



Effect of tris(1-chloro-2-propyl)phosphate and modified aramid fiber on cellular structure, thermal stability and flammability of rigid polyurethane foams



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ABSTRACT

Effect of tris(1-chloro-2-propyl)phosphate (TCPP) and modified aramid fiber (MAF) on cellular structure, thermal stability and flammability of rigid polyurethane foams (RPUF) has been investigated. RPUF with liquid TCPP and MAF alone, as well as the mix of TCPP and MAF, were prepared via a one-step process in this work. Phosphoric acid was used to modify AF, the P-OH in the MAF and the improvement of interfacial strength between MAF and PU was characterized using infrared spectrum analysis and scanning electron microscopy (SEM). Limited oxygen index (LOI) results indicated that TCPP exhibited more pronounced flame retardant efficiency than MAF for the RPUF. Gas chromatography/mass spectroscopy (GC/MS) illustrated that its flame retardancy took place in both condensed and gaseous phases. Meanwhile, the use of TCPP decreased the thermal stability of RPUF unlike MAF. The decrease by 9.4, 35.7% in the max smoke density (MSD) and peak smoke product rate (PSPR) respectively compared with RPUF showed that MAF was an environmentally friendly flame retardant. However, when TCPP and MAF were used in combination, they effectively enhanced the fire resistance and ensure macro- and micro-cellular structure of RPUF, unlike standalone use of TCPP and MAF. When 20%TCPP was simultaneously used with 5%MAF, the macro- and micro-cellular structures of the residue after cone calorimeter test (CCT) were clearly improved compared with foams prepared using MAF only. Their main advantage is related to the enhancement of compactness of the char layer and higher density. Compared with foams without flame retardants, the fire resistance of RPUF prepared with 20% RPUF and 5%MAF was enhanced; specially, the LOI was enhanced by 39.2%, MSD and peak heat release rate (PHRR) decreased by 25%, 59.6% respectively. Thus, the use of liquid and solid flame retardants in combination may effectively manufacture RPUF with high quality cellular structures and excellent fire resistance.

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1. Introduction

Rigid polyurethane foams (RPUF) is applied in refrigeration, construction, oil pipeline and furniture because of light weight and low thermal conductivity [1–6]. However, a major limitation of RPUF which possessed a large number of hydrocarbon segment, porous structure, low density and large surface area is easily flammable [7,8]. The selection of flame retardant is important to the enhancement of flame retardancy of RPUF.

Flame retardant is divided into reactive-type [9–11] and addition-type [12–19]. The addition-type flame retardants are

divided solid and liquid. Numerous works reporting the effect of addition-type flame retardants on mechanical, thermal and flame retardant properties of RPUF have been published [12,13]. However, solid flame retardant increase the viscosity in the matrix, while liquid flame retardant decrease the viscosity, thus the compounded solid-liquid flame retardants can regulate the viscosity to obtain uniform cell structure of flame-retarded RPUF. Some researchers focused on the compounded flame-retardant system in the PU nanocomposites. Modified layered silicate [14], organically-modified montmorillonite (OMMT) [15], expandable graphite (EG) [16–19], were used as nanomaterials to combine with phosphorous flame retardants in the PU nanocomposites. Solid-liquid compounded flame-retardant system not only can reduce the dosage of flame retardants, but also better flame retardancy was achieved than they were used alone. The extraordinary flame

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retardant performance is attributed to the formation of a mass of integrated, stable and tight charred layers.

Aramid fiber (AF) composed by benzene and amide is widely used in high performance composite materials owing to its light weight, high strength, modulus and excellent thermal stability, fire resistance [20]. AF has advantage in fire resistance which is decided by the macromolecular structure of high crystallization and orientation. AF will be one of the most ideal flame retardants. Given that AF modified by phosphoric acid imposes excellent flame retardancy on RPUF in condensed phase [21], tris(1-chloro-2-propyl)phosphate (TCPP) can be combined that acts in gaseous phase [22–24], which was incorporated into epoxy resin [25] and RPUF [26], because of its excellent gaseous and condensed phase [27] flame-retardant effects. This type of composition of flame retardants can result in better flame retardancy in PU foams. To our best knowledge, the effect of tris(1-chloro-2-propyl)phosphate (TCPP) and modified aramid fiber (MAF) on cellular structure, thermal stability and flammability of rigid polyurethane foams (RPUF) have not been reported.

In this study, we mixed TCPP with MAF and prepared flame-retardant RPUF. Phosphoric acid was used to modify AF. For comparison, the pure RPUF, the RPUF containing TCPP, RPUF with AF and MAF alone and the PU/TCPP/AF foams were also fabricated. The cell structure, thermal degradation and flame-retardant properties, were characterized by scanning electron microscope (SEM), thermogravimetric analysis (TGA), limited oxygen index (LOI), gas chromatography/mass spectroscopy (GC/MS), max smoke density (MSD) and cone calorimeter test (CCT). The flame-retardant mechanism and decomposition process of the PU/TCPP/MAF foams were analyzed.

2. Experimental

2.1. Materials

Polyether polyol (4110) was supplied by Langfang Huayu innovation technology Co., Ltd. (Hebei, China). The main properties were as follows: density (25 °C): 1.1 g/cm³, hydroxyl number: 430 mg potassium hydroxide (KOH) equiv/g of resin, viscosity (25 °C): 3.283 pa s, functionality: 4.1, average molecular weight: 550 g/mol. Silicone oil used as foam stabilizers, with excellent emulsification, nucleation, and stabilization, was purchased from Jining Huakai Co., Ltd. (Shandong, China). HCFC-141b was purchased from Jining Huakai Co., Ltd. (Shandong, China) and used as a blowing agent. Stannous octoate was used as catalyst and purchased from Zhangjiagang Changhua science and technology Co., Ltd. (Jiangsu, China). Triethylenediamine (TEDA; a dipropylene glycol solution of triethylenediamine; mass fraction of 33%) was also obtained from Zhangjiagang Changhua science and technology Co., Ltd. (Jiangsu, China). TEDA is another catalyst with a strongly basic, clear, colorless-to-straw liquid tertiary amine, excellent stability characteristics, and good gelling ability. TCPP was purchased from Nantong Liwei trade Co., Ltd. (Jiangsu, China). The main properties of TCPP were as follows: boiling point, 200 °C; decomposition temperature, 200 °C; phosphorus content, 9.4 ± 0.4 wt%; chlorine content, 32.4 ± 0.4 wt%. Polymeric isocyanates (MDI, 5005) was purchased from Langfang Huayu innovation technology Co., Ltd. (Hebei, China). The main performance of MDI were as follows: isocyanate equivalent weight: 126.5 g, NCO weight percent: 30%, viscosity (25 °C): 215 × 10⁻³ pa s, functionality: 2.2. All the chemicals were used as received.

2.2. Surface modification of aramid fiber by phosphoric acid

Processing: AF was impregnated in bath ratio of 1:20

phosphoric acid solution for 30 min ultrasonic, and put in the oven by maintaining a temperature of 130 °C for 5 min, then used deionized water repeatedly to clean, lastly put in the oven to dry by maintaining a temperature of 70 °C for 8 h, and put in the sealing bag to keep after drying. The chemical structure of MAF was shown in Fig. 1.

2.3. Preparation of PU foams

All the PU foams were prepared by a one-shot, free-rise method using a cast mold in our laboratory. TCPP was used as flame retardant. According to the formulations listed in Table 1, at room temperature, we pre-mixed polyether polyol (4110), TCPP, AF and MAF with an electric stirrer to obtain a uniform mixture. Silicone oil, stannous octoate, triethylenediamine, polymeric isocyanates (MDI, 5005) was then added immediately into the mixture, and the mixture was stirred again for an additional 15 s at an elevated stirring speed. Upon expansion, the mixture was instantly poured into an open mold (250 mm × 250 mm × 50 mm) to obtain free-rise foam. Finally, the foams were placed in room temperature of curing for 24 h. After foaming, the products were removed from the mold. The samples were cut into the desired shapes and sizes according to the corresponding testing standards for the evaluation of different properties. According to the method, five specimens were obtained.

2.4. Characterization

FTIR spectra recorded with a Nicolet is 10 FTIR spectrometer were used to detect the chemical structure of the flame retardant foams and some of the raw materials. Typically 100 scans within the range of 4000–500 cm⁻¹ were done for each sample with the resolution of 2 cm⁻¹ and summed up to get the spectra.

The dispersion of AF and MAF in RPUF was obtained with an X-ray diffractometer (XRD, RIGAKU Ultimate IV, Japan) using Cu K α radiation from 3° to 45°.

The photographs of the flame retardant PU foams were obtained by scanning electron microscopy (SEM). Samples were covered with gold for SEM observation.

Thermogravimetric analysis (TGA) was performed on Q500 (TA instrument). Tests were conducted on 2–5 mg sample under nitrogen atmosphere (flow of 50 ml/min) at a heating rate of 10 °C/min from 30 to 800 °C.

The limiting oxygen index (LOI) was obtained using an Automatic LOI instrument (Fire Testing Technology (LFY-605), China) according to GB/T 2406.2–2009. The sheet dimensions were 100 mm × 10 mm × 10 mm.

Gas chromatography/mass spectroscopy (GC/MS) analyses were performed on a TSQ Quantum XLS under the following conditions: the injector temperature was set at 250 °C, and the interface temperature of GC/MS was maintained at 230 °C; the temperature program began at 40 °C, was held for 4 min, and increased to 150 °C at a rate of 5 °C/min, and increased to 240 °C at a rate of 10 °C/min, was held for 5 min, the transfer line temperature was 235 °C.

Max smoke density (MSD) was obtained using Modis smoke density test instrument (XP-2, China) according to GB/T8627-2007. The sheet dimensions were 25 mm × 25 mm × 6 mm. The mass of foams before and after MSD were measured respectively, then defined as m_{bef} and m_{aft} . We defined the ratio of ($m_{bef}-m_{aft}$) to m_{bef} as the mass loss rate (MLR).

The fire behavior was characterized using an FTT cone calorimeter according to ISO5660 under an external heat flux of 25 kW/m². The dimensions of the samples were 100 mm × 100 mm × 20 mm. The specific data, including heat release rate (HRR, kW/m²), total heat release (THR, MJ/m²), total

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