

Organo-phosphorus flame retardants when applied to acrylonitrile-butadiene-styrene copolymer

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ABSTRACT

In order to find an effective halogen-free flame retardant for acrylonitrile-butadiene-styrene copolymer (ABS), organo-phosphorus compounds were studied and their flame retarding performances were determined by UL 94 vertical test. It is found that the flame retardancy strongly

Keywords: flame retardancy, organo-phosphorus flame retardant, DOPO, phosphorus content

depends on phosphorus (P) content of organo-phosphorus compounds. Only the mixture of ABS with 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl) methyl diethyl phosphinate (ODOPM-DE), which has the highest P content, i.e., 17.68 % gives V-0 rating for the 70/30 composition.

INTRODUCTION

Polymers are a large and growing fraction of the fire load in homes, commercial environment, and transportation. However, the flammability of organic polymers limits their applications and fire hazard may be greatly increased when these materials are used unsuitably [1-3]. Halogen-based flame retardants, especially aromatic bromine compounds, are the most widely used in polymeric materials. However, so that the generation of toxic, corrosive, and halogenated gases in processing and the release of polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs) in combustion might be avoided, there is a trend toward using non-halogen flame retardants in polymeric materials [4-5]. For example, EU forbids the use of polybrominated biphenyls (PBBs), polybrominated diphenylethers (PBDEs) in electric and electronic materials. Among the flame retardants containing nitrogen, silicone, phosphorus elements, organo-phosphorus compounds, generating less toxic gases and smoke, are the materials of choice [6-7]. Triphenyl

phosphate (TPP, Fig. 1(A): structure of TPP) and its analogues are widely known to be the most effective flame retardants for many polymers. But, because the evaporation temperatures of TPP and its analogues are lower than the processing temperature of various polymers, they are not suitable to avoid a considerable amount of TPP to evaporate during processing. On the other hand, aromatic bisphosphates are more thermally stable than monophosphates, tetra-2,6-dimethyl phenyl resorcinol diphosphate (DMP-RDP, Fig. 1(B): structure of DMP-RDP), is one of the phosphorus flame retardant exhibiting higher evaporation temperature compared to TPP. But, when DMP-RDP was employed to examine the flame retardancy, it didn't exhibit the UL94 V-0 rating in styrenic polymers by itself [8].

Flame retardant can be chemically bonded to the macromolecular chain (reactive type) or dispersed mechanically in the polymer matrix (additive type). So far, there have been several approaches to the use of 9,10-dihydro-9-oxa-10-

phosphaphenanthrene-10-oxide (DOPO, Fig. 1(C): structure of DOPO) by being incorporated into the backbone of the epoxy resin or the amine hardeners [9-10]. However, the phosphorus content of DOPO is low so that it also didn't exhibit the UL94 V-0 rating in styrenic polymers by itself. In this work, cyclic phosphorus compound of DOPO was used to synthesized 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl) methanol (ODOPM) via a simple addition reaction. The obtained compound with reactive methanol group was then used to continue the reaction to obtain flame retardant with high phosphorus content.

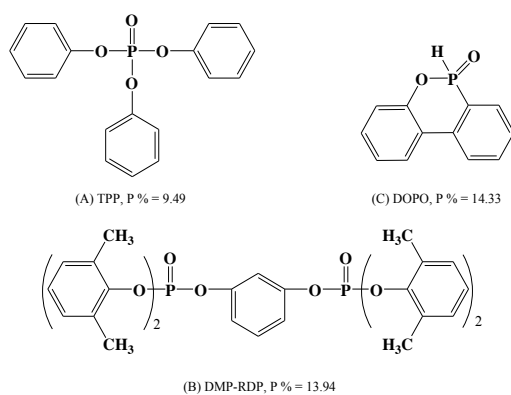


Fig. 1. Chemical structures and P contents of the studied organo-phosphorus compound: (A) TPP, (B) DMP-RDP, and (C) DOPO

MATERIALS AND METHODS

Raw Materials

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from Tokyo Kasei Kogyo Co. of Japan. 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl) methanol (ODOPM) was prepared by reacting DOPO with paraformaldehyde [8]. Paraformaldehyde was received from Aldrich and used without further purification. Xylene, dioxane, ethyl ether, triethylamine (TEA), thionyl chloride, and pyridine of reagent grades were received from Samchun Chemical Company of Korea and used

as received. Diethylphosphinic chloride was prepared in our laboratory by adopting the synthesis method found in the literature [11].

Synthesis of diethylphosphinic chloride

Diethylphosphinic acid (122.1 g, 1 mol) obtained from Cheil Industries was placed in a roundbottom flask equipped with a temperature controller and a reflux condenser. Thionyl chloride (237.94 g, 2 mol) was added dropwise. The mixture was heated to 75 °C and refluxed at that temperature for 3 h. The reaction product was concentrated on a rotary evaporator, and diethylphosphinic chloride was obtained with a yield of 94% (³¹P-NMR (CDCl₃): a singlet peak at $\delta = 76.6$ ppm).

Characterization

FT-IR spectra were recorded with an infrared spectrophotometer (Nicolet 380). ¹H- and ³¹P-NMR spectra were taken on a Varian Unity Inova 500NB spectrometer. The chemical shift of ³¹P-NMR spectrum is relative to the external standard of 85% H₃PO₄.

Differential scanning calorimeter (DSC) was carried out on a TA 2910 DSC instrument at a heating rate of 10 °C/min under a flow of N₂ gas.

The UL 94V test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bar of 127 mm in length, 12.7 mm in width, and about 12.7 mm in thickness. During the test, the specimen was subjected to two 10-s ignitions with butane gas flame. Cotton ignition would be considered if material dripping occurred during the test. After the first ignition, the flame was removed and the time for the sample to self-extinguish (t_1) was recorded. A second ignition was applied on the same sample; the self-extinguishing time (t_2) and dripping characteristic were recorded. If the sum t_1 and t_2 was less than 10 s with no dripping, the sample would be classified a V-0 ranking.

RESULTS AND DISCUSSION

Synthesis of 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl) methyl diethyl phosphinate (ODOPM-DE)

ODOPM (123.1 g, 0.5 mol), TEA (50.6 g, 0.5 mol), and dioxane (200 ml) were introduced into a 1 liter round bottom flask equipped with a nitrogen inlet, an overhead stirrer, a temperature controller, and a reflux condenser. The mixture was kept at 0 °C and diethylphosphinic chloride (70.3 g, 0.5 mol) was added dropwise over 1 h. After the completion of diethylphosphinic chloride addition, the reaction mixture was heated to 90°C and refluxed at that temperature for 5 h. The reaction mixture was cooled down to room temperature. Triethylaminehydrochloride salt was filtered off and the filtrate was evaporated under reduced pressure to give the crude product. The yellowish solid of ODOPM-DE was obtained by washing the crude product with ethyl ether thoroughly. The yield of ODOPM-DE (m.p. 110-111°C (Fig. 2)) was 90 %. The IR spectrum (KBr) exhibited absorptions at 1200–1240 and 1280 cm⁻¹ (P=O vibration), 1060 cm⁻¹ (P-O-C (aliphatic) stretching), 933 cm⁻¹ (P-O-Ph, stretching), 2880-2970 cm⁻¹ (C-H sat.), 3070 cm⁻¹ (C-H unsat.) (Fig. 3). The shift and splitting patterns of ¹H-NMR (CDCl₃) spectrum was at δ = 0.78-0.97 (m, 6H, P-CH₂-CH₃), 1.39-1.58 (m, 4H, P-CH₂-CH₃), 4.46-4.61 (m, 2H, P-O-CH₂), 7.25-8.04 (m, 8H, Ar-H). (Fig. 4). ³¹P-NMR (CDCl₃): two singlet peaks were observed at δ = 65.99 (P(O)-CH₂-CH₃) and 30.64 (-CH₂-P(O)-O-, cyclic). (Fig. 4).

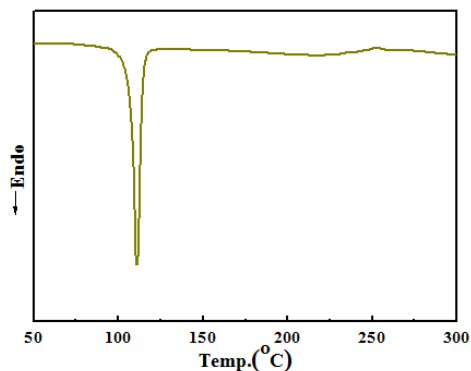


Fig. 2. DSC thermogram of ODOPM-DE

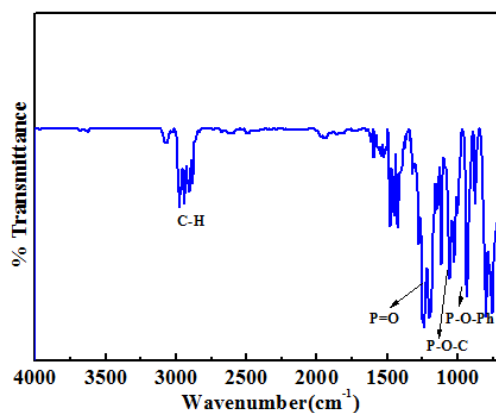


Fig.3. IR spectrum of ODOPM-DE

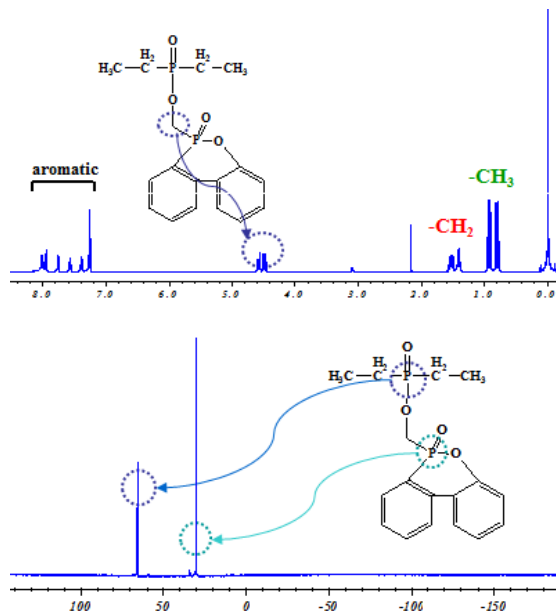


Fig.4. ¹H- and ³¹P-NMR spectra of ODOPM-DE
 UL 94V test

The UL 94V test determines the upward-burning characteristics of a solid and is considered as one of the industrial standards for determining the flame retardancy. To evaluate the efficiency of the flame retardant, 30 wt % of flame retardant

was mixed with ABS using a HAAKE Plastic-Corder mixer and undergone UL 94V test, whose results are given in Table 1. It was found that the mixture with ODOPM-DE gave V-0 rating while other mixtures burned completely. This result clearly indicated that the flame retardancy

strongly depended on phosphorus content. In other words, more effective retardancy could be achieved by employing the organo-phosphorus with higher P content, which clearly supports that our approach to synthesize this material could be justified.

Table 1. UL 94V Test Results for Various 70/30 ABS/Organo-phosphorus Mixtures.

Flame retardant	P (%) inflame retardant	P (%) in 70/30 mixture	UL 94V rating
TPP	9.49	2.85	Burning
DMP-RDP	13.94	4.18	Burning
DOPO	14.33	4.30	Burning
ODOPM-DE	17.68	5.30	V-0

CONCLUSION

Organo-phosphorus compounds derived from DOPO were synthesized successfully and their structure was confirmed by FT-IR, ^1H -, and ^{31}P -NMR spectra. Among three flame retardants used in this study, ODOPM-DE had the highest P content, i.e., 17.68 %, which was quite higher than that of DOPO. The flame retardancy of ODOPM-DE, TPP, and DMP-RDP were examined by UL 94V test for the mixture with ABS. It was found

that ODOPM-DE/ABS gave the V-0 rating for the 70/30 mixture while the mixtures with other flame retardants burned completely in the same composition. This clearly indicated that flame retardancy strongly depended on the phosphorus content.

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Hợp chất chống cháy phosphorus-hữu cơ ứng dụng trên nền vật liệu acrylonitrile-butadiene-styrene

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TÓM TẮT

Nhằm mục đích tìm ra hợp chất chống cháy phi halogen hiệu quả để ứng dụng trên nền vật liệu acrylonitrile-butadiene-styrene (ABS), các hợp chất chống cháy phosphorus-hữu cơ đã được nghiên cứu và khả năng chống cháy của chúng

được đánh giá bằng phương pháp UL94V. Kết quả cho thấy tính chất chống cháy của các hợp chất chống cháy phosphorus-hữu cơ phụ thuộc chủ yếu vào hàm lượng phosphorus. Và duy nhất hỗn hợp 70/30 ABS/(6-oxido-6H-

dibenz<c,e><1,2>oxaphosphorin-6-yl) hàm lượng phosphorus của ODOPM-DE cao nhất
methyl diethyl phosphinate (ODOPM-DE) với (17,68 %) đã đạt chuẩn tối ưu UL94V-0.

Từ khóa: phụ gia chống cháy, phụ gia chống cháy Photpho, DOPO

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