazene derivative and its application in intumescent flame retardant–EVA copolymer composites

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ABSTRACT

A novel phosphazene derivative, hexakis(dodecylamino)cyclotriphosphazene (H-12), was synthesized and characterized by Fourier-transform infrared (FT-IR), ^{1}H and ^{31}P nuclear magnetic resonance spectroscopy, and elemental analysis. H-12 was applied to an intumescent flame retardant-ethylene-vinyl acetate copolymer (EVA) composite as a synergist and compatibilizer. Integrated flame retardancy performance and good mechanical properties could be achieved simultaneously. The results indicated that H-12 can improve the compatibility of the IFRs with the EVA matrix, and enhance the flame retardancy of the composite. By replacing a portion of the IFRs with 10 wt% H-12, the LOI of the sample reached 29.1%, which is much higher than the pure EVA or its IFR composite. Furthermore, the heat release rate, total heat release, smoke production rate, and total smoke production were greatly decreased. In addition, the improved mechanical properties and the rheological measurement results indicate that H-12 can serve as an efficient lubricant and compatibilizer between the additives and EVA, endowing the materials with satisfactory processability.

1. Introduction

Ethylene-vinyl acetate copolymers (EVAs) with different acetate contents are widely used in many fields due to their excellent properties. However, these organic polymers are inherently flammable, and thus, reducing their flammability has become imperative, especially in fields such as the electronics industry in which flame retardant materials are demanded. It has been rinorganic metal hyecognized that the use of the flame retardants such as droxides [1–3] and intumescent flame retardants (IFRs) [4,5] can help to reduce the flammability of EVA materials through physical or chemical effects during combustion. However, the flame retardant efficiency of inorganic flame retardants is low; to obtain a satisfactory effect, a large amount of flame retardant must be introduced into the polymer, and the poor compatibility of inorganic flame retardant with the polymer matrix [2] undermines the flame retardant–polymer interaction. This results in the deteriorated mechanical and processing properties of the material.

A number of approaches have been attempted to solve the foregoing issues, including the use of ultrafine particles to increase the interfacial area between the flame retardant particles and polymer matrix, surface modification to improve the dispersibility and compatibility of the flame retardant particles within the polymer matrix, and synergism with other flame retardants to reduce the quantity of flame retardant added [2,6,7]. In this work, a novel phosphazene derivative, hexakis(dodecylamino)cyclotriphosphazene (H-12), was synthesized and applied to intumescent flame retardant (IFR)-EVA. The effects of different proportions of H-12 on the flame retardant performance and mechanical properties of the treated EVA were studied.

2. Experimental

Preparation of H-12: In the process, hexachlorotriphosphazene (0.0086 mol), triethylamine (0.086 mol), and dioxane (100 mL) were mixed in a 500 mL three-necked reaction vessel equipped with a reflux condenser, dry N_2 inlet, and constant pressure dropping funnel. The mixture was stirred under a flow of N_2 and heated. When the reaction temperature reached 80 °C, dodecylamine (0.0516 mol) was added dropwise over ~2 h. After the completion of the dropwise addition, the mixture was further agitated at the same temperature for 12 h. The reaction mixture was cooled slowly to ambient temperature and then filtered. The product was washed once with dioxane and twice with water, and then dried at 80 °C under vacuum to a constant weight (80% yield,

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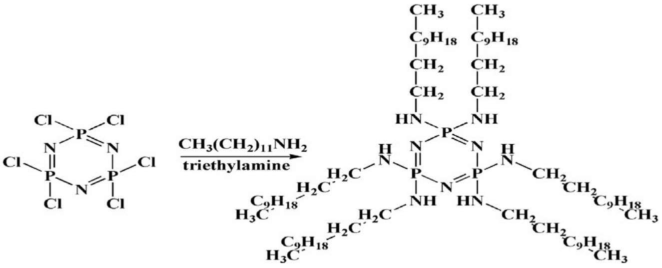

Scheme 1. Structure of H-12.

Mp 95–97 °C). The structure of H-12 is shown in Scheme 1, and it was characterized by FT-IR, ^{1}H and ^{31}P NMR, and elemental analysis.

In the FT-IR spectrum, the absorption peak at 3239 cm^{-1} was attributed to the N–H stretching vibration, and those at 1468, 2956, and 2850 cm^{-1} were assigned to C–H stretching and bending vibrations. The absorptions at 1240, 1180, 1103, and 904 cm^{-1} indicated the presence of a phosphazene ring in the skeleton of H-12. In addition, the peaks at 1378 and 721 cm^{-1} were assigned to the symmetric C–H bending vibrations of the methyl groups and the C–H bending vibrations of the methylene groups [8–9].

In the ^{1}H NMR spectrum, typical peaks were observed at δ 0.89 ($-CH_3$), 1.27 ($-C_9H_{18}-$), 1.50 ($-(C\underline{H}_2CH_2N)-$), and 2.91 ($CH_2N$) [10]. The ^{31}P resonance in the ^{31}PNMR spectrum of H-12 occurs at 14.09 ppm. By elemental analysis, the synthesized H-12 exhibited an actual N:C:H ratio 9.75:66.63:12.38, which is consistent with the theoretical value of 10.16:69.68:12.67. These results demonstrate the successful synthesis of H-12.

Preparation of the EVA composites: as the IFRs in the EVA formulations, ammonium polyphosphate (APP) and tri(1-oxo-2,6,7-trioxa-1-phosphabicyclo [2,2,2]octane-methyl)phosphate (trimer) were used in a 1:1 weight ratio. To study the effect of H-12 on the flame retardancy and mechanical properties of the EVA composites, different amounts of IFRs were replaced with H-12 in the formulations. All the composites were obtained by melt blending using a micro two-screw extruder. The temperature of the micro extruder from the hopper to the die was 95/115/125 °C, and the screw speed was 40 rpm. The formulations of the prepared samples are summarized in Table 1.

3. Methods

A Fire Testing Technology Ltd. cone calorimeter was used to evaluate the fire performance of the composite according to the standard ISO5660 under a heat flux of 35 kW/m^2 with a size of $100 \times 100 \times 3$ mm^3.

Rheological measurements were carried out on an advanced rotational rheometer (TA-AR2000EX Rheometer, TA Instruments) in air atmosphere; the measured samples were 25 mm in diameter, with a gap of 1.00 mm. Shear frequency (ω) sweeping was performed from 0.01 to 100 rad/s and at a constant temperature of 155 °C. The tensile strength (TS) and elongation at break (EAB) were measured on a UTM-4204 universal testing machine according to ISO 527-3. The crosshead speed was 20 mm/min.

4. Results and discussion

Flame retardant performance of H-12: from the data in Table 1, it is clear that the limited oxygen index (LOI) value increases initially with the increasing proportion of H-12, and then declines. The EVA composites treated with 10 wt% H-12 had the highest LOI value (29.1%). However from 10 wt% and above, the EVA composite was unable to pass the UL 94V-0 rating test and the dropping resistance property was obviously decreased. At a suitable content of H-12, the sample 8 which containing 35 wt% IFRs can also pass the UL 94V-0 rating test.

Fig. 1 presents the cone test curves for EVA and its composites. As shown in the heat release rate (HRR) versus time curves for the samples in Fig. 1(a), pure EVA is a readily flammable polymeric material; its peak heat release rate (PHRR) reaches ~828 kW/m^2 and combustion is complete after 500 s. The HRRs for the flame retardant samples – EVA/40 wt%IFRs, EVA/35 wt% IFRs/5 wt% H-12, and EVA/30 wt% IFRs/10 wt% H-12 – were obviously decreased. Most significantly, the second peaks in the heat release rates for the EVA/35 wt% IFRs/5 wt% H-12 and EVA/30 wt% IFRs/10 wt% H-12 samples were 93.28 and 38.77 kW/m^2, respectively, which were reduced by 66.6% and 86.1% compared with that of the EVA/40 wt% IFRs sample. These results demonstrate that H-12 can improve the stability of the char residue. Also consistent with these results, the EVA/35 wt% IFRs/5 wt% H-12 and EVA/30 wt% IFRs/10 wt% H-12 samples had lower total heat releases (THR), smoke production rates (SPR), and total smoke production (TSP) values.

Mechanical and rheological properties: Table 1 also reveals that the TS and EAB values for the EVA decreased considerably with the addition of the IFRs, whereas with the additions of H-12, the TS and EAB values exhibited different degrees of recovery. This could be attributed to the good compatibility of the added H-12 with the APP, trimer, and polymer matrix.

As shown in Fig. 2(a), all the samples exhibited shear thinning characteristics in their complex viscosity (η^*) curves, and the EVA/30 wt% IFRs/10 wt% H-12 had the lowest η*. Also, the storage modulus (G') curves for EVA and its composites exhibit trends that change similarly to η^* (Fig. 2(b)). The change in rheological behavior is possibly attributed to the lubricating effect of H-12,

Table 1
Properties of the EVA samples.

Sample	Composition (wt%)				LOI (%)	UL-94	EAB[a] (%)	TS [b](Mpa)
	EVA	APP	Trimer	H-12				
1	100	0	0	0	19.2 ± 0.2	NO	1413 ± 17	21.43 ± 0.41
2	60	20	20	0	26.5 ± 0.2	V-0	612 ± 11	5.34 ± 0.22
3	60	19.5	19.5	1.0	27.2 ± 0.1	V-0	770 ± 7	6.35 ± 0.27
4	60	19	19	2.0	28.3 ± 0.2	V-0	844 ± 10	6.74 ± 0.25
5	60	17.5	17.5	5.0	28.4 ± 0.1	V-0	846 ± 8	5.93 ± 0.19
6	60	15	15	10.0	29.1 ± 0.1	V-1	904 ± 9	6.04 ± 0.18
7	60	12.5	12.5	15.0	28.1 ± 0.2	V-2	948 ± 13	5.94 ± 0.23
8	65	16.63	16.63	1.75	27.1 ± 0.2	V-0	946 ± 10	7.97 ± 0.20

[a] EAB: elongation at break.
[b] TS: tensile strength.