



Enhanced polyimide proportion effects on fire behavior of isocyanate-based polyimide foams by refilled aromatic dianhydride method



Gaohui Sun^{a, b}, Lianhe Liu^{b, *}, Jun Wang^a, Hongliang Wang^a, Zhong Xie^b, Shihui Han^{a, **}

^a Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

^b Institute of Advanced Marine Materials, Harbin Engineering University, Harbin 150001, China

ARTICLE INFO

Article history:

Received 19 October 2013

Received in revised form

1 August 2014

Accepted 11 August 2014

Available online 20 August 2014

Keywords:

Isocyanate-based polyimide

Foam

Refilled

Fire resistance

ABSTRACT

Lightweight and fire-resistant isocyanate-based polyimide foams (PIFs) were rapidly formed via a simple one-pot process; polymethylene polyphenylene isocyanate (PAPI) was added into a solution containing refilled aromatic dianhydride. The obtained Fourier transform infrared spectra (FT-IR) showed that the refilled 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) reacted with isocyanate and amino groups in PIFs during the forming and postcuring process. These reactions increased the percentage of polyimide in the foams. Meanwhile, the reaction between refilled BTDA which has a higher reactivity than its derivatives and amino groups, reduced the reaction between isocyanate and amino groups. Subsequently, the generation of ureido was restrained. Thermal gravimetric analysis (TGA) and differential thermogravimetry (DTG) results presented that when the refilled BTDA dosage was increased, the percentage of polyimide and ureido were increased and reduced, respectively. However, the proportion of different ingredients in the PIFs prepared by different formulations was basically the same when the refilled BTDA dosage exceeded 50%. As such, the refilled dosage of BTDA between 50% and 60% was sufficient for this system, the refilled BTDA had extreme effects on enhancing polyimide proportion and reducing the generation of ureido. Fire resistance was characterized by limiting oxygen index (LOI) and cone calorimeter (CCT). Results showed that with the gradual increasing in polyimide proportion of the PIFs resulting from the increase in refilled BTDA dosage, their fire resistance was remarkably improved, which was mainly reflected by the following: gradual increase in LOI value, decrease in heat release rate (HRR), decrease in the peak of HRR (PHRR), decrease in total smoke production (TSP), and decrease in average specific extinction area (ASEA). Compared with the foam prepared without refilled BTDA, the foam prepared with 60% BTDA refilled dosage exhibited increased LOI value from 20.8% to 30.1%, PHRR reduction from 181.91 kW/m² to 41.54 kW/m², and significant reduction of HRR. The reduction in TSP and ASEA reached up to 78.2% and 83.1%, respectively. Meanwhile, when the refilled dosage of BTDA exceeded 60%, the LOI value also showed a slower increase. This change was possibly due to the residual BTDA in foams, which acted as a retardant packing role. The density of foams also increased when the post-additive dosage of BTDA was increased. Possible chemical reactions involved in this preparation method of isocyanate-based PIFs were also discussed in this paper.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

In the late 1960s, DuPont Company first developed polyimide foams (PIFs) based on a polyimide precursor-polyamide acid [1,2].

Afterwards, numerous studies have reported about methods to produce PIFs using polyimide precursor and powders [3]. The imide rings in the molecular skeleton endow the unique qualities of the foams, including high fire resistance, chemical resistance, and thermal stability [4–6]. Meanwhile, these foams can also have excellent acoustic absorptions and low thermal conductivities that are dependent upon foam architecture [7,8]. Given these superior properties, PIFs are widely used as thermal and acoustic insulation materials in many advanced technological applications, such as spacecraft, aircraft, marine, and high-speed trains [9–14]. At the

* Corresponding author. Tel./fax: +86 451 82568275.

** Corresponding author. Tel./fax: +86 451 82568276.

E-mail addresses: sungaohui1987@163.com (G. Sun), liulianhe@hrbeu.edu.cn (L. Liu), hsh@hrbeu.edu.cn (S. Han).

same time, the low density of PIFs is favorable for use in lightweight devices, especially in transportation [15,16].

However, PIFs prepared from polyimide precursor solutions and powders show some serious issues, which mainly due to their limited applicability and complexity of process [3]. Meanwhile, their intricate production process generates an expensive market price for PIFs. According to our market survey, the usual price of PIFs is several times higher than polyurethane and polystyrene foams, which are widely used in homes, public buildings, automobiles, and low-temperature storage industries [17,18]. Thus, the application of PIFs in these fields is limited.

In the middle-late 1960s, isocyanate-based PIFs were successfully prepared using poly-isocyanate and aromatic anhydride to simplify process routing, reduce cost of fabrication, and expand the application field of PIFs [19,20].

Over the past decades, much effort has been given to the production of isocyanate-based PIFs because of their simple preparation process and short production cycle. Horst E. Frey [19] and Gerald W. Miller [21] adopted two different preparation methods for such PIFs. In the first method, the foaming and postcuring process are all conducted at temperatures higher than 200 °C. High temperature facilitates high expansion ratio and low density for isocyanate-based PIFs. In the second method, the foaming process is realized facilely at ambient conditions by the reaction of water and isocyanate. Thus, the preparation technology is simplified compared with the first method [22–24].

However, the second preparation method for isocyanate-based PIFs also holds a challenge, which is mainly the competition of reactions between aromatic anhydrides derivatives and amino groups, as well as the reactions between isocyanate and amino groups. The reaction between aromatic anhydride derivatives and amino groups generates polyimide precursors, which can be transferred into polyimide in the postcuring process. However, the reaction between isocyanate and amino groups produces ureido, which has relatively poor thermal stability and low fire resistance compared with polyimide. Zhan MS [13] prepared an isocyanate-based PIFs by the second method; although the dosage of aromatic derivatives was in excess, a mass of ureido was generated in the foams. Therefore, to prepare foams with high fire resistance, the generation of polyimide should be enhanced, whereas the generation of ureido should be reduced. Meanwhile, little information has been reported about the fire resistance of isocyanate-based PIFs.

In the present study, a novel method for improving the generation of polyimide and reduction of ureido was proposed to fabricate isocyanate-based PIFs with excellent fire resistance. The reactions between amino groups and aromatic anhydrides or its derivatives underwent nucleophilic substitution, wherein anhydrides present higher reactivity than its derivatives [25]. Thus, the reaction between amino groups and anhydrides present a faster rate and higher extent than its derivatives, which effectively reduced the generation of ureido. However, the solubility of aromatic anhydride in polar solvent is usually poor. Therefore, in this novel method, the aromatic anhydride powder was added directly into the precursor solution. 3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA), with high electron affinity energy (E_a) of 1.55 [8], was used in this study. During the foaming process, the reaction between BTDA and amino groups effectively reduced the production of ureido and enhanced the generation of polyimide precursors. In the postcuring process, the polyimide precursor was transformed into polyimide, and the residual BTDA and isocyanate reacted further to produce polyimide. Both of these routes increased the polyimide proportion and decreased the ureido production. The effects of improved polyimide proportion on thermal stability and fire resistance were investigated by

thermal gravimetric analysis (TGA), limiting oxygen index (LOI), and cone calorimeter test (CCT). A novel and simple process was developed to fabricate isocyanate-based PIFs with improved performance. The simple preparation process and outstanding properties of these isocyanate-based PIFs enable their applications in various fields.

2. Experimental

2.1. Materials

BTDA (>99.5% purity) was supplied by Beijing Multi Technology Co., Ltd, China. BTDA was dried in vacuum for 12 h prior to use. The analytical reagents N,N-dimethyl formamide (DMF) and methanol, as well as triethylenediamine ($\geq 96\%$ purity), were acquired from Sinopharm Chemical Reagent Co., Ltd, China. Dabco-33 (33% triethylenediamine in dipropylene glycol by weight) was synthesized by dissolving 10 g triethylenediamine in a solution containing 20 g dipropylene glycol (Tianjin Guangfu Fine Chemical Institute, China) at 30 °C. The catalysts, triethanolamine and dibutyltin dilaurate (T12) used as catalysts, were also purchased from Tianjin Guangfu Fine Chemical Institute, China. The surfactants, polysiloxane-polyether copolymer (AK8805) and polyethylene glycol-600 (PEG-600), were obtained from Nanjing Dymatic Shichuang, China, and Tianjin Guangfu Fine Chemical Institute, China, respectively. Deionized water was obtained using a Milli-Q Academic ultrapure water system and used as blowing agent. Industrial-grade polymethylene polyphenylene isocyanate (PAPI) trade name PM200, which contains 31.3 wt% free isocyanate groups with an average functionality of 2.7, viscosity of 204 mPa s⁻¹ (25 °C), and isocyanate equivalent weight of 134, was obtained from Yantai Wanhua Polyurethanes Co., Ltd., China.

2.2. Samples preparation

2.2.1. Preparation of component A

First, 68.0 g BTDA was added into 100.0 g DMF at room temperature. The suspension was stirred and heated to 110 °C until BTDA was completely dissolved. To esterify BTDA completely, the solution was cooled below 60 °C, and then 14.1 g methanol (the molar ratio of BTDA to methanol was 0.5:1.05) was dropped into the solution for 5 min with magnetic stirring. Completed esterification reaction condition of BTDA with methanol was 3.5 h heating and stirring of above solution at 60 °C. Subsequently, the solution was cooled to room temperature to obtain component A. The Fourier transform infrared (FT-IR) spectrum of component A is presented in Fig. 3.

2.2.2. Composition of first solution and preparation of foams

First, 20 g component A was poured into a plastic container, then 0.4 g Dabco-33, 0.2 g T12, 1.0 g triethanolamine, 2.5 g AK8805, 2.5 g PEG-600, and 2.4 g deionized water were added into the cup in turns. The mixture was thoroughly mixed for 5 min using a glass rod to obtain a homogeneous precursor solution. BTDA powder was immediately added into the precursor solution. The resulting mixture was then stirred for 2 min using a glass rod to obtain a homogeneous suspension. The resulting suspension was named as first solution. According to our previous study, in the first solution BTDA does not react with MeOH, PEG-600, triethanolamine, and triethylenediamine, under ambient conditions. Hydrolysis between partial BTDA and water occurred under ambient condition, which generated 3,3',4,4'-benzophenone tetracarboxylic acid. This reaction could be proved by FT-IR spectroscopy of the PIF-20 first solution. Afterwards, 30 g pre-weighed PM200 (second solution) was immediately poured into the first

Download English Version:

<https://daneshyari.com/en/article/5201629>

Download Persian Version:

<https://daneshyari.com/article/5201629>

[Daneshyari.com](https://daneshyari.com)