

A reactive phosphorus-containing polyol incorporated into flexible polyurethane foam: Self-extinguishing behavior and mechanism

Wen-Hui Rao, Zong-Min Zhu, Shui-Xiu Wang, Ting Wang, Yi Tan, Wang Liao^{*},
Hai-Bo Zhao, Yu-Zhong Wang^{**}

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

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ABSTRACT

A novel liquid phosphorus-containing polyol named as PDEO was prepared via reactions between ethylene glycol and phenylphosphonic dichloride. PDEO reacts with the -NCO-terminated prepolymers and forms urethane linkages in the chain extending reaction step, thus, it was used to prepare inherently flame-retardant flexible polyurethane foams (FPUFs). The structure and properties of flame-retardant FPUFs were characterized by scanning electron microscopy (SEM), tensile measurements, limiting oxygen index (LOI), vertical burning tests, cone calorimeter tests and thermogravimetric analysis (TGA). The vertical burning test demonstrated that fire extinguished instantly after the withdrawn of the pilot flame, while the PDEO loading was only 10 php. In addition, the persistent flame retardancy of PDEO in FPUFs was proved by thermal ageing test. The corresponding flame-retardant mechanism of PDEO-containing FPUFs was investigated by pyrolysis gas chromatography mass spectrometry (Py-GC/MS), X-ray photoelectron spectroscopy (XPS), SEM and FTIR, and the results indicated a gaseous phase dominated flame-retardant mechanism of PDEO.

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1. Introduction

Flexible polyurethane foams (FPUFs) take up the largest market share of polyurethane (ca. 40%) and are widely used in furniture, mattress, automotive, handbag, luggage, footwear and textile industries based on their low density and high resilience properties [1–3]. However, because of the nature of open cell organic polymer foams, i.e. large surface area and good air permeability, FPUFs easily catch fire with high burning rates and release toxic gases such as HCN and CO during combustion [4–8]. Consequently, FPUFs are classified as high fire risk materials. Hence, it is critical to endow FPUFs with high fire safety to reduce their threat to life and property security.

To achieve this goal, flame retardants (FRs) are added and/or incorporated into the polymer network of FPUFs. Currently, concerning the impact on environment of using halogen-containing FRs, researchers are paying extensive attention on the study of

halogen-free FRs [9,10]. Furthermore, additive FRs, which are blended and physically dispersed in the resulting foams [11,12]. But the commonly used high addition amount leads to the deterioration of the mechanical properties, which affects the comfort for the users, and the flame-retardant effect would be loss during daily use because of migration of FRs. To solve these above mentioned problems, bonding FR components into the foam network, i.e. using reactive FRs, avoids possible migration and leaching, and shows better compatibility, thus are gaining much more attention [5,13,14].

The mechanical properties of FPUFs are remarkably influenced by the types of isocyanates and polyols. Long-chain polyols contribute to the soft segments and impart the foams with stretchy property, while, short-chain and highly functional polyols play a role of crosslinker and produce hard segments in the network [15–19]. In addition, incorporating phosphorus-containing polyols into the foams has the advantages of persistent flame retardancy and homogeneous distribution [5]. Based on these results, designing phosphorus-containing polyols is the most promising way for highly flame-retardant FPUFs with excellent physical and mechanical properties. El Khatib et al. [20]. synthesized some phosphonate diols as chain extenders for the preparation of

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: liaowang@scu.edu.cn, liaowang0624@126.com (W. Liao), yzwang@scu.edu.cn (Y.-Z. Wang).

polyurethane elastomers. Banks et al. [21], studied the phosphorylation of poly(vinyl alcohol) and poly(ethylene-co-vinyl alcohol). Park et al. [22], synthesized pyrophosphoric lactone-modified polyester with two phosphorus functional groups in the base resin. Velencoso et al. [23,24] developed a phosphated initiator for the polyether polyols and used the products as reactive FRs. By comparison, polyols with higher molecular weight and good flame-retardant characteristics are more favorable to prepare FPUFs in practice, since the long chain polyols can act as soft segments to increase the flexibility [25,26]. However, reports based on all of these considerations are still rare owing to the difficulties in synthesis and subsequent foaming process. Therefore, the dispute on the flame retardant function in gaseous-phase, where phosphorus-containing compound generated to reduce the effective heat of combustion of volatiles, or in the condense-phase, where phosphorus compounds decompose and form phosphoric or polyphosphoric acids to catalyze the formation of phosphorus-rich char requires further investigation [27–29].

In this study, a novel liquid phosphorus-containing polyol named as PDEO is synthesized by the reaction between ethylene glycol and phenylphosphonic dichloride, and is used to prepare a series of flame-retardant FPUFs. The microstructure, mechanical properties, thermal degradation and combustion behavior of the resulting foams are characterized and discussed in detail, and the corresponding flame-retardant mechanisms are proposed. Vertical burning test shows that PDEO endows the FPUFs with self-extinguishing capability, and has the potential to be commercially used to improve the fire safety of polyurethane foam.

2. Experimental section

2.1. Material

Polyether polyols (GEP-560s, number average molecular weight of 3000, average functionality of 3.0, OH content of 56 mg of KOH/g, technical pure grade) was obtained from Gaoqiao Petrochemical Company, Shanghai, China. Toluene diisocyanate (TDI, technical pure grade) was obtained from Chongqing Weiteng Polyurethane Products Factory, Chongqing, China. Phenylphosphonic dichloride (PPDC) was supplied by Energy Chemical, Shanghai, China. Ethylene glycol (EG), triethylamine (TEA), chloroform, and dichloromethane were supplied by Kelong Chemical Regent Factory, Chengdu, China. Dimethyl methyl phosphonate (DMMP, technical pure grade) was supplied by Energy Chemical, Shanghai, China. Modified catalyst was of technical pure grade and was supplied by Yutian Chemical Company, Liyang, China. Distilled water was used as a blowing agent and were supplied by Kelong Chemical Reagent Factory, Chengdu, China. Surfactant (technical pure grade) was supplied by Jiangsu Maysta Chemical Technology Chemical Co. Ltd. Beijing, China.

2.2. Synthesis of PDEO

Phosphorus-containing polyol (PDEO) have been prepared as summarized in Scheme 1. Ethylene glycol (EG) (0.12 mol, 7.45 g) in

200 mL of chloroform was added in a three-necked round-bottom flask equipped with a nitrogen inlet, condenser tube, and tail gas absorber. Then, phenylphosphonic dichloride (PPDC) (0.1 mol, 19.5 g) in 100 mL of chloroform was added dropwise to ensure the reaction temperature below 40 °C. After all PPDC was added, the solution was heated to 70 °C and stirring was continued for another 6 h. Then product was obtained by removing chloroform under reduced pressure. After that, the mixture was dissolved in dichloromethane, and triethylamine (TEA) was added to remove the hydrochloric acid by-products via filtration. The filtrate was poured into rotary evaporator for further purification at 70 °C under reduced pressure and the transparent viscous liquid (PDEO) was collected finally.

2.3. Preparation of FPUF

The pure and flame-retardant FPUF samples were prepared by an one-pot and free-rise method. Briefly, polyols (GEP-560s), distilled water, catalysts, surfactant, and phosphorus-containing polyol (PDEO) were well mixed in a 1 L plastic beaker through mechanical stirring. TDI was subsequently added into the beaker with vigorous stirring for 5 s. The mixture was swiftly poured into an open plastic mold (30 × 20 × 15 cm³) for free-rising of foam. The foam was cured for 24 h at 80 °C. The formulations of the FPUFs in this work were shown in Table S1 (Supporting Information). The NCO/OH ratio was 1.05.

2.4. Measurements

Fourier transform infrared (FTIR) spectra was obtained from a Nicolet FTIR 170SX spectrometer over the wave number range from 500 to 4000 cm⁻¹ by the KBr disk method.

Nuclear magnetic resonance (NMR) spectroscopy analysis: ¹H NMR was recorded on a Bruker AV 400 spectrometer using DMSO-*d*₆ as the solvent.

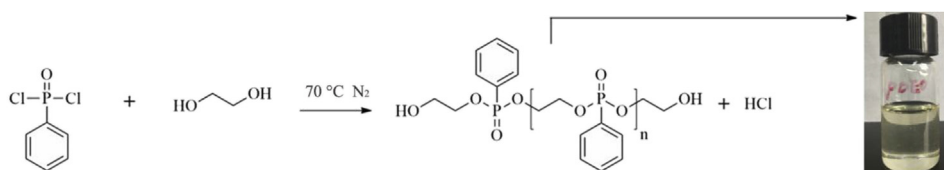
Gel-permeation chromatography (GPC) was performed on a HLC-8320 system (Tosoh Corporation, Japan) equipped with a refractive index detector. Average molecular weights of samples were measured by a Waters HPLC system equipped with a model 1515 pump and a 2414 refractive index (RI) detector. Chloroform was used as the eluent at a flowing rate of 1.0 mL/min, and sample concentration was 2.5 mg/mL. The average molecular weights (*M_n* and *M_w*) were calculated by using monodisperse polystyrenes as standards.

Limiting oxygen index (LOI) values were carried out with a HC-2C oxygen index instrument, which was performed according to ISO 4589-1:1996. The samples were used with 150 × 10 × 10 mm³.

Scanning electron microscopy (SEM) images were obtained using an INSPECTF spectrometer. The morphology of the cross-sectional with a thin gold layer was observed under a high vacuum at a voltage of 20 kV.

The average pore diameter was obtained by mercury porosimetry according to ISO 15901-1:2005 using Pore Master 33 (MIP).

The densities of the FPUF samples were measured according to standard method ISO 845:2006. The size of each specimen was no



Scheme 1. The synthetic route of PDEO.

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