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Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS

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ABSTRACT

Thermal degradation characteristics of rigid polyurethane (PUR) foam in both air and nitrogen gaseous environments were studied using thermogravimetry and differential scanning calorimetry (TG-DSC) hyphenated techniques. And in situ Fourier Transform Infrared (FTIR) was employed to investigate the characteristic functional groups of the decomposition residues at different temperatures. It is found that the thermal degradation of PUR material in air and N_2 present a three-stage and a two-stage process, respectively. And the degradation reaction rate of PUR in air is accelerated significantly due to the presence of oxygen. The thermal degradation mechanism of PUR under non-oxidizing gaseous environment was evaluated using a TGA instrument coupled with Fourier Transform Infrared and mass spectrometer (TG-FTIR-MS). HCFC-141b served as blowing agent is detected at the initial stage. The urethane bond groups of PUR start to break up into isocyanates segments and polyols segments from about 200 °C. With an increase of temperature, the polyols decompose into some kinds of aliphatic ether alcohol. In the temperature range of 350–500 °C, the dominant volatile products are primary amines, secondary amines, vinyl ethers and CO_2.

1. Introduction

Polyurethane (PU) is a kind of high polymer with a basic repetitive unit urethane bond (NHCOO). It can be produced from the polymerization of isocyanates, polyols and some kinds of additives. The products of PU materials are widely used all over the world, such as coatings, adhesives and elastomers. Rigid polyurethane foam (PUR) is one of the most important PU products, and in particular it is usually utilized to produce insulation material for building facade. However, the PUR materials are highly flammable and the flame spread quite fast in case of fire. With the increasing applications of PUR as insulation materials, more and more building fires were caused, resulting in great economic and life loss. It is generally accepted that the thermal degradation of materials is the initial step of solid combustion processes and the pyrolysis products that contain gaseous fuel support the combustion [1]. Thus, it is of great importance to study the thermal degradation characteristics and volatile products of PUR insulation materials.

Many studies have been conducted on the thermal degradation mechanism of different kinds of polyurethane materials [2–5]. 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 PUR material. Chattopadhyay et al. [6] gave a detailed review on the thermal stability and flame-retardant mechanism of various widely used polyurethane materials. Information about the processes occurring during the thermal stress, factors influencing the thermal stability, and methods to improve the thermal stability and flammability of PUs were presented. Kulesza et al. [7] investigated the thermal degradation of PUR blown with pentane by using TG–MS, TG–FTIR and Py/GC–MS. Four temperature ranges of gaseous products evolution were detected under inert atmosphere and pentane volatilized at the initial stage. It was suggested that thermal degradation of PUs based on polyester polyols might be occurred by increased bond strain of polymer chain due to temperature increasing and the sequence of thermal degradation in polymer chain is from hard segment to soft segment [8].

A large majority of the previous works focused on the influence of flame retardants on the thermal degradation behavior [9–13]. The flame-retardant mechanism of PU foams and efficiency of different flame-retardant additives were investigated. However, few literatures can be found on the degradation mechanism of PUR material itself when it is heated, especially for building facade fires. In our earlier work [14], we investigated the kinetic parameters and the decomposition products of three typical insulation materials for building insulation system applications. In this study, we attempt to

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obtain more details with respect to the degradation mechanism of PUR insulation material. The PUR employed in this study had no fire retardant (FR), and the formula used was typical for building insulation systems in the materials market. Thermal degradation characteristics of PUR foam are studied by means of thermogravimetry and differential scanning calorimetry (TG-DSC) hyphenated techniques. In order to investigate the characteristic functional groups of the decomposition residues, in situ Fourier Transform Infrared (FTIR) is employed. And the volatile products in helium are studied using a TGA instrument coupled with FTIR spectroscopy and mass spectrometer (TG-FTIR-MS). We combined the analysis results of decomposition residues and evolved products in the non-oxidizing gas environment to obtain more information on the thermal degradation mechanism.

2. Experimental

2.1. Materials

The materials were produced by Shanghai Saikun rubber and plastic products co., LTD in China. And the formula (composed of polyether polyols, isocyanates, catalyst, blowing agent and some other additives) used in this work was typical for building insulation systems in the materials market. Rigid polyurethane foams were grinded to powder in mortar for all the experiments.

2.2. TG-DSC hyphenated technique

The TG-DSC experiments were carried out on a SDT Q600 from TA Instruments in air and nitrogen, respectively. The sample weights about 4 mg, heated up to 700 °C at a heating rate of 10 °C/min, and the flow rate of the both gases was 100 mL/min.

2.3. In situ FTIR tests

Changes in the functional groups of decomposition residues at different temperatures were characterized by in situ FTIR spectroscopy (Nicolet 8700 from Thermo Electron Corporation). The pressed-disk technique was utilized with KBr and CaF_2 in air and nitrogen, respectively. Therefore, one of the spectral ranges was from 4000 to 400 cm^{-1} while the other was 4000–1000 cm^{-1}.

2.4. TG-FTIR-MS experiment

On-line testing of gaseous products obtained during the thermal degradation was performed using a Perkin Elmer Pyris 1 TGA coupled with Frontier FTIR spectroscopy spectrophotometer and a Clarus SQ 8T mass spectrometer (TG-FTIR-MS). The sample was heated from room temperature up to 800 °C at a heating rate of 10 °C/min in helium, with a gas flow rate of 75 mL/min. The connections for gas transportation between the apparatuses were set at 190 °C to allow the decomposition products in a gaseous state.

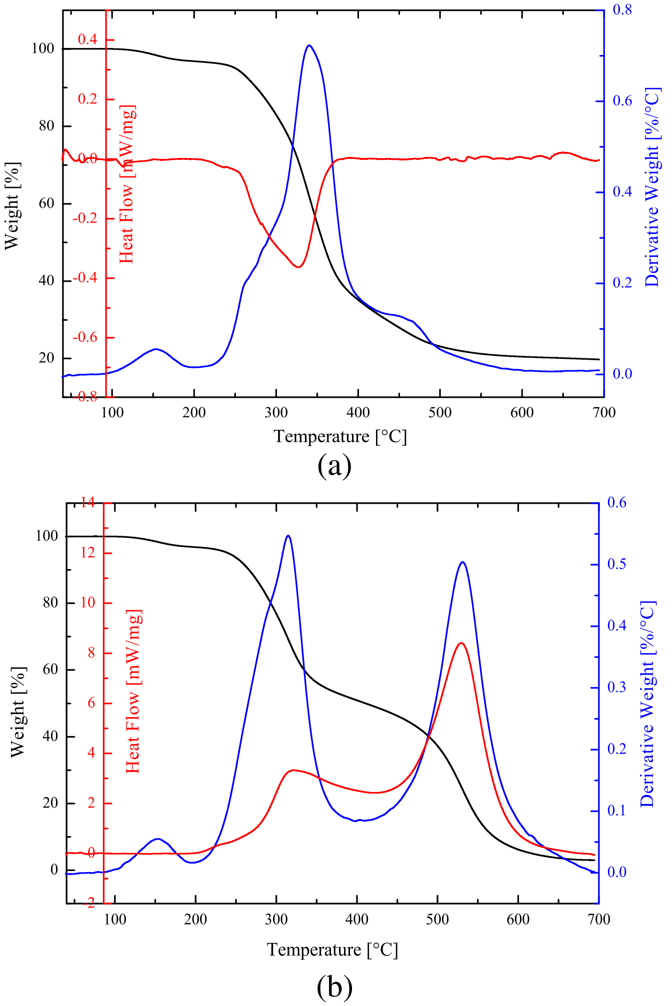

Fig. 1. TG and DSC curves of rigid PU foams in (a) nitrogen and (b) air atmospheres at 10 °C/min.

3. Results and discussion

3.1. Thermal degradation behavior

Fig. 1 shows the TG and DSC curves of rigid PU foams in (a) nitrogen and (b) air at a heating rate of 10 °C/min. It is obvious that the thermal degradation of rigid polyurethane foam (PUR) in nitrogen and air show a two-stage and three-stage process, as presented in Fig. 1(a) and (b), respectively. Table 1 gives the parameters obtained from TG and DSC results during the thermal degradation of PUR. In both air and nitrogen, small amount of weight loss (about 3%) can be observed between 110 and 190 °C, as listed in Table 1. It indicates that the evaporation of water and some small molecules products predominate in this stage and most of the chemical bonds have not begun to break up (which will be confirmed later).

Table 1
Parameters obtained from TG and DSC results of the thermal degradation of PUR.

Atmosphere	The temperature range of each stage (°C)	Weight loss (%)	T_{max} (from DSC curve)	Residue (%)	Heat (J/g)
N_2	110–190	3	340 °C	20	−156.42 (absorption)
	220–600	76.5			
Air	110–190	2.7	314 °C, 530 °C	3	+7201.52 (release)
	210–397	46			
	397–670	48.3			