

# A Phosphorous-based Polyol for Flame Retarded Rigid Polyurethane Foam

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## Abstract

A phosphorus-containing polyol (P-polyol) was synthesized with diethyl ethylphosphate (DEEP) and trihydroxymethyl phosphane oxide (THPO) via transesterification reaction, which was introduced into rigid polyurethane foam (RPUF) by in-situ chemical reaction. The optimum synthesis conditions of P-polyol were investigated as follows: butyldihydroxychlorostannane as catalytic agent, the molar ratio of DEEP to THPO was 1:1 at 120-170°C, the yield was over 85%, the apparent viscosity of P-polyol was 1400 MPa.S with the hydroxyl value about 480 mg KOH/g and the acid value about 100 mg KOH/g. With the increase of adding P-polyol, the flame retardant properties of the RPUF increased continuously. When the P-polyol amount in white material was 40%, the LOI reached 24.7% and vertical combustion test rated UL 94 V-0. TGA results show that the P-polyol promotes the degradation and the formation of char residue of RPUF significantly. The polyurethane foam had the characteristics of condensation phase. Simultaneously, the compressive strength of RPUF was increased by 50 % and 21% in horizontal and vertical direction, respectively, compared with neat RPUF.

## Keywords

Phosphorus-containing Polyol; Rigid Polyurethane Foam; Flame Retardant; Mechanical Property; Transesterification Reaction.

## 1. Introduction

Rigid polyurethane foams have been applied in many industrial applications for their light weight, thermal insulation performance, excellent insulating property and superior mechanical properties. Therefore, the demand of related industries for flame retardancy of rigid polyurethane foam products is also increasingly demanding. The flame retardant materials must meet the requirements of both flame retardant standards and mechanical properties. According to existing research, there were many flame retardants for polyurethanes, including reactive flame retardants, additive flame retardants and coating flame retardants. Among them, reactive flame retardants can be bonded to the main chain of polyurethane by chemical bond, which can improve the flame retardancy while reducing the negative impact on mechanical properties [1-2]. DMOP was synthesized from dimethyl methylphosphonate and diethanolamine, which was applied in polyurethane soft foam to promote the flame retardancy by Rao et al.[3]. The addition amount reached to 10 php (about 6.3wt%), and the tensile strength and tear strength were correspondingly improved, and the flame retardant polyurethane foam could pass the vertical combustion test V-0 level. Yan Li et al.[4] and Rao et al.[5] synthesized phosphorus-containing long-chain diols with phenyl phosphonyl dichloride and ethylene glycol which was used to prepare flame retarded rigid polyurethane foam and polyurethane flexible foam respectively. The results showed that when the phosphorus content was 1.82%, the flame retardancy and mechanical properties of flame retardant PUF were improved simultaneously. Rong et al. [6] used the hexa-(phosphite-hydroxyl-methyl-phenoxy)-

cyclotriphosphazene (HPHPCP) in rigid polyurethane foams. Results suggested that HPHPCP enhanced the density, comprehensive strength and thermal stability, as well as increasing the flame retardancy. Dong et al. [7] introduced a novel compound containing phosphorus and nitrogen DOPO-NIBAM in polyurethane foam. It demonstrated that DOPO-NIBAM could improve the flame retardancy and mechanical properties of polyurethane foam. So it was suggested that the reactive flame retardants can comprehensively improve the flame retardancy and mechanical properties of RPUF.

In this paper, phosphorus-containing polyol (P-polyol) was prepared by transesterification of diethyl ethyl phosphonate (DEEP) and trimethylolphosphine oxide (THPO), and used to react with flame retardant rigid polyurethane foam (RPUF). The optimal reaction conditions and the mechanical properties, flame retardancy, and thermal stability of flame retardant RPUF were studied also.

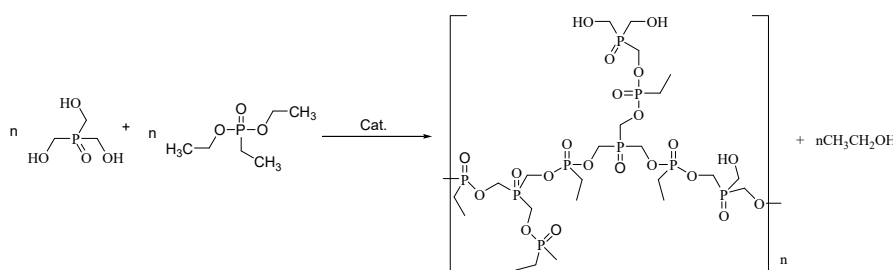
## 2. Experimental Section

### 2.1. Materials

Polyether polyol (white material) was obtained from Tuohan Trade Industry Co., Ltd. (Nanjing, China). Polymethyl polyisocyanate (black material) was provided by Wanhua Polyurethane Co., Ltd. (Yantai, China). Water-based silicone oil (DMS) was supplied by Damao Chemical Reagent Factory (Tianjin, China). Stannous octanoate ( $C_{16}H_{30}O_4Sn$ ) was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Distilled water ( $H_2O$ ) prepared by our laboratory. Triethanolamine (TEA) and Glycerol were supplied by Beifang Tianmedical Chemical Reagent Factory (Tianjin, China). Diethyl ethyl phosphate (DEEP) was provided by Moore Chemical Co., Ltd. (Linyi, China). Tris(hydroxymethyl)phosphine oxide (THPO) was supplied by Alfa Chemical Co., Ltd. (Zhengzhou, China). Dihydroxybutyltin chloride was provided by Weng Jiang Reagent Co., Ltd. (Wengyuan, China).

### 2.2. Synthesis of Phosphorus-Containing Polyol

The equivalent THPO and DEEP was added into a 250ml three necked circular bottom flask, with 0.4wt.% of dihydroxybutyltin chloride as catalyst. The reaction temperature was increased slowly and maintained at 120 °C, 140 °C, and 170 °C for a period of time. At the same time, the vacuum degree of the system was increased to ejecting ethanol until the reaction was completely completed. The reaction scheme of P-polyol was shown in Fig.1:



**Fig 1.** The transesterification of DEEP and THPO

### 2.3. Preparation of Rigid Polyurethane Foams

Using water as the foaming agent and water-based silicone oil as the stabilizing agent, RPUF was prepared according to the formula in Table 1. Polyether polyols, P-polyols, and other additives were stirred evenly in a plastic cup to obtain white material. Then, black material PAPI was added to the white material, stirred at high speed for 20 seconds, and poured into the

mold for free foaming. After being placed at room temperature for 1 hour, it was placed in a vacuum oven and matured at 80 °C for 24 hours to obtain flame-retardant RPUF.

**Table 1.** The formula of RPUF containing P-polyol

code	PAPI /g	4110 /g	Stannous octanoate /g	Triethylamine /g	silicone oil /g	glycerol /g	Water /g	P-polyol /g
1	15	10	0.7	0.21	0.55	0.6	0.15	0
2	15	8	0.7	0.21	0.55	0.6	0.15	2
3	15	6	0.7	0.21	0.55	0.6	0.15	4
4	15	4	0.7	0.21	0.55	0.6	0.15	6

## 2.4. Measurements

Fourier transform infrared spectroscopy (FTIR) was performed with a AVATAR380 spectrometer (Nicolet, USA). The wavenumber ranged from 400 to 4000  $\text{cm}^{-1}$  with a spectral resolution of 8  $\text{cm}^{-1}$  and 32 scans.  $^1\text{H}$ ,  $^{31}\text{P}$  NMR spectra were obtained on a Bruker Avance spectrometer (400 MHz, Bruker, Germany) using deuterated chloroform as the solvent. Hydroxyl value and acid value were referred to the method of GB12008.3-1989, 0.5 g and 1 g of phosphorus-containing polyol were weighed and tested for hydroxyl value and acid value using pyrimidine, imidazole, phthalic anhydride and dioxane reagents.

The foam core was prepared the specimen with the size of 50 mm  $\times$  50 mm  $\times$  50 mm according to GB/T6343-1995, and tested it after 72 hours of sample making to researching apparent core density. The sample size of 10 mm  $\times$  10 mm  $\times$  2 mm small sample strips were quickly cut into small slices of approximately 1 mm thickness to observe the vesicle structure.

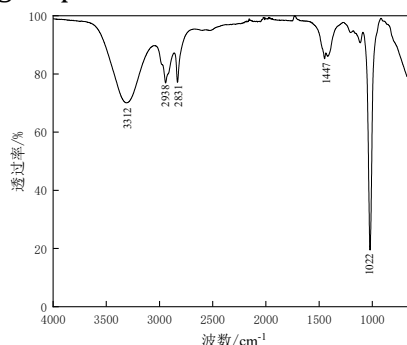
Compression tests were carried out using an electronic universal testing machine (Autograph AGS-X, Shimadzu) with a crosshead speed of 5  $\text{mm}\cdot\text{min}^{-1}$  according to GB/T 8813-2008 standard with a specimen size of 50 mm  $\times$  50 mm  $\times$  50 mm. The LOI values of the RPUFs (dimensions: 150  $\times$  10  $\times$  4  $\text{mm}^3$ ) were obtained using an oxygen index meter according to ISO 4589-2:1996.

The thermal stability of the RPUFs were measured by thermogravimetric analysis (TGA; HCT-3, Hengjiu). Samples (approximately 6-8 mg each) were heated between 30 and 600 °C at a rate of 10 °C  $\text{min}^{-1}$  under nitrogen flow.

## 3. Results and Discussion

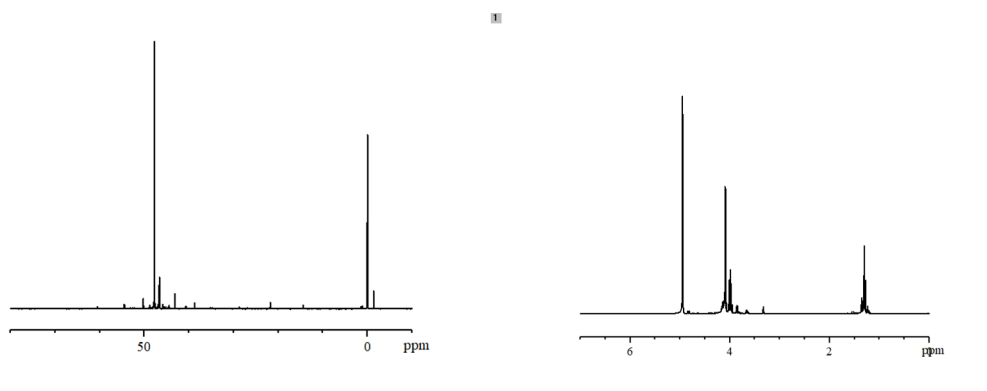
### 3.1. Synthesis and Characterization of P-polyol

Fig.2 revealed the FTIR spectrum of P-polyol. It exhibited a broad band around 3000  $\text{cm}^{-1}$ , corresponding to the O-H, a band around 1447  $\text{cm}^{-1}$  corresponds to P=O and a band around 1022  $\text{cm}^{-1}$  corresponds to P-O-C. The bands around 2938  $\text{cm}^{-1}$  and 2831  $\text{cm}^{-1}$  were attributed to the C-H stretching from aliphatic groups.



**Fig 2.** The FTIR spectrum of P-polyol

There are two types of phosphorus elements located on the main chain of phosphorus containing polyols in  $^{31}\text{P}$ -NMR spectrum (fig. 3a). The peak at 50ppm represents the phosphorus element on the phosphonate ester, which has a greater shielding effect. The peak at 0ppm represents the phosphorus element on THPO, which has a greater shielding effect. And it has multiple peaks for the polydispersity of phosphorus containing polymers. From  $^1\text{H}$ -NMR spectrum (Fig. 3b), it can be seen that the hydrogen near 1.3ppm and 4ppm is the hydrogen in the ethyl and ester groups of DEEP, while the hydrogen near 5ppm is the methylene in the unreacted hydroxymethyl group at the end group.



**Fig 3.**  $^{31}\text{P}$ -NMR and  $^1\text{H}$ -NMR spectra of P-polyol

The effects of reaction temperature, feed ratio, etc. on the degree of reaction are shown in Table 2. When feeding at a molar ratio of 1:0.6, the reaction functionality is relatively close and cross-linking occurs, which cannot be used for preparing RPUF. While feeding at an equal molar ratio, a viscous P-polymer can be obtained. Fixing the feeding ratio 1:1, when the temperature increases from 120 °C to 140 °C, the conversion rate of the reaction significantly increases, and the increase in conversion rate slows down when the temperature rises from 140 °C to 170 °C. But the acid value increased along with the increase in temperature, which may be due to the high reaction temperature, which partially decomposes DEEP into phosphoric acid, leading to an increase in the acidity of the system. Fixing the feeding ratio 1:1 and maintaining the reaction temperature 170 °C, the optimal reaction time is measured by the amount of by-product ethanol generated. Therefore, the reaction time is controlled within 12-14h.

**Table 2.** The effects of reaction conditions on apparent viscosity, hydroxyl value and acid value

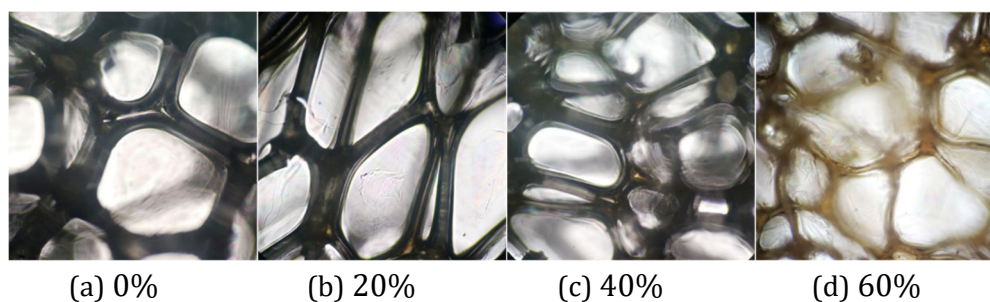
Ratio DEEP/THPO (mol/mol)	Temperature °C	Ethanol yield(%)	apparent viscosity mPaS	acid value mg KOH/g	hydroxyl value mg KOH/g
1: 0.6	120	79.31	Cross-linked		-
1: 0.8	120	87.42	Cross-linked		-
1: 1	120	86.74	1100	100	534
1: 1	140	94.05	1400	103	480
1: 1	170	95.51	1350	230	582

## 3.2. The Performances of RPUF Containing P-polyol

### 3.2.1. The Foam Pore Structure

The foam pore structure of polyurethanes with P-polyol 0wt.%, 20wt.%, 40wt.% and 60wt.% of white materials was observed by microscope as shown in Fig.4. The neat RPUF has the uniform distribution pore structure which is similar to spherical shape. The cell size of polyurethane foam decreases with the increase of addition amount from 20wt.% to 40wt.% of white materials. It causes the increase of the apparent density. But with the increase of P-poly, the size and shape of bubbles become more irregular, with uneven distribution and poor stability. With the additional amount is 60%, the pore structure exhibits inhomogeneous seriously, leading to the decrease of mechanical performances.

This is due to the foaming process of polyurethane foam as follows: nucleation and growth. When the amount of P-polyol is limited, the system viscosity is relative large, which slows down the foaming speed, making the polyurethane foam fully nucleate, thus increasing the foam pores. A small amount of P-polyol acts as a nucleating agent in this process. When the addition of P-polyols gradually increases, the viscosity of the system gradually decreases, and the internal force of polyurethane is uneven, resulting in uneven pore size and shape.



**Fig 4.** Pore structure of polyurethane foam with different content of P-polyols

### 3.2.2. Density and Compressive Strength of Polyurethane

The effect of P-polyol on the density and compressive strength of RPUF was listed in Table 3. With the increase of P-polyol, the density gradually increases due to more dense cellular structure. The mechanical properties of RPUFs in the vertical direction are obviously stronger than those in the horizontal direction.

Comparing the neat RPUF with the RPUF made of 40wt.% P-polyol, it can be seen that the phosphorus-containing RPUF has better mechanical properties than the neat RPUF in both horizontal and vertical directions. From the density data, the greater is the density of phosphorus-containing RPUF, the stabler structure and the better mechanical performances they are.

**Table 3.** The effect of P-polyol on the density and compressive strength

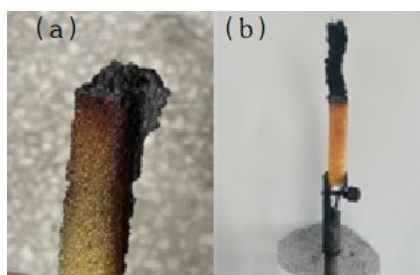
code	Density (g/cm <sup>3</sup> )	Compressive Strength (horizontal)/(MPa)	Compressive Strength (vertical)/(MPa)
1	0.052	0.092	0.145
2	0.057	0.103	0.156
3	0.065	0.137	0.175
4	0.061	0.082	0.128

### 3.2.3. Flame Performance

The combustion properties of phosphorus containing polyurethane are listed in Table 4. The oxygen index LOI of polyurethane foam with phosphorus containing polyols increased gradually. When the amount of P-polyol in white materials exceeds 40wt.%, LOI is 24.7% and reached UL-94 V-0 for vertical combustion. This is mainly due to the promoting charring effect of P-polyol and the residue layer exhibits the excellent expansibility. As shown in Figure 5, the char residuals were found on the surface of the sample after burning. It effectively prevented the matrix from further degrading. It indicates the condensed phase flame retardant mechanism of P-polyol.

**Table 4.** Flame performance of phosphorus-containing RPUF

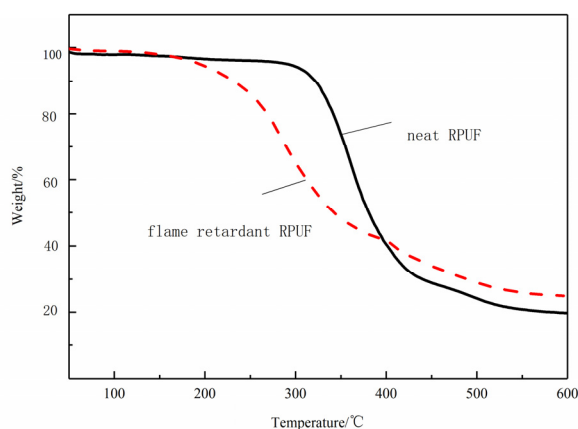
code	LOI %	Combustion time s	UL-94
1	17.0	25.40s	---
2	21.1	6.48s	V-1
3	24.7	1.22s	V-0
4	25.5	1.17s	V-0



(a)after vertical combustion test (b) after LOI test

**Fig 5.** RPUF residues digital photos after flame tests

### 3.2.4. Thermal Stability Analysis



**Fig 6.** TGA curves of neat and flame retardant RPUF

Fig.6 depict the TG curves of the neat RPUF and flame retardant RPUF at heating rates of 10 °C/min. The curves show two inflection points, which indicate that there were two thermogravimetry stages in the thermo-decomposition process of RPUFs. Neat RPUF

has two degradation stages at 300-450°C and 450-550°C. The weight loss in the first stage was due to the pyrolysis of urethane bonds, and the polyurethane is decomposed into polyisocyanates and polyols. Then the polyisocyanates are degraded into imide structure and then decomposed into some isocyanates and volatile gases. The mass loss in the second stage took place because the further degradation of the substances generated in the first stage, which produce amines, carbon dioxide, and hydrocarbons [8-10]. The flame retardant RPUF shows two degradation stages at 200-400°C and 400-550°C with introducing P-polyol. The lower initial decomposition temperature indicates that phosphorus-containing compounds have a certain catalytic effect on the decomposition process of polyurethane foam, in addition, the bond energy of the P-O-C bond is lower than urethane bond. Although the decomposition is advanced, the polyphosphoric acid and polymetaphosphate formed after the decomposition of P-O-C bonds play a role in promoting the carbonization of the material [11]. The carbon residue of phosphorus containing polyurethane foam is 25.08% during thermal decomposition at 600°C, which has the characteristics of condensed phase flame retardant.

#### 4. Conclusion

A phosphorus-containing polyol (P-polyol) was synthesized with diethyl ethylphosphate (DEEP) and trihydroxymethyl phosphane oxide (THPO) via transesterification reaction. The optimum synthesis conditions of P-polyol were investigated as follows: butyldihydroxychlorostannane as catalytic agent, the molar ratio of DEEP to THPO was 1:1 at 120-170°C, the yield was over 85%, the apparent viscosity of P-polyol was 1400 MPa.S with the hydroxyl value about 480 mg KOH/g and the acid value about 100 mg KOH/g. P-polyol was introduced into RPUF to increase flame and mechanical performances simultaneously. When the content of P-polyol in the white materials is 40%, the LOI is 24.7% and reaching UL-94 V-0 level. Furthermore, the compressive strength of RPUF was increased by 50 % and 21% in horizontal and vertical direction, respectively. The results of TGA and combustion testing show the characteristics of condensed phase flame retardancy.

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