

## Synthesis of polyhydric alcohol/ethanol phosphate flame retardant and its application in PU rigid foams

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**ABSTRACT:** Two types of polyhydric alcohol/ethanol phosphates (PAEPs) were synthesized by a two-step reaction using phosphorus oxychloride, ethanol, and polyhydric alcohol (glycerol and pentaerythritol). First, phosphorus oxychloride was reacted with ethanol to form a mixture of diethyl chlorophosphate and tri-ethyl phosphate, and then PAEPs were prepared by the reaction between the above mixture and polyhydric alcohol. The chemical structures of PAEPs were characterized by <sup>1</sup>H NMR, and the elemental compositions were analyzed by X-ray photoelectron spectroscopy (XPS). The degradation behavior of the PAEPs and their solubility in polyols were studied. The results indicated the PAEPs could be well dissolved in polyols. When PAEPs were used as flame retardant for PU rigid foams at a content of 8 wt %, the char residue of polyurethane foam at 800°C increased from 17.2 to 28% in average, and the peak heat release rate (pHRR) of polyurethane foam decreased significantly from 207 to 133 kW/m<sup>2</sup>. In addition, PURF with PAEPs showed remarkable intumescent property. The results indicated that PAEPs were effective condensed phase flame retardant with char catalytic and intumescent property. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42298.

**KEYWORDS:** degradation; flame retardance; polyurethanes

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### INTRODUCTION

Polyurethane rigid foam (PURF) has been widely used as an important type of insulation material.<sup>1,2</sup> However, its applications have been restricted by its good flammability. In recent years, the enhancement of PURF's flame retardant property has drawn much attention.

Among the flame retardants, phosphorus-containing compounds have been widely studied and used as efficient flame retardant for PURFs,<sup>3</sup> such as ammonium polyphosphate,<sup>4,5</sup> cyclotriphosphazene,<sup>6</sup> and some other type phosphorus flame retardants.<sup>7–9</sup>

Generally, phosphorus-containing flame retardants can be divided into two kinds according to their effects.<sup>10</sup> One mainly plays an important role in gas phase by interrupting the sustainable combustion, whereas the other mainly is mostly effective in condensed phase. The mechanism of phosphorus-containing flame retardants in condensed phase is complex. First, thin char layers are generated after the degradation of PURFs to flammable fragments. The degradation reaction of PURFs can be catalyzed and accelerated by phosphorus-containing flame retardants, reducing the production of flam-

mable fragments and facilitating the formation of char layer. The enhanced char formation can bring two benefits, i.e., reducing the generation of flammable gas and forming a protective char layer.<sup>11,12</sup>

The catalytic effect of phosphorus-containing flame retardants is closely related to the efficiency of its degradation to products with acidic structures. The char-forming capability of flame retardants is dependent on the reaction between the acidic structures and PURF.<sup>13,14</sup> Among phosphorus-containing flame retardants, polybasic alcohol phosphate and ammonium salt of polyphosphate are known to be easily degradable to acids below the degradation temperature of polyurethane. For example, 1-oxo-2,6,7-trioxo-1-phosphabicyclo[2,2,2] octane (PEPA)<sup>15</sup> and ammonium polyphosphate (APP)<sup>16</sup> are typical representatives of polybasic alcohol phosphate and ammonium salt of polyphosphate, respectively.

Although APP and PEPA are advantageous for flame retardant of PURF in condensed phase, their poor solubility in polyols brought to great disadvantages to the industrial foaming process, especially by high pressure foaming machine. In addition, when phosphorus flame retardant compounds in solid state is used combined with nanomaterials, a negative interaction might

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**Table I.** Component of Different PURF

Component by weight	Pure PURF	PURF with GEP	PURF with PEP
Polyol-1	35	35	35
Polyol-2	25	25	25
HCFC-141B	23	23	23
Triethylenediamine	0.2	0.2	0.2
Dibutyltin dilaurate	0.8	0.8	0.8
Foam stabilizer	0.3	0.3	0.3
GEP	—	16	—
PEP	—	—	16
Total Polyols	84.3	100.3	100.3
PAPI	100	100	100
Isocyanate index (%)	140	140	140

The number represented part by weight of each raw material.

be observed.<sup>13</sup> In contrast, the liquid phase phosphates, such as triethyl phosphate, are less effective in condensed phase because of their relative low boiling points.

For the flame retardant of PURF, it is important to prepare a kind of condensed phase phosphorus flame retardant, which has good solubility in polyols. Significantly, the diethyl phosphate structure, which has high phosphorus content, could be used as basic unit of phosphorus flame retardant. The reactive position in diethyl phosphate can be used to synthesis flame retardants by bonding to a proper structure. Steven *et al.*<sup>17</sup> has reacted dialkyl phosphate with wood dust and successfully improved the char residue of the modified wood dust. The polyhydric alcohols are usually used as initial agent for preparation of polyols. Therefore, it was chosen as the “matrix” to form phosphorus flame retardant for application in PURF.

In this work, a novel liquid phosphorus-containing flame retardant was designed by bonding the diethyl phosphate structure to polyhydric alcohol with different structures. Two types of polyhydric alcohol/ethanol phosphates (PAEPs), namely glycerol/ethanol phosphate (GEP) and pentaerythritol/ethanol phosphate (PEP), were prepared and characterized. Their degradation behavior, solubility in polyols, and flame retardant effect in PURF were studied.

## EXPERIMENTAL

### Materials

Ethanol, glycerol, pentaerythritol and phosphorus oxychloride ( $\text{POCl}_3$ ) were purchased from Sinopharm Chemical Reagent Co., Shanghai, China.

Polymeric MDI (PAPI), with commercial grade designation 5005, was provided by Huntsman Corporation with average functionality of 2.7–2.8, the NCO content was 30.5%.

Polyols was supplied by Collodion Company Group, Shanghai, China. It was composed by the following ingredients.

Polyol-1 was a kind of polypropylene glycol with end group –OH. The hydroxyl value was 480–520, average functionality was 5.5, and the commercial grade designation was 635.

Polyol-2 was a kind of polyester polyol based on phthalates with end group –OH. The hydroxyl value was 390–430, average functionality was 3.3, and the commercial grade designation was 8410.

Foam stabilizer was Matestab AK8803 purchased from Jiangsu Maysta Chemical Co., Jiangsu, China.

Triethylenediamine, dibutyltin dilaurate, and HCFC-141B were purchased from Sinopharm Chemical Reagent Co., Shanghai, China.

### Synthesis of PAEPs and Preparation of PURFs

**Synthesis of PAEPs.** A 500-mL three-necked flask was equipped with condenser and drying pipe. Phosphorus oxychloride was added to the flask and kept at 0°C. Ethanol was dropped to the flask with the speed of one drop/s. After the dropping process, the reaction was kept first under 0°C for 2 h, and then the temperature was raised to 50°C and kept for 4 h. Afterward, the temperature was raised to 80°C and kept refluxing for 2 h.

At last, the mixture was cooled to room temperature. Polyhydric alcohol was added to the mixture, the reaction was kept for 1 h at room temperature. Then, the reaction temperature was gradually raised to 100°C with the heating rate of 10°C per hour.

The product was treated by reduce pressure distillation at 150°C and –0.098 MPa, until no steam escaped. Then the mixture was washed by ethanol and purified by reduce pressure distillation at 75°C and –0.098 MPa for three times. The product was obtained.

**Preparation of PURFs.** The component of different foam was shown in Table I. PURFs were made by first stirring the flame retardants with polyols until the mixture became transparent. PAPI was added into the mixture, meanwhile the mixture was stirred with a glass stick until it began to foam. Finally, the as-formed PURFs were kept at 50°C for 24 h. The characteristic parameters of different PURF were shown in Table II.

### Characterization

Thermogravimetric analysis (TGA) was performed on a TG analyzer (Perkin Elmer Co., USA) from 50 to 800°C with a heating rate of 20°C/min in nitrogen atmosphere.

<sup>1</sup>H and <sup>31</sup>P nuclear magnetic resonance (NMR) measurements were conducted on a Bruker DMX 500 spectrometer at room temperature with D<sub>2</sub>O or CDCl<sub>3</sub> as solvent.

X-ray photoelectron spectroscopy (XPS) spectra were acquired on an X-ray photoelectron spectrometer (PHI 5000C ESCA, PHI Co., USA) with aluminum target, 14.0 kV of high voltage,

**Table II.** Characteristic Parameter of Different PURF

Parameter	Pure PURF	GEP/PU	PEP/PU
Cream time (s)	25	30	30
Rise time (s)	50	65	65
Gel time (s)	80	90	90
Density of the foam /(kg/m <sup>3</sup> )	40	48	54

and 300 W of power. Binding energy correction was performed by using Cl1s = 284.6 eV as reference.

The stability of solution of PAEPs in polyol was tested by Turbiscan instrument (Turbiscan TAB Expert, Formulation Co., France). The solution was made by stirring PAEPs (16 part) and polyols (84 part) to transparent and even-colored and put into the Turbiscan instrument. During the test, the transmittance of different height of the solution was recorded every 30 min.

The density of PURF was tested by Buoyancy method, the sample was 50 × 50 × 50 mm.

PURFs' limited oxygen index (LOI) was tested according to Chinese standard GB2406-1993, LOI was tested on a LOI testing instrument (HC-3, Fangfen Instrument Co., China). The sample was 10 × 10 × 120 mm.

The combustion performance of PURF was examined with a Low Oxygen Standard Cone Calorimeter (CONE, FTT, USA) at an incident heat flux of 50 kW/m<sup>2</sup>, according to standard ISO 5660-1. The size of all samples was 100 × 100 × 25 mm. All sides of the samples were wrapped in aluminum foil except for the upper face, which was exposed to the heat flux.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Polyhydric Alcohol/Ethanol Phosphates (PAEPs)

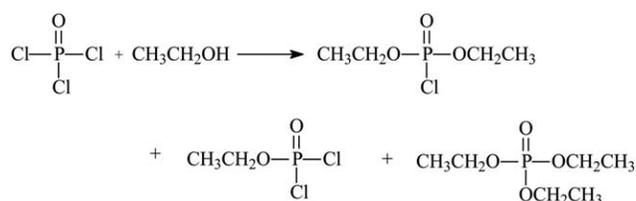
Because both polyhydric alcohol (PA) and POCl<sub>3</sub> compounds were multifunctional molecules, their direct reaction can result in the formation of gel by the cross-linking reaction. Even in the presence of excessive POCl<sub>3</sub>, the generation of cyclophosphate cannot be avoided. Therefore, to minimize the by-products, in this work, the PAEPs were synthesized by two sequential steps, i.e., the synthesis of diethyl chlorophosphate (Step 1) and synthesis of PAEPs (Step 2).

**Synthesis of Diethyl Chlorophosphate.** After the reaction between ethanol and POCl<sub>3</sub>, a mixture of diethyl chlorophosphate (EP-Cl), ethyl dichlorophosphate (EP-Cl<sub>2</sub>), triethyl phosphate (TEP), and a small amount of some other compounds were formed. The reaction was shown in Scheme 1.

A method for the synthesis of dialkyl chlorophosphate was reported by Steven in Ref. 18. Through the reaction of alcohol and POCl<sub>3</sub> at a molar ratio of 2 : 1, EP-Cl was obtained with the presence of a small portion of EP-Cl<sub>2</sub> and TEP.

In this work, the product was not intended to be purified and would be directly used in Step 2 reaction. Based on the fundamental, the product by Step 1 should be mainly EP-Cl. EP-Cl<sub>2</sub>, which might cause cross-linking in Step 2 reaction, should be controlled to low level or none. TEP had less influence on the reaction between the mixture and PA, and a certain amount of TEP was even preferred as the thinner.

The reaction was controlled by adjusting the ratio of ethanol to POCl<sub>3</sub>. The fundamentals of controlling ethanol to POCl<sub>3</sub> ratio were (1) avoiding EP-Cl<sub>2</sub>, (2) increasing EP-Cl, and (3) providing a proper viscosity for Step 2 reaction. The increase of ratio of ethanol to POCl<sub>3</sub> was in favor of avoiding the product of EP-Cl<sub>2</sub>, but it would also result in increase of TEP and decrease



**Scheme 1.** Reaction between ethanol and phosphorus oxychloride.

of EP-Cl. Even a certain amount of TEP was preferred as thinner for EP-Cl with PA, excessive ethanol would definitely decrease the total product rate. The ratio of ethanol to POCl<sub>3</sub> was controlled to 2.1–2.5 to 1. When different ratio of ethanol was added to POCl<sub>3</sub>, the state of Step 2 reaction was observed and listed in Table III.

According to results in Table I, the proper ratio of ethanol to POCl<sub>3</sub> was chosen to be 2.3–2.5 : 1. The viscosity of the mixture in Step 2 was too thick to be well mixed by the magnetic stirrer, when the ratio of ethanol to POCl<sub>3</sub> was 2.1 or 2.2 to 1.

When the ratio of ethanol to POCl<sub>3</sub> was 2.3 : 1, the viscosity of the mixture was suitable for the Step 2 reaction. The resultant product was characterized by <sup>31</sup>P NMR. The result (discussed in the characterization section) indicated that there was no EP-Cl<sub>2</sub> existing in the mixture obtained in Step 1. It should be noted that there was no need to increase the ratio of ethanol to POCl<sub>3</sub> as it would decrease the EP-Cl content. Hence, the ratio of ethanol to POCl<sub>3</sub> was optimized to be 2.3 : 1 in Step 1.

**Synthesis of PA/Ethanol Phosphate.** The reaction of PA with product in Step 1 was conducted based on the calculation as shown in Scheme 2.

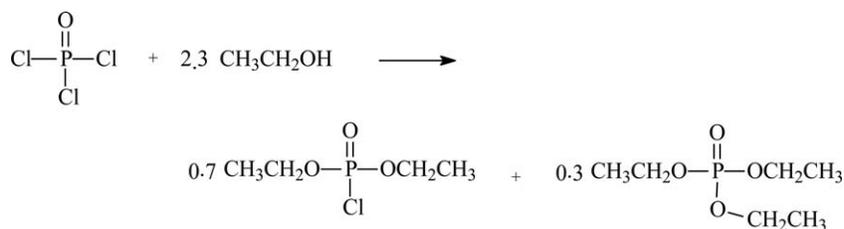
When 0.1 mol POCl<sub>3</sub> was added, about 0.07 mol EP-Cl would be generated. In Step 2, EP-Cl was about 15% over weight than the added PA, which means 0.2 mol glycerol or 0.15 mol pentaerythritol was added to the mixture.

Glycerol/ethanol phosphate (GEP) and pentaerythritol/ethanol phosphate (PEP) were synthesized by the reaction shown in Scheme 3.

During the preparation of PAEPs, it was important to control the temperature of the reaction Hydrogen chloride (HCl), produced by the reaction of EP-Cl and PA, was slowly generated and gradually released from the reaction system when the temperature was increased in the mention way shown in the Synthesis of PAEPs section. The generation of HCl was accelerated

**Table III.** Influence of Ratio of Ethanol/POCl<sub>3</sub> on State of Step 2 Reaction

	Ratio of ethanol to POCl <sub>3</sub>	Viscosity of mixture in step 2
M1	2.1	Lose fluidity
M2	2.2	Too thick for magnetic stirrer
M3	2.3	Thick liquid
M4	2.4	Thick liquid
M5	2.5	Good flowing liquid



**Scheme 2.** Theoretical reaction of phosphorus oxychloride and ethanol.

at high temperature. The side reaction between HCl and EP-Cl or PAEP would be increased with high concentration HCl at 100°C. The reaction was shown in Scheme 4. If reaction was kept at the room temperature, it was too long for the reaction to complete.

For the preparation of PAEPs, no acid gas release from the reaction system was set as the reaction end point.

**Characterization of PA/Ethanol Phosphate and the Intermediate Product.** The product by M3 was characterized by  $^{31}\text{P}$  NMR (see Supporting Information Figure S1), all the characteristic peaks were assigned, such as 4.4–4.6 ppm for EP-Cl,  $-1.2$  ppm for diethyl phosphate (DEP),  $-2.6$  ppm for TEP, and a small peak for EP-Cl<sub>2</sub> at 6.9 ppm. In addition, DEP might be generated by the hydrolysis of EP-Cl because of the moisture in the air. Based on the  $^{31}\text{P}$  NMR spectrum, the required precursor was successfully synthesized.

The GEP synthesized by the mentioned process was characterized by  $^1\text{H}$  NMR (see Supporting Information Figure S2) and XPS. The chemical shift peak at 1.05–1.40 ppm was ascribed to hydrogen in  $-\text{CH}_3$  group, and the peak at 3.90–4.25 ppm was the chemical shift of hydrogen in the  $-\text{CH}_2$  and  $-\text{CH}$ , in which the carbon atom was directly bonded with oxygen in phosphate group. There was a small peak at about 4.5 ppm, which could be attributed to the hydrogen in  $-\text{OH}$  group.

The standard  $^1\text{H}$  NMR of glycerol mainly showed two chemical shifts which were 3.3–3.5 ppm for hydrogen atom in C–H structure and 4.4–4.6 ppm for hydrogen atom in hydroxyl. The difference in  $^1\text{H}$  NMR spectra of GEP and glycerol indicated that glycerol was successfully reacted with EP-Cl. However, the small

peak at about 4.5 ppm illustrated that a small amount of  $-\text{OH}$  groups existed in the product.

The integral ratio of the peak at 3.90–4.25 ppm to the peak at 1.05–1.40 ppm was approximately 17.5 : 18, which was close to the theoretical value of 17 : 18.

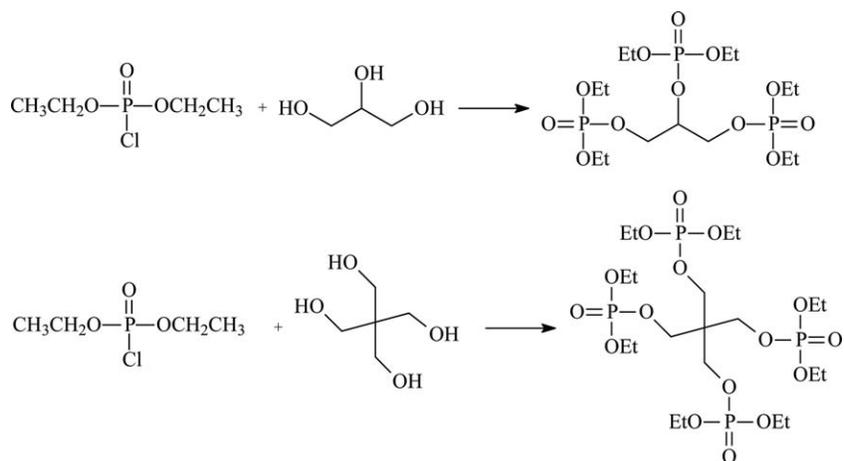
GEP was also analyzed by XPS to study the elemental composition. The results were listed in Table IV.

According to the product shown in Scheme 3, the theoretical ratio of carbon, oxygen, and phosphorus was 5 : 4 : 1. It could be seen that the actual content of phosphorus was slightly lower than the theoretical value. This indicated that the product was not as perfect as the structure in Scheme 3.

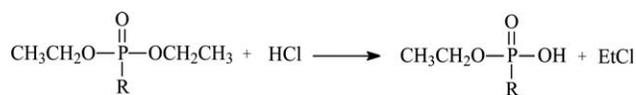
To further study the structure of GEP, its C1s spectrum was shown in Figure 1. The C1s spectrum in Figure 3 illustrated two types of carbon bonds were existed in GEP. From the bonding energy to know they were C–C and C–O bonds. The ratio of C–O and C–C was 1.57 : 1, which was also higher than theoretical value of 1.5 : 1.

From above characterization, it could be speculated that the three hydroxyls of glycerol were not completely reacted with EP-Cl generated by Step 1. We assume that the secondary hydroxyl group in glycerol was not completely reacted owing to the steric hindrance. And the GEP was a mixture of tri-ester and di-ester.

The structure of PEP was characterized by  $^1\text{H}$  NMR (see Supporting Information Figure S3), the peak at 1.3–1.4 ppm was assigned to hydrogen in  $-\text{CH}_3$  group, and the peak at 4.1–4.2 ppm was the chemical shift of hydrogen in the  $-\text{CH}_2$ , in which the carbon atom was directly bonded to oxygen in phosphate



**Scheme 3.** Synthesis of glycerol/ethanol phosphate and pentaerythritol/ethanol phosphate.



**Scheme 4.** Possible side reaction between HCl and phosphate.

group. There was no peak at about 4.5 ppm, confirming that absence of  $-\text{OH}$  group in the product. These results indicated the successful synthesis of PEP.

### Study on PAEPs as Flame Retardant of PURF

**Thermal Degradation Property of PAEPs.** The flame retardant effect of PAEPs in PURF was closely related to its thermal degradation property. Taking GEP as an example, its thermal degradation behavior was studied by TG and XPS. The results were shown in Figure 2.

As shown in TG and DTG curves, the degradation of GEP was in the temperature range from 160 to 350°C and the peak value temperature of weight loss consisted in 240°C. The degradation temperature was lower than that of PURE. The char residue of GEP at 800°C was still 41 wt %.

The elemental content of char residue of GEP generated at different temperatures was analyzed by means of XPS and the results were listed in Table V.

As shown in Table III, when the treating temperature was higher, the phosphorus and oxygen contents were decreased and the carbon content was increased in the char residue. The results indicated that GEP was gradually degraded to acidic phosphate and the weight loss of GEP was caused by the generated water and some phosphate.

The C1s spectra of the char residues of GEP generated at different temperatures (shown in Figure 3) were further analyzed to investigate the degradation process of GEP.

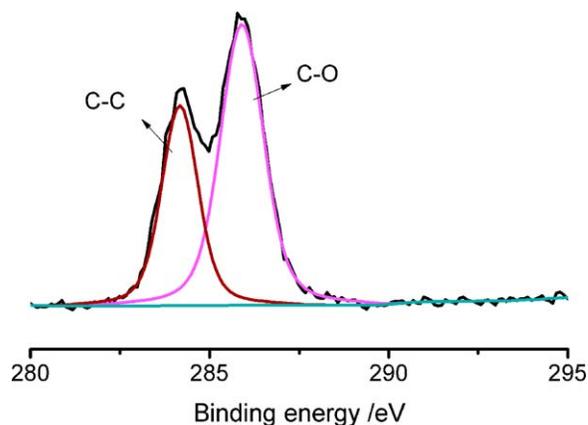
By comparing the results in Figures 1 and 3, one could see that the degradation of GEP led to a marked decrease of the peak at 286 eV in C1s spectra, which was ascribed to the carbon atoms bonded with oxygen. At the same time, the peak at 283 eV assigned to C–C carbon atoms was also decreased when GEP was treated at high temperature.

In Figure 3, when GEP was treated at high temperature, the peaks at 285 and 288 eV were attributed to C=C and C=O, respectively. The peak at 288 eV was possibly from the oxidation of the char layer by the environment, but the peak at 285 eV was caused by the degradation of GEP.

By comparing the results in Figure 3(A,B), the higher the degradation temperature was, the more the C=C bonds were generated. On the basis of the above study, the degradation of GEP

**Table IV.** The Element Content of GEP

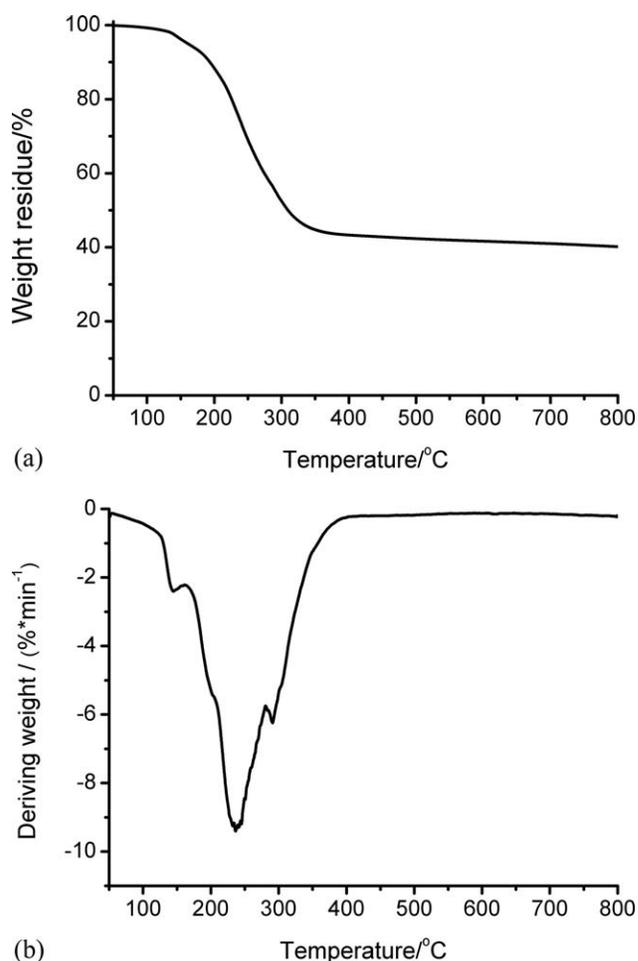
Type of element	Content (mol %)
C	49.5
O	40.8
P	9.7



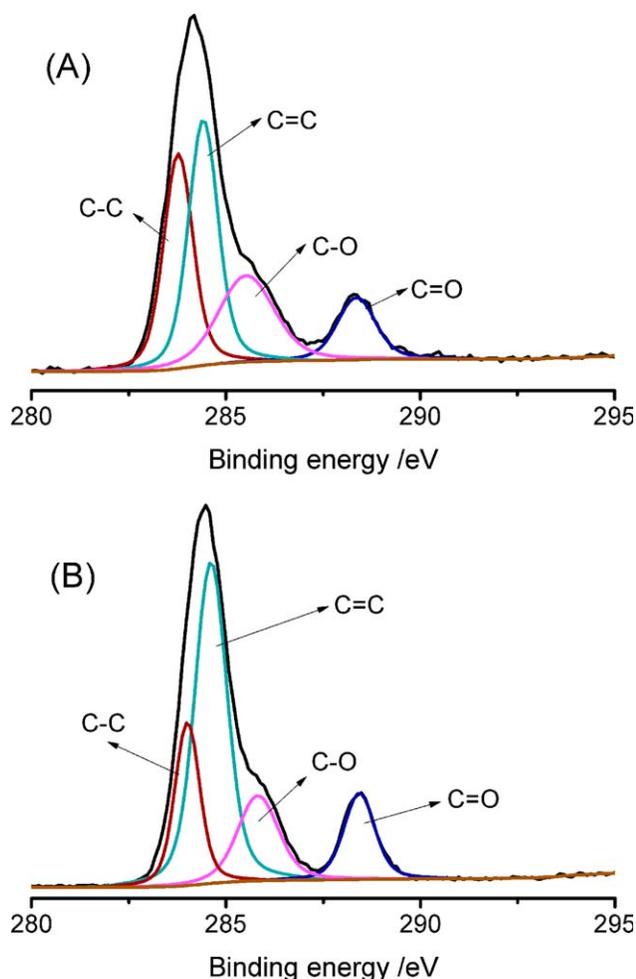
**Figure 1.** C1s spectrum of GEP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

was based on  $\beta$ -H transfer of ethyl or glycerol and generate C=C bonds. The result was in accordance with the  $\beta$ -H transfer decomposition process of phosphates<sup>18</sup>

When GEP was treated by even higher temperature, more acidic phosphates were produced, and char with more carbon element was generated at the same time. It is understandable that when



**Figure 2.** TG and DTG curves of GEP in nitrogen environment.



**Figure 3.** C1s spectra of char residue of GEP. (A) Char residue at 300°C. (B) Char residue at 400°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

GEP was used in PURF, the generated acid would react with PURF and catalysis the char formation. Thus, the GEP was expected to act as a flame retardant in PURF in condensed phase.

PEP has the similar structure to GEP, so their degradation behavior was nearly the same. Both GEP and PEP could degrade to acidic phosphates, which could facilitate the char formation in PURFs.

**Solubility of PAEPs in Polyols.** Solubility and stability of solution of GEP and PEP in polyols were tested (see Supporting Information Figure S5). The photos of the solution are shown in Figure 4.

**Table V.** Element Content of Char Residue of GEP

Sample	Element content (mol %)		
	C	O	P
Char residue at 300°C	61.8	34.0	4.2
Char residue at 400°C	68.6	28.5	2.9



**Figure 4.** Photos of polyols with PAEPs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

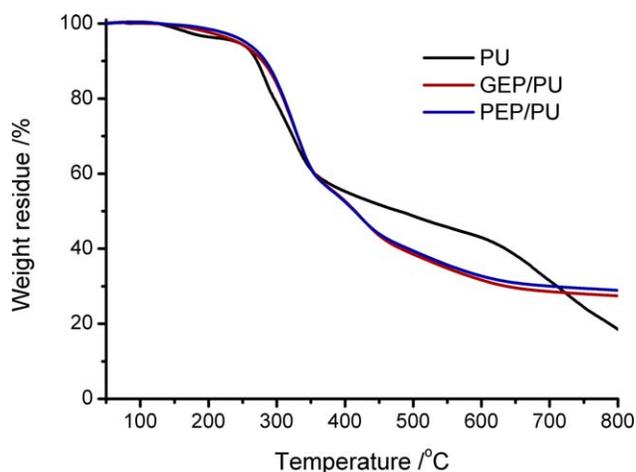
The results showed that both GEP and PEP could be easily dissolved in polyols with merely hand stirring of the mixture. The solutions were still transparent after 1 month.

**Thermal Degradation of PURF with PAEPs.** PAEPs were used in PURFs by 8 wt %. TG of PURF with GEP or PEP was tested and the curves were displayed in Figure 5.

As shown in Figure 5, the weight loss of neat PURF was mainly in two temperature ranges at 250–400°C and 550–800°C. Weight loss at 250–400°C was attributed to hard segments in PURF and the weight loss at 550–800°C was ascribed to the gradual degradation of oxygen-containing soft segments.

When GEP or PEP was added individually, the thermal degradation behavior of PURFs was totally changed. Both GEP and PEP showed good char promotion effect and the char residue rate at 800°C reached 27.7 and 29.0%, respectively.

The difference in TG result of PURFs with GEP and PEP was mainly in three parts. First, PU with GEP (GEP/PU) showed more weight loss than PURF with PEP (PEP/PU) in the initial degradation at 150–220°C; then PEP/PU performed the larger weight loss than GEP/PU at 300–350°C; at last, the weight loss of PEP/PU was lower than GEP/PU at 420–600°C.



**Figure 5.** TG curves of PURF with PAEPs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table VI.** LOI of Different PURFs

Samples	LOI (%)
PURF	19.0
GEP/PU	23.5
PEP/PU	23.5

The results might be related to the degradation behavior of GEP and PEP. As illustrated in the Thermal degradation property of PAEPs section, the degradation of PAEPs was by  $\beta$ -H transfer effect. Glycerol had  $\beta$ -H structures, whereas pentaerythritol did not. Therefore, the degradation of GEP was easier than PEP at lower temperature. The peak position of GEP/PU and PEP/PU was all the same, which indicated that GEP and PEP performed similar effect in degradation in PURFs.

From TGA data of GEP/PU and PEP/PU, GEP and PEP were both effective condensed phase flame retardant for PURF.

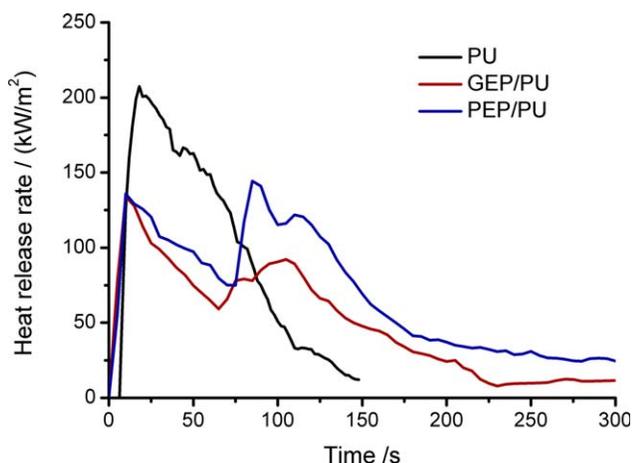
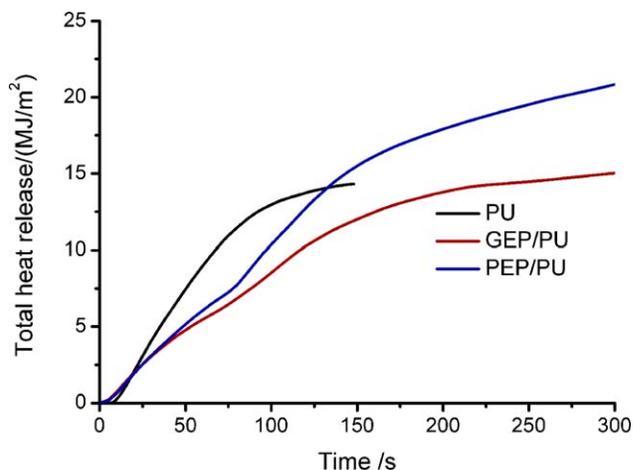
**Combustion Behavior of PURFs with PAEPs.** LOI of PURFs with 8 wt % PAEPs or without flame retardant was tested and the results were listed in Table VI.

From Table VI, both GEP and PEP could increase the LOI of PURFs. The increase of LOI was similar to other condensed phosphorus flame retardants, but lower than that of gas phase flame retardants.

The combustion behavior of PURFs with 8 wt % PAEPs or without flame retardant was studied by cone calorimeter. The peak heat release rate (pHRR) (Figure 6), total heat release (THR) (Figure 7), smoke release rate (SPR) (Figure 8), and mass loss rate (Supporting Information Figure S6) of different PURFs were reported accordingly.

From Figure 6, the heat release rate of GEP/PU and PEP/PU showed double-peak process. The first peak was related to the char formation and intumescent process, whereas the second peak presented after the formation of the char layer.

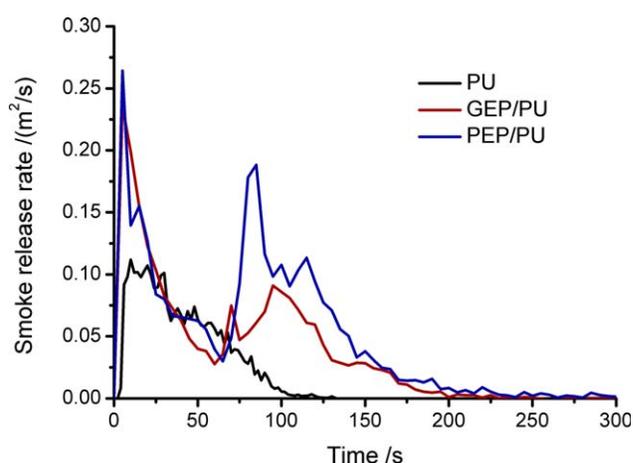
According to the data in Figure 6, pHRR of GEP/PU and PEP/PU was 133 and 135  $\text{kW/m}^2$ , respectively. During this process,

**Figure 6.** Heat release rate of PU and PAEPs/PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 7.** Total heat release of PU and PAEPs/PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the heat release was contributed by the surface part of PURF. The data were similar for GEP/PU and PEP/PU, indicating that GEP and PEP performed similar char promotion effect. In the same period, the intumescence of the char layer was different. The difference in intumescence of the char layer resulted in completely different performance of succeeding heat release peak.

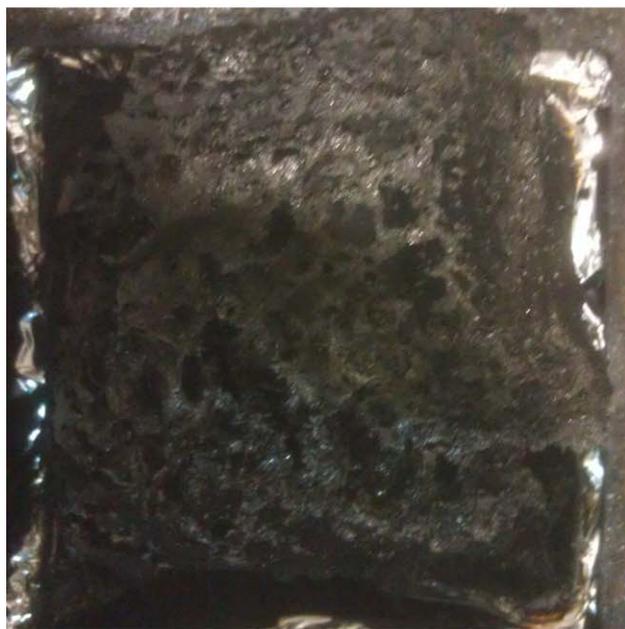
As shown in Figure 6, the second pHRR of GEP/PU was 90  $\text{kW/m}^2$ ; however, the second pHRR of PEP/PU was about 140  $\text{kW/m}^2$ . The difference was due to the effect of the char layer. The char layer of GEP/PU was compact, so that the second pHRR was lower for its better protective effect. The char layer of PEP/PU was intumescent to large volume and became unconsolidated. The second pHRR was even greater, when the char was destroyed by the radiation and the pressure of the fragment.

The performance of GEP/PU and PEP/PU was related to their degradation behaviors. As was shown in Figure 8, the weight loss of PEP/PU was more intensive at about 320°C. It meant the gas release process was intensive, which was in accordance with the violently intumescent process. The weight loss of GEP/

**Figure 8.** Smoke release rate of PU and PAEPs/PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a)



(b)

**Figure 9.** The appearance of char layer of GEP/PU (left) and PEP/PU (right). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

PU was in a larger range, so it was not as intensive as the performance of PEP/PU. The comparable mildly intumescent process resulted in more compact char layer.

In addition, the HRR of GEP/PU and PEP/PU, other data were adopted to further explain the performance of GEP/PU and PEP/PU.

As displayed in Figure 7, the total heat release was different for different PURFs. THR was more related to the mass of the sam-

ples. The heat release of all samples was nearly 12.8 MJ/kg. The results confirmed that PAEPs was effective condensed phase flame retardant and less effective in gas phase.

As shown in Figure 8, the smoke release rate (SPR) of PURFs increased when GEP and PEP were used. The reason could be ascribed to the char promotion effect of GEP and PEP, which disturbed the sufficient burning of PURF. The performance in SPR was simultaneous with that of HRR.

In the whole radiation process, the mass loss rate of GEP/PU and PEP/PU were the same except for the small difference at 85–100 s. At the time range 85–100 s, the mass loss rate of PEP/PU was higher than that of GEP/PU.

Based on the results, the differences of GEP/PU and PEP/PU consisted mainly in the period 85–100 s. At this period, the char layer was already formed. The performance of PURFs could be also attributed to the protection effect of the char layer.

After the cone test, the appearance of char layers of GEP/PU and PEP/PU was shown in Figure 9.

From Figure 9, it could be seen that the char layer of GEP/PU was more compact than that of PEP/PU, and this was in accordance with the results of cone calorimeter test.

Based on the results, both GEP and PEP were effective condensed phase flame retardant for PURF. The performance of PURF in cone calorimeter with different PAEPs was mainly affected by the state of the generated char layer during the combustion. If the intumescent process of PAEPs/PU was controlled by other parameter, PAEPs/PU might have better performance in flame retardant for PURF.

## CONCLUSION

In summary, two types of polyhydric alcohol/ethanol phosphates (PAEPs) were synthesized by a two-step reaction. Results of NMR and XPS confirmed that both glycerol/ethanol phosphate and pentaerythritol/ethanol phosphate were synthesized successfully.

PAEPs had good solubility in polyols and the solutions were stable. In addition, PAEPs showed favorable degradation behavior as a condensed phase flame retardant, which performed remarkable char promotion property for PURFs and led to notable intumescence of the char layer. PAEPs could significantly improve the flame retardancy of PURFs, especially for GEP, which could decrease the peak heat release rate of PURF from 207 to 133 kW/m<sup>2</sup>.

The advantages of PAEPs make it a suitable condensed phase flame retardant for industry application in PURF.

## REFERENCES

1. Szycher, M. *Szycher's Handbook of Polyurethanes*[M]; CRC press, 1999, 78, 81.
2. Demharter, A. *Cryogenics* 1998, 38, 113.

3. Chattopadhyay, D. K.; Webster, D. C. *Prog. Polym. Sci.* **2009**, *34*, 1068.
4. Awad, W. H.; Wilkie, C. A. *Polymer* **2010**, *51*, 2277.
5. Meng, X.; Ye, L.; Zhang, X.; Tang, P.; Tang, J.; Ji, X.; Li, Z. *J. Appl. Polym. Sci.* **2009**, *114*, 853.
6. Qian, L.; Feng, F.; Tang, S. *Polymer* **2014**, *55*, 95.
7. Semenzato, S.; Lorenzetti, A.; Modesti, M.; Ugela, E.; Hreljaa, D.; Bescoa, S.; Michelina, R. A.; Sassib, A.; Facchinb, G.; Zorzic, F.; Bertania, R. *Appl. Clay Sci.* **2009**, *44*, 35.
8. Huang, G.; Gao, J.; Wang, X. *Appl. Surf. Sci.* **2012**, *258*, 4054.
9. Lorenzetti, A.; Modest, M.; Gallo, E.; Schartel, B.; Besco, S.; Roso, M. *Polym. Degrad. Stab.* **2012**, *97*, 2364.
10. Lorenzetti, A.; Modest, M.; Gallo, E.; Schartel, B.; Besco, S.; Roso, M. *Polym. Degrad. Stab.* **2012**, *97*, 2364.
11. Liu, W.; Chen, D. Q.; Wang, Y. Z.; Wang, D. Y.; Qu, M. H. *Polym. Degrad. Stab.* **2007**, *92*, 1046.
12. Wang, G.; Xu, W. *Polym. Degrad. Stab.* **2013**, *98*, 2323.
13. Lorenzetti, A.; Besco, S.; Hrelja, D.; Roso, M.; Gallo, E.; Schartel, B.; Modesti, M. *Polym. Degrad. Stab.* **2013**, *98*, 2366.
14. Zheng, X.; Wang, G.; Xu, W. *Polym. Degrad. Stab.* **2014**, *101*, 32.
15. Jiang, W. Z.; Hao, J. W.; Han, Z. D. *Polym. Degrad. Stab.* **2012**, *97*, 632.
16. Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1984**, *17*, 1605.
17. Steven, R.; van Es, D. S.; Bezemer, R.; Kranenbarg, A. *Polym. Degrad. Stab.* **2006**, *91*, 832.
18. Li, Y.; Koper, O.; Atteya, M.; Klabunde, K. *J. Chem. Mater.* **1992**, *4*, 323.