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Effects of hydrotalcites and tris (1-chloro-2-propyl) phosphate on thermal stability, cellular structure and fire resistance of isocyanate-based polyimide foams

Gaohui Sun [a], Lianhe Liu [b, *], Jun Wang [b], Hongliang Wang [a], Wenpeng Wang [a], 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

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ABSTRACT

Isocyanate-based polyimide foams (PIFs) with different dosages of liquid tri (1-chloro-2-propyl) phosphate (TCPP) and micro-sized hydrotalcites (LDHs) particles alone, as well as different mixing ratios of TCPP and LDHs, were prepared via a one-step process in this work. Limiting oxygen index (LOI) and cone calorimeter test (CCT) results indicated that TCPP exhibited more pronounced flame retardant efficiency than LDHs for isocyanate-based PIFs. However, scanning electron microscopy images and digital macrostructural images results showed that, in contrast to LDHs, when the dosage of TCPP exceeded 10% it caused a clear cracking effects on the macro-cellular structure and opening cell effects on the micro-cellular structure for isocyanate-based PIFs. Because the dramatically volatilization of TCPP during the postcuring process caused obvious cellular contraction in the isocyanate-based PIFs. Meanwhile, the use of TCPP also obviously decreased the thermal stability of isocyanate-based PIFs unlike LDHs. However, when these two flame retardants were used in combination, they could effectively enhance the fire resistance and ensure macro- and micro-cellular structures of the isocyanate-based PIFs, unlike stand-alone use of TCPP and LDHs. When 10% TCPP was simultaneously used with 10% LDHs, the macro- and micro-cellular structures of the resultant foams were clearly improved compared with foams prepared using TCPP only. These results were believed to be attributable to LDHs dispersion in the foams, which enhanced the strength of cellular windows and skeletons, then restrained the cell contraction. Compared with foams without flame retardants, the fire resistance of the isocyanate-based PIFs prepared with 10% TCPP and 10% LDHs was obviously enhanced; specially, the LOI was enhanced by 29.4%, and the peak of heat release rate (PHRR) decreased by 36.1%. Thus, the use of liquid and solid flame retardants in combination may effectively yield isocyanate-based PIFs with high quality cellular structures and excellent fire resistance.

1. Introduction

Polyimide foams (PIFs) present pronounced performance, including low density, outstanding flame and chemical resistance, and thermal stability, all of which are attributed to the molecular structure of polyimide. The thermal insulation, acoustic absorption, and shock absorption properties of foams mainly depend on the cellular structure in foams [1–9]. Because of these excellent properties, PIFs are recognized as ideal thermal and acoustic insulation materials for application in many high technology fields. The preparation methods of PIFs mainly include powder and friable microsphere foaming processes; however, high thermal energy and economic costs limit the applicability of these techniques [7]. Another process for preparing PIFs is through utilization of a first solution of aromatic dianhydride or its derivatives and a second solution of isocyanate via the free-foaming approach; the foams formed from this process are called isocyanate-based PIFs [7,10–12]. Isocyanate-based PIFs also present excellent thermal

* Corresponding author. Tel./fax: +86 451 82568275.
** Corresponding author. Tel./fax: +86 451 82568276.
E-mail addresses: liulianhe@hrbeu.edu.cn (L. Liu), hsh@hrbeu.edu.cn (S. Han).

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stability, acoustic absorption, and thermal insulating properties [7,10]. The free-foaming process significantly simplifies the technical route, thereby decreasing process costs and material prices. This makes it possible that PIFs can be used in common applications such as in homes, low temperature processes, and public building industries that require inexpensive acoustic absorption and thermal insulating materials. Now, these industries mainly use polyurethane and polystyrene foams as acoustic absorption and thermal insulating materials [13,14]. Unlike PIFs, polyurethane and polystyrene foams present poor thermal stability and service lives. Thus, isocyanate-based PIFs are being widely studied by many scientists and suitable for a wide range of applications.

Unfortunately, some properties of isocyanate-based PIFs, such as their fire resistance, are fairly low because of the presence of the vast flammable by-products, including ureido and urethano groups in the macromolecular chains; which restricts the wider application of isocyanate-based PIFs. Utilizing of flame retardants is the most effective and economic route to enhance the fire resistance and application security of polymeric foams in polymeric foamed material filed. However, unlike other polymeric foamed materials, the preparation of isocyanate-based PIFs requires high-temperature postcuring process. Most flame retardants exhibit volatilization or decomposition behavior during the postcuring process. May be for this reason, only a few detailed studies on flame retardants used for isocyanate-based PIFs and their effects on thermal stability, fire resistance, cellular structure, and other isocyanate-based PIFs performance parameters have been reported.

Hydrotalcites are layered double hydroxides (LDHs) used in different applications because they are abundant, non-toxic, environment-friendly and inexpensive, the general chemical composition of LDHs is expressed as $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[(Y)^{m-}_{x/m}]\cdot nH_2O$ [15,16]. The general formula of hydrotalcites with Mg^{2+} and Al^{3+} is $[Mg_{1-x}Al_x(OH)_2]^{x+}[(CO_3)^{m-}_{x/m}]\cdot nH_2O$; this material widely used as an effective and environment-friendly inorganic flame retardant because of its synergistic effect in flame-retarded polymers between MH and ATH [16–18]. Flame-retardant LDHs function as a heat release rate (HRR) reducer and smoke suppressant [16]. LDHs act in both the condensed and gas phases during a fire, and the thermal decomposition process of LDHs follows an endothermic reaction that results in a decrease in the temperature of matter and release of water into the gas phase to dilute flames [19,20].

Tri (1-chloro-2-propyl) phosphate (TCPP) is a liquid flame retardant widely used in polymeric foamed materials such as polyurethane and polystyrene foams because of its low price and pronounced flame retardant efficiency, which is ascribed to chlorine and phosphate groups in its molecular structure [21]. The efficacy of TCPP is due to the catching of radical patterns in the gas phase and char formation mode in the condensed phase [21]. Compared with solid-state LDHs, liquid-state TCPP can disperse better in the modular solution used to prepare foamed materials, which ensures uniform dispersion in foams. Although studies on the application of flame retardants in isocyanate-based PIFs have been reported, these reports mainly concentrate on the singular use of solid organic phosphate flame retardants [11]. Few studies on the effects of inorganic flame retardants on the fire-retarding behavior of isocyanate-based PIFs, as well as the synergistic effects of combined inorganic and liquid flame retardants on the fire-retarding behavior, cellular structure, and other performance parameters of isocyanate-based PIFs have been reported.

Therefore, more studies are required to understand the influence of different types of flame retardants on the fire resistance and other performance parameters of isocyanate-based PIFs. LDHs and TCPP are excellent solid and liquid flame retardants, respectively. The present study attempts to investigate the individual and synergistic effects of these two flame retardants on enhancing the fire resistance of isocyanate-based PIFs. A simple preparation process for fabricating isocyanate-based PIFs with high fire resistance is used. The effects of these two flame retardants on the thermal stability, cellular structure, and morphology of isocyanate-based PIFs are also discussed. This study attempts to determine suitable conditions and formulas for manufacturing isocyanate-based PIFs with enhanced fire resistance and uniform inner cellular structures to allow their wider use in common technological fields in the future.

2. Experimental section

2.1. Raw materials

3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) with a purity exceeding 99.5% was supplied by Beijing Multi Technology Co., Ltd, China, it was dried in vacuum for 12 h prior to use. Analytical reagents N, N-dimethyl formamide (DMF) and methanol were acquired from Sinopharm Chemical Reagent Co., Ltd, China. The catalysts, triethanolamine and dibutyltin dilaurate (T12), 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 used as blowing agent and obtained using a Milli-Q Academic ultrapure water system. 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. Industrial-grade tris (1-chloro-2-propyl) phosphate, which has a purity level exceeding 99.5%, decomposition temperature higher than 230 °C and viscosity of 65 mPa s^{-1} (25 °C), was supplied by Qingdao United Chemical Co., Ltd., China. ALCAMIZER®1-C hydrotalcites (LDHs) with a purity level exceeding 99.5% was acquired from Dandong Songyuan Chemicals Co., Ltd., China. TCPP and LDHs were used as flame retardants.

2.2. Preparation of the first solution

The first solution was a mixture of component A, catalysts, surfactants, water, and flame retardants. Component A was produced by esterification reaction of BTDA with methanol according to the procedures previously reported [22]. Firstly, 20 g of component A, 0.5 g of T12, 1.0 g of triethanolamine, 3.0 g of AK8805, 3.0 g of PEG-600 and 2.5 g of deionized water were each added into a plastic container. The mixture was thoroughly mixed for 5 min using a glass rod to obtain a homogeneous precursor solution. Flame retardants were then immediately added into the precursor solution. The resulting mixture was then stirred for 2 min using a glass rod to obtain a homogeneous system that was labeled as the first solution.

The first solutions with different flame retardant dosages and flame retardant matching were prepared according to the formulations listed in Table 1. We now presented four sets to study the individual and synergistic effects of these two different flame retardants on the properties of isocyanate-based PIFs. The mass fraction of LDHs and TCPP for every formulation listed in Table 1 was the mass ratio of $w2/w1$ (i.e., $w2$ was the corresponding dosage of each flame retardant). The first set of samples contained only LDHs (i.e., 0, 5, 10, 15, and 20 wt%) and were marked as PIF-1 to PIF-5. The second set of samples contained only TCPP (i.e., 0, 5, 10, 15, and 20 wt%) and were marked as PIF-1 and PIF-6 to PIF-9. The