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Synthesis and characterization of flame retardant rigid polyurethane foam based on a reactive flame retardant containing phosphazene and cyclophosphonate

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ABSTRACT

A reactive flame retardant hexa-(5,5-dimethyl-1,3,2- dioxaphosphinane-hydroxyl-methyl-phenoxyl)-cyclotriphosphazene (HDPCP) was synthesized by using 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide and hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene via P-H addition reaction. And it was used to prepare flame retardant rigid polyurethane foams (FR-RPUFs). The effect of flame retardant HDPCP on physical-mechanical, thermal degradation and fire behavior properties of FR-RPUFs system has been investigated. The results suggested that HDPCP showed no obviously negative influence on physical-mechanical property of RPUF. The thermal stability and char residue at 700 °C of RPUF were enhanced by introducing HDPCP. HDPCP is benefit to improve flame retardance of RPUF. The limiting oxygen index (LOI) increased from 19 to 25% with incorporation of 25% HDPCP. Moreover, the peak heat release rate (PHRR), total heat release rate (THR), total smoke rate (TSR) and total smoke production (TSP) of RPUFs decreased due to a good char-forming ability of HDPCP.

1. Introduction

Thermal insulation materials have been the object of attention in the last decades due to the increasing requirement of energy efficiency and environmental protection [1]. In general, the lower thermal conductivity the better thermal insulation, in that case, rigid polyurethane foams (RPUFs) are one of the promising insulation materials since its thermal conductivity is the lowest among common insulation materials. Besides that, with the advantages of good dimensional stability, adhesion strength, low density, high specific strength, and simple construction, RPUFs have been widely used as insulation materials in new construction especially in high-rise building [2]. However, RPUFs are inflammable with a limiting oxygen index (LOI) around 17–19%, which is a potential for deadly fire. Meanwhile, the foam structure leads to a fast flame and smokes propagation speed. In that case, flame retardance modification is a prerequisite for application of RPUFs [3–5].

There are two main ways to introduce the flame retardant into RPUFs. One is blending or coating, in which there is no chemical bond between flame retardant and RPUF [6–8]. The other is using a reactive flame retardant with hydroxyl or amino group which can react with -NCO group in the foaming process [9,10]. With the advantage of no migration and volatilization, the reactive flame retardants would endow a permanent flame retardance effect to RPUFs. Therefore, reactive flame retardants received considerable attention in thermoset materials [11–14]. Recently, mono-component flame retardant containing multiple flame retardant groups such as P/P (phosphazene/phosphaphenanthrene [15,16], phosphazene/phosphonate [17]), P/N (phosphonamidate [18], phosphaphenanthrene/triazine-trione [19], ammonium polyphosphate/piperazine [20], ammonium polyphosphate/diethylenetriamine [21], PEPA/triazine/diethylenetriamine [22]) P/Si (phosphaphenanthrene/silsesquioxane [23]), becomes the hot topic due to high efficiency induced by a synergistic effect of different flame retardance elements and structures. Hexachlorocyclotriphosphazene (HCCP) is an important member of the cyclophosphazene series with six reactive chlorine atoms which can be modified with reactive hydroxyl or amino group in the resulting flame retardant by nucleophilie substituted reaction [15–17,24,25]. In our previous work [17], a reactive flame retardant

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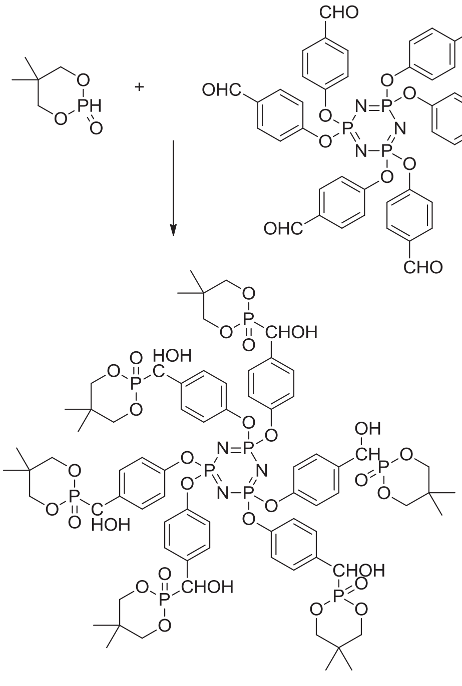
(HPHPCP) containing cyclophosphazene and phosphonate was synthesized and used to prepare flame retardant RPUF. The FR-RPUFs showed better thermal stability and flame retardancy due to the hexa-functionality and high phosphorus content of HPHPCP. The efficiency and mechanism of phosphorus flame retardant can be effected by chemical structure and valency of phosphorus [8,26]. Compared to diethyl phosphite, 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide is a alkyl-phosphate with a P-H group and a hexatomic ring. However, the cycle structure is easy to form chars and play a role in the condensed phase [27].

Therefore, in this article, a novel reactive flame retardant hexa-(5,5-dimethyl-1,3,2- dioxaphosphinane-hydroxyl-methyl-phenoxyl)-cyclotriphosphazene (Scheme 1) containing phosphazene and cyclophosphonate was synthesized and used to prepare flame retardant RPUFs. The influence of HDPCP on physical-mechanical property, thermal stability as well as flame retardancy in FR-RPUFs was investigated in details.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene was purchased by Zibo Lanyin chemical Co., Ltd (Shandong China). Neopentyl glycol, and *p*-hydroxybenzaldehyde was purchased by Aladdin Industrial Corporation (Shanghai China). Phosphorus trichloride was purchased by Xiya reagent Corporation (Chengdu China). Polyether polyol (GR-4110) was purchased by Sinopec Shanghai Gaoqiao Company. The main performance were as follows: typical hydroxyl value, 430 ± 10 mg KOH equiv/g; water content≤0.1 wt%; viscosity (25 °C), 2000–4000 mPa s. Polymethylene polyphenyl isocyanate (PAPI) was purchased by Wanhua Chemical Group Co., Ltd. The main performance indices of PAPI were as follows: viscosity (25 °C): 150–250 mPa s, -NCO weight percent: 30%, and density (25 °C): 1.22–1.25 g/cm^3. Silicone oil was purchased by Nanjing Dearmate Shichuang Chemical Co., Ltd. Hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene (HAPCP) was synthesized in our early reference, [17] and 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide was synthesize according reference [28]. All other reagents were commercial and used as received.



Scheme 1. Synthesis of flame retardant HDPCP.

2.2. Synthesis of reactive flame retardant hexa-(5,5-dimethyl-1,3,2-dioxaphosphinane- hydroxyl-methyl-phenoxyl)-cyclotriphosphazene (HDPCP)

HAPCP (17.23 g), 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (22.5 g), triethylamine (20 ml) and 200 ml THF were loaded into a 500 ml three-necked flask, which was equipped with a nitrogen inlet, condenser and a mechanical stirrer. After that, the mixture was refluxed for 12 h and then the solution was poured out. The crude product was washed with water three and four times and white power product was obtained. ^{1}H NMR (500 MHz, DMSO): δ (ppm) = 7.39 (d, 12H, *Ar*-C), δ = 6.91 (d, 12H, *Ar*-O), 6.43 (m, 6H, Ar-C*H*), 5.26 (m, 6H, C-O*H*) 4.44, 3.95 (m, 24H, $-CH_2$), 1.14, 0.84 (m, 36H, $-CH_3$). ^{31}P NMR (400 MHz, DMSO): 12.92 (s, 6P, PO), 8.29 (d, 3P, P_3N_3). The characteristic peaks of HAPCP are as follows: ν_{max} cm^{-1} 3285 (-OH), 2968, 2896 ($-C_2H_5$), 1265 (P=O), 1181 (P-*O*-C), 955 (P-*O*-Ph).

2.3. Preparation of rigid polyurethane foam

All the rigid polyurethane foams were prepared following the same procedure. The typical procedure of RPUF was as follows: polyols were premixed at room temperature with a small amount of silicone oil AK8805 (surfactant), N,N-dimethyl cyclohexylamine (catalyst), HCFC-141B, flame retardant and water. The mixture was stirred with a propeller stirrer for 3–5 min at approximately 1500 rpm to ensure a homogeneous mix and then mixed with PAPI using the a propeller stirrer (2000 rpm) for 6–8 s at constant NCO/OH ratio 1.1:1 to guarantee that each OH group was reacted, and poured into a plastic box. The obtained rigid polyurethane foams were put in an oven for complete cure for 72 h at 30 °C in order to complete the polymerization reaction, before carrying out characterization. The compositions of rigid polyurethane foam and flame retardancy rigid polyurethane foams are shown in Table 1.

2.4. Characterization

2.4.1. Chemical structure

Fourier-transform infrared (FTIR) spectra were measured with a Nicolet 6700 FTIR spectrometer using sample films and transmission mode. NMR spectra (^{1}H, 500 MHz; ^{31}P, 500 MHz) of resulting polymers were recorded on a Bruker AVANCE III 500 NMR apparatus. Samples were dissolved in DMSO. The elements contents of carbon (C), nitrogen (N), oxygen (O) and hydrogen (H) of HDPCP were measured by elemental analyzer (PerkinElmer EA 2400). And phosphorus (P) content of HDPCP was detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES Vista-AX, Varian).

Table 1
Formulations of rigid polyurethane foams.

Sample	RPUF	RPUF/HDPCP15	RPUF/HDPCP20	RPUF/HDPCP25
GR-4110/g	100	100	100	100
AK-8805/g	2.2	2.2	2.2	2.2
HCFC-141b/g	15	15	15	15
H_2O/g	1	1	1	1
PC-8/g	1.8	1.8	1.8	1.8
HDPCP/g	0	36	48	60
PAPI/g	120	120	120	120