



Material Behaviour

Thermal degradation study of rigid polyurethane foams containing tris(1-chloro-2-propyl)phosphate and modified aramid fiber



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ARTICLE INFO

Keywords:

Polyurethane foam
Thermal degradation
TG-FTIR
GC-MS
Aramid fiber

ABSTRACT

The rigid polyurethane foams (RPUF) were prepared using tris(1-chloro-2-propyl)phosphate(TCPP) and modified aramid fiber(MAF) as flame retardants. The thermal degradation behaviors of RPUF and flame retardant RPUF were investigated by thermogravimetric analysis/infrared spectrometry (TG-IR), gas chromatography-mass spectrometry (GC-MS). Char residue for PU composites at different temperatures was analyzed by fourier transform infrared spectra (FTIR). The TGA curves suggested that aramid fiber(AF) has good ability of char formation. In TG-IR measurement, simultaneously use of TCPP and MAF in the RPUF exhibited lower smoke and toxicant production and increased char residue compared to RPUF containing TCPP. Production of toxic gases such as hydrogen cyanide (HCN) was significantly decreased, nonflammable gases carbon dioxide (CO₂) and water were increased. GC-MS illustrated that TCPP and MAF exerted barrier effect in the condensed phase and the quench effect in the gaseous phase. Based on these facts, a potential thermal degradation mechanism was primarily proposed.

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]. More and more building fires are caused by the RPUF, resulting in great loss of life and economic risk [9]. The application of RPUF is limited in the construction industry due to the strict requirements on the flame retardancy. This further necessitates the use of flame retardant (FR) in the manufacturing of RPUF for reduction in smoke/toxic fumes production. Pyrolysis products are important component parts of the smoke gases. So, the research work of pyrolysis process and products is very necessary for fire hazards of flame-retardant RPUF.

Many studies have been conducted on the thermal degradation mechanism of different kinds of polyurethane(PU) materials [10–13]. With different types of isocyanates, polyols or additives, PU can have different molecular structures and properties. And the thermal degradation behavior depends on the structure of the PU material. Chattopadhyay et al. [3] gave a detailed review on the thermal stability and flame-retardant mechanism of various widely used polyurethane materials. Tris(1-chloro-2-propyl)phosphate(TCPP) is one of the most popular halogenated flame retardants used in RPUF because it is

economical and efficient [14,15]. The thermal decomposition and flammability of PU with TCPP was reported by Refs. [16–18]. The thermal degradation of TCPP in the PU foams was investigated by Georg Matuschek et al. [16], who found that TCPP is not only active in the gas phase but also in the condensed phase with a high char-forming ability, in which the phosphorus is active in the condensed phase and the chlorine in the gaseous phase. Liu et al. [17] investigated the pyrolysis process and products of RPUF containing TCPP by using thermogravimetric analysis/infrared spectrometry (TG-IR) and pyrolysis-gas chromatography-mass spectrometry (Py/GC-MS). It was indicated that the use of TCPP results in an increase in the smoke toxicity of PU as large amount of toxic and corrosive gases such as carbon monoxide (CO) and hydrogen chloride (HCl) are released during the combustion process [18], which are not conducive to evacuation and rescue operations. Phosphoric acid and chloropropanol are formed in the presence of acids and bases. To substitute the halogenated flame retardants, development of new and efficient environment friendly halogen-free flame retardants are needed. Addition of recycled environmental friendly fiber in RPUF can make up the increment of smoke fumes production. Aramid fiber (AF) has become one of the most ideal environmental friendly flame retardant and been attracted tremendous attention owing to its excellent fire resistance and smoke suppression [19–21]. AF suffers from a poor interfacial interaction with polymer matrix due to its chemical inert and smooth surface [22,23]. The

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modification of AF proves to be necessary to increase active groups, such as -COOH, -OH, =CO and -NH₂ on the surface of fiber to improve bonding strength with the matrix [24–26]. Deng ting-ting et al. had studied the modification of para-aramid fiber by phosphoric acid [27]. The results showed that -P-OH groups were introduced to the surface of AF. Chen et al. studied a recycled environmental friendly flame retardant by modifying para-aramid fiber with phosphorus acid for thermoplastic polyurethane elastomer(TPU) [21]. The results revealed that aramid fiber modified by phosphorus acid (AF-P) had improved flame retardant effect and thermal stability of TPU, more importantly reduced the release of carbon dioxide (CO₂) at the beginning. Many investigations on thermal degradation behavior of TCPP and modified aramid fiber(MAF) standalone in the PU materials have already been reported, but there is a lack of data concerning the TG-IR and gas chromatography-mass spectrometry (GC-MS) characterization of volatile compounds from RPUF containing TCPP and MAF.

In this study, TCPP was mixed with MAF in the RPUF. Phosphoric acid was used to modify AF. For comparison, the pure RPUF, the RPUF containing TCPP, RPUF with MAF alone were also fabricated. The thermal behavior of RPUF was analyzed using TG-IR. FTIR spectra of residue for PU/TCPP/MAF at different temperatures and GC-MS analyses were further carried out to elaborate the thermal decomposition mechanism of flame-retardant RPUF and to study the effect of TCPP and MAF on their gaseous and condensed phase action.

2. Experimental

2.1. Materials

Polyether polyol (4110, 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) was supplied by Langfang Huayu innovation technology Co., Ltd. (Hebei, China). Silicone oil used as foam stabilizers, with excellent emulsification, nucleation, and stabilization, were purchased from Jining Huakai Co., Ltd. (Shandong, China). 1,1-dichloro-1-fluoroethane (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 di-propylene glycol solution of triethylenediamine; mass fraction of 33%), which is an effective catalyst for RPUF, was also obtained from Zhangjiagang Changhua science and technology Co., Ltd. (Jiangsu, China). Tris(1-chloro-2-propyl)phosphate(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%. Aramid fiber(AF) was purchased from Tongxiang Xuantai Composite materials Co., Ltd. (Zhejiang, China). The basic properties of AF are as follows, density: 1.44 g/cm³ (ISO1183); short cut fiber length: 3 mm; filament diameter: 11.6 μm; elastic modulus: 80 GPa (ISO527-2); fracture strength: 19.4cN/dtex (ISO6383-1). Phosphoric acid was purchased from Guoyao chemical reagent Co., Ltd. Polymeric isocyanate (MDI, 5005, isocyanate equivalent weight: 126.5 g, NCO weight percent: 30%, viscosity (25 °C): 215 × 10⁻³ pa s, functionality: 2.2) was purchased from Langfang Huayu innovation technology Co., Ltd. (Hebei, China). 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.

Table 1
Formulations of TCPP and fiber in the matrix.

No.	TCPP	AF	MAF
RPUF-1			
RPUF-2	20		
RPUF-3		5	
RPUF-4			5
RPUF-5	20	5	
RPUF-6	20		5

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, AF and MAF were used as flame retardants. 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 isocyanate (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 24h. 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.

2.4. Characterization

The thermal stability and the thermal decomposition performance of the samples were tested by a thermogravimetric analyzer(DT-50) (Setaram Instrumentation Co., Led., France) at a heating rate of 20 °C/min under the nitrogen flow of 60 mL/min, the needed sample is about 10 mg, placed in an alumina crucible and temperature ranged from 30 to 700 °C. The components analysis of the pyrolysis gas from TG analyzer was performed by a FTIR spectrometer (170SX) (Shimadzu, Japan), and the wavenumber range was set from 4000 to 500 cm⁻¹.

Changes in the functional groups of decomposition residues at different temperatures were characterized by a Nicolet is 10 FTIR spectrometer. 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.

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.

3. Results and discussion

3.1. Thermogravimetric analysis

Thermal behavior of the RPUF and flame-retardant RPUF in nitrogen were investigated by TGA and DTG, the results are shown in Fig. 1 and summarized in Table 2. The thermal degradation of the RPUF shows two main stages: in the first stage RPUF was decomposed into 1,1-dichloro-1-fluoroethane, small molecule water, polyol and isocyanates; in the second stage polyol and isocyanates were decomposed into small molecule amine compounds, carbon dioxide, alkene and water [2,10]. Nevertheless, the change in weight associated with each step, the onset of decomposition temperature(T_{5%}), the residue at high temperature, the temperature of the maximum rate of weight loss and the mass loss rate in the main decomposition step are different for the

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