

Study of thermal properties of intumescent additive

Pentaerythritol phosphate alcohol

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Abstract Bicyclic compounds containing phosphorus on their skeleton such as 2,4,6-trioxa-1-phosphabicyclo[2,2,2]octane-4-methanol phosphate (PEPA) having three active ingredients required for intumescence have been synthesized. The structural characterization of PEPA was carried out by FT-IR, ^1H and ^{13}C NMR. The thermal behaviour of the material was studied using TGA, TGA-MS and pyrolysis GC-MS. Thermogravimetric analysis reveals that PEPA undergoes several stages of degradation with a char of about 12% at 800 °C. The TGA-MS studies indicate that the material degrades with the liberation of water, formaldehyde, alkene and alcohols as the major degradation products. Pyrolysis GC-MS results reveal that PEPA isomerizes in the acidic medium. PEPA and/or isomers of PEPA react with formaldehyde, one of the degradation products, to form cross-linked structure and cyclic products with the elimination of water molecule. The thermal degradation mechanisms for PEPA are presented and discussed.

Keywords Intumescence · Thermal degradation · Thermogravimetry-mass spectrometry · Pyrolysis GC-MS · Degradation mechanism

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Introduction

Today's modern life increases the fire hazards, because of the development of electrical and electronic items and consumption of comfort items, etc. These are generally made up of petroleum products and having high energy content; therefore, they catch fire easily and release large amount of heat. The released heat helps the fire propagation. This formed fire having secondary effect induces release of highly toxic corrosive gases and smoke. This secondary effect causes the unpredictable damages to materials and/or fire deaths.

Combustion process is a complex phenomenon which comprises exothermic and endothermic reactions. Combustible materials cannot be made 100% non combustible. Combustibility of the material can be retarded by using flame retardants [1–3]. The causes of fire influence many researchers to develop fire-retardant materials. Fire retardants are chemicals which are added to combustible materials to make the material more resistant to fire by modifying pyrolysis reactions or oxidation reactions. Flame retardants interfere in the combustion of materials physically or chemically during heating, decomposition, ignition or flame spread [1, 4]. An ideal flame retardant should fulfil the appropriate mandatory fire requirements and rules, be easy to incorporate in the material involved, be compatible with the material involved, not alter the mechanical properties of the material, be colourless, have good light stability, be resistant towards ageing and hydrolysis, match and begin its thermal behaviour before the thermal decomposition of the material, should not cause corrosion, should not emit or at least emit low level of toxic gases, must not have harmful physiological and environmental effects, be commercially available and cost efficient. In flame-retardant-treated materials, the ignition

parameter depends on the mechanism of flame-retardant materials and its performance in combustion process [5, 6].

Nowadays, environmental-friendly phosphorus-based flame retardants are a major focus. They generate less smoke, toxic and corrosive gases, and low loading is enough to show the flame retardancy [7]. Elemental red phosphorus, phosphine oxides, phosphonates, phosphinates and phosphonic acid derivatives are some examples of phosphorus-based flame retardants. Phosphorus containing flame retardant reduces the heat of combustion by about 70 kcal mol^{-1} , and its flame retardant mechanism depends on the nature of combustible materials [1, 8, 9]. In the combustion process, phosphorus-based flame retardants act both in the gaseous and condensed phases. In gas phase, it generates free radical scavengers such as P_2 , PO , PO_2 during the combustion and reduces the exothermic reaction thus suppressing the combustion of materials. In condensed phase, it modifies the chemical reactions in combustion processes and forms carbon char rather than producing pollution gases CO and CO_2 . The formed char covers the surface of the materials thus preventing the underlying materials [7, 8, 10, 11].

Phosphorus compounds in combination with carbonifics (pentaerythritol, mannitol and sorbitol) and spumifics (urea, dicyandiamide, melamine, polyamides, etc.) show intumescent behaviour. Intumescence is a phenomenon in which substrate swells and forms multicellular charred layer as a result of heating, there by increasing its volume and decreasing its density. The intumescent char restricts the mass transfer from combustible material to fire and entrance of the atmospheric oxygen to substrate. Intumescent process should occur just before the decomposition temperature of the combustible materials [12]. The main aim behind the development of the intumescent materials is thermal protection. Different types of intumescent coating materials have been produced from time to time, to increase the escaping time during fire [13]. The mechanism of intumescent process may be the phosphate ester formation [14]. When the three active ingredients are added separately to combustible materials, water solubility and migrations are the main problems associated with this technique. Those problems are overcome by synthesizing single compound which provides all the functions necessary for intumescence [15, 16].

Halpern et al. [17] synthesized the intumescent flame retardant, 2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane-4-methanol phosphate and studied its fire retardancy behaviour with thermoplastics, mainly polypropylene. PEPA is a good environmental-friendly flame retardant suitable for many purposes. Camino et al. [14] reviewed the formation of swollen char on heating the intumescent materials. Earlier development of intumescent coatings and the recent development of intumescent additives for polymers are

also discussed by taking the example of melamine salt of bis(2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane-4-methanol) phosphate. Chemical reactions responsible for the intumescence process are described in detail by taking ammonium polyphosphate-pentaerythritol (APP-PER) system. Allen et al. [18] discussed the salient molecular features for intumescent behaviour by synthesizing different derivatives of pentaerythritol phosphate alcohol using acid anhydrides, methacryloyl chloride and with excess diketene.

Li et al. [19] studied the combustion and thermal degradation behaviour of PEPA incorporated diglycidyl ether of bisphenol-A epoxy resin. The incorporation of PEPA not only enhances the flame retardancy and thermal stability of the epoxy resin but also acts as smoke inhibitor. Balabinovich [16] studied the volatile and solid decomposition product of PEPA and its blend with melamine phosphate (PEPAMP) which is less stable to oxidative degradations. Gao et al. [20] synthesised the novel phosphorus-nitrogen intumescent flame retardant by reacting bis(2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane-4-methanol) chlorophosphate and diaminodiphenyl methane. An UL-94 test, thermogravimetry and in situ FT-IR studies reveal that the presence of P-N intumescent flame retardant along with poly urethane in poly (butylene terephthalate) increases flame retardancy and thermal stability.

The effect of metal chelate on a novel oligomeric intumescent flame retardant, poly(4,4'-diaminodiphenylmethane-*o*-bicyclicpentaerythritolphosphate-phosphate) (PDB PP) on flammability of polypropylene was studied by the Song et al. [21]. It was concluded that the metal chelate forms cross-linked network with polyphosphoric acid and enhance the flame retardancy of PP/PDBPP as evidenced by Raman spectroscopy, IR spectroscopy, SEM, LOI analysis and cone calorimetry. Gaële et al. [15] studied the flame retardancy and thermal stability of melamine salt of both 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide and bis(1-oxa-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-4yl-methanol) phosphate (PP/NI-FR) with and without zinc borates using LOI, UL-94 V-O, cone calorimetry and TG analyses. Phosphorus containing flame retardant such as 4-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yloxymethyl)-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]-octane-1-oxide (MOPO) was synthesised by Wang et al. [22]. They prepared intumescent flame retarded EVA system with different ratios of APP and MOPO. The addition of intumescent flame retardant additive significantly decreases the total heat release rate and increases the char yield.

The study of the degradation pattern of the intumescent materials is an important factor since its applicability can be assessed only on these grounds. In the present investigation, PEPA was synthesized and its structure was

confirmed using FT-IR, ^1H and ^{13}C NMR spectral data. Its thermal properties were studied using TGA. The main interest was to study the degradation products obtained during pyrolysis and it was followed using TGA-MS, pyrolysis GC-MS and the results are discussed.

Experimental

Materials

Dioxane and hexane purchased from SD Fine Chemicals Ltd, Mumbai, India, pentaerythritol got from Alfa Aesar, Johnson Matthey GmbH, Karlsruhe, Germany and phosphorus oxychloride obtained from Loba Chemie Pvt. Ltd. Cochin, India were used as such without any further purification.

Synthesis of 2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-4-methanol phosphate (PEPA)

A 1000-mL three-necked round-bottom flask was equipped with a mechanical stirrer, reflux condenser, thermometer, addition funnel, dry nitrogen inlet and aqueous sodium hydroxide trap. The flask was charged with 525 mL of dioxane and 105 g (0.77 M) pentaerythritol. About 50% (70 mL) of the total POCl_3 (1.54 M) was added at 95 °C, the remaining at reflux condition over a period of 7 h. After the complete evolution of HCl the reaction mixture was cooled slowly to room temperature and filtered. The white solid was washed once with dioxane and twice with hexane. The product was dried at 70 °C under vacuum to a constant mass. Approximately 80% (110 g) yield was obtained [17].

Methods

Structural studies

The FT-IR spectrum of the material was run on Fourier transform infrared-8400S spectrophotometer, Shimadzu, Japan using KBr disc. The ^1H and ^{13}C NMR spectral analyses were performed using DMSO- d_6 and CDCl_3 as solvent, respectively, on Bruker 300 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal standard.

Thermal studies

Thermogravimetric analysis was performed from 100 to 800 °C at a heating rate of 10 °C min^{-1} in nitrogen atmosphere in a TGA-50 thermogravimetric analyzer,

Shimadzu, Japan. TA-60 WS software was used for analysis of thermogram. Approximately 10 mg of the sample was used. TG-MS study was carried out in a Netzsch TGA coupled to a Pfeiffer quadrupole mass spectrometer. The pyrolysis was performed in an SGE Pyrojector attached to the injector of the GC-MS. Approximately, 0.5 mg of the sample was taken for the pyrolysis. The pyrolysis was done at 500 °C for 5.0 min. The separation of the components of the volatile fraction resulting from the thermal decomposition of the materials was done in a Thermo Scientific, Trace GC ultra gas chromatograph containing a Thermo TR-5 MS SQC general purpose 15 m capillary column coated with cross-linked silicone gum. The separated components were identified by a Thermo Scientific, DSQII MS, quadrupole mass spectrometer which was coupled to the gas chromatograph. The data analysis was performed using a work station. The following GC-MS settings were employed for the separation and identification of the pyrolysis products: injector temperature, 250 °C; equilibration time, 0.5 min; carrier gas, helium; total column flow, 5.0 mL min^{-1} ; septum purge, 0.9 mL min^{-1} ; initial temperature, 50 °C; heating rate, 10 °C min^{-1} ; initial time, 5.0 min; detector temperature, 270 °C; splitless on time, 0.0 min; injection volume, 1 μL ; mass scanned, 20 to 300 amu; open-split purge, 0.8 mL min^{-1} ; final temperature, 250 °C; solvent delay, 1.00 min and final time, 5.0 min.

Results and discussion

Spectral characterization

The structure of the synthesized PEPA was confirmed with specific absorption at 1292 (*vs*, P=O), 1024 (*vs*, P-O-C), 1168 (*vs*, $\text{C}(\text{CH}_2)_4$), 959 (*vs*, $\text{CH}_2\text{-OH}$), 862, 764, 661, 625 (*vs*, typical of cyclic structure), 2955 (*vs*, asymmetric -CH_2 stretching) and 2906 (*vs*, symmetric -CH_2 stretching) in the FT-IR spectrum, which is consistent with previous report [19].

^1H NMR (300 MHz, d_6 -DMSO) (ppm): 2.5 (S, -OH), 3.3 (S, $\text{C-CH}_2\text{-OH}$), 4.5–4.7 and 4.1–4.4 (d, $\text{C-CH}_2\text{-O-P}$) and ^{13}C NMR (300 MHz, CDCl_3) (ppm): 39–41 (m, $\text{C}(\text{CH}_2\text{OH})_4$), 58 (S, $\text{-CH}_2\text{-OH}$), 77 (d, $\text{-CH}_2\text{-O-P}$) peaks ascertain the placement of hydrogen and carbon, respectively, and confirms the structure of PEPA.

Thermogravimetric analysis

The recorded TG and DTG traces of PEPA in nitrogen atmosphere at a heating rate of 10 °C min^{-1} are presented in Fig. 1. Thermogram shows that PEPA starts to degrade above 250 °C and has a residual mass of about 12% at 800 °C. In between 250 and 350 °C, two overlapping

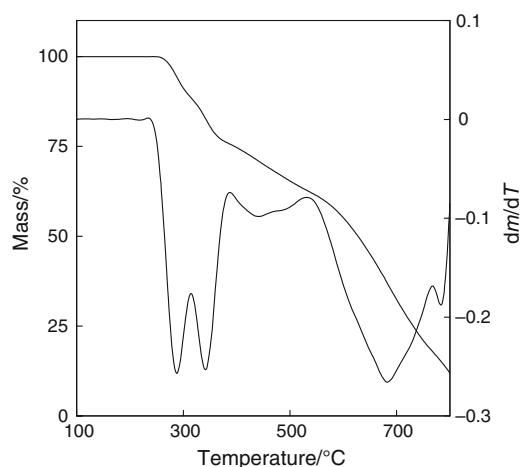


Fig. 1 TG and DTG traces of pentaerythritol phosphate alcohol at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

degradations were observed. About 20% mass loss was associated with these two degradations, and the maximum for these degradations are noted at 280 and 340 °C, respectively. After 375 °C, the degradation of the material is slow and a multistep degradation was registered, which proceeds till 530 °C. The mass loss noted during this temperature range is about 10%. After this degradation, the rate of degradation of PEPA was found to be faster. Here also (550–780 °C), a multistep degradation behaviour is noted and the mass loss observed in this region was about 50%. The degradations occurring in the temperature range 250–350 °C may be associated with the eruptive release of volatile products from the degrading PEPA.

TG–MS study

The profile of evolution of different low molecular mass gaseous products from degrading PEPA was made by thermogravimeter coupled to a mass spectrometer. During thermogravimetric analysis of PEPA, single ion monitoring was made and the ions monitored are $m/z = 18, 28, 30, 46, 110$ and 142 . The evolution profiles of monitored ions are shown in Fig. 2. It is interesting that water ($m/z = 18$) is released from PEPA in two steps, and the maximum release is at 250 and 300 °C (Fig. 2a). These two sharp peaks may be responsible for the ether formation (Scheme 1) and the transesterification reaction [16] leading to the formation of phosphate ester linkages. Small amount of water is before 100 °C, and this may be attributed to the release of absorbed water or surface moisture. The evolution of CO/ C_2H_4 is investigated by monitoring the ion, $m/z = 28$. Its evolution profile, depicted in Fig. 2b, shows bimodal release of these compounds and the maxima are at 270 and 320 °C. Above 500 °C, the elimination of CO/ C_2H_4 increases gradually up to 800 °C.

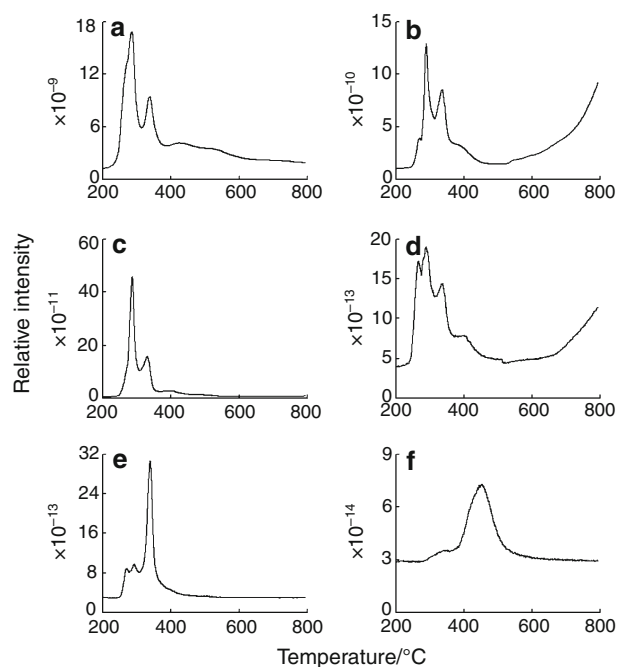
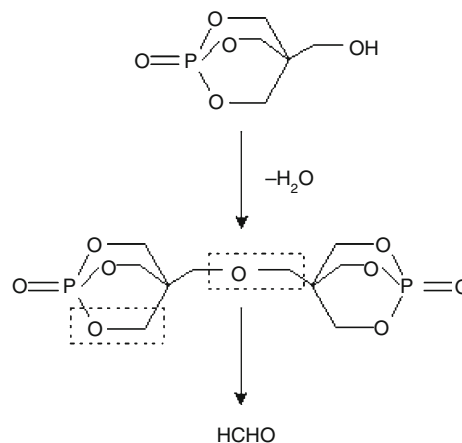


Fig. 2 TG–MS study of PEPA: evolution profile of various gaseous products monitored by SIM technique



Scheme 1 Mechanism of elimination of water and formaldehyde from PEPA

The evolution profile of formaldehyde from degrading PEPA is followed by monitoring the ion $m/z = 30$ (Fig. 2c). The release of formaldehyde starts around 250 °C, and the maximum release is noted at around 280 °C. Up to 400 °C, the evolution of formaldehyde gradually decreases, and after 500 °C, the release of formaldehyde is not detectable. The plausible mechanism of formation formaldehyde from PEPA is presented in Scheme 1. The formed formaldehyde is highly reactive and is homogeneously fixed in the condensed phase, and hence escape to the gaseous phase is not profound. This reactive

compound readily attacks different nucleophiles generated in the course of the intumescent process and can lead to various cross-linking reactions [23, 24]. The occurrence of fragment with $m/z = 46$ is due to the evolution of formic acid/ethanol. Thermal oxidation of formaldehyde leads to the production of formic acid, which may, on further heating, release carbon monoxide and carbon dioxide and can act as blowing agent during the intumescent process. The mechanism of formation of ethanol from degrading PEPA is presented in Scheme 2. The evolution of formic acid/ethanol occurs in multi-stages in the temperature region 200–350 °C (Fig. 2d). The formation of all the low molecular mass gaseous products is occurring within a short temperature region and thus permitting the production of foamed char. Evolution profile of $C_2H_7O_3P$ and $C_4H_9O_4P$ is followed by monitoring the ions $m/z = 110$ and 142, respectively (Fig. 2e, f). The evolution maximum $m/z = 110$ is noted at around 320 °C whereas the $m/z = 142$ shows the maximum at 440 °C. Further it is obvious from the intensities that the release of phosphorus compounds from the degrading PEPA is very less.

The acidic environment created during the degradation of PEPA favours etherification and transesterification reactions. The isomerization of PEPA is also a favourable route during the thermal degradation of PEPA, which triggers the formation of ethanol, substituted phosphoric acid. Most of the low molecular mass gaseous products (H_2O , CO/C_2H_4 and $HCHO$) are released from the degrading PEPA matrix nearly in the same temperature region. Volatile phosphorus compounds are released in minor amounts indicating the retention of phosphorus in the char.

Pyrolysis GC–MS study

Pyrolysis GC–MS study for PEPA is carried out in helium atmosphere. The material was pyrolyzed at 500 °C for 5 min and the formed degradation products were injected in GC and the product identification was done using a mass spectrometer. The recorded total ion chromatogram is presented in Fig. 3 and the identified compounds are listed in Table 1. Gaseous products like CO and CO_2 are

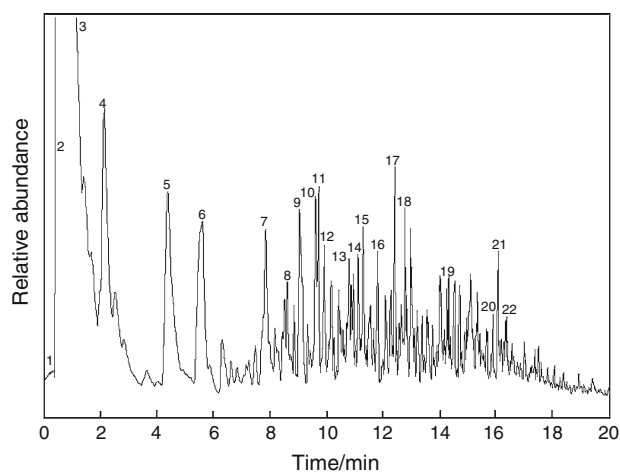


Fig. 3 Total ion chromatogram of volatile degradation products obtained by pyrolyzing PEPA (500 °C, 5 min)

registered in the TIC. From the evidences collected from the TGA–MS studies of PEPA, one can safely assume that the thermal degradation of PEPA is a complex process and involves several types of reactions viz. dehydration, decarboxylation, deformylation, etc. Occurrence of several complex, parallel and consecutive reactions in PEPA makes the degrading system to produce highly reactive and sterically hindered methylenecyclopropene, which is amenable to isomerisation, Diels–Alder reaction and polymerization. Formation of such highly reactive compound is essential for the production of several condensed aromatics from the degrading PEPA (Scheme 3).

Under pyrolysis condition the compound methylenecyclopropene isomerizes to yield cyclobutadiene, $CH \equiv C-CH=CH_2$, $CH_2=C=C=CH_2$, etc. The polymerization of these isomeric products may be the possible reason for the formation of several substituted aromatics (alkyl-substituted benzenes) and condensed aromatics (benzofuran, substituted indane and several alkyl-substituted naphthalenes) (Table 1).

In the Pyrolysis GC–MS studies of PEPA, phosphorus containing volatiles are not registered amongst the volatile degradation products (Table 1). But in the case of TG–MS studies, minor amounts of volatile phosphorous compounds are detected ($m/z = 110$ and 142) (Fig. 2e, f). From this, it

Scheme 2 Thermal degradation of PEPA: the formation of alkene and alcohol

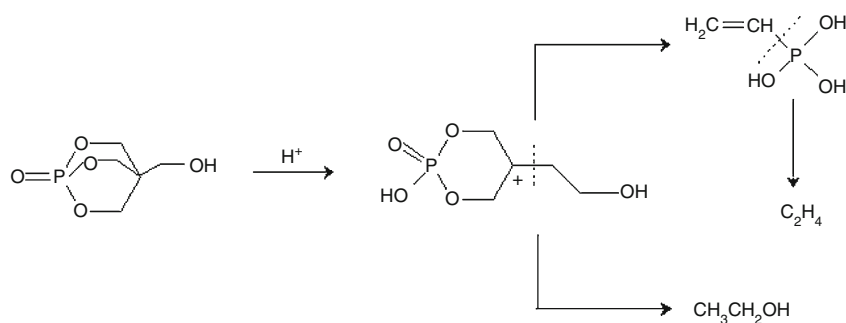
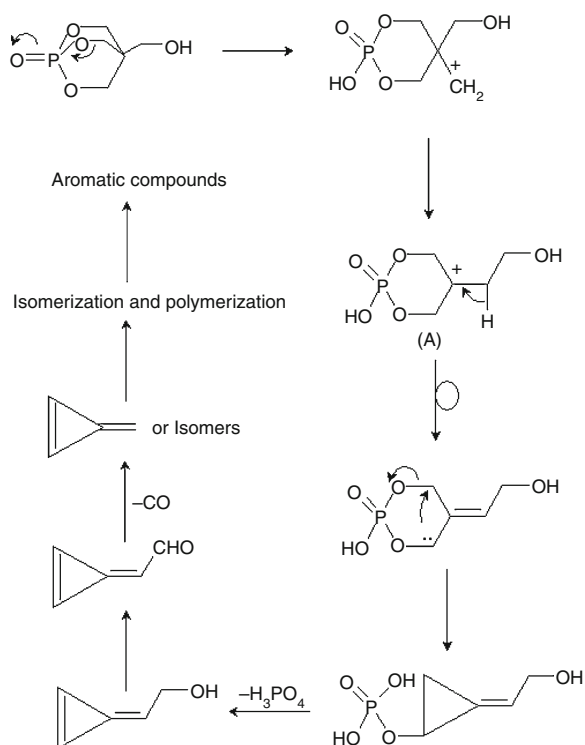
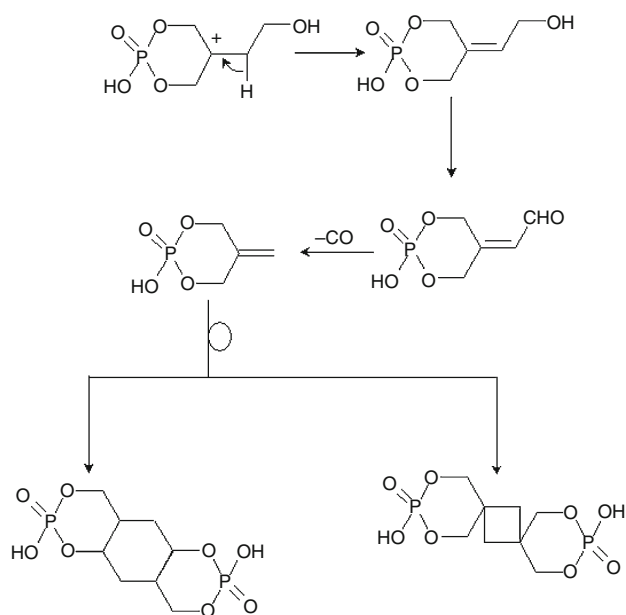


Table 1 Possible structure for the various m/z value ions in pyrolysis GC–MS study

S.No.	Retention time/min	Molecular mass	Molecular formula	Name of the product
1	Smaller molecular mass compounds CO and CO ₂			
2	0.71	70	C ₄ H ₆ O	Methacrolein
3	0.94	84	C ₅ H ₈ O	2-Butenal-2-methyl
4	2.15	106	C ₈ H ₁₀	Xylene
5	4.38	120	C ₉ H ₁₂	Ethylmethylbenzene
6	5.57	120	C ₉ H ₁₂	Isomer of #5
7	7.84	134	C ₁₀ H ₁₄	1,4-Dimethylethylbenzene
8	8.51	134	C ₁₀ H ₁₄	Isomer of #7
9	9.03	130	C ₁₀ H ₁₀	1,2-Dihydronaphthalene
10	9.60	134	C ₉ H ₁₀ O	4-Ethylbenzaldehyde
11	9.71	134	C ₉ H ₁₀ O	Isomer of #10
12	9.90	146	C ₁₀ H ₁₀ O	Ethylbenzofuran
13	10.82	144	C ₁₁ H ₁₂	2,3-Dimethylindene
14	11.12	148	C ₁₁ H ₁₆	Pentamethyl benzene
15	11.30	142	C ₁₁ H ₁₀	Benzocycloheptatriene
16	11.82	160	C ₁₂ H ₁₆	Unknown
17	12.42	158	C ₁₂ H ₁₄	1,2,3-Trimethylindene
18	12.79	156	C ₁₂ H ₁₂	1,7-Dimethylnaphthalene
19	14.32	170	C ₁₃ H ₁₄	1,4,5-Trimethylnaphthalene
20	15.88	184	C ₁₄ H ₁₆	1,2,3,4-Tetramethylnaphthalene
21	16.06	184	C ₁₄ H ₁₆	Isomer of #20
22	16.38	184	C ₁₄ H ₁₆	Isomer of #20

**Scheme 3** Mechanistic route to the formation of methylenecyclopropene from PEPA during thermal degradation**Scheme 4** Formation of phospho-carbonaceous structure during the intumescent process

is possible to say that during the thermal degradation of PEPA, most of the phosphorous is retained in the solid phase as phospho-carbonaceous char (Scheme 4).

Phosphoric acid derivatives produced from the degrading PEPA undergo condensation by the elimination of water molecules, and the polyphosphoric acid produced catalyses the carbonization of the material.

Conclusions

The bicyclic phosphorous containing intumescent compound 2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-4-methanol phosphate (PEPA) was synthesized and characterized. From the TG and DTG curves of the compound PEPA, it is clear that the material shows intumescent behaviour at around 250 °C and multistage degradation behaviour. The TG–MS study of PEPA reveals that the release of low molecular mass compounds (H₂O, CO/C₂H₄ and HCHO) in a short temperature region is responsible for production of intumescent foamed char. Hence the release of these low molecular mass compounds within a narrow temperature region testifies the complexity of thermal degradation of PEPA and the formation of these products can be explained due to dehydration, decarboxylation and deformylation reactions. The identification of aromatics and condensed aromatics amongst the pyrolysis products of PEPA indicates the formation of highly reactive sterically strained molecule methylenecyclopropene from PEPA. This molecule undergoes isomerisation and polymerization in the degrading PEPA matrix. Further the absence of organo phosphorous volatiles in the degradation products of PEPA hints that majority of the phosphorus is retained in the char that is formed as a phospho-carbonaceous char. This study indicated that PEPA is an efficient intumescent material.

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References

- Mostashari SM, Mostashari SZ. Combustion pathway of cotton fabrics treated by ammonium sulfate as a flame retardant studied by TG. *J Therm Anal Calorim.* 2008;91:437–47.
- Troitzsch JH. Methods for the fire protection of plastics and coatings by flame retardant and intumescent system. *Prog Org Coat.* 1983;11:41–69.
- Hernangil A, Rodriguez M, Leon LM, Ballesterio J, Alonso JR. Experimental design of fire-retarded formulation. Low viscosity polyester resins. *J Fire Sci.* 1999;17:281–306.
- Atikler U, Demir H, Tokatli F, Tihminlioğlu F, Balköse D, Ülkü S. Optimisation of the effect of colemanite as a new synergistic agent in an intumescent system. *Polym Degrad Stab.* 2006;91: 1563–70.
- Košík M, Reiser V, Blažej A. Thermoanalytical studies of combustion of cellulose and activity of fire retardants. *J Therm Anal Calorim.* 1982;23:51–64.
- Morrey EL. Flame retardant composite materials. *J Therm Anal Calorim.* 2003;72:943–54.
- Huang Z-G, Shi W-F. Effect of poly(bisphenol A acryloxyethyl phosphate) on the activation energy in thermal degradation of urethane acrylate. *J Therm Anal Calorim.* 2007;88:833–41.
- Green J. Mechanism for flame retardancy and smoke suppression—a review. *J Fire Sci.* 1996;14:426–42.
- Dombrowski R. Flame retardants for textile coatings. *J Coat Fabrics.* 1996;25:224–38.
- Chen X, Hu Y, Jiao C, Song L. Thermal and UV-curing behaviour of phosphate diacrylate used for flame retardants coatings. *Prog Org Coat.* 2007;59:318–23.
- Perret B, Pawlowski KH, Scharrel B. Fire retardancy mechanism of arylphosphates in polycarbonate (PC) and PC/acrylonitrile-butadiene-styrene. *J Therm Anal Calorim.* 2009;97:949–58.
- Anderson CE Jr, Ketchum DM, Mountain WP. Thermal conductivity of intumescent char. *J Fire Sci.* 1988;6:390–41.
- Green J. A review of phosphorus-containing flame retardants. *J Fire Sci.* 1996;14:353–66.
- Camino G, Costa L, Martinasso G. Intumescent fire retardant system. *Polym Degrad Stab.* 1984;23:359–76.
- Fontaine G, Bourbigot S, Duquesne S. Neutralized flame retardant phosphorus agent: facile synthesis, reaction to fire in PP and synergy with zinc borate. *Polym Degrad Stab.* 2008;93:68–76.
- Balabinovich AI. Thermal decomposition study of intumescent additives: Pentaerythritol phosphate and its blend with melamine phosphate. *Thermochim Acta.* 2005;435:188–96.
- Halpern Y, Mott DM, Niswander RH. Fire retardancy of thermoplastic materials by intumescence. *Ind Eng Chem Prod Res Dev.* 1984;23:233–8.
- Allen DW, Anderson EC, Shiel LE. Structure-property relationships in intumescent flame retardant derivatives of 4-hydroxy methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-1-oxide. *Polym Degrad Stab.* 1994;45:399–408.
- Li X, Ou Y, Shib Y. Combustion behaviour and thermal degradation properties of epoxy resins with a curing agent containing caged bicyclic phosphate. *Polym Degrad Stab.* 2002;77:383–90.
- Gao F, Tong L, Fang Z. Effect of novel phosphorus-nitrogen containing intumescent flame retardant on the fire retardancy and thermal behaviour of poly(butylene terephthalate). *Polym Degrad Stab.* 2006;91:1295–9.
- Song P, Fang Z, Tong L, Jin Y, Lu F. Effect of metal chelate on a novel oligomeric intumescent flame retardant system for polypropylene. *J Anal Appl Pyrolysis.* 2008;82:286–91.
- Wang DY, Cai XX, Qu MH, Liu Y, Wang JS, Wang YZ. Preparation and flammability of novel intumescent flame retardant poly(ethylene-co-vinyl acetate) system. *Polym Degrad Stab.* 2008;93:2186–92.
- Li G, Liang G, He T, Yang Q, Song X. Effects of EG and MoSi₂ on thermal degradation of intumescent coating. *Polym Degrad Stab.* 2007;92:569–79.
- Harashina H, Tajima Y, Itch T. Synergistic effect of red phosphorus, novalac and melamine ternary combination on flame retardancy of poly(oxy methylene). *Polym Degrad Stab.* 2006;91: 1996–2002.