

ORIGINAL RESEARCH ARTICLE

Flame Retardant Effect of Isocyanate Trimer on Polyisocyanurate Foam

Mingyang Du, Chunze He, Canhui Zhou

School of Materials Science and Engineering, Chengdu Jiaotong University, Sichuan, China

ABSTRACT

The effect of Isocyanate trimer on the flame retardancy mechanism of polyisocyanurate (PIR) foam was studied through 3 aspects including the mechanism of thermal decomposition stage in condensed phase, the barrier mechanism of carbon layer formation on the surface in condensed phase and the mechanism in gaseous phase by using infrared spectroscopy, scanning electron microscopy, thermal analysis, cone calorimeter, high temperature pyrolysis gas chromatography mass spectrometry. The results show that the trimer can improve the thermal stability of the PIR foam and is not easily decomposed in the combustion. The trimer can increase the carbon content of the PIR foam to 29.9% than that of the polyurethane (PU) foam. The carbon layer formed is denser, and it can retard heat and oxygen and thus improve the flame retardant properties; trimer can reduce the release of flammable polyol gas, decompose into more carbon dioxide which is inert gas and it has certain flame retardant effect in the gaseous phase.

KEYWORDS: Polyisocyanurate foam; Isocyanate trimer; Flame retardant mechanism

Polyisocyanurate Foam (PIR) is a new type of insulation material used in building construction. Due to the introduction of the isocyanate trimer structure in the foam molecular structure, the temperature and flame resistance of the foam can be improved, in which its thermal stability and flame retardancy are higher than that of the PU foam [1,2].

On the flame retardant mechanism of polymers, the classical flame retardant theory is based on the combustion process designed which including the following aspects: the mechanism of thermal decomposition stage in condensed phase, the barrier mechanism of carbon layer formation on the surface in condensed phase and the mechanism in gaseous phase [3]. Zhan et al. [4,5], Kulesza et al. [6] and Kunze et al. [7] determined the thermal decomposition characteristic of polyurethane (PU) foam at different temperatures and qualitatively analyzed the entire thermal decomposition process of PU by using Thermogravimetric Analysis and Fourier Transform Infrared Spectroscopy (TG-FTIR), thermogravimetric analysis and mass spectrometry (TG-MS) and Pyrolysis gas chromatography mass spectrometry (Py/GC-MS). By using TG and SEM characterization, Hu et al. [8] found that the addition of expandable graphite and dimethyl phosphonate in PIR-PU foam caused its surface carbon layer structure became denser and the thermal stability of the material was increased after combustion. Gao et al. [9] studied the synergistic effect of expandable graphite, ethyl diethyl phosphonate and organic modified montmorillonite by using a cone-shaped calorimeter (CONE) and it shows that the flame retardant property of PIR foam increased, this is due to the formula can promote the formation of carbon layer in which can isolate oxygen and heat effectively.

As a reactive flame retardant structure, the trimer structure has a great effect on the flame retardancy of PIR foam, but the study on the mechanism of its action is still not completely. In this paper, the effect of Isocyanate trimer on the flame retardancy mechanism of polyisocyanurate (PIR) foam was studied through 3 aspects including the mechanism of thermal decomposition stage in condensed phase, the barrier mechanism of carbon layer formation on the surface in condensed phase and the mechanism in gaseous phase by using infrared spectroscopy, scanning electron microscopy, thermal analysis, cone calorimeter, high temperature pyrolysis gas chromatography mass spectrometry.

1. Experimental part

1.1. Experimental materials

Polyester Polyol (PS-3152): Industrial grade, Nanjing Jinling Steinpan Chemical Co., Ltd.; Diphenylmethane diisocyanate (Desmodur44V20L): Industrial grade, Kesiqi Polymer (China) Co., Ltd. Silicone stabilizer (L-6920): Industrial grade, supplied by Kesi Polymer (China) Co., Ltd.; N, N-Dimethylcyclohexylamine (POLYCAT-8): Industrial Grade, Jiangdu Dajiang Chemical Plant; (PU-1792): industrial grade, Jiangdu Dajiang Chemical Plant; HCFC-141b (hydrochlorofluorocarbon-141b): industrial grade, industrial grade, Changshu three love rich fluoride Chemical Co., Ltd..

1.2. Foam test recipe and sample preparation

Due to many elements, the approved design was three months later than planned. Half time has been used for design and construction preparation so the time pressure is very big for the project, how EPC contractor can completes the project is one of the key tasks in run over the project.

Experimental used Foam systems and Foam formulations as shown in Tab. 1

Component	PU	PIR
44V20L (index)	110	350
PS-3152	100	100
PC-5	0.3	0.3
Water	0.5	0.5
HFC-141B	15	20
L6920	4	4
PC-8	1.5	0
PU-1792	0	5

Tab. 1 Foaming formulation of PIR and PU foam

Polyurethane foam preparation: refer to Tab. 1 This study used two foam systems, one group as a reference sample PU foam, the other group is PIR foam, two kinds of foam are not added flame retardant. The preparation of the foam has two main processes: Firstly, polyol, catalyst, blowing agent and the surfactant are mixed and stirred at room temperature to obtain a mixture called white matter (if in the summer, it should be stored into the refrigerator, the control temperature is 20 °C); secondly, isocyanate is quickly added to the white material, stir in high-speed for 6s and then quickly put into the mold (150mm × 150mm × 100mm), observe the characteristics of foam reaction, record the duration of white matter formation, gel formation and foam formation by using stopwatch. At the end, the foam become hardened and recovered to room temperature, then the foam is placed into the oven at 80 °C for 24 hours.

1.3. Testing and characterization

1.3.1 Thermogravimetric analysis (TGA):

NETZSCH-STA449C thermogravimetric analyzer (German resistant company), the heating rate of 20 °C / min, the temperature range of 20 ~ 800 °C, air atmosphere.

1.3.2 Infrared Spectroscopy (FT-IR):

EQUINOXSS / HYPERION 2000 Infrared Spectrometer (Germany BRUKER Spectrometer), spectral range 7500 ~ 370cm⁻¹, resolution <0.5cm⁻¹. High temperature infrared preparation: the foam sample placed in the muffle furnace for 5 mins at the set temperature, and then the sample is undergo infrared testing.

1.3.3 Pyrolysis gas chromatography mass spectrometry (Py / GC-MS) analysis:

QP-2010 Ultra type pyrolysis gas chromatography mass spectrometry (Shimadzu Corporation), the mass range (m / z) of 1.5 ~ 1090, The pyrolysis temperature ranges from 350 to 750 ° C..

1.3.4 Scanning Electron Microscope:

S-2360N Scanning Electron Microscope (Hitachi, Japan) The desired sample is the residual carbon residue after the foam is measured by the cone calorimeter. Before the observation, it is necessary to cut the section and then spray the gold.

1.3.5 Limit oxygen index determination:

HC-2A limit oxygen index instrument (Nanjing Jiangning Analytical Instrument Co, Ltd.) in accordance with GB / T 2406 test, the sample size is 120mm long, 10mm wide, 4mm thick, working pressure of 0.1MPa , The timer accuracy is not less than 0.1s, igniter flame length (5 ~ 50) mm can be adjusted, the purity of gas source is not less than 98% of the oxygen and nitrogen.

1.3.6 Cone calorimeter test:

The use of the United Kingdom FTT's FTT0007 cone calorimeter is to conduct a real combustion behavior assessment on foam, that is, to determine the amount of smoke, mass loss rate, oxygen consumption analysis, CO₂ and heat release rate. Thermal radiation power of 50kW / m²; sample size of 100mm × 100mm × 25mm; implementation of the standard GB / T 16172 or ISO 5660-1. RSR is the smoke release rate, m² / (s · m²); TSR is the total amount of smoke released, m² / m²; HRR is the heat release rate, kW / m²; THR is the total heat release, kJ / m².

2. Results and discussion

2.1. Combustion model

Through the comprehensive analysis of the literature, the polyurethane combustion flow chart is shown in Fig. 1 [3]. It is aimed at judging the mechanism of flame retardant by its combustion process. In Part 1, the thermal decomposition process in condensed phase of polyurethane foam is mainly the process where the thermal decomposition products to break through the carbon layer into the gaseous phase. In Part 2, the combustible gas in the gas phase undergo combustion and the inert gas release; In Part 3, the surface of the carbon layer, some thermosetting plastics in the combustion will produce surface carbon layer, and the surface carbon layer has flame retardant effect.

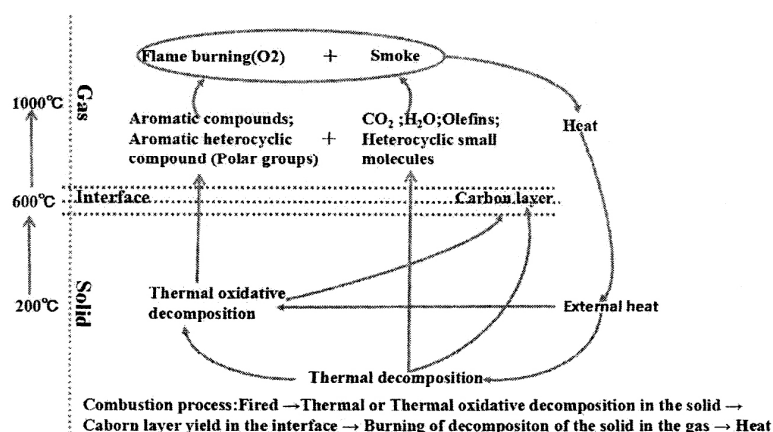


Fig. 1

Therefore, the flame retardant mechanism of the trimer structure on the PIR foam is studied from the mechanism of thermal decomposition stage in condensed phase, the barrier mechanism of carbon layer formation on the surface in condensed phase and the mechanism in gaseous phase.

2.2. PU and PIR foam combustion performance comparison

The PU used as the blank control group in order to study the effect of trimer structure on the flame retardancy of PIR foam, the changes of the flame retardant in foam was tested in the present of trimer. The infrared characteristic peak of the trimeric structure is usually located at about 1410 cm⁻¹ [10] Fig. 2 shows the infrared spectrum of PIR foam and PU foam, indicating that PIR foam has a stronger absorption peak at the 1406cm⁻¹ than that of PU foam, and carbon peak position of PIR foam is shifted to lower wave compared to the PU. It can be seen from the reaction formula (Fig. 3) in which the isocyanate is trimerized to form a trimeric structure. Since the carbonyl group in the PIR foam is linked

to the trimeric structure, it may be due to the conjugation that causes the above changes. Results also indicates that PIR foam contains a large amount of isocyanurate ring structure. The combustion performance of PIR and PU foam can be studied by using cone calorimeter and limit oxygen index. Fig. 4 and Fig. 5 are the heat release rate and smoke release rate of PIR and PU foams, respectively. Tab. 2 shows the combustion performance of the two foams and the combustion performance is mainly compared through the following data, firstly the maximum heat release rate, PU has the maximum heat release rate of 279.8kW / m², significantly higher than that of the PIR which is 143.6kW / m², the higher the heat release rate, the better combustion performance of the material, and correspondingly the flame retardant performance is poor. And the total heat release of PU is also higher than the PIR, indicating that combustion of PU is completely than PIR. The release of smoke from the combustion process can also reflect the flame retardancy of the foam, and the amount of smoke released by the PIR in the combustion is less 4.5 m² than that of the PU. The final burning carbon residue from PIR foam is also higher than that of the PU foam. In addition, the limiting oxygen index is also a measurement of plastic and other polymer materials relative to the combustion test in order to determine the degree of difficulty in combustion of the material in contact with the flame in air, the higher oxygen index, the greater the flame retardant properties of materials. From Tab. 2, it can be seen that the limit oxygen index of PIR foam is 22%, which is greater than 19% of PU foam, which further shows that PIR foam has better flame retardancy than PU foam. In summary, it can be seen that the presence of trimeric structures can improve the flame retardancy of PIR foams.

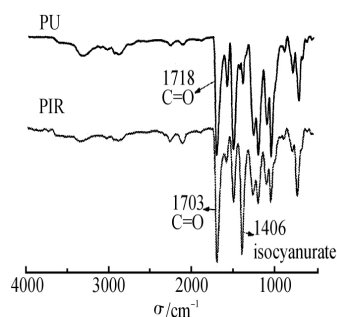


Fig. 2

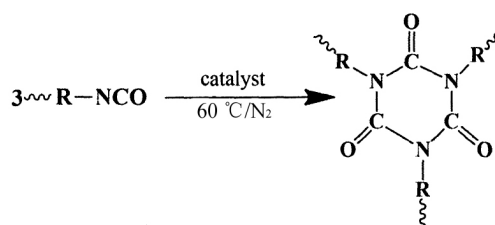


Fig. 3

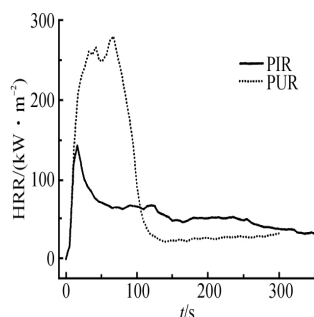


Fig. 4

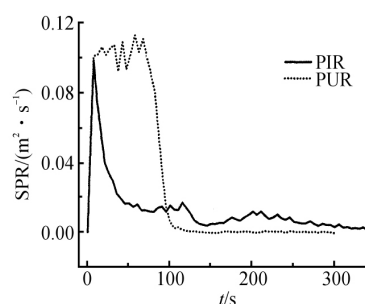


Fig. 5

Sample	HRR / (kW·m-2)	THR / (MJ·m-2)	TSP / m2	Char residue /%	LOI /%
PU	279.8	26.8	8.7	14.6	19
PIR	143.6	22.8	4.2	29.9	22

Tab. 2

2.3. The mechanism of thermal decomposition stage in condensed phase

The mechanism action of trimer structure in increasing the flame retardancy of PIR was studied, analyzed and discussed in 3 different part as mentioned in the following. Firstly, in the mechanism of the thermal decomposition stage in condensed phase, which mainly to study the rate of residual decomposition and to understanding the segments of decomposition at different temperatures by using thermogravimetric analysis and infrared analysis. Fig. 6 and Fig. 7 shows that, in the atmospheric air condition, both PIR and PU foam show two significant heat loss stages, the significant heat loss peak fall at 330 °C and 540 °C, respectively. As shown in Tab. 3, the decomposition residual rate of PIR at 330 °C and 540 °C was significantly higher than that of PU. Compared with PU, the decomposition residual rate of PIR

increased from 65.8% to 82.7% at 330 °C, whereas the rate increased from 18.8% to 31.7% at 540 °C. It indicates that the trimer structure has high thermal stability and is not easily decomposed at high temperature, thus it slows down the thermal decomposition process during the combustion of the foam and increases the flame retardancy of the foam. The infrared analysis curves of polyurethane foams from different temperatures are shown in Fig. 8: (1) at room temperature, 1703cm⁻¹ is the stretching vibration peak for C = O, 1597cm⁻¹ and 1513cm⁻¹ is vibration peak of the benzene ring skeleton, 1406cm⁻¹ is the peak position of trimer structure, 1223cm⁻¹ is the C-O stretching vibration peaks, 1067cm⁻¹ and 1008cm⁻¹ are C-O-C ethers stretching vibration peaks, and 816cm⁻¹, 755cm⁻¹ and 711cm⁻¹ are C-H outer swing characteristic peaks for para, ortho and meta respectively in the aromatic hydrocarbon structure, all infrared characteristic peaks above are the classical peaks for PIR foam. (2) The infrared characteristic peaks are significantly weakened at 330 °C, including C-O and C-O-C were significantly decreased or disappeared, this shows that the first heat loss stage was mainly the fracture and decomposition of the carbamate structure, while the characteristic peak intensity of the trimer structure at this stage was still significant stronger, these indicating that the thermostability of the trimer structure is high at this temperature stage; (3) at 540 °C, the infrared curve is more smooth, only at 1578cm⁻¹ is the benzene ring C = C vibration peak and at 1214cm⁻¹ is the C-O stretching vibration peak, indicating that most of the structure of this stage of thermal decomposition more thorough, some cross-linked structure tends to carbonize. The above analysis shows that the trimer structure enables the PIR foam to have good thermal stability, causing the foam is not easily decomposed at high temperature, slowing down the thermal decomposition process of foam in condensation phase, thus playing a flame retardant effect.

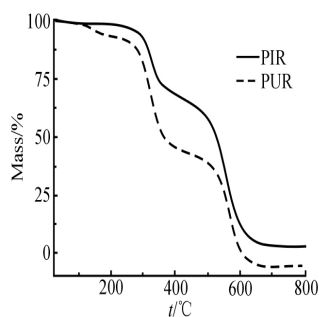


Fig. 6

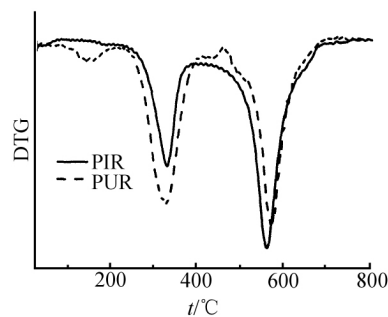


Fig. 7

2.4. The barrier mechanism of carbon layer formation on the surface in condensed phase

In order to observe the mechanism of the carbon layer, the optical camera and the scanning electron microscopy (SEM) were used to test on the foam combustion residue which left after the cone calorimeter test. Fig 9 shows the carbon residual decomposition of PU and PIR foam. It is clear that the carbon residue of the PIR foam (Fig.9b) is quite complete, while the carbon residue of PU foam (Fig. 9a) has many holes and cracks. This phenomenon can also be observed more clearly by SEM. Fig. 10 shows that the surface of PU foam residue has many obvious holes, and the structure is more loose. This may be due to the fact that the carbamate segments are easily released through the carbon layer under the action of combustion heat, and causing the more pores and cracks to form on the carbon layer surface. And the PIR foam tends to become charcoal due to the presence of a large number of isocyanurate rings during combustion, and the cross-linked isocyanurate structure is the primary factor in the formation of carbon, resulting in the formation of a dense and firm carbon layer in PIR foams after combustion. In addition, results of the cone calorimeter test shows that the presence of the trimer structure increased the carbon residue after the combustion of the foam, it greatly increased from 14.7% in PU to 29.9% in PIR. In summarize, the results show that the trimer structure cause the PIR foam to form a more dense carbon layer than the PU during combustion, and it effectively blocking the oxygen and heat, thus to increase the flame retardancy of the PIR foam.

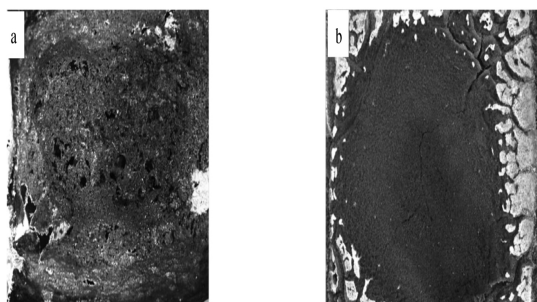


Fig 9

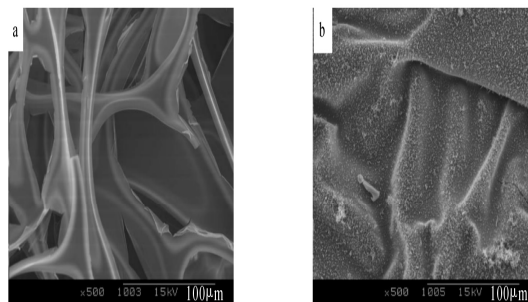


Fig 10

2.5. The mechanism in gaseous phase.

In this paper, the gaseous composition of thermal decomposition in PIR and PU foam was demonstrated by using pyrolysis gas chromatography mass spectrometry, and the mechanism of flame retardation in gaseous was explored. The foam combustion surface temperature is about 600 °C tested by using temperature measurement probe. The analysis of the carbon layer in previous experiment was also assumed at 600 °C. Therefore, the test conditions of Py / GC-MS were set at 600 °C and the helium atmosphere is the gaseous composition used to simulate the real combustion. According to the mechanism of gas-phase flame retardancy, the high temperature pyrolysis experiment is mainly analyzed the content of decomposed inert gas CO₂ composition, including the content of combustible gas. Fig 11 shows high temperature pyrolysis gas chromatogram of PIR foam at 600 °C and Fig. 12 shows the corresponding high temperature pyrolysis mass spectrometry of PIR foam at 600 °C, integrated to qualitative and quantitative analyze the gas composition. Fig 13 and Fig. 14 show the finding of the high temperature pyrolysis gas chromatographic and mass spectrometric analysis of PU samples. Since different peaks correspond to different thermal decomposition compounds, the changes in CO₂ content is determined by comparing the surface area of the different peaks. Partial decomposition structure of phthalic anhydride in phthalic acid polyester polyol found to be stay at peak b correspond at the time of 18.936 min in PIR and at 18.978 min in PU due to the content of the two in the formula is the same, and the structure is more stable, thus it is selected as the reference peak. Peak a of CO₂ were found to be at 2.244 min in the PIR and in the PU was 2.197 min. In addition, the content changes of flammable gas polyol peak c (residence time at 10.883 min and 10.917 min, respectively) was also investigated.

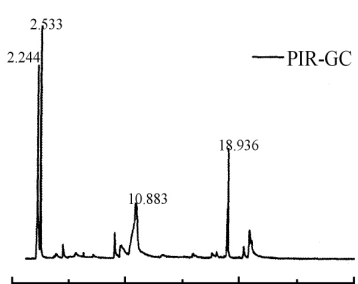


Fig 11

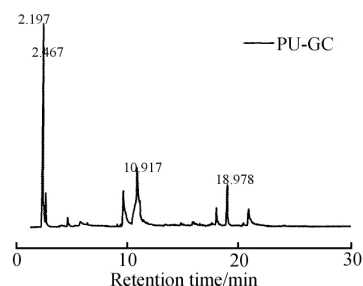


Fig 13

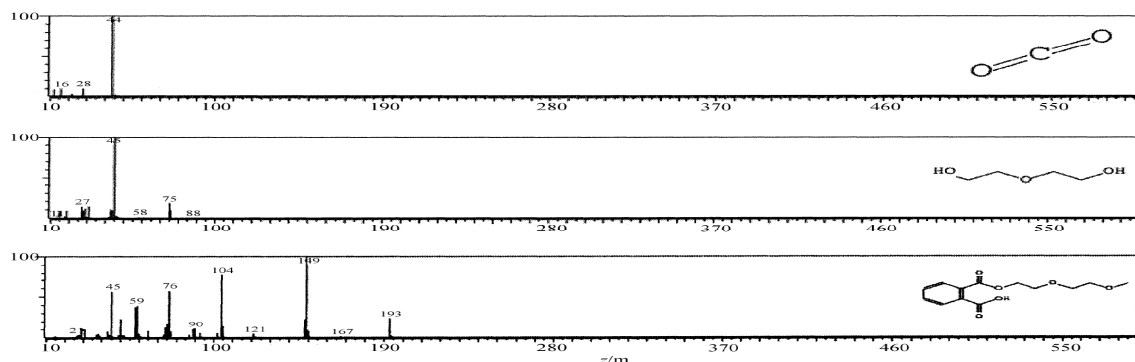


Fig 12

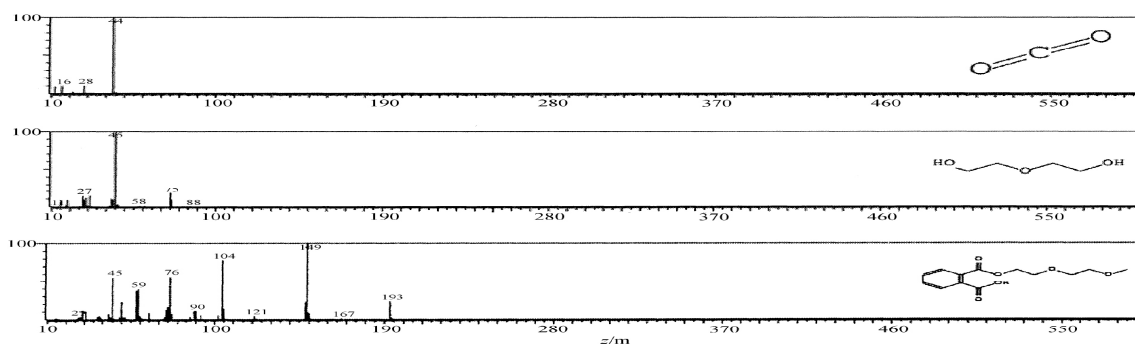


Fig 14

Data in Tab. 4 shows the integration and comparison of different peaks and peaks area, respectively. Statistics show that the CO₂ content in the PIR foam decomposition in gas phase is 79.3% higher than that of the PU, and the flammable gas polyol is reduced by 36.4%. These indicate that the trimer structure can effectively increase the content of inert gas in the gas phase, dilute the flammable gas concentration, and also reduce the flammable gas content in the gas phase, thus improving the flame retardancy of the PIR foam.

3. Conclusion

In this paper, the trimer structure is proved to induce flame retardancy effect in PIR foam by using infrared, thermal analysis and high temperature pyrolysis gas chromatography.

(1) TG test results show two biggest heat loss stage and decomposition residual formed at 600 °C. PIR foam have a higher residual rate compared to PU foam and this demonstrates that the trimer causes the PIR foam to have higher heat stability. The high temperature infrared test structure indicates that the trimer structure is more thermally stable than the carbamate structure, and it needs to absorb more heat when decomposing, causing the foam is not easily decomposed at high temperature and slower the thermal decomposition process in condensed phase and thus induced flame retardant effect.

(2) By observing the morphology of the carbon layer, it can be seen that the trimer structure favors the formation of charcoal and the residual carbon content from 14.7% of PU to 29.9% of PIR and causing the PIR foam to form more dense carbon layer, and effectively blocking the oxygen and heat in the combustion, thereby enhancing the flame retardant properties of the foam.

(3) Thermal decomposition of polyurethane in gas phase was tested using Py / GC-MS. The results show that the trimer in the PIR reduces the release of the flammable polyol gas by 36.4% relative to the PU foam, while also increasing the content of the inert gas carbon dioxide by 79.3%, further supporting the trimer induced flame retardant effect in gas phase.

Reference

1. Chen Jun. Polyisocyanate Foam [J]. *Plastics*, 1989, 18 (2): 4-10. Chen J. Polyisocyanurate foam plastics [J]. *Plastics*, 1989, 18(2): 4-10.
2. Tang Mingjing, Zhou Qiuming, Tian Chunrong. Polyurethane Modified Polyisocyanurate Foam Heat Resistance Can study [J]. *Plastics Industry*, 2010,38 (10): 17-20. Tang M J, Zhou Q M, Tian C R. Study on the heat resistance of PU-PIR foam [J]. *China Plastics Industry*, 2010,38 (10): 17-20.
3. Zhang Jun, Ji Kuijiang, Xia Yanzhi. *Polymer combustion and flame retardant technology* [M]. Beijing: Chemistry Industrial Press, 2005.
4. Zhang Y, Xia Z, Huang H, Chen H. Thermal degradation Polyurethane based on IPDI [J]. *J. Anal. Appl.*, 2009, 84: 89-94.
5. Zhang Y, Xia Z, Huang H, Chen H. A degradation study of Waterborne polyurethane based on TDI [J]. *Polym. Test.*, 2009,28: 264-269.
6. Kulesza K, Pielichowski K, German K. Thermal decomposition of bisphenol A-based polyetherurethanes blown with pentane: Part I-Thermal and pyrolytical studies [J]. *J. Anal. Appl.* 2006, 76: 243-248.
7. Kunze R, Schartel B, Bartholmai M, et al. TG-MS and TG FIIR applied for an unambiguous thermal analysis of intumescent Coatings [J]. *J. Therm. Anal. Calorim.*, 2002, 70: 897-909.
8. Hu X M, Wang D M, Wang S L. Synergistic effects of expandable Graphite and dimethyl methyl phosphonate on the mechanical Properties, fire behavior, and thermal stability of a polyisocyanurate- Polyurethane foam International [J]. *J. Min. Sci. Technol.*, 2013,23: 13-20.
9. Gao L P, Zheng G Y, Zhou Y H, et al. Synergistic effect Expandable graphite, diethylethylphosphonate and organically modified Layered double hydroxide on flame retardancy and fire Behavior of polyisocyanurate-polyurethane foam nanocomposite [J]. *Polym. Degrad. Stab.*, 2014, 101: 92-101.
10. Modesti M, Lorenzetti A. An experimental method for comparison Isocyanate conversion and trimer formation in polyisocyanate-Polyurethane foams [J]. *Eur. Polym. J.*, 2001, 37: 949-954.